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WATER SECURITY

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Chad Staddon

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The monograph is devoted to problems of water services economics and policy, water usage, sewerage, management, quality and pollution of waters, monitoring, measures to improve the state of water objects, quality of water, system and technology of sewage treatment.
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The book is written for scientists, lecturers, postgraduate students, engineers and students who specialize in the field of environmental researches, where the object of study is water.

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Dedicated to the 25th anniversary of
the Petro Mohyla Black Sea National University

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FOREWORD

Water was given a magic power to become the force of life on Earth
Leonardo da Vinci

The European Union considers environmental security as an important component of European stability. Environmental protection is defined as a priority area of cooperation between Ukraine and the European Union. Integration of Ukraine into the EU in the field of environmental protection, rational management of natural resources, and ensuring of environmental security should be achieved through the creation of a harmonized legal, regulatory, methodological, and organizational base that should meet the requirements of national and European environmental security.

Water security is one of the priorities of national and European policies to ensure the goals of sustainable development. It is important to note that Ukraine has a number of topical environmental issues of water security and, at the same time, has an important role in ensuring environmental sustainability in Europe. Ecologically destructive models of development in many countries of the world have led to the degradation of water resources, which is reflected in their volume and quality. The need arises to ensure the optimal use of water, protection of freshwater resources, monitoring of water resources, the search for new technologies and methods of wastewater treatment, the investigation of the quality of drinking water.

Over the past decades in water management in many countries use an ecosystem approach. Ecosystem water management is carried out by the state and society through basin management based on paid water use. Basin principle is this method of water management, which basic unit is the area of the river basin, where the latter is a system of established environmental and socio-economic connections. Now the river basin approach enables to foresee the effects of anthropogenic activities for early warning of environmental catastrophe.

Among the methods of wastewater treatment is more effective and promising biological methods that have shown good results in water preparation.

The urgency of the problems of management, monitoring, and forecasting of water resources in conditions of intense water use, drinking water quality are the issues related to technology, methods of wastewater treatment, biological and biochemical aspects of municipal and industrial wastewater treatment i.e. a wide range of scientific research subjects, where an object is water has caused the publishing of collective monograph under the general name «Water Security. Issue 2».

The main thematic modules of the monograph:

- Water services economics and policy.
- Water use and sewerage.

- Water management.
- Quality and pollution of waters.
- Water monitoring.
- Measures to improve the state of water objects.
- Quality of drinking water and its impact on health.
- System and technology of sewage treatment.
- Enviromental education in the field of the water security.

The book would be impossible without the support of the Erasmus+ Programme of the European Union. There are chapters of scientists from Ukraine, Slovakia, Poland, and Georgia on the pages of the book. There is especially the wide geography of Ukrainian scientists on the pages of the monograph.

The monograph is the result of the scientific achievements of scientists, leading specialists from universities and organizations:

Petro Mohyla Black Sea National University; University of the West of England, United Kingdom; Comenius University, Bratislava, Slovakia; Prešov University in Prešov, Slovakia; Batumi Shota Rustaveli State University, Georgia; Maria Curie-Skłodowska University, Lublin, Poland; Lviv Polytechnic National University; Taras Shevchenko National University of Kyiv; Vinnytsia National Technical University; O.M. Beketov National University of Urban Economy in Kharkiv; National University of Water and Environmental Engineering; Institute of Colloid and Water Chemistry of National Academy of Sciences of Ukraine, Kyiv; Kamianets-Podilskyi National Ivan Ohiienko University; Kharkov National University of Construction and Architecture; National University of Civil Defense of Ukraine; Sumy State University; Ipris-Profile LLC; A. S. Makarenko Sumy State Pedagogical University; Odessa State Environmental University; Pavlo Tychyna Uman State Pedagogical University; National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»; Institute of Hydromechanics of National Academy of Sciences of Ukraine; UC Kharkivvodocanal; Institute of Telecommunications and Global Information Space of the National Academy of Sciences of Ukraine; Department of Ecology and Natural Resources of the Mykolaiv Regional Public Administration.

We express our sincere thanks to all the authors, esteemed colleagues, who in a short time presented the own, original, interesting researches on the problems of water security, contributing to this book was published.

In the future we hope that the scientific works are on the pages of this edition will find creative affiliate cooperation through successful joint implementation of actual ideas, proposals, scientific and practical developments.

We would like to thank the Erasmus+ Programme of the European Union for supporting the publication of the book within the framework of the Jean Monnet project.

Prof. Olena Mitryasova & Prof. Chad Staddon

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ENSURING THE ENVIRONMENTAL SAFETY OF AQUATIC ECOSYSTEMS: IDENTIFYING THE DISADVANTAGES OF REGULATORY AND PROSPECTS OF STENOBIONTIC APPROACHES

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ABSTRACT

The dynamics of aquatic ecosystems in most regions of the world has long been characterized by negative trends. In view of this, based on the analysis of the causes of this degradation, the authors argue the methodological inefficiency of the modern concept (normative) to ensuring ecological safety and regulation of anthropogenic pressure on the environment, which is based on the use of «maximum allowable concentration». A number of disadvantages have been identified due to which component-by-component standardization of abiotic environment parameters does not reflect the objective state of both water resources and the water ecological system as a whole. This is based on calculations of the energy response of the water ecosystem (for example, the Dnieper-Bug estuary) at each level of the food chain: despite the constant state of water quality in the estuary over the past 40 years, the level of ecological safety of the ecosystem has deteriorated. In addition, based on a synthesis of the results of toxicological studies by other scientists, it is proved that the method of biotesting, which is the basis for determining most of the maximum allowable concentrations, does not provide complexity in assessing the state of aquatic ecosystems. The reason for this should be considered insufficient justification of the process of selection of test organisms, without taking into account their environmental survival strategies. It should also be noted that in Ukraine, for example, 75% of the existing maximum allowable concentrations justified based on medical research and production facilities, the purpose of which is to ensure the health for human, but not the safety for ecosystems. It was also found that among scientists there is no unified approach to the choice of model toxicant and test organism for the development regulation standards of anthropogenic impact. Therefore, having identified the key aspects of methodological imperfection of the normative concept, the stenobiont approach to ensuring the ecological safety of water ecosystems and standardization of anthropogenic impact on the environment is proposed. The list of indicator species and the obligation to integrate a number of biosphere laws (tolerance, complication, emergence and internal dynamic equilibrium) in the theoretical and methodological basis of a new, stenobiontic, approach are substantiated.

Key words: stenobiontic approach, ecological safety of aquatic ecosystems, disadvantages of anthropogenic influence regulation on the environment; energy response of ecological systems

INTRODUCTION

Currently, the leading place in the system of environmental safety of the environment, in particular aquatic ecosystems, is occupied mainly by the regulatory approach. Its main tool is the concept and indicator of the "maximum permissible concentration" of pollutants in the environment. And work with it is quite simple: if the actual concentration does not exceed the standard, the conditions for the release of pollutants into the environment are considered safe. However, the global scale and the use of this approach are are not unambiguous. Moreover, in many countries around the world, compliance with standards does not mean the formation of a safe environment for humans, and the state – for ecosystems. On the contrary, the world community notes the pervasive deterioration of the environment, the depletion of ecosystems and the growing scarcity of natural resources [21].

A special place in this process is occupied by aquatic ecosystems, the regulatory, supporting, providing and cultural functions of which are leveled every year. Although more than 20 years ago, the United Nations recognized their critical importance in the development of human civilization, social, economic and environmental value. It is aquatic ecosystems that determine the momentum of matter and energy flows in the trophic chains of the biosphere. Given the regularity of the substances cycle (including anthropogenic origin) and energy in nature, aquatic ecological systems are mostly a mandatory and often the final source of their flow.

Take into account the current destructive phenomena and processes in all aquatic ecosystems, despite the periodic revision and strengthening of the criteria for regulatory control of the intensity of anthropogenic impact on water bodies, understanding the biological, economic and strategic value of water resources, there is no doubt the need to develop new approaches to ensuring their environmental safety.

METHODS AND EXPERIMENTAL PROCEDURES

This study is based on the principles of a systematic approach, the content of which is very well reflected in one of the environmental laws of B. Commoner: "everything is connected to everything else" [14]. That is, gases released into the atmosphere or waste buried in the soil will sooner or later come into contact with water and living organisms in all parts of the food chain.

The purpose of the study was to theoretically and methodologically substantiate the stenobiont approach to ensuring the environmental safety of aquatic ecosystems. With this in mind, the following tasks were set:

- substantiate the theoretical basis of the stenobiont approach, taking into account the provisions of biosphere laws;
- identify the advantages and disadvantages of modern approaches to ensuring the environmental safety of aquatic ecosystems;
- assess the possibility of using stenobionts in the process of ensuring the environmental safety of aquatic ecosystems.

The methodological basis of the study is based on the use of methods of analysis, synthesis, comparison, generalization and formalization to substantiate the point of view on the effectiveness of modern and proposed tools for assessing and ensuring environmental safety. Structurally, the problem is based on the analysis of the content of modern systems of anthropogenic pressure normalization on the environment, comparing their advantages and disadvantages, highlighting the problem niche and synthesis of potential activities to fill it. During the presentation of results the actual data of ecotoxicological experiments of other scientists were generalized and formalized. The own calculations of the size of the energy niche of the human in the context of action of water chronic toxicity on ecological safety and sustainability of ecosystem services flow of the river are stated. On this basis, the expediency of the relevant theoretical and methodological provisions of the stenobiont approach is substantiated.

THE RESEARCH RESULTS AND DISCUSSIONS

In many countries around the world, the basis of environmental protection activities is the system of anthropogenic pressure regulation on the environment (SAPRE). Within its limits, four directions find practical application: substantiation of maximum permissible concentrations (MPC) of pollutants in the environment; identification of environmental risks (risk-oriented approach); bioindication approach with analysis of the ecosystem`s biotic component state "in situ" and historical-cultural approach.

Based on the comparison of their advantages and disadvantages, there is an opinion that the most promising in this list of SAPRE directions is the use of biota indicators [9]. This can be argued by examples of modern practical transformation of environmental protection principles in different countries.

In the United Kingdom, for example, in the run-up to the 2017 elections, some political party programs have stated that toxicological experiments on animals are an unacceptable component of SAPRE and this approach should be completely abolished based on the principles of humanity and science [3, 24]. Moreover, since 2000, this country has effectively used its own system of bioindication of aquatic ecosystems – RIVPACS (River Invertebrate Prediction and Classification System) [49].

In the United States, the "Rapid Bioassessment Protocols. For Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates, and Fish" has been officially approved and mandatory since 1999 [47]. It determines the procedure for biomonitoring the state of surface watercourses, taking into account the economic efficiency and scientific feasibility of using biota.

In Canada, the national biomonitoring system is called CABIN (Canadian Aquatic Biomonitoring Network), in Australia (since 1994) – AUSRIVAS (Australian River Assessment System), in Spain (since 2009) – MEDPACS (MEDiterranean Prediction And Classification System). All of them are adapted to regional climatic conditions, based on the Trent Biotic Index, which was first used by Woodiwiss in 1964 [55, 56], and has since been tested in almost every country in Western Europe. To this list could be added the Belgian Biotic Index, which is used as the national water quality standard in Belgium, or the French Indice Biotique in France.

The use of biota to assess the status of aquatic ecosystems within the European Union has been enshrined in the Water Framework Directive since 2000 [11].

Given the above, quite fair statement Tolochyk I.L. that an objective assessment of water quality of watercourses should take into account the parameters of both the aquatic environment and the indicators of the biotic component. In this case, an objective assessment is impossible without a comprehensive approach, as the property of self-cleaning of aquatic ecosystems is influenced by both external and internal patterns of their functioning, abiotic and biotic factors [51]. That is why changes in the quality of the environment and the state of the ecosystem are observed at the organismal, population and coenotic levels [4]. And many scientists emphasize the importance of using biological methods to assess the state of aquatic ecosystems [1, 2, 7, 43].

Also valid is the opinion of Tsibulskyi O. I. that the current widespread application of the one-sided concept of anthropogenic pressure regulation on the basis of the MPC does not take into account the effects of synergism and antagonism of several pollutants. In addition, derivatives of these relationships are more toxic than the parent compound alone [52].

Therefore, destructive changes in aquatic ecosystems, in particular the deterioration of water resources, occur even at concentrations that do not exceed the regulated MPC. The use of maximum permissible values allows water companies to dissolve discharges to the level of the standard, artificially adjusting the concentrations of pollutants to the required parameters.

Therefore, some researchers claim that the MPC concept does not provide reliable protection for aquatic ecosystems [16, 33]. Moreover, the analysis of the appendix №2 of Ukraine Sanitary Norms and Rules №4630-88, which is in force, showed that 75% of the standards set out there are developed by medical institutions, and the purpose of the document, according to, is to ensure human health and not a word about fauna and flora .

The bias and failure of the normative concept of ensuring the environmental safety of ecosystems, including aquatic ones, is set out in the materials of federal hearings held by the US Environmental Protection Agency in 1999 [25].

The document states that the developers of the LD_{50} test (on which the entire biotesting system and the process of establishing the MPC are now built) recognized its serious shortcomings in 1927, outlining the possibility of its use only for limited medical purposes.

In particular, it is emphasized that minor changes in testing conditions (toxicological experiments) can lead to very different consequences. Numerous documentary evidence has been found that factors such as species, hereditary information, age, weight, sex, health, nutrition, restriction of access to food before the test, method of application of the substance, ambient temperature and animals housing conditions were affected on LD_{50} results [25].

At least this list of factors leads to the fact that the results of laboratory biotesting are very different. It is also likely that humidity, weather, noise, the light-dark cycle, and the behavior of laboratory personnel may affect the test result.

Thus, the value determined by the LD_{50} test is not a biological constant and is not of great importance in determining the toxicity of pollutants [25]. According to the definition of Gelashvili D.B. and Karandashova A.A. [20], the concept of MPC is the worst environmental paradigm that humanity is actively using in practice.

Therefore, it is quite natural that the current state of the relationship between man and nature can no longer be objectively assessed and regulated by the normative concept. At the same time, it is impossible to talk about a complete abandonment of it, because it is effectively used in the drinking water supply system and can ensure the quality of the production environment (shops, hangars, local industrial sites, etc.). The principle of its application is as follows: the environment will be safe for humans if it is safe for the most sensitive animals and plants, in response to a set of environmental factors.

Regarding the substantive difference between the normative (based on biotesting) and bioindication approaches, despite the similar goals, procedurally they differ significantly. Bioindication is aimed at assessing the state of the ecosystem, and biotesting – specifically water resources (consumer orientation) [12, 35].

Bioindication is carried out at the level of the organism and the population in "in situ" conditions, and the obtained results quantitatively or qualitatively characterize the tendencies of changes in the state of ecosystems, processes, phenomena. During the application of the method, the indicator organisms do not die and remain in the ecosystem. It is important to note that this area of SAPRE, due to the principle of complexity, most effectively assesses the quality of the environment and is a generally accepted indicator of sustainable development [12].

Biotesting is an artificial, highly specialized area of regulatory approach. The object of study is usually a molecule, cell or organism, and the result is the possible consequences of environmental pollution [31, 36]. However, the method has some methodological shortcomings, including the justification for the choice of test organisms, which affect its accuracy and objectivity in practice.

An important difference between the schemes of SAPRE aproaches is the consideration of the time factor (Fig. 1).

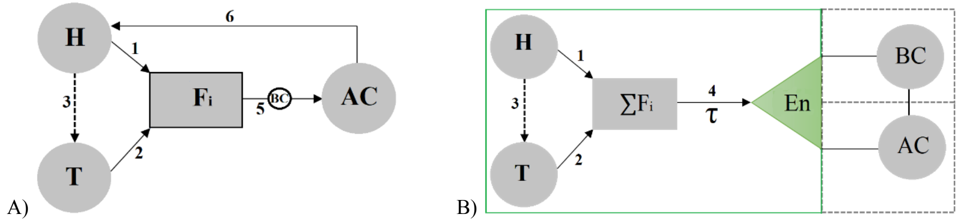

Fig. 1. Simplified schemes of SAPRE: *H* – human; *T* – technology; F_i – environmental factors, *En* – environment, *AC* – abiotic components, *BC* – biotic components

Thus, the modern regulation system (Fig. 1A) works with each pollutant separately (F_i), which is a consequence of anthropogenic activity (1 and 2; 3 – technology management). During toxicological experiments 5 it is established how F_i, getting into the *AC*, will pour 6 on *H*. Here the main tool of the regulatory approach is the method of biotesting. The result of its application is the establishment of an MPC for each individual substance. And only later attempts are made to aggregate these standards into a one-dimensional index complex system. However, even under such conditions, it is impossible to establish the influence of natural factors (temperature, light, humidity, etc.) on the level of anthropogenic hazards, which are determined to be safe in the laboratory.

Despite its simplicity, this approach has not developed into a generally accepted practical tool for objectively assessing water quality. After all, many chemical compounds dissolved in water at the level of MPC are determined quite time-consuming, expensive and inaccurate [35, 51].

According to Melnyk V.Y. [37], given the many years of experience in the practical application of the regulatory approach, at most points of water quality control MPC are exceeded, and the existing system based on them does not provide reliable protection of aquatic ecosystems nationwide.

In the context of assessing the quality of water by its chemical analysis, Maltsev V.I. and others talk about the difficulty of determining the danger to humans and aquatic organisms of pollutants, if their concentrations are insignificant. In addition, synergistic effects and discharges in the past are not taken into account [35].

The bioindication approach (Fig. 1B) has not only an ecosystem orientation (both man and technology are part of the triangle *En*, not external autonomous entities), but also reflects the historical trace of anthropogenic impact 4. In addition, the assessment of the *En* is taking into account both biotic (*BC*) and abiotic components (*AC*) in terms of multifactorial and temporal heterogeneity. Obviously, the evaluation results obtained in system B (Fig. 1) can be considered more comprehensive and objective. The only practical unresolved issue is the methodological organization of this process.

Therefore, there is no doubt about the urgency of developing new comprehensive methods for assessing and ensuring the safety of aquatic ecosystems and resources based on the response of their biotic component in nature, taking into account the specifics of each water body for a number of abiotic and biotic characteristics [52]. It seems possible to implement this on the basis of the stenobiont approach, taking into account the fundamental laws of the biosphere.

Most MPCs are calculated on experimental animals by converting the dose-effect indicators per kilogram of human weight. This eliminates such important objective factors as the time of exposure, physiological characteristics of organisms, the number of active factors, the location of experiments, spatial distribution, species set of indicators, artificial lighting, photo mode and many others. Given the significant list of milestones in the formation of the MPC, it should be emphasized that the new approach should take into account the provisions of biosphere laws, in particular such as: Shelford's tolerance (optimality) [48], Roulier's complication [13, 32], emergence [17, 32] and Reimer`s internal dynamic equilibrium [40] (Table 1).

Table 1. The content of biosphere laws in the stenobiontic approach to ensuring the environmental safety of aquatic ecosystems

Biosphere Law	Content	Relationship with the stenobiont approach
Shelford's tolerance (optimality)	The number or spatial distribution of organisms can be determined by certain factors in cases where their level exceeds the maximum or minimum tolerance limits of this organism.	Proves the need to reorient the modern regulation of anthropogenic impact on the environment from the reactions of the human body (or similar) to stenobionts – the most sensitive "receptors" of ecosystems.
Complication	The historical development of living organisms (as well as all other natural systems) leads to the complication of their organization, through the increasing differentiation (division) of functions and organs (subsystems) that perform these functions.	Stenobionts are often the basis of most energy, material and information connections in ecosystems. Therefore, their reaction reflects the general state of the ecological system. The bifurcation and saturation point of the ecosystem is postponed for an indefinite period of time according to the above three parameters.
Emergence	The whole has new, special properties that are absent in its constituent elements (for example, the forest has more properties than one tree).	Analysis of the response of several species of stenobionts in laboratory and field conditions allows to reduce the numerical error rates in determining the critical values of the action of negative factors on the same experimental animals
Reimer`s internal dynamic equilibrium	Changes in the flow of matter, energy and information and dynamic properties of ecosystems will inevitably cause structural-functional, quantitative and qualitative deformations of their parameters.	The dynamic stability of the species composition of stenobionts and their numbers is a criterion for assessing the state of the aquatic ecosystem over a certain period of time. The duration and dynamics of the intensity of the influence of negative factors are taken into account.

The content of the proposed stenobiont approach is that the regulation of anthropogenic pressure on the environment, which is based on the assessment of ecological characteristics of stenobionts, will contribute (not violate) the complexity of functional and material-energy relationships in ecosystems and evolutionary bifurcations, increasing their stability and self-balancing properties. This, in turn, will help ensure their environmental safety.

The main problem of the modern SAPRE should be sought in the methodological diversity of the criteria for selecting a reference pollutant and test-organisms to substantiate the MPC.

Indicative, in terms of differences in the reactions of organisms to pollutants, are the results of studies by Michiel A. Daam et al. [15] and Rachelle C. Riegerix et al. [41]. Their synthesis perfectly demonstrates the heterogeneity of reactions of living organisms to the same pollutant (Fig. 2).

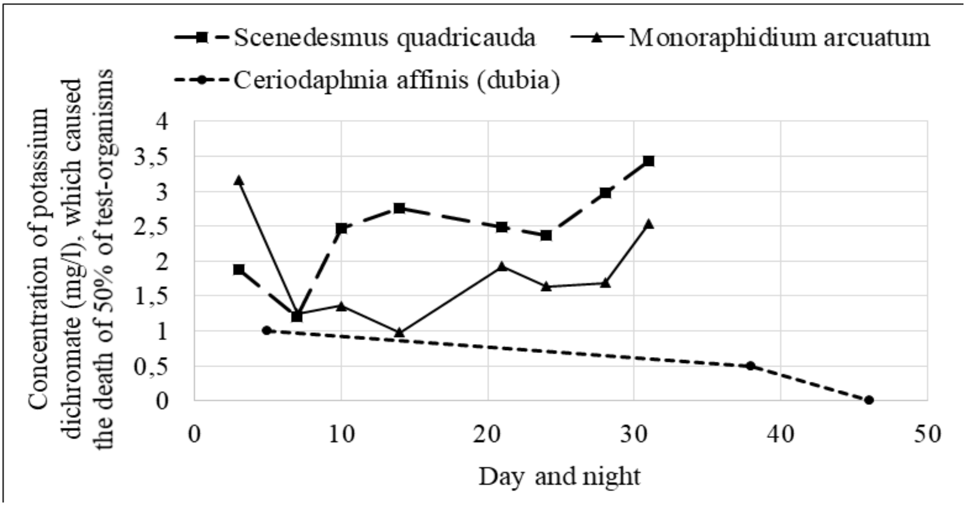

Fig. 2. Differences in toxicological reactions of different organisms to potassium dichromate

Thus, regardless of the selected indicator organism, in the practice of environmental protection, an approach is implemented when anthropogenic impact is regulated by the subject of influence, ie the human (safety of the pollutant is assessed). Although, clearly, it should be the opposite.

It is obvious that the choice of indicator organisms is a fundamentally important task in the process of ensuring the environmental safety of aquatic ecosystems on the basis of biotesting and bioindication.

Potassium dichromate, as the reference experimental pollutant (model toxicant), is chosen by many ecotoxicologists only on the grounds that metals are more chemically stable in the aquatic environment, so they are best suited for short-term experiments. However, from an ecosystem point of view, it is hardly possible to liken the multifactorial multi-intensity irregular anthropogenic impact on the environment of the toxic effects of potassium dichromate on test-organisms.

In addition, some authors determine the relationship between the toxicity of a certain concentration of contaminants on test organisms over a long period of time, while others, on the contrary, seek a concentration that in 3 or 5 days will kill 50% of experimental groups of living organisms. Summarizing the above, it is seen (Fig. 2) that different test-organisms react differently and do not give an unambiguous model reaction, which should be regulated anthropogenic impact.

Due to the significant differences between species, what is relatively safe for test-organisms can be extremely toxic to humans and vice versa (chocolate, for example, is harmless to humans but toxic to many animals) [19]. In addition, it takes into account the wide range of synergetic and cumulative processes that may occur in the aquatic ecosystem during the discharge of pollutants. In particular, the example of pesticides that have been washed away from fields to water bodies has been shown to increase their toxic effects over time [46]. In ecotoxicology and environmental risk assessments, the phenomenon of time-cumulative toxicity is often ignored, which undoubtedly contributes to the deterioration of the environment [45].

Some authors rightly consider biotesting more as a tool for regulating the concentration of certain pollutants in the aquatic environment [30]. And the experimental data obtained by them are very valuable for substantiating the stenobiontic approach.

Thus, the study noted that individuals of *Ceriodaphnia affinis* can be used to establish environmental standards of water quality [30]. Based on the obtained results, without highlighting their statistical significance, the authors determined the range of sensitivity of test organisms *Ceriodaphnia affinis* (determined by the change in their behavior, namely the rate of immobilized individuals) in the range of $1.45 < EC_{50-24} < 2.91$ (mg/dm^3). Given this, a number of practical questions arise, such as "for which pollutants should these test organisms be used?", "how can the reference chemical $K_2Cr_2O_7$ be a toxicant that is closely related to water quality?", "How extrapolate the results to the process of ensuring the quality of water resources?","which ecological or biological properties of *Ceriodaphnia affinis* determined the standard (or "ecosystem") of this species?","what are the toxicological responses of other organisms?" and other.

Lacerda A. C. F. et al., for example, note that to assess water pollution by petroleum products, it is more appropriate to use individuals of the family Chironomidae, because it is the most common group in the benthic community, they simply keep and manipulate them in the laboratory [34]. However, the reactivity (tolerance to contamination) of these organisms is not taken into account.

Therefore, the focus in biotesting on the reactions of living organisms, cells or organs of certain species, the peculiarities of changes in their behavior in a toxic environment is a limited reflection of ecosystem changes, and the assessment (conclusion) can not be considered comprehensive. Especially since test organisms are selected without reference to their environmental properties. However, the practical value of biotesting is seen in its application in the operational control of aquatic ecosystems, for example, in cases of accidental wastewater discharges.

Biotesting within the regulatory approach is aimed at expanding the scope of control of individual components of the abiotic environment (establishment of new MPCs for new pollutants) and is practically detached from ecosystems both in content (methodologically) and in form (methodically).

In particular, Francisco Sánchez-Bayo and Henk A. Tennekes draw attention to this problem [44]. Although the overall framework is well established, the methodologies used at each stage of the assessment face a number of shortcomings. Despite the subjectivity of risk assessment, there is skepticism in scientific circles about the appropriateness of existing methodologies, because after so many years of assessment, humanity is still unable to predict the negative effects on the environment from the use of certain chemicals in their own activities.

Confirmation of these views is found, in particular in the study of Gredelj A. et al. [22]. Thus, an alternative to ecotoxicological testing model for assessing the environmental safety of the aquatic ecosystem (AQUATOX) was developed, which, according to the authors, takes into account chemical, physical, biological and ecological processes in the river, but is based on the same MPC for one species (it was assessed mass of individuals due to water pollution by synthetic surfactants). This scheme of scientific research allowed the authors to argue that neglecting the role of environmental processes in extrapolation from laboratory tests to ecosystems leads to insufficient threshold concentrations of chemicals.

Even if we abstract from aquatic ecosystems and focus on the categories of industrial or domestic wastewater, there are virtually no productions that are sources of discharge of water contaminated with one or even two substances. It is always a set of natural and anthropogenic factors that constantly interact with each other, both weakening and strengthening each other.

Therefore, the concept of environmental safety of the aquatic environment should be focused on the use of factors and indicators that are formed under the influence of external and internal factors, are relatively stable in space and time and can assess the quality of the environment on an ecosystem scale (eg macrozoobenthos energy in the system, redox potential of the aquatic environment, etc.).

Given the complexity and multifactorial process of ensuring the ecological safety of aquatic ecosystems, the existing difficulties in the methods of bioindication and biotesting, the proposed stenobiontic approach can be implemented in two directions (Table 2): ecosystem (based on the assessment of the constancy of flows of matter, energy and information – ecosystem response) and democological (identification of species and populations that are stenobionts in the study area and determination their ecological characteristics; the transition from the principle of "biota for abiota" to "stenobiota for biota").

Table 2. Structural and hierarchical content of the stenobiontic approach

STENOBIONTIC APPROACH				
Ecosystem response			Democological direction	
Matter	Energy	Information	Bioindication (stenobionts)	Biotesting (stenobionts)

Indicative in this context are the results of studies of the ecosystem response to the increase in the intensity and power of negative anthropogenic factors in the Dnieper-Bug estuary (Ukraine). Using well-known patterns of energy flow in ecosystems (10% rule), it was found that prolonged pollution of the aquatic ecosystem by domestic and industrial wastewater leveled, for example, the possibility of commercial fishing for predatory fish (pike perch, perch, catfish, asp, pike, etc.). The energy niche of these consumers of different orders is currently completely depleted (Table 3) [5].

Table 3. The size of the energy niches of the Dnieper-Bug estuary trophic chain components

Aquatic ecosystem	Producers	First order consumers	Second order consumers	Third order consumers (predatory fish)	Fourth order consumers (human)
$625{,}32 \cdot 10^{12}$ kcal	$12{,}5 \cdot 10^{12}$ kcal	$1{,}25 \cdot 10^{12}$ kcal	$0{,}125 \cdot 10^{12}$ kcal	$0{,}0125 \cdot 10^{12}$ kcal	$0{,}00125 \cdot 10^{12}$ kcal
%	2	10	10	10	10

In material terms, the energy provided in the ecosystem for fourth-order consumers corresponds to 1200 tons of fish. Currently, this indicator of fishing for predatory fish in the Dnieper-Bug estuary is almost zero [5]. Therefore, the decrease in the dynamics of industrial fish productivity can be considered evidence of the formation of chronic water toxicity, when most regulations often meet the approved standards, but the productivity of the aquatic ecosystem is constantly declining.

Stenobionts are represented in each component of the trophic chain, in which there is a unidirectional flow of matter, energy and information between living organisms and the abiotic environment. With this in mind, the development of a new approach to ensuring the environmental safety of aquatic ecosystems must take into account the ecological responses of the aquatic organism (as presented in Table 3). Stenobionts will continue to be the first to respond to negative anthropogenic factors, which will cause either their temporary or permanent absence and, as a consequence, the corresponding "disruptions" in the productivity of ecosystems.

Regarding the democological direction (Table 2), the methods of bioindication and biotesting should be focused on the use of ecological response functions of stenobionts – the most sensitive organisms to changes in the living conditions. In the case of aquatic ecosystems, we consider representatives of macrozoobenthos as a valuable indicator group (Table 4).

Table 4. Stenobionts of freshwater ecosystems

Indicator organisms	Satisfy the conditions
Stonefly (*Plecoptera*)	1) sensitivity to the presence of pollutants in the water [6]; 2) occupies an important place in the food chain [11]; 3) economic and practical accessibility [12, 29]; 4) life cycle involves a sedentary lifestyle [6, 12] 5) wide area of distribution [12]
Mayfly (*Ephemeroptera*)	
Caddisfly (*Trichoptera*)	
Alderfly, dobsonfly and fishfly (*Megaloptera*)	
Amphipod (*Amphipoda*)	

Thus, if safe conditions for stenobionts are provided, they will, a priori, be safe for other aquatic organisms, whose tolerance zone to the active factors is much wider.

In the context of the above, it is worth paying attention to the ecological feasibility of selecting the above five groups of aquatic organisms as stenobionts, based on the ecological characteristics of which it is proposed to create new approaches to environmental safety of aquatic ecosystems.

It is a well-known fact that zoobenthos is considered to be a very indicative bioindicator of the state of aquatic ecosystems. For benthic organisms is characterized by a settled strategy of life. Therefore, unlike fish, in most cases they can not avoid volley dumps, hiding in the tributaries. Zoobenthos has a much longer life cycle than, for example, plankton [52]. In particular, Mikhailova L.V. notes [38] that the plankton population, given the rate of adaptive responses in the polluted environment, can not be used as an objective criterion for assessing the complex pollution of the water body.

The state of zoobenthos clearly characterizes not only the ecological state of the reservoir or watercourse in general, but also specific areas of the aquatic ecosystem [7, 39, 42].

According to the research of Yavorsky V. Yu. [57], representatives of macrozoobenthos are important and indicative indicators of the aquatic ecosystems state, which have a fairly long life cycle and reflect changes in the environment over a long period of time. At the same time, aquatic ecosystems are characterized as spatially integral, ie upstream activity is necessarily reflected in the state of the river ecosystem downstream. In particular, it was noted that amphipods, stoneflies and caddisflies were regularly found in the plain part of the Desna River, the reference class of water quality of which is defined as 2-3 class, which is a natural phenomenon within the Polissya zone.

It is also noted that of all the variety of proposed methods of biological analysis and assessment of water quality by structural and functional characteristics of zoobenthos, now there is no single and generally accepted [57]. Probably, this can be explained by the fact that in each case it is necessary to take into account local (regional) natural conditions.

The known results of chemical, physical and biological studies of water bodies show that the representatives of *Ephemeroptera* are bioindicators of water quality, showing a rapid response to changes in their environmental conditions [3, 11, 18, 47, 49]. At the same time, about 20% of the species of this family worldwide can be endangered due to pollution, invasion of alien species, loss and degradation of habitats and climate change [26].

Due to the global trend of increasing salinity of rivers and lakes, no less important influencing factor, in addition to anthropogenic pollution, is the concentration of dissolved salts in water. According to the results [23, 28], for *Ephemeroptera* individuals, the salinity of water from about 1.4 g / l is critical for life (recalculation of NaCl moles in grams was performed according to mathematical models in [24, 27, 54]). With increasing salinity, macrozoobenthos develops more slowly, increases the mortality of young individuals and impoverishes the food chain in the ecosystem [23].

Mayflies are also very sensitive to pollution, and are usually found only in high-quality, minimally contaminated areas. Along with babies and freckles, they are one of the three most common indicators of the "health" of aquatic ecosystems. Because mayflies could be found in a wide variety of habitats and are so sensitive to pollution, they are a valuable indicator of water pollution [53].

The fact that members of the families *Plecoptera*, *Ephemeroptera*, *Trichoptera*, *Megaloptera* are indicative indicators of freshwater quality and pollution, is given in the classification materials of the Department of Environmental Protection of West Virginia, USA [50, 10]. Since 1998, Department specialists have been using bottom macrozoobenthos data to measure the biological health of rivers and lakes within the federal territory [10]. Currently, the network has 6450 observation stations.

A similar conclusion is given by Maltsev V.I. and others, emphasizing that stoneflies, mayflies and some species of caddisflies are demanding indicators of clean water [35].

Representatives of macrozoobenthos provide reliable and comprehensive information on water quality and habitat and have been used as biological indicators in many parts of the world for almost 100 years. In some cases, it may be difficult to identify contaminants and stressors in streams with only chemical data that only provide information regarding sampling time. Even the presence of fish may not indicate the state of the stream, as the fish may swim far to avoid contaminated water or adverse living conditions and then return when conditions improve. Many uterine invertebrates at the bottom are not as mobile as fish, and cannot move to avoid contamination. Therefore, the quantitative and qualitative diversity of benthic aquatic species living in the stream may indicate water quality conditions in the past. In addition, benthos are an excellent tool for assessing water quality, as they are extremely diverse, providing a wide range of sensitivity and response to stressors such as metals, nutrients and sediments. Finally, they are widespread and available for field work, making them valuable practical tools for assessing water quality in aquatic ecosystems [10].

Benthos insects spend most of their lives (about 1 month to 4 years, depending on the species) in water and only appear as adults in a few hours (or days) to mate and complete their life cycle. The movement of benthos larvae includes swimming, crawling on the bottom of the stream and drifting downstream [10]. Regarding the requirements of all five groups of organisms for water purity, in particular amphipods, it was made a corresponding conclusion based on the analysis of worldwide studies [8].

Regarding the indicators by which the ecological safety of aquatic ecosystems can be assessed, the dynamics of stenobiont numbers, their species diversity, population density, spatial distribution, toxicological resistance and seasonality should be considered.

CONCLUSIONS

1. The use of stenobiontic approach in the process of assessing the environmental safety of aquatic ecosystems will facilitate the practical integration of the ecosystemness principles in the process of ensuring the environmental safety of aquatic ecosystems, in particular by taking into account the provisions of biosphere laws in environmental assessment and management. A rational and, obviously, the most objective solution to the problem of representativeness of the anthropogenic pressure regulation on the environment, in the context of harmonious development of man and nature, is at the intersection of modern approaches, where stenobiontic approach should take the main methodological place. Its meaning is that the choice of indicator organisms will take into account the functional requirements of the biota ecological valence and its ecological survival strategies.

2. The main theoretical and methodological principle of the stenobiont approach to ensure the environmental safety of aquatic ecosystems is that stenobiont organisms are the first among other biological species to respond to changes in the state of the ecosystem. Accordingly, if their

living conditions are safe for them, then, a priori, will be the same for other living components of ecosystems, including humans.

3. Based on the differences identified in the toxicological reactions of different organisms to the reference substance potassium dichromate, calculated material-energy response of the aquatic ecosystem to long-term anthropogenic impact and generalization of the results of the application of the MPC concept, the practical inability of the latter to ensure the environmental safety of aquatic ecosystems was confirmed.

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WATER REMEDIATION WITH FUNCTIONAL CAPABILITIES OF ZEOLITIC NANOCOMPOSITES: A REVIEW

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ABSTRACT

Ammonia/ammonium used to be removed from waters based on its concentration with ion exchange mostly onto natural zeolite clinoptilolite or some other selective synthetic resins, air stripping, chemical precipitation with magnesium and phosphate salts to fertiliser magnesium ammonium phosphate or break point chlorination. The most traditional or environmentally feasible method is biological nitrification - denitrification or recently explored and already industrially applied Anammox process. The described investigations on zeolites (clinoptilolite based rock) for the removal of various kinds of aqueous pollutants lead to the conclusion that this natural resource can be considered an alternative cost-effective adsorption material, either with or without surface treatment, depending on the type of water to be purified. A special attention is focused on the clinoptilolite´s competitive effectivity, environmental availability, and economic feasibility in specific ammoniacal nitrogen removal from various water and wastewater streams. Therefore, the pilot deammonification of drinking water with overlimitted ammonium concentration as well as pilot tannery wastewater deammonification onto clinoptilolite are discussed finally.

Keywords: natural zeolite of clinoptilolite type, deammonification, nanocomposite, water treatment

INTRODUCTION

Ammonia - a colorless gas with a very sharp odor - is a chemical that is produced by both humans and nature. It is an essential mammalian metabolite for DNA, RNA, and protein synthesis and is necessary for maintaining acid-base balance. Ammonia is excreted primarily as urea and urinary ammonium compounds through the kidneys. Most of the ammonia in the environment comes from the natural breakdown of manure and dead plants and animals [1]. In water, ammonia NH_3 is in equilibrium with the ammonium ion NH_4^+. The ammonia-ammonium ion equilibrium is highly dependent on the pH and, to a lesser extent, the temperature of the medium. In acidic waters and neutral waters, the equilibrium favours the ammonium ion. Ammonia toxicity can be a major issue that leads to mass mortality under unfavourable aquacultural conditions [1; 2]. The sea fauna and especially corals are extremely sensitive to anthropogenic pollution. Ammonia has often caused the fish hyperplasia of the branchial apparatus. However, certain fish species can accumulate high levels of ammonia in the brain or defense against ammonia toxicity by enhancing the effectiveness of ammonia excretion through active NH_4^+ transport, manipulation of ambient pH, or reduction in ammonia permeability through the branchial and cutaneous epithelia [2]. About 80% of all manufactured ammonia is used as fertiliser. Agriculture is responsible for 95% ammonia emisions using fertilizers which contribute to production of respirably harmful aerosols [3]. Elevated concentrations of ammonia in water are usually due to effluent discharges from sewage treatment plants or industrial processes, or runoff from fertilised fields or livestock areas [4]. In water, ammonia can volatilize to the atmosphere, be removed by microbial processes, or adsorb to sediment and suspended organic matter. In surface water, groundwater, or sediment, ammonia can undergo sequential transformation by two processes in the nitrogen cycle, nitrification and denitrification, which would produce ionic nitrogen compounds, and from these, elemental nitrogen. Elemental nitrogen formed from the anaerobic process of denitrification is lost by volatilization to the atmosphere. The ionic nitrogen compounds formed from the aerobic process of nitrification, NO_2^- and NO_3^-, can leach through the sediment or be taken up by aquatic plants or other organisms [5]. High concentrations of nitrate in groundwater can cause methemoglobinemia in childreen when contaminated water is ingested. Eutrophication in rivers and lakes is mainly caused by high concentrations of ammonium and phosphate. Soils usually obtain additional ammonia from natural or synthetic fertiliser application, animal excreta, decaying organic matter, or natural fixation from the atmosphere [6]. At the beginning of the 20th century, most nitrogen was fixed into usable forms (e.g., NH_3) by lightning strikes and microbial nitrogen fixation [4].

CURRENT AND TRADITIONAL WATER TREATMENT TECHNIQUES FOR AMMONIA REMOVAL

Ammonia/ammonium used to be removed from waters based on its concentration with ion exchange mostly onto natural zeolite clinoptilolite or some other selective synthetic resins, air stripping, chemical precipitation with magnesium and phosphate salts to fertiliser magnesium ammonium phosphate or break point chlorination [7]. The most traditional or environmentally feasible method is biological nitrification - denitrification or recently explored and already industrially applied Anammox process [8]. All of the above mentioned methods have particularly some benefits but also disadvantages, e.g. the efficiency of the process of air stripping and biological processes used to be significantly influenced by the low temperature in winter. Air stripping process is critisized by public for the noise and when the stripped ammonia is not recovered by fertiliser production, also for air pollution [9]. The improper input of chlorine into treated water by breakpoint chlorination may potentially produce risky and cancerogenic chloramines, N_2O or NO intermediates [10]. Chemical precipitation with magnesium and phosphate salts means simultaneously salinization of treated waters. In general, all the aforementhioned physico-chemical processes are effective to remove the higher ammonia concentration in waters. On the other hand, ion exchange is more competitive method for a little influence of the low temperature in winter as well as for sufficient high selectivity toward ammonium/ ammonia. Except that, ion exchange equipment can be automatically controlled, requiring only occasional monitoring, inspection and maintenance [11].

The exchanger currently favoured for this use is clinoptilolite, a zeolite, which occurs naturally in several extensive deposits in the western United States, Mexico, Eastern Europe, Italy, Turkey and some other regions. Slovakia belongs to the countries that mine large tonnages of zeolite mineral (of clinoptilolite type). Over 170 000 metric tonnes of high grade clinoptilolite tuff were exploited from the industrial open-pit mine at Nižný Hrabovec (Eastern Slovakia) in 2018, making it one of the world´s major natural clinoptilolite producer [12,13].

BRIEF CHARACTERIZATION OF ZEOLITIC AND OTHER ADSORPTION MATERIALS STUDIED FOR AQUEOUS POLLUTANTS REMOVAL

NATURAL ZEOLITE (CLINOPTILOLITE)

As Table 1 illustrates, a broad range of various zeolite-based, natural or even commercial adsorption materials, including the inland natural zeolite of clinoptilolite type, were examined for the commonly occuring environmental pollutants removal, in order to compare them to each other. The reason for such as broad selection of model pollutants and adsorbents was to demonstrate objectively how the natural zeolite (clinoptilolite) after surface treatment enhances its native adsorption potential also to anionic and even organic types of aqueous pollutants, despite originally its cation exchange behaviours. Based on the Table 1, it may be observed that the GEH (granulated ferric hydroxide) and ODA (octadecylammonium) -surfactant coated zeolite possess rather universal properties suitable to remove most of the pollutants examined [14,15]. Actually, mostly surface untreated clinoptilolite tuff can compete with other natural materials or even waste products, as occurring in the markets of many countries at very low prices. Furthermore, the clinoptilolite can be considered also as an alternative cost-effective adsorption material, either with or without surface treatment, depending on the type of water pollutants [15,16]. The physicochemical and mineralogical specification of the inland clinoptilolite based rock examined in this study including zeolitic crystal structure and surface morphology presents Table 2. The crystal structure of the HEU-type zeolites is characterized by a 3-dimensional aluminosilicate framework. Clinoptilolite framework contains narrow 4- and 5-membered rings in parallel sheets arrangement, as well as broad 8- and 10-membered rings constituting intraframework micropores perpendicularly to these parallel sheets, capable to host extra-framework cations in association with mobile water molecules [17]. Except that, it is necessary to highlight natural zeolite (Slovak clinoptilolite´s) cation selectivity according to following sequence:

$Cs^{+} > Ag^{+} > Pb^{2+} > Ba^{2+} > NH_4^{+} > Zn^{2+} > Co^{2+} > Fe^{2+}$

$NH_4^{+} > K^{+} > Na^{+} > Mg^{2+} > Zn^{2+} > Ca^{2+}$

NATURAL OR INDUSTRIAL WASTE PRODUCTS AND COMMERCIAL ADSORBENTS

<u>Montmorillonite-rich bentonite</u> originated from the deposit Stará Kremnička – Jelšový Potok in the Slovak Republic, which is the most popular and long mined ore of the country. Basically, bentonite belongs to a group of natural nanomaterials composed predominantly of crystalline mineral particles from the group of dioctahedral smectites – montmorillonite (less than 0.2 mm). <u>Granulated ferric hydroxide (GEH</u>) is an approved commercial adsorbent manufactured by GEH Wasserchemie GmbH & Co. KG Osnabrück (Germany). The main components of GEH are

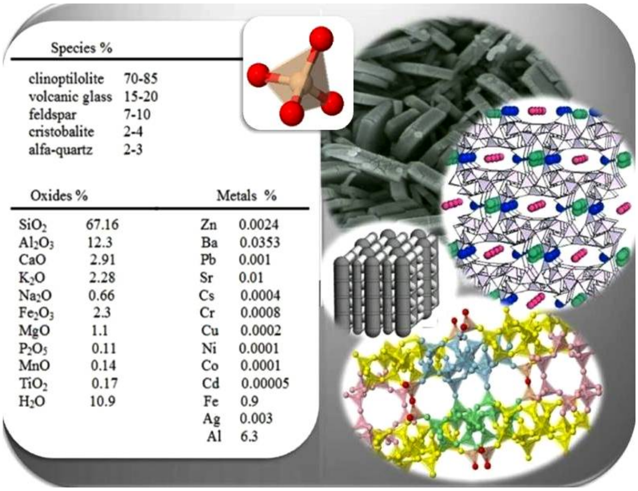
akaganeite (ß–FeOOH) and goethite [α-FeO(OH)]. Slovakite decodes an commercial adsorbent manufactured by IPRES Engineering, Ltd. Bratislava from domestic dolomite, bentonite, diatomic clays, alginite and zeolite, justified only with clinker and final pressurizing. Alginite fossil was from the southeastern Slovak deposit Pinciná and it is an ecological raw material which originates from the algae stock deposition.

Table 1. Overall View of All the Examined Adsorbents Toward a Broad Range of Model Pollutants (x—Positive Adsorption, Although With Various Efficiency).

adsorbent / pollutant	ammonium	metal cations	phenol	cefazoline	diclofenac	n-decane	m-cresol	Sb-species	acid red	phosphate	aluminum	orthosilicate	chromate	arsenate	nitrate	sulfate	halide
Beringite		x		x				x		x	x				x		
Shungite		x	x	x	x	x	x		x		x						
ODA-zeolite		x	x	x	x	x	x	x	x	x		x	x	x	x	x	x
Natural zeolite	x	x			x					x	x						
Active coke		x	x	x	x	x	x		x		x						
FeO(OH)-zeolite		x		x	x	x		x			x		x	x		x	
MnOx-zeolite		x						x			x		x	x			
Fe alginate-zeolite		x						x	x	x	x	x	x	x	x	x	x
Chitosan		x		x	x	x			x		x				x		
Chezacarb			x	x	x	x	x		x		x	x					
Nanofer					x		x	x		x							
Slovakite				x				x	x	x							
Montmorillonite			x						x	x							
Lignite								x									
Alginite		x				x			x		x						
Carbonized zeolite			x	x	x	x	x		x								
Absodan Peat SB 18				x	x				x								
Spillkleen SK2				x	x						x						
Spillkleen SK1				x													
Absodan DN 2			x		x												
GEH	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	

This fossil possesses a high humus content, macro- and micronutritive and trace elements with considerable dehydration ability, which supports its utilization as a soil fertilizer, pharmaceutical additive or environmental adsorbent. The superior adsorption performance of active coke may result from its large specific surface area and microporosity. Commercially available active coke is usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as a precursor for the fabrication of active coke. Coal is the most commonly used precursor for active coke production. This fossil is a mixture of carbonaceous materials and mineral matter, resulting from the degradation of plants. The adsorption properties of individual coal is determined by the nature of the original vegetation and the extent of the physicochemical changes occurring after deposition (low quality coal used to be classified as lignite). Carbonaceous fossil lignite was of domestic origin. The industrial ashes Chezacarb (amorphous carbon) was supplied from Chemopetrol Litvínov (Czech Republic). Beringite is basically aluminum silicate rock made up of albite, barkevikite and orthoclase [18,19].

Table 2. The mineralogical and chemical composition of the clinoptilolite from the open pit mine Nižný Hrabovec (left) and principal sketch of clinoptilolite framework (right), columnar model of 2-dimensional channel arrangement of HEU framework; tabular crystal shapes of clinoptilolite (surface morphology) and basic tetrahedra unit at the top.



Species %	
clinoptilolite	70-85
volcanic glass	15-20
feldspar	7-10
cristobalite	2-4
alfa-quartz	2-3

Oxides %		Metals %	
SiO_2	67.16	Zn	0.0024
Al_2O_3	12.3	Ba	0.0353
CaO	2.91	Pb	0.001
K_2O	2.28	Sr	0.01
Na_2O	0.66	Cs	0.0004
Fe_2O_3	2.3	Cr	0.0008
MgO	1.1	Cu	0.0002
P_2O_5	0.11	Ni	0.0001
MnO	0.14	Co	0.0001
TiO_2	0.17	Cd	0.00005
H_2O	10.9	Fe	0.9
		Ag	0.003
		Al	6.3

Nanofer is commercially produced Fe(0) (Zero Valent Iron - ZVI) stabilized in the aqueous suspension by Nanoiron, Ltd. Rajhrad (Czech Republik). It has been successfully applied for large scale remediation process at several industrial regions. Commercial Absodan and Spilkleen products (Great Britain) are composed from natural resources, like cellulose, calcium carbonate, clays and natural silicate minerals. Peatsorb means high-quality peat. Peat consists of lignin, cellulose, fulvic and humic acids as major constituents that bear polar functional groups, such as alcohols, aldehydes, ketones, phenolic hydroxides and ethers, being used in chemical bonding. In the last decade, chitin and its deacetylated product chitosan respectively appear as potential biosorbents, too. Chitosan possesses appropriate mechanical strength, rigidity and settling characteristics, which are a perfect alternative to other adsorbent-biomass, despite fragile structure and poor mechanical strength. Chitin is found in fungi, arthropods and marine invertebrates. Shungite is a natural carbonaceous mineral with amorphous structure, abundant in West Russia. Recently it has been stated that the mineral has important amount of fullerenes, mainly C60. Shungite rocks are characterized by highly dispersed silicate mineral grains distributed in the shungite carbon matrix. It may replace coke, graphite, carbon black and serve as a complex raw material, quite effective also in water treatment processes [15,20].

ZEOLITE-BASED NANOCOMPOSITES

Colour recorded rows in the Table 1 mean surface modified zeolites, accomplished in order to enhance their cabilities for as much as broad spectrum of pollutants (Fig.1). While the sol-gel process was suitable wet route for the synthesis of hydrophobized, i.e. surfactant coated ODA - clinoptilolite, carbonized zeolite was prepared in a pilot scale plasmachemical reactor (pyrolytic chamber) installed at the laboratory, using the waste vegetable together with some twigs of garden or park bushes. In that case clinoptilolite was actually chosen as the interface carrier for amorphous carbon, beside some individual carbon nanotubes explored. While surface carbonization by means of carbonaceous biomass pyrolysis provided the host zeolite rock with an embedded carbon layers of about 5 μm thickness in various surface interstitial spaces and cavities, the hydrophobization with octadecylammonium (ODA) surfactant provided the host zeolite with various structure of ODA aggregates, which thickness was of one order of magnitude lower than those of carbonized zeolite [21]. Some interesting remarks of living cells are based on the excretion of biogenic surfactants or specific biopolymeric acids like alginic acid and their salt alginate. Alginate is a copolymer of the isomers mannuronic and guluronic acids. These biogenic compounds enhance colloidal stability and the dense packing of submicrometer-sized particles in natural suspensions.

Fig. 1. Illustration of zeolite based adsorbents synthesized at laboratory. FeO(OH)-MnOx-zeolite, Fe(III)alginate zeolitic beads, ODA-zeolite and carbonized zeolite (from the left to the right).

Also clinoptilolite was combined with biogenic alginate to obtain an amphoteric product with specific properties. Thus, the flexible component alginate biopolymer with a rigid component (powdered) zeolite was crosslinked using Fe(III) and Ca(II) salts. While Fe(III) cationic sites of new pelletized biosorbent are in process of water purification responsible for electrostatic uptake of oxyanionic pollutants, exchangeable Ca cations from inside structure work as cation exchanger. According to aforementioned, such alginate–zeolite composed adsorbent is enhancing considerably the uptake performance of zeolite as well as stabilizing its overall technological properties [22]. Scientists developed a model for surface-induced metal oxide formation and have used this as a guiding principle for the synthesis of metal oxide nano-particles in other natural or engineered architectures. Many iron oxyhydroxide or bimetallic iron oxyhydroxide-manganese polyoxides coated zeolites since the last several decades have been synthesized to upgrade natural zeolite properties toward environmental pollutants, respectively. Metal oxides based adsorbents are effective, low cost adsorption materials for heavy metals and other pollutants removal together with pathogen detection. Their sorption process is mainly controlled by complexation. When their particle size is reduced to below 20 nm, the specific surface area of normalized adsorption capacity increases 10-100 times, suggesting a „nanoscale effect“. They may be combined with other carriers or pelletized or enriched with a broad range of functional groups and thus separated magnetically. Current immobilization techniques usually result in significant loss of treatment efficiency. Therefore, research is needed to develop simple, low-cost methods to immobilize nanomaterial without significantly impacting their performance. Nevertheless, to overcome a potential human risk from environmental spreading, nanomaterials need to be embedded in a solid matrix, respectively, to have minimum release until they are disposed of. Due to the very high price of commercial Fe-oxyhydroxide (GEH) on our market, which was quite frequently used for As and Sb removal from some underground water reservoirs in Slovakia, we prepared and compared the chemically pretreated FeO(OH)-zeolite with the above GEH product. Biomimetic sol-gel synthesis in alkaline solution of iron (III) nitrate nonahydrate was used for ecnomically feasible FeO(OH)-zeolite preparation, while grain-sized zeolite based on nanoporous structure and its channel dimensions of (0.33 x 0.46 nm; 0.3 x 0.76 nm and 0.26 x 0.47 nm) served during this synthesis as template or nanoreactor [23]. Active surface induced removal of aqueous Mn(II) and Fe(II) pollutants onto silicious sand or gravel coated with catalytically affecting high valency manganese sesquioxides have been in water purification process applied for decades. Therefore, also the MnOx-zeolite, prepared by simple and inexpensive redox-synthesis at ambient temperature using the contacting the grain-sized zeolite with the 5% $KMnO_4$ solution, was compared with above mentioned products. An zeolitic nanocomposite may be defined hereto as a combination of a various, potentially nanosized substance immobilized onto surface of the inorganic e.g. zeolite carrier to avail advantages of both zeolitic and embedded constituents as well. Accordingly, such technique can be used to modify organic or inorganic materials and such hybrids should therefore be considered as the new generation of composites that may encompass a wide variety of applications [14]. The conversion of inorganic ion exchange materials into hybrid nanoscale ion exchangers is considered to be now-a-day the latest development of discipline. The nanomaterials are drawing a great attention as they exhibit a high efficiency and rate of sorption with short diffusion path toward environmental pollutants. Advances in nanoscale science and engineering are today providing unprecedent opportunities to develop more cost effective and environmentally acceptable water purification processes, respectively. Finally, for the water purification, besides the metal-containing nanoparticles, carbonaceous materials and dendrimers, also the zeolites are being evaluated recently as the most progressive functional and nanosized materials of this millenium.

BRIEF FEATURES AND PERFORMANCE DATA OF THE MOST EFFECTIVE ZEOLITE BASED ADSORBENTS

The above described investigations on zeolites (clinoptilolite) for the removal of various kinds of aqueous pollutants lead to the conclusion that this natural resource can be considered an alternative cost-effective adsorption material, either with or without surface treatment, depending on the type of water to be purified. Previously discussed chemical treatments necessary for the enhancement of their adsorption performance for various water pollutants would certainly increase the price of these commodities as a consequence of the use of chemicals and energy consumption, however, they are not as high as those of the currently marketed commercial products [15,21]. The graphical plots in Fig.2a)d), are a couple of examples that illustrate considerable increasing of uptake capacities toward Cs^+ and I^-, especially when natural clinoptilolite was simply and inexpensively ion exchanged into Na^+ and Ag^+ forms. On the other hand, the use of ODA surfactant or alginate biopolymer for zeolite benefication, caused the increasing of uptake capacity, respectively, however, for their energy consuming synthesis, more complicated chemicals were required (Fig.2b)c)). In contrast to the clays, the surface of which has so far been coated with surfactant modifiers, natural zeolitic minerals modified with hydrophobic long-chain amines present a fairly new potential in water protection, especially due to their superior hydraulic characteristics, which are absent in clays.

The presence of surfactants, usually quaternary ammonium salts, such as hexadecyltrimethyl-ammonium chloride (HDTMA), cetylpyridinium chloride (CPC) and others on solid zeolitic surfaces can enhance and also univerzalise their adsorption properties for different nonpolar organic pollutants and inorganic anions as well. Long-term, experimental work has confirmed the high affinity of Slovak clinoptilolite toward Cs^+ and Ag^+, therefore, this natural zeolite was recommended as an excellent adsorption and ion exchange material, preferably for remediation processes of environments impacted by nuclear accidents [15,25].

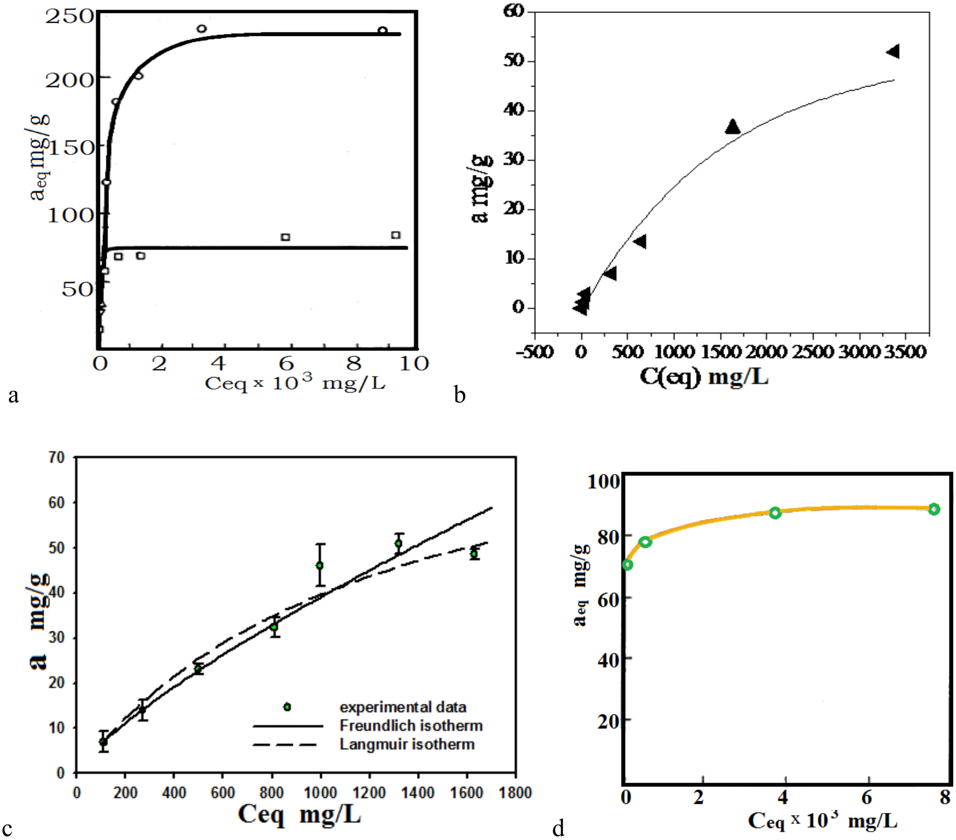


Fig. 2. a) Ion exchange isotherms for Na- and natural clinoptilolite vs. CsCl solution (downwards); b) Adsorption isotherm for ODA-clinoptilolite and arsenate solution; c) Adsorption isotherms for nitrate and Fe-alginate zeolitic pellets; d) Adsorption isotherm for Ag-clinoptilolite and KI solution.

Indeed, natural zeolites (mainly of clinoptilolite type) were used effectively for the cleanup of the nuclear reactor disaster at Chernobyl (former USSR) in 1986 and for the remediation of the environment after this nuclear accident. Most of the ca. 500,000 tons of zeolite were used for the construction of barriers that limited the spread of radionuclides, as well as for remediation activities, such as filtering of drainage waters from the encapsulated reactor, decontamination of the Dnieper River water, and reduction of cesium activity levels in agricultural and veterinary products [24,25]. Studies showed that a mixture of some natural minerals, such as bentonite, mordenite, and clinoptilolite in the form of compact layers with a thickness of some tens of centimeters may satisfactorily act as buffer materials to protect against radioactive contamination for many years. In this context, natural zeolites are employed as a natural barrier for the migration of radionuclides in the polluted areas around nuclear power station accidents or where nuclear weapons have been stored, such as Chelyabinsk (Russia), Semipalatinsk (Kazakhstan), and Krasnoyarsk (Siberia) [26]. A combination of raw, surfactant-modified, and Ag-impregnated herschelite, which included a Na-zeolite with a chabazite structure, was also utilized, along with coagulation, sedimentation, and desalination for the removal of Cs^{137}, Sr^{90}, Tc^{99m}, and I^{129} from saline radioactive waters after the accident at the Fukushima Daiichi Nuclear Power Plant (Fig.2a)d)) [28]. A zeolite based permeable barrier (PRB) was also designed in Russia to prevent the further migration of Cs-137 and Sr-90 from the site of the underground nuclear explosion "Kraton-3", which was conducted for peaceful purposes in 1978. Investigations during the period 2007-2008 showed the presence of Cs-137 and H-3 in the water of the region. Zeolitic tuff from Khonguruu (Yakutiya) containing 70% - 95% HEUtype zeolite (clinoptilolite) was selected for the PRB on the basis of laboratory and modeling studies [26,27]. Fig. 3 below displays the surface morphology of the natural clinoptilolite and ODA surfactant coated clinoptilolite using the Atomic Force Microscopy (AFM) and the Scanning Electron Microscopy (SEM). Photomicrographs of the clinoptilolite tuff shows well-defined, tabular-shaped crystals with excellent crystal edges. When surface coverage with the polymeric ODA surfactant occurred, smaller, more agglomerated crystals and more poorly defined crystal edges were observed in about 1-µm scale SEM image. The apparent sharpness of the image decreased with increasing surfactant coverage (Fig.3 right).

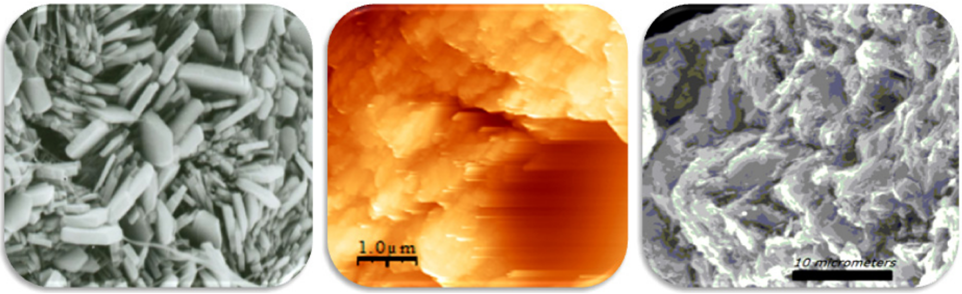


Fig. 3. SEM micrograph of raw clinoptilolite tuff from Nižný Hrabovec (East Slovakia) - magnification of 3700 X, AFM of ODA-clinoptilolite tuff, SEM of clinoptilolite tuff hydrophobized with octadecylammonium surfactant (ODA) (from the left to the right).

The SEM image of the synthesized beads of alginate pelletized clinoptilolite in Fig.4 displays a rough, nearly ropes-like surface morphology, and thus a profound change of the original tablets of the natural clinoptilolite morphology. Some examination of the SEM micrograph indicates the presence of many pores, cracks and oval shapes objects on the surface, too. Several swollen, alginate-pelletized, clinoptilolite beads were observed, especially after a curing the beads in calcium or iron solutions overnights.With regards to both micrographs (SEM) and (STM) in Fig.4, considerable difference of the morphology could be observed. Scanning Tunneling Microscopy STM did not display the clinoptilolite surface with such as sharped edged crystals as the Scanning Electron Microscopy did, however, with regards to the rounded ones, the typical layered texture remained also by the STM micrograph for alginate pelletized clinoptilolite. According to the AFM image and 2D topography, the surface texture of (FeIII) alginate pelletized clinoptilolite presents sharply edged parallel rods growing from the beads inside to the outer surface, what was observed in the 3D topography and phase image as well.

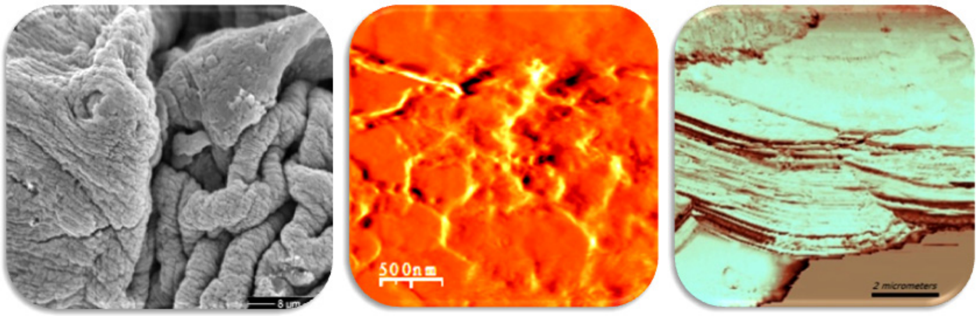


Fig. 4. SEM, AFM and STM micrographs of Fe-alginate pelletized clinoptilolite tuff (from the left to the right).

PILOT WATER AND WASTEWATER DEAMMONIFICATION ONTO CLINOPTILOLITE TUFF

FIXED BED EXPERIMENTS SCENARIO FOR AMMONIA REMOVAL

In this section, a special attention is focused on the clinoptilolite´s competitive effectivity, environmental availability, and economic feasibility in specific ammoniacal nitrogen removal from various water and wastewater streams. While at the end of the nineteenth century biological treatment of wastewater accounted mostly for organic matter (biological oxygen demand) removal and had not significantly progressed beyond then, after World War II, the rapid technological development of biological deammonification, i.e. nitrification and denitrification has become remarkable. In general, the environmentally acceptable biomimetic solutions have been considered since that time among the latest trends of development for all the water cleanup processes. Specifically, for the complementary or tertiary removal of ammoniacal nitrogen from the wastewater, in other words the subsequent polishing step, also adsorption/ion exchange onto natural clinoptilolite, as highly selective toward ammonium, has been alternatively applied [6,15,26-28]. Most of the considerable progress and research regarding sorption processes can be performed through laboratory-scale with either a batch mode or fixed bed mode. All the equilibrium data derived from the batch mode do not directly correspond with wastewater treatment plants, where most ion exchange and adsorption processes operate through fixed bed columns. A fixed bed scale can provide more useful insights into sorption equilibrium and dynamics, which are necessary for predicting column behaviour in large scale operations. Fixed bed column efficiency is usually appraised through two important concepts, which are breakthrough and exhaustion points calculated from exit concentration versus time or bed volume (BV). Determination of the above mentioned points is required for providing the fundamental data necessary for successful design of a continuous adsorption system. Complete (total) exhaustion occurs when the concentration of effluent equals the concentration of influent. Breakthrough time, curve shape, exhaustion time and ion exchange properties strongly depend on a variety of operational parameters, such as bed height, flowrate, influent concentration and chemical composition of adsorbent. The breakthrough curve gives insights into the fixed bed column performance by plotting (C/C_0) on the Y-axis against time (in min, hr) or against BV on the X-axis. Basically, nanomaterials based adsorbents can achieve the requirements of a green circular economy since it is characterized by admirable physicochemical characteristics, such as a large surface area, numerous surface active sites, high sorption efficiency, low cost, environmental compatibility and recyclability. From economic and environmental perspectives, reusability of saturated (spent) sorbent is of great importance because it is considered a true criterion for judging the sorbent quality and its applicability for large industrial scales through consecutive sorption/desorption cycles. A successful operational desorption process is not limited to reducing the overall cost of such used processes, but also paves the recovery of extracted substances captured from examined aqueous solutions (i.e. tannery process), hence using them as feedstocks for various industrial sectors. Fundamentally, an effective regeneration (recovery) process depends on adsorbent type, adsorption mechanism, and an appropriate desorption scenario [11,15]. Fig.5 illustrates some experimental data measured at the laboratory for ammonia removal from drinking and communal wastewater with Slovak clinoptilolite tuff, as well as after their saturation the zeolite regeneration curves using the 2% NaCl solutions [6].

Fig.5. The laboratory-scale experiments with fixed bed mode for ammonium removal from (a) drinking water with the flowrate through the zeolite bed 15 BV/h; (b) communal wastewater with the flowrate 40 BV/h; (c) ammonia elution curves from saturated zeolite beds depending on pH of 2% NaCl regeneration solutions; (d) comparable efficiency for ammonia elution from zeolite bed using the 0.3 M NaCl and 0.004 M $Ca(OH)_2$ regenerants; (e) ammonia elution efficiency from the zeolite bed upon the numbers of regenerant´s BV.

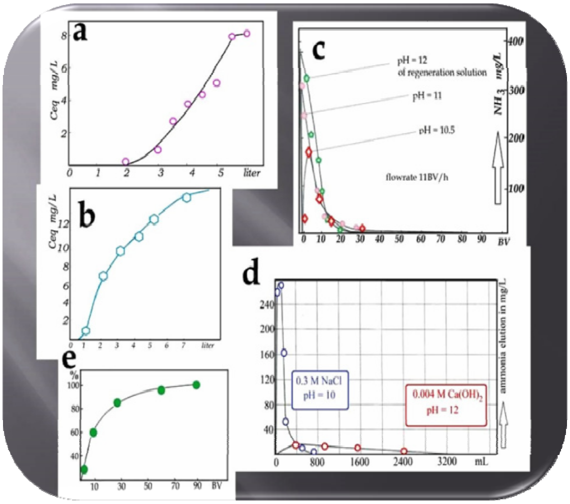


Fig.5 a) outlines a typical S-shaped breakthrough curve obtained by filtration of synthetically prepared tap water with a high concentration of NH_4^+ (8 mg/L) across a clinoptilolite column with the flowrate of 15 BV/h. A rather long adsorption zone with up to 2L of water treated without any ammonium leakage was recorded. Full saturation or exhaustion of a zeolite column with ammonium was observed after filtration of 6 L of water, when the influent and effluent ammonia concentrations were equalled. In another case, an untypical breakthrough curve was plotted after a lab-experiment with real communal wastewater treated for ammonia removal onto a clinoptilolite column, most probably due to a high flowrate of water filtration, i.e. 40 BV/h (Fig.5b). The initial ammonium concentration in the wastewater equalled 17 mg/g. The first leakage with very low ammonium concentration through a zeolite bed occured after filtration of a half liter of this water, the filtration of another half liter caused leakage with the ammonium concentration in the effluent of 1 mg/L, and filtration of 9 L of communal wastewater saturated the clinoptilolite column thoroughly. In most industrial operations, zeolite columns are usually regenerated with 2 – 5% NaCl solutions in order to use the zeolitic bed as long as possible. Therefore, several attempts on how to regenerate the inland clinoptilolite bed most effectively were proposed in laboratory before the pilot operation in field or at wastewater treatment facility was implemented. Fig.5c) clearly demonstrates the tendency to increase ammonia elution from the zeolite bed with an increase of pH in the most frequently used 2% NaCl regenerant solutions (Fig.5c). Despite the best result with the ammonia elution, which used a quite agressive pH = 12, these strong alkalic solutions pose a negative impact on the aluminosilicate skeleton by gradual dealumination and destruction of the zeolite structure. Based on this fact, lower pH values of regenerant solutions are recommended. Two types of regenerants, which differ from each other in regard to concentrations about 100-times, where the low and very economic 0.004 M $Ca(OH)_2$ lime was alkalized with strong NaOH to pH = 12 and thus enriched with additional Na ions, and the other commonly used and relatively costly 0.3 M NaCl of pH = 10 were examined for elution efficiency. Fig.5d) clearly illustrates a much higher efficiency of 0.3 M NaCl solution to exchange ammonium out of zeolitic channels and cavities, probably due to a higher affinity of clinoptilolite toward Na ion, as well as its higher concentration gradient. Moreover, the use of economic lime for filter regeneration is usually excluded due to the identification of unwanted calcium carbonate between zeolite grains, causing a so-called „chanelling effect“ or filter plugging. The last experimental results plotted in Fig.5e) concern the dependence of the numbers of bed volumes loaded across the column to eluate ammonia and thus prepare the column for a new cycle in ammonium removal. It was found that regenerating a zeolite filter by 70 - 80% (20 – 30 BV) or eluating the ammonia out of the loaded zeolite bed by this efficiency was satisfactorily for maintaining a solid time schedule and the required water quality (Fig.5e). Industrial ion exchange facilities with chemical regeneration prefer such as schedule as well. The time and solution consuming 100% regeneration process is thus useless due to the unfavourable economy. As can be seen from the curve in Fig.5e), there is only about a 15% difference in elution performance between the 30 and 90 BV, as extrapolated along the X-axis [6,7,10,15].

PILOT DEAMMONIFICATION OF DRINKING WATER WITH OVERLIMITTED AMMONIUM CONCENTRATION

During the autumn 1986, the zeolite ion exchange pilot installation (ZIEPI) with a hydraulic loading rate of 900 L/h (~13 Bed Volumes BV/h) was situated at the field experimental facility of Water Research Institute in Vajnory, the closed vicinity of Bratislava. This pilot facility treated the tap water which was enriched by ammonium chloride to the initial concentration of 1 mg/L ammonium. Two pressure steel columns operating in series, each one filled with 70 L or 56 kg of clinoptilolite of size-granulation 0.4-1 mm, as the part of above desribed pilot facility, provided the drinking water purification with the high efficiency for several weeks. Bottom of each column was filled with 14 L of about 3 mm grain-sized sand as the drainage support layer. The zeolite filters were operated in downflow mode during the common working service and upflow mode during the chemical regeneration. For the chemical regeneration of the loaded zeolite filter 2% NaCl solution of pH ~9 was used. Two hours lasted chemical regeneration required approximately 25 BV of 2% NaCl solution. To regenerate a zeolite filter by 85% or to eluate the ammonia out of the loaded zeolite bed by this effectivity was satisfactorily for maintaining a solid time schedule and the required water quality. To provide a permanent running of the whole facility (ZIEPI) and the uninterrupted water purification, ammonia exhausted regenerants thereafter needed to get recovered by means of air stripping, to be again recycled for filter regeneration. HDPP plastic tower of the total height 6.5 meter, assembled from 6 modules of the ground-plane measures 980 x 650 mm, was applied for ammonia stripping. To strip ammonia out of the regenerant brine a large quantity of air through the tower was necessary, therefore the design of stripping tower was improved by installation of two lateral air blowers at its bottom module (each one with the blowing capacity of 450 L/s). Stripping ammonia out of the exhausted regenerant solutions was then processed in countercurrent tower configuration, by which the entire air flow entered the bottom, while the treated regenerant was pumped to the top (with the same hydraulic loading rate as into the ZB, *i.e.,* 900 L/h) and falled across the vertical waves-like shaped laminated slats to the bottom of the tower. The whole regenerant volume was air stripped without the mass closed loop operation, because the ZIEPI with the rather low operation capacity did not affect the surrounded air quality in that time significantly. Therefore, the stripped ammonia was at that pilot facility discharged only into atmosphere, however the higher-grade facility would need to be provided already with ammonia recycling. The entire volume of regenerants (1800 L) was recycled through the tower during 150 minutes to decrease the initial ammonia concentration of 50 mg/L to less than 10 mg/L. In the first stripping cycle 47% of ammonia was stripped out, therefore also the second stripping cycle was necessary [29,15].

Fig. 6. Laboratory pilot for ammonium removal out of the simulated drinking water (upper left photograph) and typical breakthrough curves during the process studied (left down). Principal sketch of zeolite ion exchange pilot installation (ZIEPI) situated at the field experimental facility of Water Research Institute (right down).

The major factors which affected design and process performance of air stripping tower were the tower configuration, the air flow and the pH. For recovery of 1L of regenerant solution the consumption of 3.8 m^3 air was necessary. To maintain pH ~ 11 of regenerant solutions in stripping process and to compensate some loss of sodium ions in regenerant effluents, regular addition of NaOH into effluents was provided during the operation of ZIEPI. Under above described operation, one zeolite column was able to treat 85 m^3 of drinking water with enhanced ammonium concentration up to the limited value of 0.5 mg/L (the laboratory equipment only a volume of 675 L), which means that the 4 days operated zeolite filter removed 81 gram of ammonium from the whole treated volume of water. The operation principle of two pilot zeolite columns (zeolite beds ZB) was as follows: Single or one ZB was under the operation service till the ammonium concentration in effluent reached the limited value of 0.5 mg/L and then the second new ZB was connected with the first one in series to load the capacity of the first ZB totally. When the first ZB was loaded to its maximum capacity, the column was disconnected from the operation in series and started to get regenerated, while the second ZB operated as single column. There was sufficient time for ammonium loaded ZB to get regenerated and to prepare it for the sequenced operation in the next process of drinking water purification. The longer time operating ZB was used to be joint in series always at the inffluent end, backed up by another ZB with lower loading level. Using this strategy of operation, the number of bed volumes throughput (volumes of treated water by ZB) during the operation service increased effectively by about 50%. A half an hour of ZB backwashing using the tap water to about 30% bed expansion followed the chemical regeneration with alkalic NaCl solution additively, as a requirement to decrease pH of the treated water filtered through ZB, which remained due to its contact with the alkalic brines. In the year 1986, the cost of 1 m^3 water treated by means of ion exchange onto the clinoptilolite tuff including chemical regeneration and regenerant recovery by air stripping, was calculated to 0.37 Czechoslovakian crowns (0.012 Euro), however in respect to that time low electricity price, this total cost of water purification was low. To the total cost the consumption of zeolite, chemicals, energy for pumping, air stripping, filtering and backwashing was calculated. Any pathogenic microorganism occurence during the water purification by this method was detected. According to the hygienic and sanitary expertise performed this aluminosilicate was not classified as toxic or carcinogenic and it did not proveany oral or dermal toxicity [30]. Some standardized fibrogenity procedure using the intratracheal application of powderized zeolite with less than 5 µm grain-size in physiological solution was tested by means of the rat species Whistar, respectively. Only less than 3% of respirable, pure SiO_2 (free quartz) content in the zeolite samples was identified. Based upon this fact it was concluded that above content may not expose or endanger the human health during the treatment process. Moreover, epidemiological studies to date have not revealed any evidence of a relation between exposure to natural clinoptilolite and diseases of the respiratory tract beyond general effects of dust [31]. Despite the positive results presented, the technology of ion exchange by clinoptilolite tuff has not been applied industrially since that time in Czech or Slovak Republics, probably due to a very rare occurrence of such a specifically polluted drinking water collectors [15].

PILOT TANNERY WASTEWATER DEAMMONIFICATION ONTO CLINOPTILOLITE TUFF

Similar operation with the same hydraulic loading rates through the zeolite beds as by the drinking water purification units was used for ammonia removal of mixed tannery and sewage sludge wastewater at Shoe Manufactury Wastewater Reclamation Plant in Otrokovice (former Czechoslovakia) in the 1987.

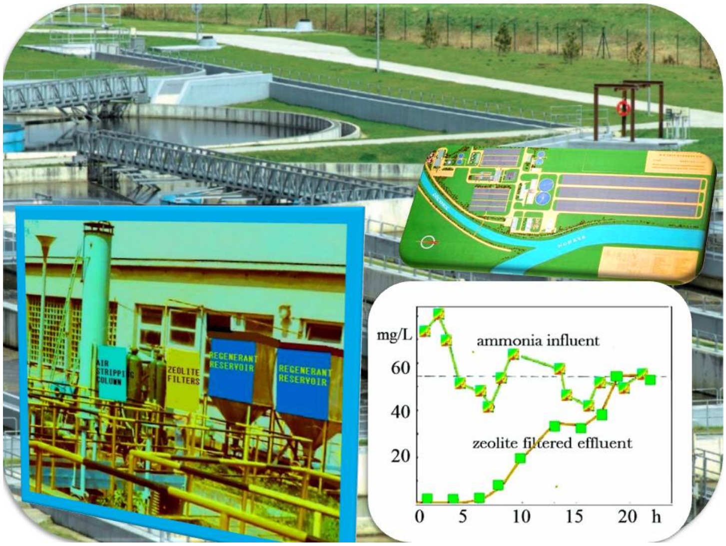


Fig. 7. Pilot ammonia removal with clinoptilolite tuff of mixed tannery and sewage wastewater at Shoe Manufactury Wastewater Treatment Plant in Otrokovice (former Czechoslovakia) in the 1987 (left). An original design layout of Sewage Treatment Works in Otrokovice with closed Drevnice and Morava rivers (upper right). Graphical recording of ammonium influent and effluent concentrations during the column filtration in WWTP Otrokovice (right down).

A higher ammonium concentration in wastewater (in average 50 mg/L) increased the ion exchange capacity of zeolite considerably (approximately 10-times higher in regard to the drinking water purification) [32-34]. Three columns operation (two ZB under stream while the third ZB being regenerated) as well as much more complicated management of the entire ZIEPI valving and piping was required at this wastewater treatment facility. Comparing to the sufficient long, *i.e.,* 4 days lasting drinking water service of ZB, ammonia removal from the wastewater by ZB reached the limited value of 3 mg/L in effluent already after 15 h. Consequently, the time of regeneration including ammonia stripping was necessary to shorten to get the entire operation system permanently running. The 3-fractional regeneration and adequate ammonia stripping process used for regenerant recovery and recycling in this zeolite ion exchange pilot installation was therefore proposed. Only the highest, on ammonia mostly concentrated elutriant solution was stripped in air stripping tower. Ammonia stripping process was intensified and considerably shorten by the injection of the mixed hot waste steam and air (1: 3) at the bottom of the tower against the regenerant solution pumped to the top of this tower (Fig.7). The stripped ammonia was proposed to get absorbed into water to produce the technological grade solution to be recycled. For the recovery of 1 L of highly concentrated elutriants (regenerant solution) the consumption of 20 m^3 air was necessary. After several months of ZIEPI operation, the Centroproject Zlin provided, based on the submitted pilot experimental data, some economic calculations for model capacity of treated wastewater 6000 m^3/day. At that time the investment for the construction of zeolite ion exchange and regeneration and air stripping recovery units for the proposed capacity was calculated 550 000 Euro, whereas the investment for ammonia removal by means of biological nitrification -

denitrification method was estimated 700 000 Euro. Nevertheless, the operation cost of ion exchange technology using the natural zeolite per one cubic meter of treated water was a bit higher than the operation cost of the comparable biological nitrogen removal using the nitrification-denitrification method. Concluding, the examined technology of zeolitic ion exchange appeared technically and financially competetive to the traditional biological methods. TOMA industrial Facility and the whole municipality in Otrokovice delivers up to 55 000 cubic meters of wastewaters per day, while conventionally treating with activated sludge process a volume of 18 000 m^3/ day (200 L/s), therefore the process of zeolite ion exchange including regeneration and air stripping by mass closed loop operation was designed for the entire capacity. The proposed wastewater treatment plant consisted of three series of zeolite beds (ZB) or pressure columns, each of sets composed from five ZB (1 pentade), with the zeolite weight per one bed 8 tons. The set of 5 ZB was proposed to operate simultaneously. A large air stripping tower (total volume of 140 m^3) with the same elutriant loading rate as the ZB filtration rates, *i.e.,* 40 L/s, was proposed to provide elutriants recovery, while consuming 80 m^3/s air, by regeneration and air stripping of 1 ZB lasting not longer than 3 h.

CONCLUSIONS

The above described investigations on zeolite (clinoptilolite tuff) for the removal of various kinds of aqueous pollutants lead to conclude that this natural resource can be considered as an alternative cost-effective adsorption material, either with or without surface treatment, depending on the type of water pollutants. Natural zeolite may be advantageously proposed especially for complementary water purification. Mostly surface untreated clinoptilolite based rock can compete with other natural materials or even waste products, as occurring in the markets at very low prices. Previously discussed chemical treatments necessary to enhance their adsorption performance for various water pollutants would certainly increase the price of these commodities as a consequence of the use of chemicals and energy consumption, however, by far not as high as those of the currently marketed commercial products.

ACKNOWLEDGMENTS

The author thanks for the cooperation by pilot ammonia removal with clinoptilolite tuff of mixed tannery and sewage wastewater at Shoe Manufactury Wastewater Treatment Plant in Otrokovice to facility and operation managers J. Švancer, M.Eng. and J. Konečný, M.Eng. as well as Dr. Z. Bošan, PhD.

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THE STATE OF THE SURFACE WATERS OF THE NORTH-WESTERN BLACK SEA COAST

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ABSTRACT

This section presents the general assessment results of a state of the surface waters in the North-Western Black Sea region according to a complex of indicators of a surface water quality and technogenic loading on the water bodies. The assessment and classification of the surface water quality using the various methodological approaches, as well as the assessment of the technogenic loading based on the calculation of the technogenic load module on the water bodies.

Keywords: water bodies, quality, assessment, technogenic loading, module.

INTRODUCTION

The regions of the North-Western Black Sea Coast (NWBSC), which include the Odesa, Mykolaiv and Kherson regions of Ukraine, are multifunctional territories. They are used for agricultural, industrial, transport, maritime, recreational and other purposes. Within this area there is a significant number of technogenic objects that adversely affect the condition and the quality of the components of the environment, including the surface waters. The area covers the lower parts of the Danube, Dniester, Southern Bug and Dnieper basins, the coastal zone of the northwestern part of the Black Sea with estuaries and is used mainly for agricultural, fishery and recreational purposes [1].

The assessment of a state of the surface waters in the NWBSC regions is a subject of a long-term research for many scientists, including the authors [2, 3]. These are the works concerning the complex estimations of the Odessa region water resources as a whole and the separate objects, their hydroecological condition [4 – 6], the works which are devoted to the estimation of the qualitative characteristics of the Odessa region rivers and lakes [7 – 11]. Some works relate to the methodological aspects, namely improving the methods for assessing the surface waters quality [12, 13]. Also in the work [14] a general estimation of a surface waters quality in the Mikolayiv region for a long-term period is presented, in the work [15] a new approach to estimating the ecological risk of the water objects deterioration is offered, and also a state of the Ingulets river basin within the region is analyzed.

METHODS AND EXPERIMENTAL PROCEDURES

Several methods for assessing a water quality, which we believe are optimal for using, have been identified. Such methods included a graphical method, a method of assessing the land surface water quality by the hydrochemical parameters, a method of assessing the ecological state of the water bodies by the content of *Biochemical Oxygen Consumption*$_5$ *(BOC*$_5$*)*.
The graphical method is based on drawing up a graphical model of a surface water quality, which is a cyclogram with scales-radii corresponding to a certain hydrochemical index. The division value of each radius is equal to a maximum value of the indicator concentration, which determines a water suitability for a particular type of water using [16]. The application of this method makes it possible to determine simultaneously an excess of the maximum permissible concentration (*MPC*) by the content of all quality indicators, which are monitored.
The method of assessing a land surface water quality by the hydrochemical parameters [17] allows to perform a comprehensive assessment of a surface water quality using the combinatorial pollution index (*CPI*). It allows you to take into account any list of indicators and to determine a water quality based on the number of indicators.
The assessment of a state of the water bodies by the content of BOC_5 [18, 19] is an indirect tool for determining the ecological state in the absence of systematic data by the hydrobiological quality indicators.
To assess the technogenic loading on the surface waters, a module of technogenic loading on the water bodies (M_{WB}) by the indicators of the return waters and pollutants discharges in their composition was used. It is defined as a volume of wastewater or pollutants discharges (thousand tons) for 1 year, attributed to the area of the administrative district or the region [20].

THE RESEARCH RESULTS AND DISCUSSIONS

In the territory of the Odessa region the surface waters are distributed rather unevenly. The northern and central parts of the region are characterized by limited water reserves, and the south and the west, which belong to the lower parts of the Dniester and Danube basins, have significant reserves [21]. The drainage in the region is carried out into the Black Sea basin, the Dniester, the Khadzhibey and other estuaries, as well as into the surface water bodies.

The analysis of the pollutants in the composition of wastewater discharging into the water bodies of the region showed that the maximum volumes are observed for phosphates and dry residue, the minimum – for heavy metals, calcium and sodium.

The assessment of a surface water quality of the Odessa region using a graphical method was performed for the Danube and Dniester river basins. It can be noted that in the waters of the Danube basin during 2005 – 2018 there were exceedances of the *MPC* by fishery standards for the content of nitrites, manganese, copper and chromium (VI). The excess in the manganese content in all years was maximum. Thus, according to other studies [22], a high content of manganese in the Danube waters is characteristic. High concentrations of nitrites indicate a significant organic pollution of the Danube. According to economic and drinking standards, the maximum permissible concentrations were exceeded by the content of copper and, in some years, by the content of phenols.

In the waters of the Dniester river basin, according to fishery standards, there were constantly increased concentrations of sulfates, nitrites, iron, in some years phosphates, as well as the excess of the *MPC* for total mineralization. According to the economic and drinking requirements, constant exceedances of the MPC were observed in the total mineralization. Increased concentrations of nitrogen and phosphorus compounds in the waters of the Dniester basin are the result of agricultural activities.

Fig. 1 – 2 show the results of calculating the *CPI* in the waters of the Danube and Dniester river basins. The maximum value of *CPI* for the Danube basin surface waters (Fig. 1) according to

fishery standards was noted in 2017, the minimum – in 2018. From 2005 to 2017 there was a tendency to increasing the *CPI*. According to economic and drinking standards, the maximum *CPI* was noted in 2009. During the study period the index was ranging from 20 to 30 units (except in 2018). The marked in 2018 minimum for both types of water using is explained, first of all, by reducing the number of reviewed water quality indicators from 16 to 11. Also in 2018 there were no data on the content of indicators in the water, which almost constantly have the significantly exceeded *MPC* in 2005 – 2017, primarily by the fishery requirements (copper and manganese).

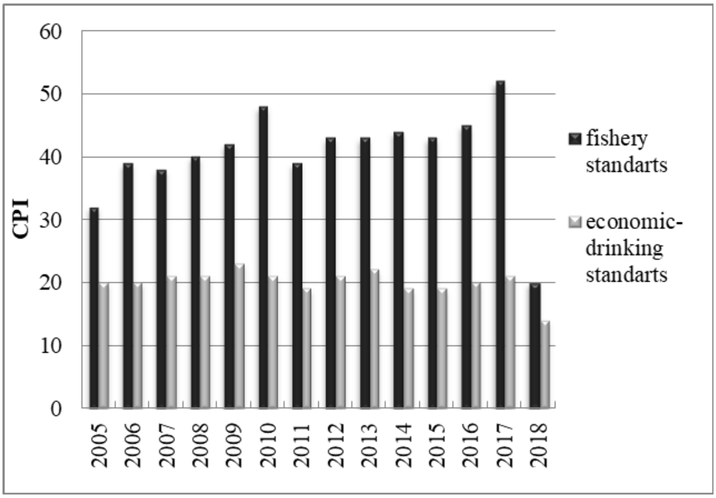


Fig. 1. The dynamics of changing the *CPI* in the waters of the Danube basin within the Odessa region

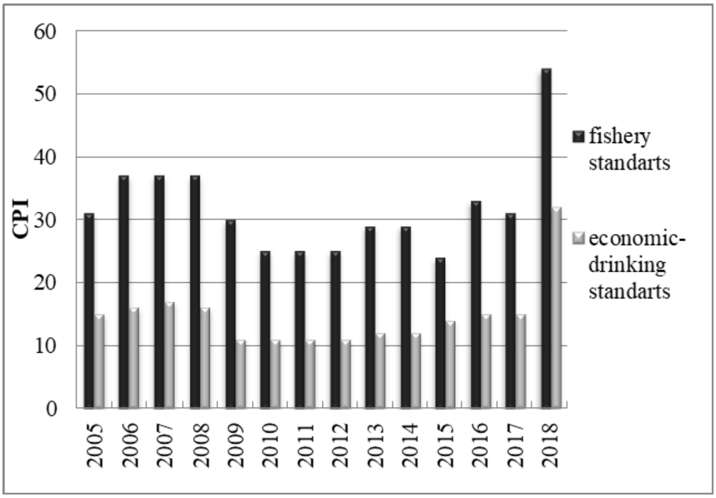


Fig. 2. The dynamics of changing the *CPI* in the waters of the Dniester river basin within the Odessa region

For the waters of the Dniester river basin (Fig. 2) by the fishery requirements, the maximum value of *CPI* was noted in 2018, the minimum was in 2015. In general 2009 – 2017 is a period of minimal pollution. According to the economic and drinking standards, the maximum *CPI* was also observed in 2018, the minimum values were observed in 2009 – 2012. These maxima for both types of water using were explained by increasing the number of reviewed water quality indicators in 2018, as well as a significant increase of the BOC_5 content in some observed sites.

Table 1 shows the results of the water quality classification in the Danube and Dniester river basins within the Odessa region. In general by the fishery standards, the water quality of the Dniester river basin is worse compared to the waters of the Danube river basin. The waters of the Danube basin are mostly characterized by quality classes IIIa – IIIb, category "dirty". The water quality of the Dniester river basin in different years is characterized by classes IIIa – IIIb (category "dirty") – IVa (category "very dirty"). According to the economic and drinking standards, the waters of the both rivers basins are characterized by the same indicators – class II, category "polluted" (except in 2018 for the Dniester).

Table 1 – The classification of a surface water quality of the Odessa region

Year	The Danube river basin		The Dniester river basin	
	fishery standards	economic and drinking standards	fishery standards	economic and drinking standards
2005	II, contaminated	II, contaminated	IIIб, dirty	II, contaminated
2006	IIIa, dirty	II, contaminated	IVa, very dirty	II, contaminated
2007	IIIa, dirty	II, contaminated	IVa, very dirty	II, contaminated
2008	IIIa, dirty	II, contaminated	IVa, very dirty	II, contaminated
2009	IIIa, dirty	II, contaminated	IVa, very dirty	II, contaminated
2010	IIIa, dirty	II, contaminated	IIIb, dirty	II, contaminated
2011	IIIa, dirty	II, contaminated	IIIb, dirty	II, contaminated
2012	IIIa, dirty	II, contaminated	IIIb, dirty	II, contaminated
2013	IIIa, dirty	II, contaminated	IIIb, dirty	II, contaminated
2014	IIIa, dirty	II, contaminated	IIIb, dirty	II, contaminated
2015	IIIa, dirty	II, contaminated	IIIb, dirty	II, contaminated
2016	IIIa, dirty	II, contaminated	IVa, very dirty	II, contaminated
2017	IIIb, dirty	II, contaminated	IIIa, dirty	II, contaminated
2018	II, contaminated	II, contaminated	IVa, very dirty	IIIa, dirty

The results of the assessment of the Danube waters by the value of BOC_5 are given in table 2. As it can be seen, in the vast majority a state of the Danube basin waters by the level of pollution is characterized by category "moderately polluted" and by the ecological state – a threshold stage. The data on the values of BOC_5 in the waters of the Dniester River were unsystematic. Thus according to the available data, a state of water in general is also characterized by the level of pollution by category "moderately polluted", by the ecological state – a threshold stage.

In the Mikolaiv region the problem of surface water objects pollution is also acute. Due to the lack of domestic and industrial emissions high-quality treatment, the situation in the region is significantly complicated.

In terms of surface water reserves, the Mykolayiv region belongs to the basins of the Southern Bug River, the Dnieper River and some rivers of the Black Sea region [23]. The region local water resources are very limited and depend on the inflows from other regions.

Table 2. The classification of the Danube water quality according to the value of BOC_5

Year	Pollution level	Ecological condition
2005	Moderately polluted	Threshold stage
2006	Contaminated	Stage of irreversible changes
2007	Moderately polluted	Threshold stage
2008	Contaminated	Stage of irreversible changes
2009	Contaminated	Stage of irreversible changes
2010	Moderately polluted	Threshold stage
2011	Moderately polluted	Threshold stage
2012	Moderately polluted	Threshold stage
2013	Moderately polluted	Threshold stage
2014	Clean	Stage of reversible changes
2015	Clean	Stage of reversible changes
2016	Moderately polluted	Threshold stage
2017	Moderately polluted	Threshold stage
2018	Moderately polluted	Threshold stage

According to the available data [24, 25], the maximum volumes of discharges are observed for such an indicator as dry residue. Also in recent years there has been an increase in discharges of nitrogen and phosphorus compounds.

The dynamics of changing the indicators of the Mikolayiv area surface waters quality was analyzed using a graphic method. In almost all the years, the maximum exceedances of the *MPC* in the waters of the Southern Bug River Basin by the fishery standards were noted for the content of copper and manganese. There were also significant exceedances of the *MPC* for fishery needs in terms of nitrites, phosphates, sulfates, total iron, zinc and nickel. The obtained data are consistent with the previous studies of the authors [26]. However the authors considered the Southern Bug water quality only for economic-drinking and communal purposes. According to economic and drinking requirements, the excess of *MPC* was noted in terms of chlorides, magnesium, total iron and the amount of surface water mineralization.

The calculation of the Mikolayiv region surface waters *CPI* (fig. 3) showed that according to the fishery standards the CPI value is 3 – 4 times higher than by the economic and drinking standards. In general for both types of water using there is a decrease in the overall level of water pollution from 2010 to the present. The minimum *CPI*, noted in 2016 and significantly different from other years (primarily by the fisheries standards), is the result of several reasons:

- reducing the number of analyzed indicators from 16 to 7;

- in 2016 the analysis did not take into account the substances for which there were previously constant and significant exceedances of the *MPC* (nitrites, magnesium, phosphates, total iron, copper, zinc, nickel and manganese).

On the basis of the received data the classification of the Mikolayiv region surface waters quality for the long-term period is executed (tab. 3). In all the years, except for 2016, the surface waters quality of the region according to the fishery standards is characterized by class VIa, category "very dirty", according to the economic and drinking standards – the only class II, category "polluted". Compared with the surface waters of the Odessa region, the waters of the Mikolayiv region are characterized by the worse quality according to the fishery standards.

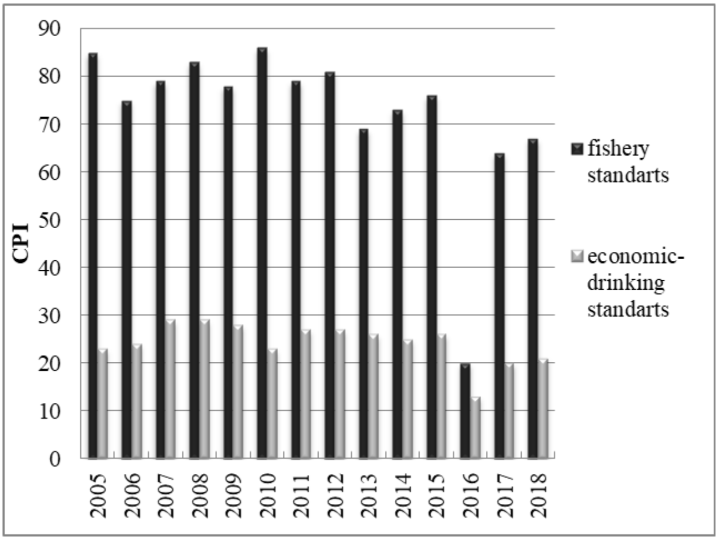


Fig. 3. The dynamics of changing the surface waters *CPI* in the Mikolayiv region

Table 3. The classification of a surface water quality in the Mikolayiv region

Year	Fishery standards	Economic and drinking standards
2005	VIa, very dirty	II, contaminated
2006	VIa, very dirty	II, contaminated
2007	VIa, very dirty	II, contaminated
2008	VIa, very dirty	II, contaminated
2009	VIa, very dirty	II, contaminated
2010	VIa, very dirty	II, contaminated
2011	VIa, very dirty	II, contaminated
2012	VIa, very dirty	II, contaminated
2013	VIa, very dirty	II, contaminated
2014	VIa, very dirty	II, contaminated
2015	VIa, very dirty	II, contaminated
2016	IIIa, dirty	II, contaminated
2017	VIa, very dirty	II, contaminated
2018	VIa, very dirty	II, contaminated

The results of the classification of the Mykolayiv region surface waters by the value of BOC_5 are given in table 4. As it can be seen the surface waters of the region by the level of pollution are mainly characterized by categories "moderately polluted" – "polluted", by the ecological state – a threshold stage and a stage of irreversible changes. Compared to the Odessa region, the surface water bodies of the Mikolayiv region are characterized by the worst ecological state indicators.

Table 4. The classification of the Mikolayiv region surface water quality by the value of BOC_5

Year	Pollution level	Ecological condition
2005	Moderately polluted	Threshold stage
2006	Clean	Stage of reversible changes
2007	Contaminated	Stage of irreversible changes
2008	Contaminated	Stage of irreversible changes
2009	Moderately polluted	Threshold stage
2010	Moderately polluted	Threshold stage
2011	Moderately polluted	Threshold stage
2012	Moderately polluted	Threshold stage
2013	Moderately polluted	Threshold stage
2014	Contaminated	Stage of irreversible changes
2015	Contaminated	Stage of irreversible changes
2016	Contaminated	Stage of irreversible changes
2017	Contaminated	Stage of irreversible changes
2018	Moderately polluted	Threshold stage

26 rivers flow through the territory of the Kherson region, including the Dnieper River with the Kakhovka Reservoir, the Ingulets River. The waters of the Dnieper feed the Kakhovka magistral canal and the North Crimean canal [27]. The largest water users in the region are agriculture and utilities, as well as industrial enterprises.

Sewage is discharged into the Kalanchak River, the Kalanchak Estuary and the Black Sea [28]. The maximum volumes of discharges according to [29, 30] data are observed for dry residue, sulfates and chlorides.

Analyzing the dynamics of changes in the Kherson region surface water quality indicators using the graphical method shows that in 2005 – 2008 there were significant exceedances of the MPC by the fishery standards (> 10 *MPC*) for nitrites, chromium (VI), copper and nickel. Maximum excesses were observed in the content of chromium (VI). Significant exceedances of the fishery standards were also noted in the content of sulfates, phosphates, manganese, values of BOC_5 and mineralization. According to the economic and drinking requirements, the excess of MPC was most often observed in such indicators as mineralization, BOC_5, nickel.

The increased content of nitrogen and phosphorus compounds in the water is a consequence of agricultural production in the Kherson region. The Ingulets River flows through the region, the chemical composition of its waters is formed under the influence of highly mineralized wastewater from the Kryvyi Rih iron ore basin.

The CPI of the Kherson region surface waters was calculated (Fig. 4). The analysis of the given figure shows that the maximum value of CPI for both types of water using was noted in 2008. This is explained by the fact that that year the number of analyzed indicators was maximum (17), that influenced the results of the *CPI* calculation. The index value for the fishery requirements, as for other regions of the NWBSC, is much higher than for drinking. In 2014 – 2015, there is a minimum *CPI*, which is caused by several factors:

- reducing the number of analyzed indicators to 10 – 11;

- a lack of available data when analyzing the indicators that significantly degraded a quality of the surface waters in the region (chromium (VI), copper, nickel, etc.).

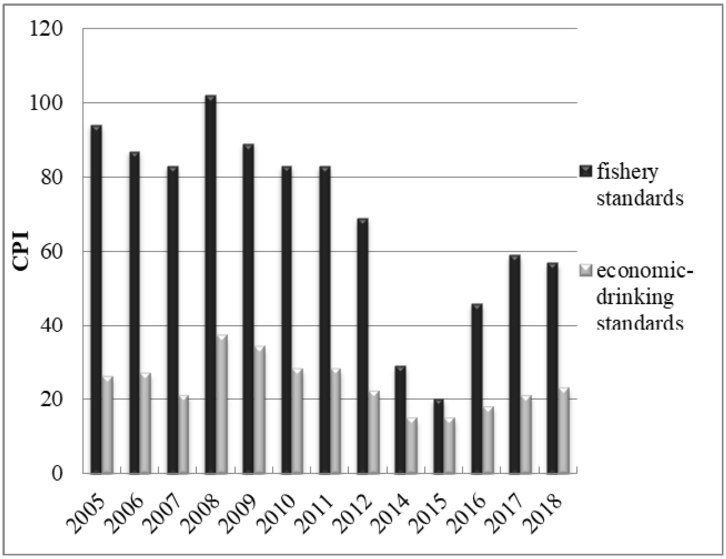


Fig. 4. The dynamics of changing the surface waters *CPI* in the Kherson region

In 2016 – 2018 the list of indicators almost did not differ from the list of 2005 – 2012. However there is a significant decrease in the *CPI* value.

In most cases a quality of the surface waters of the region (Table 5) according to the fishery requirements is characterized by classes IVa – IVg, category "very dirty", for drinking water – class II, category "polluted", class IIIa, category "dirty".

The ecological condition of the Kherson region surface waters was also assessed according to the content of BOC_5 (Table 6). Thus almost the whole period the surface waters of the region are characterized by the worst indicators in terms of pollution ("dirty") and in terms of the environmental state ("stage of irreversible changes").

If we compare the indicators of a surface water quality in the regions of the NWBSC, the waters of the Kherson region are characterized by the worst quality in terms of hydrochemical indicators and in terms of the ecological state (content of BOC_5).

We calculated the projected trends in the dynamics of the surface water pollution level in the regions of the NWBSC (Fig. 5 – 7). The presented drawings show that for the Mikolayiv and Kherson regions a stable tendency towards a decrease in the surface waters pollution within the next 10 years is noted. As for the Odessa region, in general, pollution indicators tend to increase. Thus the probability of the surface water quality deterioration in the regions of the NWBSC is observed for the basins of the Danube and Dniester rivers within the Odessa region.

An important factor in analyzing the state of the components of the environment, including the state of the water bodies, is the assessment of technogenic loading.

Table 5. The classification of the surface water quality of the Kherson region

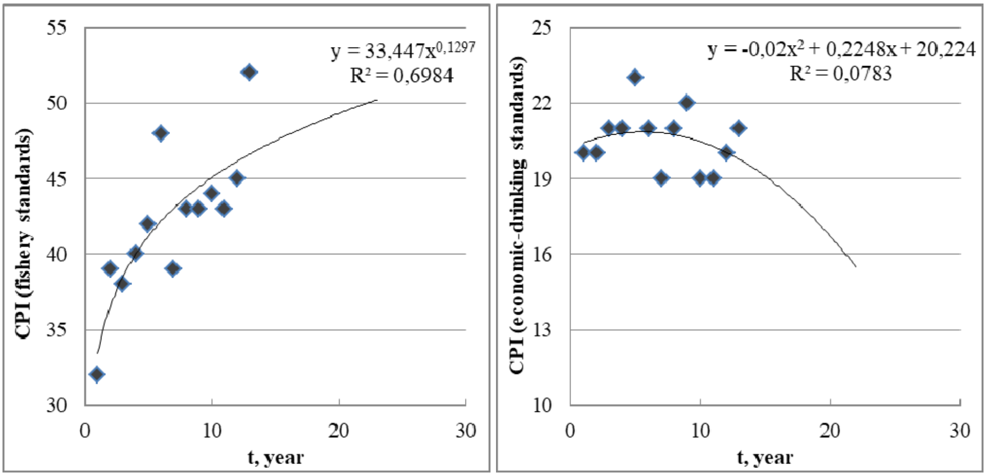
Year	Fishery standards	Economic and drinking standards
2005	IVg, very dirty	II, contaminated
2006	IVc, very dirty	IIIa, dirty
2007	IVc, very dirty	II, contaminated
2008	IVc, very dirty	IIIa, dirty
2009	IVb, very dirty	II, contaminated
2010	IVc, very dirty	IIIa, dirty
2011	IVc, very dirty	IIIa, dirty
2012	IVa, very dirty	II, contaminated
2014	IIIa, dirty	II, contaminated
2015	IIIa, dirty	II, contaminated
2016	IVa, very dirty	II, contaminated
2017	IVa, very dirty	II, contaminated
2018	IVa, very dirty	II, contaminated

Table 6. The classification of the Kherson region surface water quality by the value of BOC_5

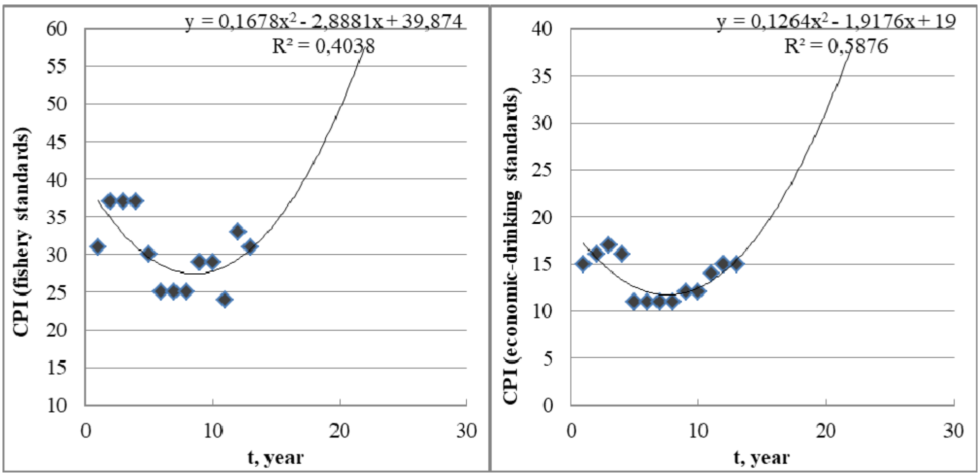
Year	Pollution level	Ecological condition
2005	Dirty	Stage of irreversible changes
2006	Dirty	Stage of irreversible changes
2007	Dirty	Stage of irreversible changes
2008	Dirty	Stage of irreversible changes
2009	Dirty	Stage of irreversible changes
2010	Dirty	Stage of irreversible changes
2011	Dirty	Stage of irreversible changes
2012	Dirty	Stage of irreversible changes
2014	Moderately polluted	Threshold stage
2015	Dirty	Stage of irreversible changes
2016	Dirty	Stage of irreversible changes
2017	Dirty	Stage of irreversible changes
2018	Dirty	Stage of irreversible changes

In the Odesa region, there are 132 enterprises that discharge pollutants into the surface water bodies. The main pollutants are utilities, namely “Infoxvodokanal” (Odessa), “Chornomorskvodokanal”, “Artsyz Vodokanal”, “Podilskvodokanal”, “Belgorod-Dniestrovskvodokanal”, “Teplodarvodokanal”, “Baltavodokanal” and also a cellulose-cardboard factory (Izmail) [31].

The largest volumes of water intake are carried out from the surface sources (95 % of the total water intake in the region). According to using the water for various needs the use for drinking needs took the first place until 2012, since 2013 the first place has been occupied by using the water for irrigation. Minimum water using indicators are observed in the agricultural sector.



the Danube river basin



the Dniester river basin

Fig. 5 – The projected assessment of the surface water pollution level in the Odessa region

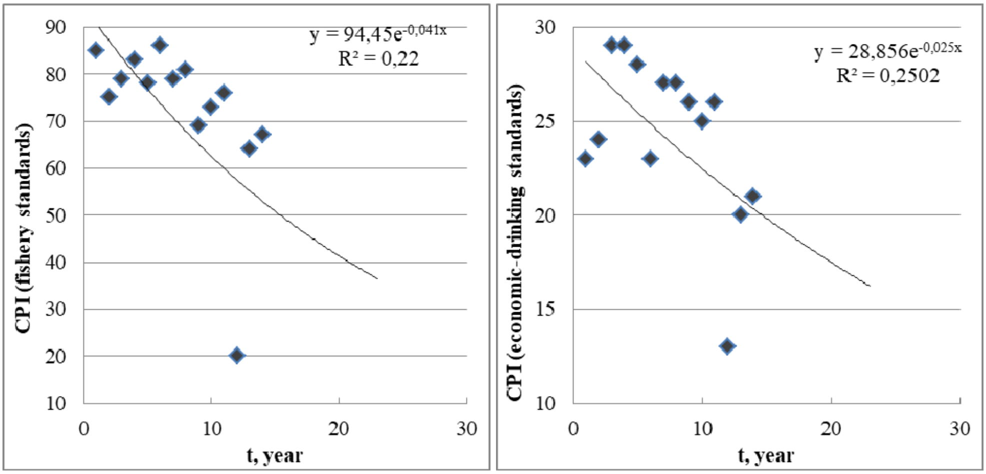


Fig. 6. The projected assessment of the surface water pollution level in the Mykolayiv region

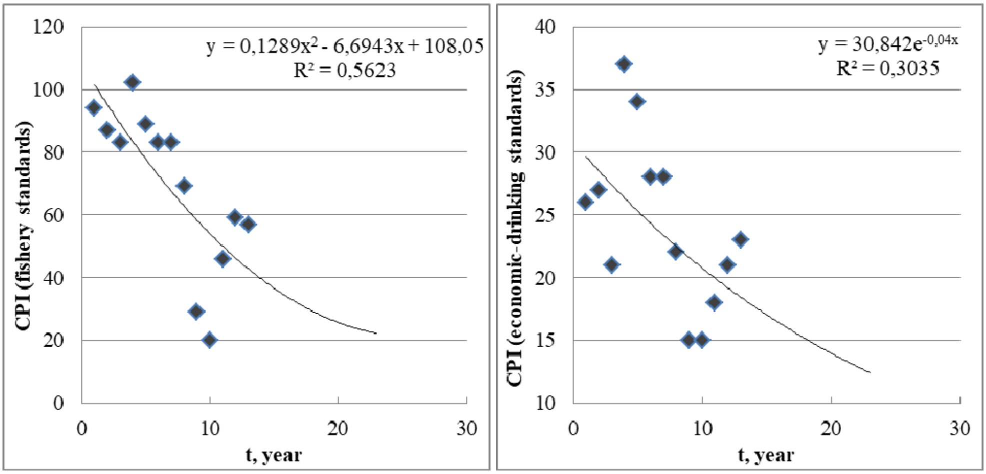


Fig. 7. The projected assessment of the surface water pollution level in the Kherson region

Sewage and other return waters are discharged mainly into the surface water bodies. At present, 40 – 50 % of discharged pollutants are characterized as "normative cleaned". In recent years, there has been a significant increase in return water discharges, which may be due to an increase in the water abstraction in the region.

By the types of economic activity, the main water-consuming industries are housing and communal services and agriculture.

The assessment of technogenic loading on the Odessa region water bodies according to the indicators of wastewater and pollutants discharges in their composition was performed using the M_{WO} indicator (Fig. 8). Thus from 2009 to 2016 there was a decrease in the total loading on the surface water bodies in the region due to a decrease in wastewater discharges. In 2017 – 2018, this figure increased significantly, which, as noted above, is due to an increase in discharges. Until 2013, with the overall decrease in the volume of wastewater discharges, the number of pollutants in their composition had been increasing.

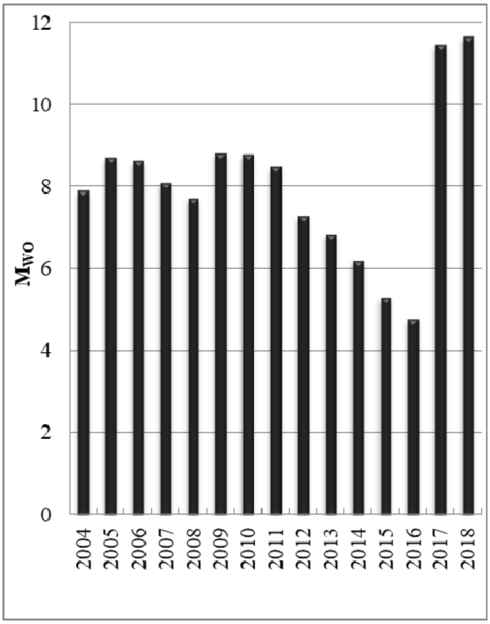
The analysis of the discharge volumes from the main polluting enterprises showed that the Odesa region water objects receive the maximum technogenic loading according to the indicators of wastewater discharges under the influence of the “Infoxvodokanal” activity. Among other enterprises the largest discharge rates are observed for the cellulose-cardboard factory in Izmail.

The analysis of the prognostic load indicators on the Odessa region surface water bodies (Fig. 9) testifies to the tendency of increasing the indicators, first of all by the volumes of wastewater discharges.

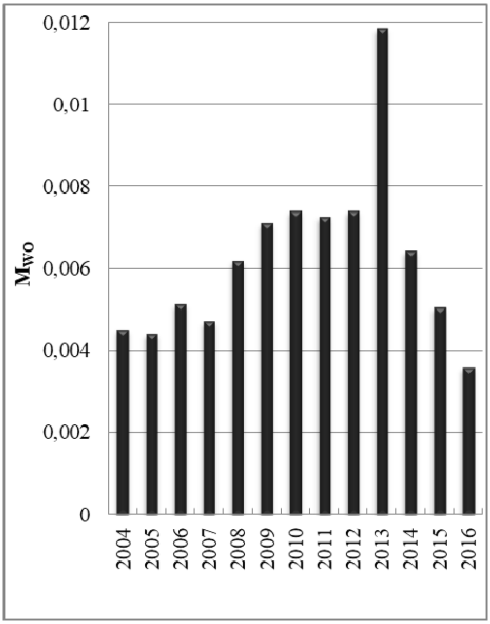
In the territory of the Mikolayiv region about 160 enterprises having the permission for water using are operating nowadays. The main water bodies polluters in the region are the vodokanal enterprises, namely "Mykolayivvodokanal", "Olshanske", "Pervomaisky city vodokanal", "Pribuzke", Bashtanka "City vodokanal", "Ochakivvodokanal".

In the Mikolayiv region from 2003 to 2010 the water intake indicators decreased almost in 1,5 times and at present they are fluctuating within 226 – 290 million m^3. The water using indicators have also declined. The maximum water consumption is observed for the production needs, the minimum – for the agricultural needs without taking into account the irrigation needs.

There is also a significant decrease in the values of indicators from 2003 to the present in terms of wastewater discharges. The largest amount of wastewater is discharged into the surface water bodies (more than 90 %). Untreated water prevails in the wastewater composition. The share of "normatively cleaned" wastewaters is very low. This is a consequence of inefficient operation of the municipal sewage treatment plants.

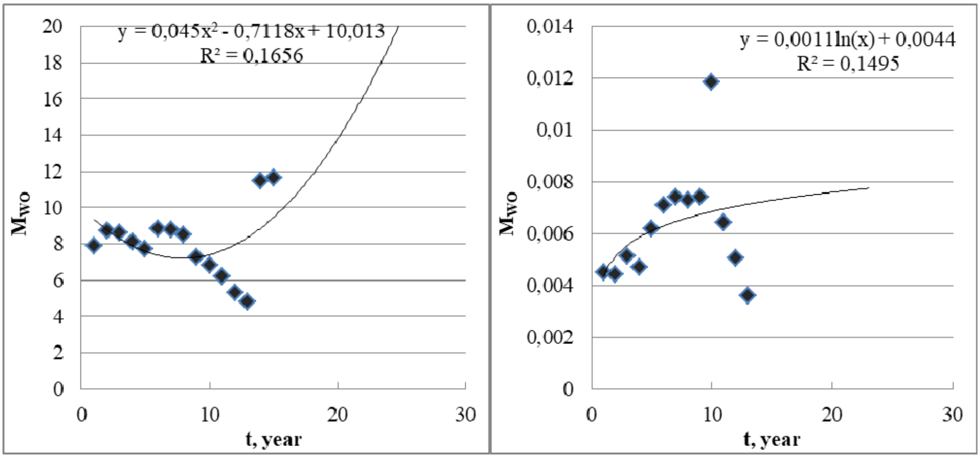


by the volumes of wastewater discharges



by the volumes of pollutants discharges

Fig. 8. The value of the M_{WO} indicator in the Odessa region in 2004 – 2018

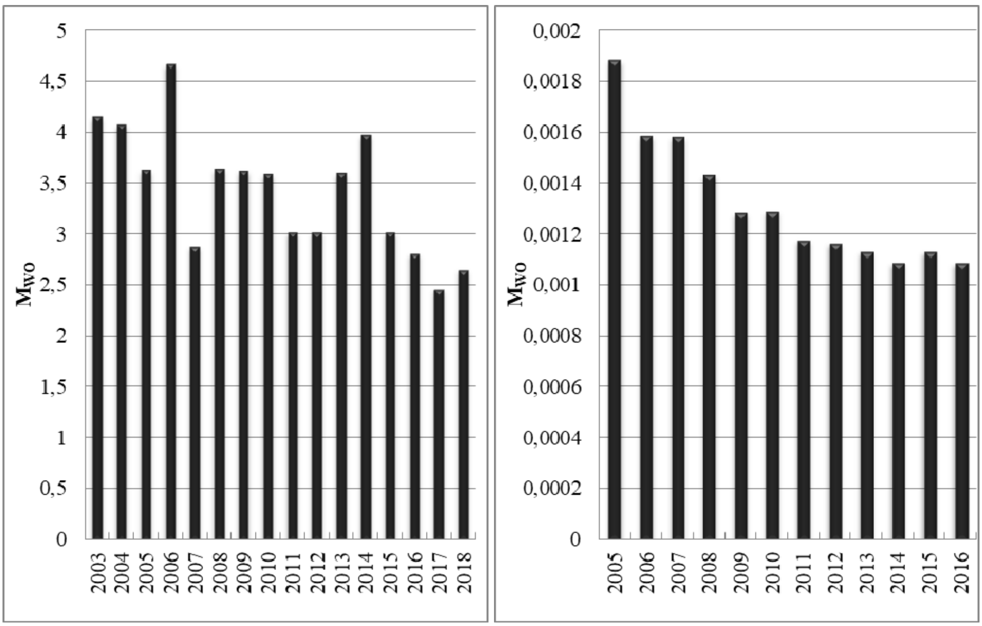


wastewater pollutants

Fig. 9. The projected assessment of the level of technogenic loading on the Odessa region water bodies

By the types of economic activity the most water-consuming industries are agriculture (taking into account the irrigation and fish farming needs) and energy. Significant water consumption indicators are also observed for the housing and communal service needs.

The estimation of technogenic loading on the Mikolayiv region water objects of (fig. 10) is done. In terms of wastewater discharges, the M_{WO} value has decreased by almost 1.5 times since 2006. According to the pollutants discharges indicators, there has been a steady decrease in loading almost 2 times since 2005. This is a consequence of the reduction of wastewater discharges and, accordingly, pollutants in their composition.

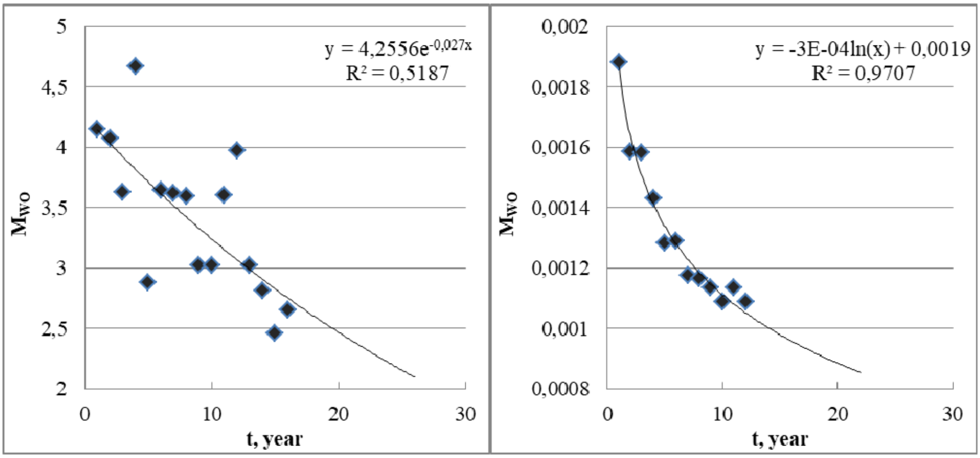


by the volumes of wastewater discharges by the volumes of pollutants discharges

Fig. 10. The value of the M_{WO} indicator in the Mykolayiv region in 2003 – 2018

The analysis of loading from the main enterprises-polluters showed that the volumes of discharges from "Mikolayivvodokanal" exceed the corresponding indicators of other enterprises by 1 – 2 orders. Among the other enterprises, in recent years the maximum discharge volumes have been observed for Pervomaisky Vodokanal.

The received projected indicators (fig. 11) testify to the tendency to reducing the level of technogenic loading on the Mikolaiv region water objects.



wastewater pollutants

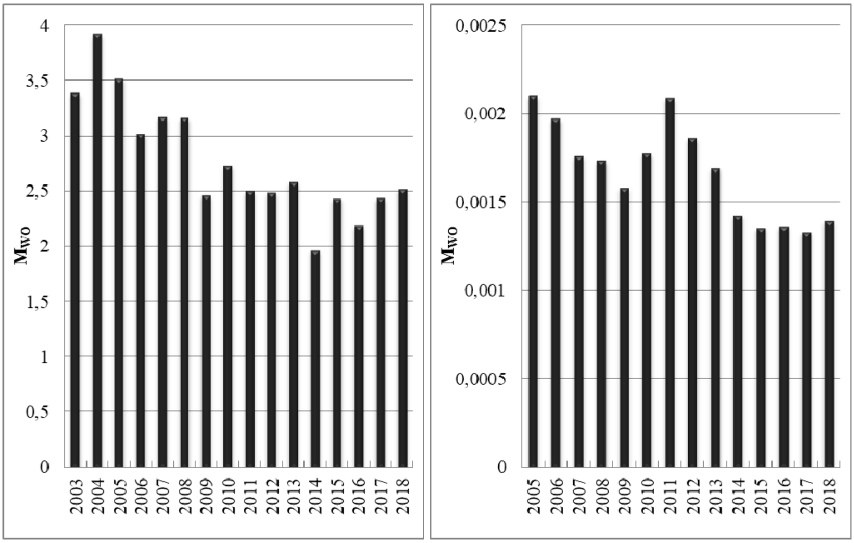
Fig. 11. The projected assessment of the level of technogenic loading on the Mykolaiv region water bodies

According to [32] data in 2019 in the Kherson region 1161 water users were registered. In recent years the main water bodies polluters are the "Palada" plant (Kherson), the Kherson river port and such enterprises as "Source" of the Kalanchak village council, "Rice of Ukraine", "Zhukova" and "Southern" (village Oleksiyivka), "Sewage treatment plants" of the Skadovsk city council [28].

The analysis of water intake in the region showed that there is a steady increase in all indicators. The largest water intake is from the surface water sources, the smallest – from the sea sources. With the increase in water intake, there is an increase in water using. The maximum volumes are marked for the irrigation needs, the minimum are for other agricultural needs. With the general increase in water intake, there is a decrease in wastewater discharges. The maximum number of wastewater discharges is carried out into the surface water bodies. In terms of the degree of purification constantly clean wastewater is dominated.

By the types of economic activity the greatest needs in water resources in the region are observed for the agricultural enterprises compared to other industries.

The estimation of the level of technogenic loading on the surface water bodies of the region according to the volumes of wastewater discharges and pollutants in their composition (Fig. 12) indicates a significant decrease in the M_{WO} indicator (by almost 30 %).



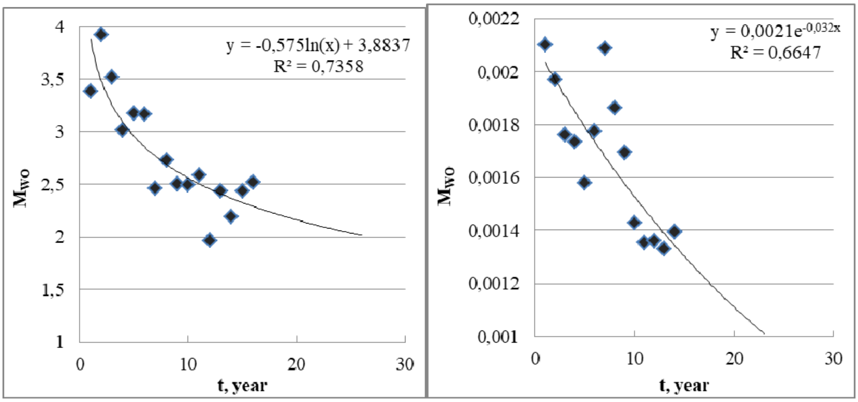
by the volumes of wastewater discharges by the volumes of pollutants discharges

Fig. 12. The value of the M_{WO} indicator in the Kherson region in 2003 – 2018

The analysis of technogenic loading on the water bodies from the main polluting enterprises of the Kherson region showed that the discharge volumes from the Kherson water supply system exceed the corresponding ones by 1 – 2 orders of magnitude. Among other enterprises, the significant discharge volumes are noted for “Rice of Ukraine”.

The projected values of technogenic loading on the water bodies indicate their decrease during the next 10 years (Fig. 13).

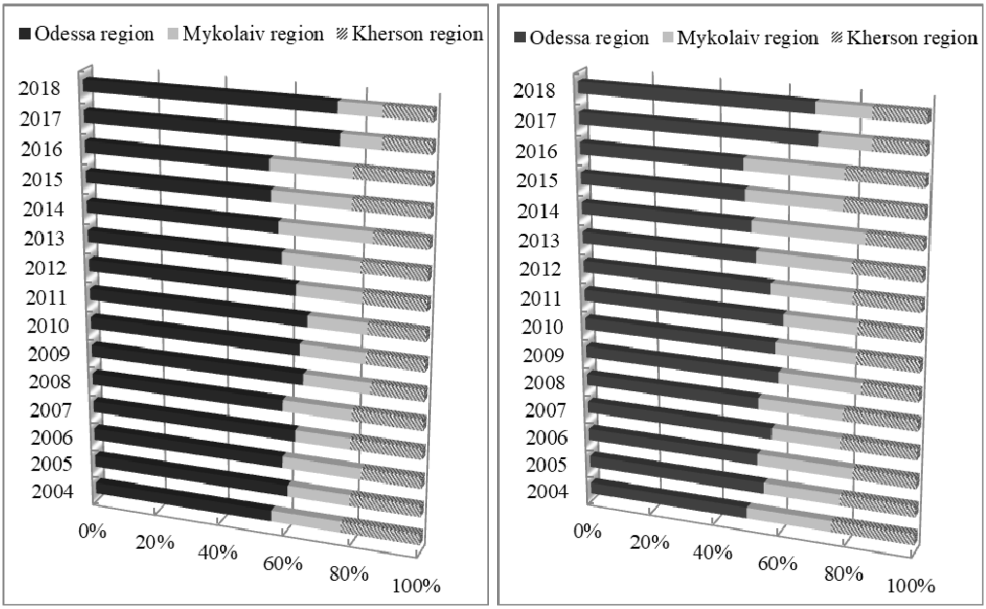
A comparative analysis of technogenic loading on the surface water bodies of the NWBSC regions was also performed (Fig. 14 – 15). As it can be seen from both figures, the greatest loading is on the surface water bodies of the Odesa region (55 – 75 % of wastewater discharges and 60 – 75 % of pollutants discharges from the total volumes). The second place is taken by the Kherson region. According to the value of the M_{WO} indicator, the maximum level of loading is also noted for the Odesa region. According to the wastewater discharges indicators, after the



wastewater pollutants

Fig. 13. The projected assessment of the level of technogenic loading on the Kherson region water bodies

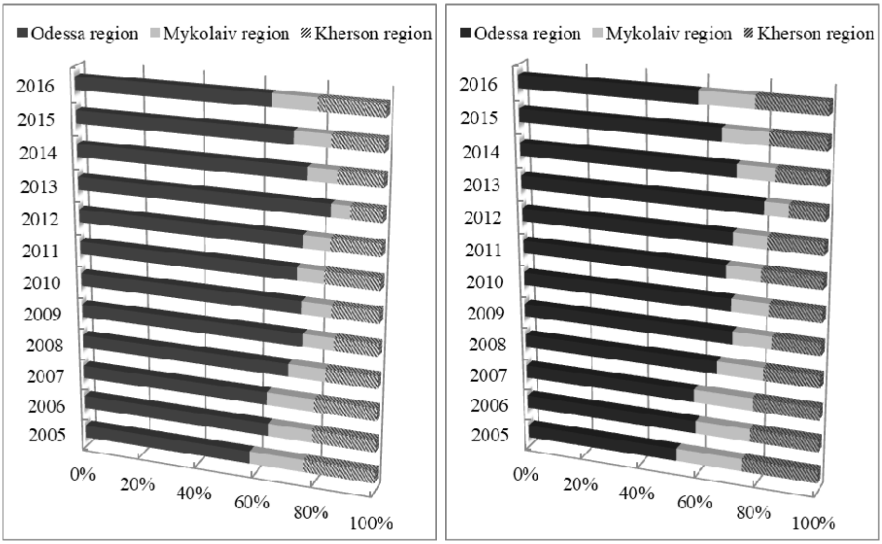
Odesa region, the value of M_{WO} is the largest in the Mykolayiv region as a whole, and according to the volume of pollutants discharges it is the largest in the Kherson region.



by the volumes of wastewater discharges by the value of M_{WO}

Fig. 14. The comparative analysis of technogenic loading on the regions of the NWBSC in terms of wastewater discharges into the surface water bodies

The analysis of materials for a long-term period and the obtained calculations show that the maximum level of technogenic loading is observed for the Odesa region, the minimum – for the Kherson region in terms of the volumes of wastewater discharges into the surface water bodies.



by the volumes of pollutans discharges by the value of M_{WO}

Fig. 15. The comparative analysis of technogenic loading on the regions of the NWBSC in terms of pollutant contaminants in the wastewater discharging into the surface water bodies

CONCLUSION

The section presents the general assessment results of a state of the surface waters in the North-Western Black Sea region according to a complex of indicators of a surface water quality and technigenic loading on the water bodies. The obtained calculations allow us to draw the following conclusions:

1. In all regions of the NWBSC, a non-compliance with the standards was most often noted for fishery requirements. According to the value of *CPI* the Odessa region surface waters were characterized by quality classes IIIa – IVa (category "dirty" – "very dirty") according to fishery standards, the Mykolaiv region – mainly class VIa (category "very dirty"), the Kherson region – classes IVa – IVg (category "very dirty"). According to economic and drinking standards, the water quality in the regions was characterized by class II – IIIa (categories "polluted" – "dirty"). The estimation of an ecological state of the waters showed that waters of the Odessa region are characterized as "moderately polluted" with a threshold stage of an ecological condition, the Mikolayiv region – "moderately polluted" and "polluted" (accordingly a threshold stage and a stage of irreversible changes), the Kherson region – "dirty" with a stage of irreversible changes.

2. The comparative analysis showed that the waters of the Kherson region are characterized by the worst quality for the fishery and drinking requirements, as well as by the ecological condition.

3. According to the volumes of wastewater and pollutants discharges into the surface water bodies, the maximum level of technogenic loading is observed for the Odesa region, the minimum – for the Kherson region.

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ASSESSMENT OF THE LANDFILL FILTRATE IMPACT OF THE SOLID WASTE BY ENVIRONMENT

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ABSTRACT

The object of the study is the drainage water of solid waste landfills (SWL) and the assessment of the impact of solid waste landfills on the main components of the environment, including the hydrosphere and lithosphere. In particular, the analysis revealed that the main source of environmental pollution is leachate and biogas, which are derived from the operation of landfills. groundwater for 3 quarters, at one of the landfills of Ukraine (Zaporizhzhia).

Keywords: leachate, solid domestic waste, monitor, method, protective shield, efficiency, environment.

INTRODUCTION

Municipal solid waste landfills are complex multicomponent systems with active-negative impact on the environment. The main purpose of monitoring such systems is to identify the dynamics of quantitative and qualitative changes in the state of the environment, both on the landfill and in the surrounding areas.

The main factor of negative impact of the solid waste landfill on the environment is the impact of leachate, which generated as a result of waste decomposition.

The filtrate is a brown-brown liquid component of landfills, with an unpleasant odor (usually ammonia, putrefactive compounds), which is formed due to waste moisture, precipitation infiltration, biochemical processes that result in the release of water. Its temperature can reach 38 gr. Landfill wastewater is very dangerous in sanitary and epidemiological terms for the environment and human health.

The filtrate is formed as a result of anaerobic decomposition of solid waste in the body of the landfill, penetration into the body of the landfill, the amount of which exceeds the amount of moisture. evaporating from the surface of the landfill. The average annual volume of the filtrate is 2-3 thousand m3 / ha.

In practice, it is accepted to divide filtration waters into 2 categories:

– "young filtrate" formed at the initial stage of landfill operation in the acetogenic phase of solid waste destruction after 2-7 years of solid waste storage and disposal. Filtration waters are characterized by an average pH value of 6, high values of COD (up to 60,000 mgO_2 / dm^3) and BOD (sometimes up to 40,000 mgO_2 / dm^3), high content of ammonium nitrogen and iron (on average 750 mg / l). The composition of organic impurities is represented by volatile organic acids of the fatty series

– "old filtrate" is formed at the stages of methanogenesis, ie mainly during post-operational periods. The filtrate of old landfills ("old filtrate"), has a pH of 8, significantly reduces the valuesof COD - up to 3000-4000 mgO_2 / dm^3 and BOD - up to 180 mgO_2 / dm^3, high ammonium nitrogen (750 mg / l) and low iron content.

Qualitative characteristics of drainage wastewater has been given in table. 1.

Drainage waters of landfills are characterized by high BOD and COD, the presence of a component of organic nature, the content of petroleum products, zinc, nickel, copper, chromium, nitrogen, nitrates and nitrites. increased salt content and the presence of suspended solids.

Table 1. Qualitative characteristics of the drainage water of the landfill

Name of the indicator	Research period		
	Autumn	Winter	Spring
Solids, mg/dm^3	22614,3	18352,7	23200,5
BOD_5, mgO/dm^3	182,1	167,7	165,3
COD, mg/dm^3	1007,5	1215,6	999,8
chromatic level , gr.	180	167	159
Suspension particles, mg/dm^3	251,4	268,07	209,7
pH	7,6	7,1	7,4
Nitrogen, mg/dm^3	67,7	262,3	76,24
Nitrates, mg/dm^3	109,4	120,2	107,8
Sulphates, mg/dm^3	1630,1	2154,8	2376,8

According to the classification of the filtrate, depending on age, the filtrate of this qualitative composition can be attributed to the "old" filtrate, but it should be noted that in most cases a mixture of filtrates of different periods is formed at landfills due to constant mixing of portions that was formed at the stage of methanogenesis.

METHODS AND EXPERIMENTAL PROCEDURES

At the present stage, the pollution of the aquatic environment is controlled by sampling water for chemical analysis from surface watercourses and wells located along the contour of the object, and in the direction of surface and soil runoff. This approach is not correct enough, as the presence of contaminants is recorded, and the nature of their formation is ignored. This point is extremely important due to the fact that the pollution of the hydrosphere occurs not only due to leachate from waste storage sites, but also due to other factors, such as surface runoff from agricultural land, sewage, etc. .

At the landfill for solid waste it is necessary to constantly monitor the amount and composition of the treated filtrate discharged into the sewer system of the settlement. The control is carried out by analyzing the composition of wastewater before and after the complex of local facilities for leachate treatment, in control wells (including in the absence of local treatment facilities), as well as measuring the amount of wastewater discharged in control wells.

Sampling is a very important step in the technological cycle of eco-analytical control, as the results of even the most accurate (and expensive) analysis lose all meaning in the case of incorrect sampling. Errors caused by incorrect sampling, as a rule, can not be corrected in the future. Therefore, the reliability and accuracy of further analysis largely depend on the correct choice of method and thorough sampling.

Should also consider that every spring, after the snow melts or after heavy rains, the landfill dramatically increases the volume of leachate.

One of the most common ways to dispose of solid waste is to dispose of it in landfills, where waste decomposition processes have been going on for decades. The latter leads to local or global changes in the sanitary - epidemiological situation of the surrounding areas.

Discharge of leachate into the municipal drainage network is allowed only if the volume and composition of the leachate meet the requirements of the "Rules of acceptance of wastewater from enterprises in municipal and departmental sewerage systems of cities and towns of Ukraine" [1] in consultation with local sanitary-epidemiological service (SES).

The leachate collection and disposal system must be operational from the beginning of the landfill operation, as well as after its closure.

The development of devices for the collection and disposal of filtrate, as well as biogas, which is formed in large quantities in the layers of solid waste continues. One of the latest developments is presented in Figure 1 [2].

To protect groundwater and surface water from pollution during the construction of landfills, the following measures are envisaged:

– pumping the filtrate from the body of the landfill with subsequent removal to treatment plants;

– creation of a multilayer protective screen on the bottom and slopes of the pit, which houses the landfill.

The composition of the filtrate directly depends on the stage of the life cycle of the landfill. Each stage corresponds to a certain stage of biochemical decomposition of waste, which underlies the formation of quantitative and qualitative characteristics of drainage water.

So today, we don't have any universal effective technology for purification and disposal of filtrate. One of the reasons - the variability of its composition, it determines the scheme of purification - physico - chemical, physical, biological or a combination thereof.

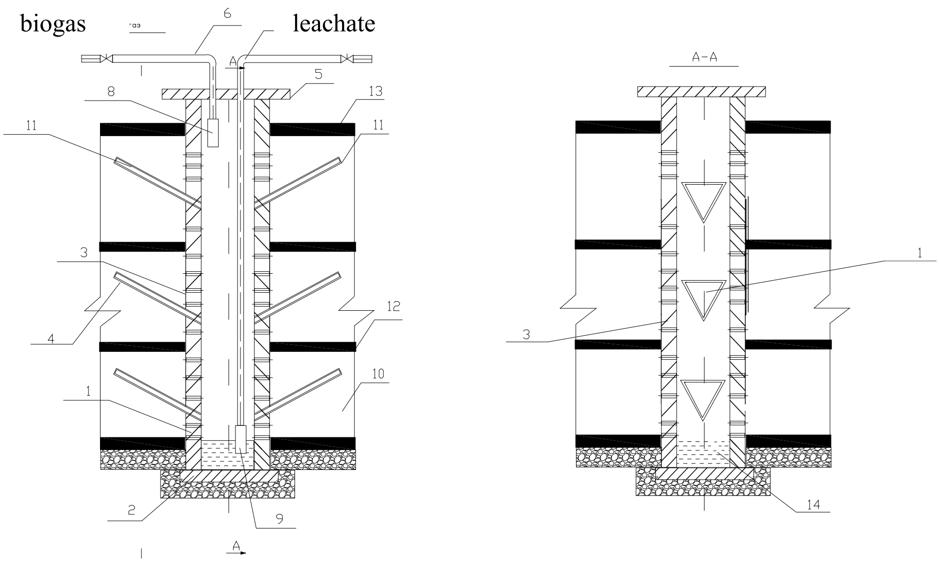


Fig. 1. Filtrate and biogas collection system: 1 – polymer pipe; 2 – bottom; 3 – well vertical drainage; 4 – additional drainage; 5 – lid; 6 – vertical pipes; 7 – polymer pipeline; 8 – biogas sensor; 9 – filter level sensor; 10 – first layer of waste; 11 – plugs; 12 – insulating layer of sludge or sand, 13 – waterproofing; 14 – filtrate

On March 1, 2017, new rules for designing solid waste landfills [3] came into force in Ukraine, in particular, measures to protect soils and groundwater from the effects of leachate were strengthened and this is stated in amendment N 1 to state construction norms state buildings norms .B 2.4-2-2005 "Landfills of solid household waste. Basic design provisions", which was published in the official printed publication of the Ministry "Information Bulletin of the Ministry of Regional Development, Construction and Housing of Ukraine" No. 11 of 2016.

The document provides for:

- proper design and construction of landfills for briquetted household waste, biogas collection and disposal systems, collection and disinfection of leachate at landfills (including existing ones), as well as effective implementation land reclamation after the closure of the landfill
- optimization of estimated costs required for the construction of the landfill in solid waste in accordance with the requirements of legislation in the field of waste management; health of people, animals, plant protection, as well as property and the environment.

In particular, certain design decisions made in accordance with the requirements of state buildings norms B 2.4-2-2005 "Landfills for solid waste. The main design provisions " led to the cessation of construction of landfills or their reclamation and re-approval of the developed projects.

In turn, the supervisory authorities and experts referred to the impossibility of violating the relevant provisions of state buildings norms B.2.4-2-2005 "Landfills for solid waste. Basic design provisions" [3].

This applies in particular:

- the requirements of paragraph 3.130 for the installation of a protective screen during the reclamation of land after the closure of the landfill, which provides for the use of increased volumes of loam, extraction and transportation to the landfill is a costly measure; § 3.19 on determining the slope of the pit of the landfill,
- the requirements of § 3.74 on determining the requirement for the utilization of biogas generated by anaerobic decomposition of the organic component of municipal waste mandatory;
- the requirements of 3.85 for the use of rotary drilling rigs with unsuitable drilling diameters for drilling wells for biogas collection,
- requirements of 3.32 for clarification of the requirements for prohibited solid household waste briquettes, etc.

In addition state buildings norms B.2.4-2-2005 is supplemented with new appendices, in particular: Annex K Form of sanitary-technical passport of the solid waste landfill; Annex L Basic methods of filtrate disposal.

Analysis of the new version of the normative document allows us to draw conclusions about strengthening control over the environmental component of the landfill operation process and minimize the negative impact on the environment.

THE RESEARCH RESULTS AND DISCUSSIONS

Uncontrolled accumulation of waste at landfills poses a significant risk to the environment and directly to humans. The vast majority of existing solid waste landfills (SWL) are filled to 90% of the project volume or overcrowded, which requires the alienation of new areas for the arrangement of regular sites (queues) for waste disposal.

The analysis revealed that the main source of environmental pollution is leachate and biogas, which are derived from the operation of landfills.

In the process of increasing the thickness of the waste layer, aeration conditions deteriorate, methane and ammonia are formed.

After showers and snowmelt, the landfill is saturated with water, which gets the decomposition products of organic matter. At the same time, the filtration capacity of soils increases and the processes of environmental pollution are more active than the processes of self-cleaning.

Monitoring of waste storage areas should include control over the state of the hydrosphere (groundwater and surface water), atmosphere, soils, noise pollution within the range of the landfill.

The system of observations should include:

– preliminary inspection of the landfill site and adjacent areas to identify the main objects of control and determine background concentrations;

– implementation of a system of continuous environmental monitoring, and creation of conditions for normal operation;

– forecast of the dynamics of the state of the environment in the phase of active operation of the landfill, and after reclamation,

– development and implementation of recommendations to prevent deterioration of the quality of controlled areas.

To protect groundwater and surface water from contamination by leachate in modern conditions during the construction of new landfills, the following measures are envisaged:

– pumping of filtrate from the landfill body with subsequent transportation to treatment facilities;

– creation of a multilayer screen on the bottom and slopes of the pit, which houses the landfill.

According to of state buildings norms B.2.4-2-2005 [4], groundwater at the site of landfills must be at a depth of at least 2 m from its foundation.

To minimize the effects of harmful effects of contaminated areas, various measures: reclamation, rehabilitation, reclamation. The direction of reclamation determines the following targeted use of these areas.

To confirm the potential threat to the environment, a number of studies were conducted at landfills in Ukraine (Zaporizhzhia, Kharkiv, Kyiv, Odessa), which showed a negative influence of leachate on groundwater and soil of adjacent territories. Values, the content of cadmium exceeds the norm by 1.5 times, lead 4-6 times, petroleum products more than 10 times. Thus, there is an excess of a large number of controlled indicators throughout the observation period with increasing concentrations, which is due to the activation of chemical processes in the body of the landfill.

The geological section in the area of the landfill allows to estimate the filtration coefficient of each layer and therefore the potential degree of impact on groundwater (table 1).

The study evaluated the impact of drainage water on groundwater in several observation wells. It should be noted that well №1 is a background reference point located in the northeastern part of the landfill site, and well №5 is drilled directly in the landfill body (equipped in 1999) and allows to assess the quality of the filtrate, has the greatest depth – 17 m.

All 4 observation wells are equidistant from the 5 wells and therefore the effect of the filtrate is observed at all five control points (Figure 2).

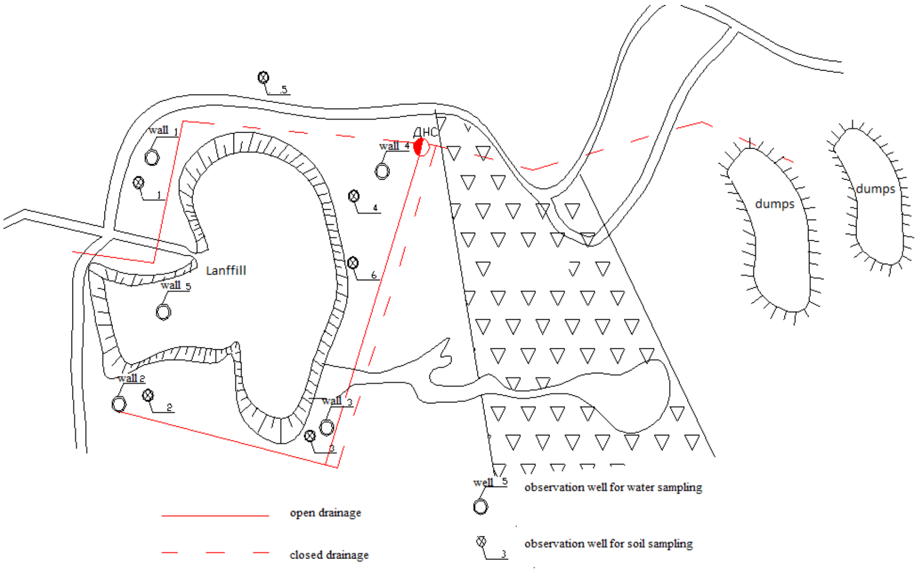


Fig. 2. Layout of the landfill and collector-drainage system for drainage water drainage

Table 1. Coefficients of filtration of lithological layers of the landfill of the city of Zaporizhzhia

Tumber in order №	Layer thickness, m	Layer name	Filtration coefficient, m/day
1	0,3-0,4	The soil and vegetation layer is humified loam.	-
2	0,0-2,2	Loess loam	0,2-0,25 0,22
3	0,0-4,1	Loess loam, light, water-saturated.	0,6-1,1 0,75
4	1,8-4,1	Loess loam, medium	0,3-0,45 0,35
5	0,0-4,3	Loess loam, light, water-saturated Loess loam, medium, water-saturated	0,4-0,6 0,45
6	3,0-9,0	Loess loam, heavy, water-saturated	0,17-0,25 0,2
7	3,3-8,5	Sandy clay	0,05-0,10 0,06
8	0,7-3,0	Secondary kaolin, sandy, loamy	0,008-0,03 0,015
9	0,7-2,6	Fine-grained sand, water-saturated	0,01-0,04 0,03
10	1,9	Sand medium-grained, water-saturated	1,0-2,5 1,5
11	9,0	Grit granite with sandy aggregate	3,5-5,6 4,2
12	> 0,5	The soil and vegetation layer is humified loam	-

Analysis of the results of qualitative indicators of groundwater taken in wells 1-5 show that there is a significant excess of concentrations of groundwater contaminants compared to background (well 1). The average excess over the background is as follows:

- Ammonium nitrogen – 30 times;
- BSC_5 – 2.5 times;
- Suspended matter – 1.5 times;
- Copper – 8.5 times;
- Mineralization – 30.5 times;
- Nitrites – 8 times;
- SPAR – 7.5 times;
- Sulfates – 15.5 times;
- Phenols – 9.5 times;
- Chlorides – 55–80 times;
- COD – 4.3 times.

Hydrochemical studies are carried out from control wells or observation wells located above and below the landfill body along the groundwater flow.

It should be noted that there is a non-uniformity impact of drainage waters on hydrosphere objects, in particular groundwater and surface water bodies, where landfill drainage waters may enter.

The multicomponent composition of the filtrate is due to the heterogeneity of waste and uneven decomposition, the filtrate accumulates lenticularly and has a local distribution.

Determining the location of the filtrate is necessary to record the trajectory of the filtrate in the geological environment and the development and implementation of special environmental measures.

During the research was obtained and analyzed the following dynamics , at one of the landfills of Ukraine (Zaporizhzhia). Samples from several control wells located on the landfill site and in the immediate vicinity were analyzed. The analysis data are shown in diagrams 2-4.

Thus, the analysis of studies on the impact of the landfill on the environment, in particular, landfill derivatives, showed a high degree of pollution, which negatively affects the state of water resources, atmosphere and lithosphere, and limits their subsequent post-reclamation use. Thus, it is necessary to prevent the landfill filtrate from entering surface water and groundwater, or to minimize their negative impact, in particular through local treatment plants.

Physical, chemical, biological methods are used to treat highly concentrated drainage water from landfills, and also their combination [5, 6]:

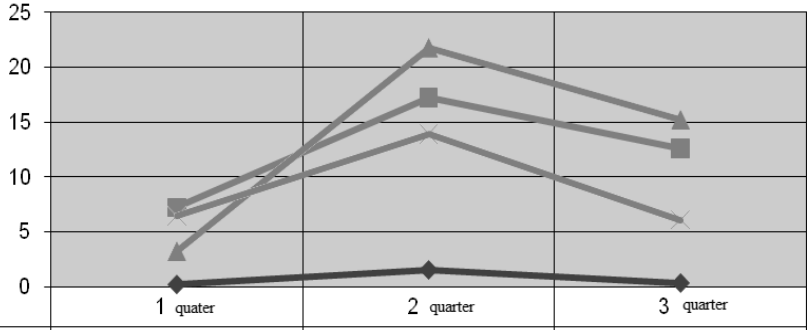
 the use of sorption purification at the stage of methanogenesis is recommended for low-concentration filtration waters;

 when using galvanocoagulation and reagent coagulation at the stage of acetogenesis, the BOD is reduced to 60%, chromaticity up to 85%;

 when using membrane purification technologies at the stages of aceto-and methanogenesis without pre-treatment there is a rapid clogging of membranes and the formation of concentrate, difficult to further dispose of, the method due to the complexity of operation and relative high cost, can not be recommended as the main, but can be used as additional treatment at any stage of the landfill.

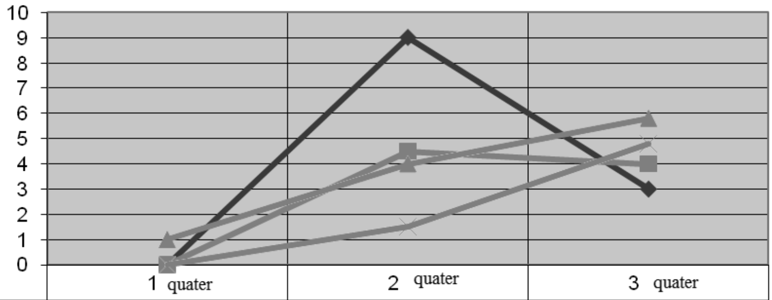
Application of aerobic methods for purification of the filtrate in the stage of methanogenesis is possible during the preliminary physico-chemical and chemical treatment, because the effluents have a high salt content, the presence of organochlorine compounds.

Also effective is a technology that involves reagent treatment using an activated solution of aluminum sulfate coagulant [7, 8].



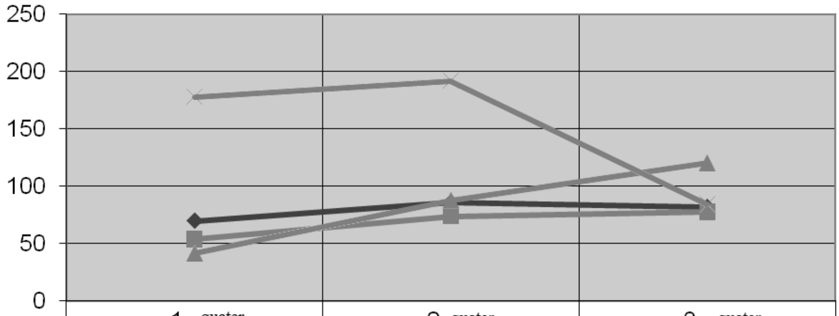
	1 quater	2 quarter	3 quarter
well 1	0,194	1,5	0,32
well 2	7,23	17,2	12,6
well 3	3,25	21,74	15,2
well 4	6,48	13,9	6,1

Fig. 3. Concentration of ammonium nitrogen in groundwater



	1 quater	2 quater	3 quater
well 1	0	9	3
well 2	0	4,5	4
well 3	1	4	5,8
well 4	0	1,5	4,8

Fig. 4. Dynamics of changes in BOD_5 in groundwater



	1 quater	2 quater	3 quater
well 1	70	86	82
well 2	54	74	78
well 3	42	88	120,4
well 4	178	192	84,6

Fig. 5. Change in the concentration of suspended solids in groundwater

CONCLUSION

Thus, the operation of the landfill, even in compliance with modern requirements for their design, (including drainage system, protective screen) has a multifactorial negative impact on the environment, in particular, the hydrosphere (surface and groundwater) and the lithosphere.

In particular, during the analysis of the level of soil contamination, within the sanitary protection zone (landfill in Zaporizhzhia), the following data were obtained: the content of zinc, chromium, copper and nickel does not exceed acceptable values, the cadmium content exceeds the norm in 1,5 times, lead 4-6 times, petroleum products more than 10 times.

There is an excess of normative values of controlled indicators during the whole time of observation with increasing concentrations, which is explained by the activation of chemical processes in the body of the landfill.

Analysis of the results of groundwater quality indicators taken at control points in observation wells shows a significant excess of groundwater contamination concentrations compared to background (well 1). Namely: Ammonium nitrogen – 30 times; BOD_5 – 2.5 times; Suspended matter – 1.5 times; Copper – 8.5 times; Mineralization – 30.5 times; Nitrites – 8 times; Surfactants – 7.5 times; Sulfates – 15.5 times; Phenols – 9.5 times; Chlorides – 55–80 times; COD – 4.3 times.

For a comprehensive solution to the problem of leachate accumulation and its negative impact on the environment, the first step is the sorting of garbage in the places of its formation (businesses, enterprises), will lead to a significant reduction in the amount of garbage and areas occupied under landfills, will minimize the amount of leachate, will lead to monomization of its composition, and simplify the treatment scheme.

It is expected that these measures will improve the areas under landfills, reduce their area and improve the overall environment. Eliminates the need for the alienation of new areas for the installation of landfills.

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ASSESSMENT OF SURFACE WATER QUALITY OF THE PRIPYAT RIVER BASIN IN UKRAINE

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ABSTRACT

Water quality and the aquatic environment state of water bodies in Pripyat River basin (within the district of right-bank tributaries in the middle part of the river) were assessed. The methodology of environmental assessment of surface water quality by the relevant categories (by I_e index) was used. The assessment showed that the water bodies belong to the II class by the average quality values (2–3 categories) and they are characterized as "clean" and "clean enough". According to the worst quality indicators – to II–III classes, and characterized as "very clean"–"slightly polluted"–"moderately polluted". More than a third (37% of control sites) of the region's surface waters are eutrophic, for the rest the trend is even more threatening: polytrophic – 46%, hypertrophic – 17%. Predictable deterioration in water quality was observed in rivers below the discharges of industrial and communal enterprises, within cities and other settlements. The analysis has shown three periods of the change in the quality of surface water, which caused by economic and climate reasons: 1 – deterioration, from 1964 to 1990; 2 – improvement, from 1990 to 2000; 3 – stabilization and decrease of water quality of some rivers by the worst indicators after 2000.

Keywords: ecological index, environmental assessment, surface water quality, rivers

INTRODUCTION

Deteriorating surface water quality as a result of increasing pollution is one of the attributes of the global water crisis [3]. This is seen as a decrease in the ability of the environment to meet social and economic goals and needs, as a loss of the ability to provide ecosystem services – those resources and benefits that people and society are received from ecosystems [4, 11]. The quality of surface and groundwater is a function of natural factors and human impact [8]. Water quality deteriorates by increased input of nutrients and toxicants (e.g. from diffuse sources such as run-off from agriculture, or point sources such as wastewater discharges), change in oxygen level, acidity, and temperature [11, 12]. In the second part of the XX century quality of surface water in Ukraine deteriorated significantly due to human impact; the process is continuing now, in particular, some water bodies in the Pripyat River basin are polluted and much polluted [9]. The aim of the study is ecological assessment of quality of surface waters of the Pripyat River basin (within the area of right-bank tributaries in the middle part of the river) [5].

METHODS AND EXPERIMENTAL PROCEDURES

Study area. Investigated waterbodies. The objects of the study were water bodies in the Pripyat River basin (within the area of right-bank tributaries in the middle part of the river) within the 16th European ecoregion by the Water Framework Directive (2000) [10] and

Freshwater Ecoregion 425: Dnieper – South Bug by the Freshwater ecoregions of the world [1]. The water bodies are located in north-western part of Ukraine. Hydrochemical studies were carried out in 2008-2014 at 83 control sites located in the Rivne Oblast (region): on 19 rivers of different lengths, 3 reservoirs, and 5 lakes (fig.1).

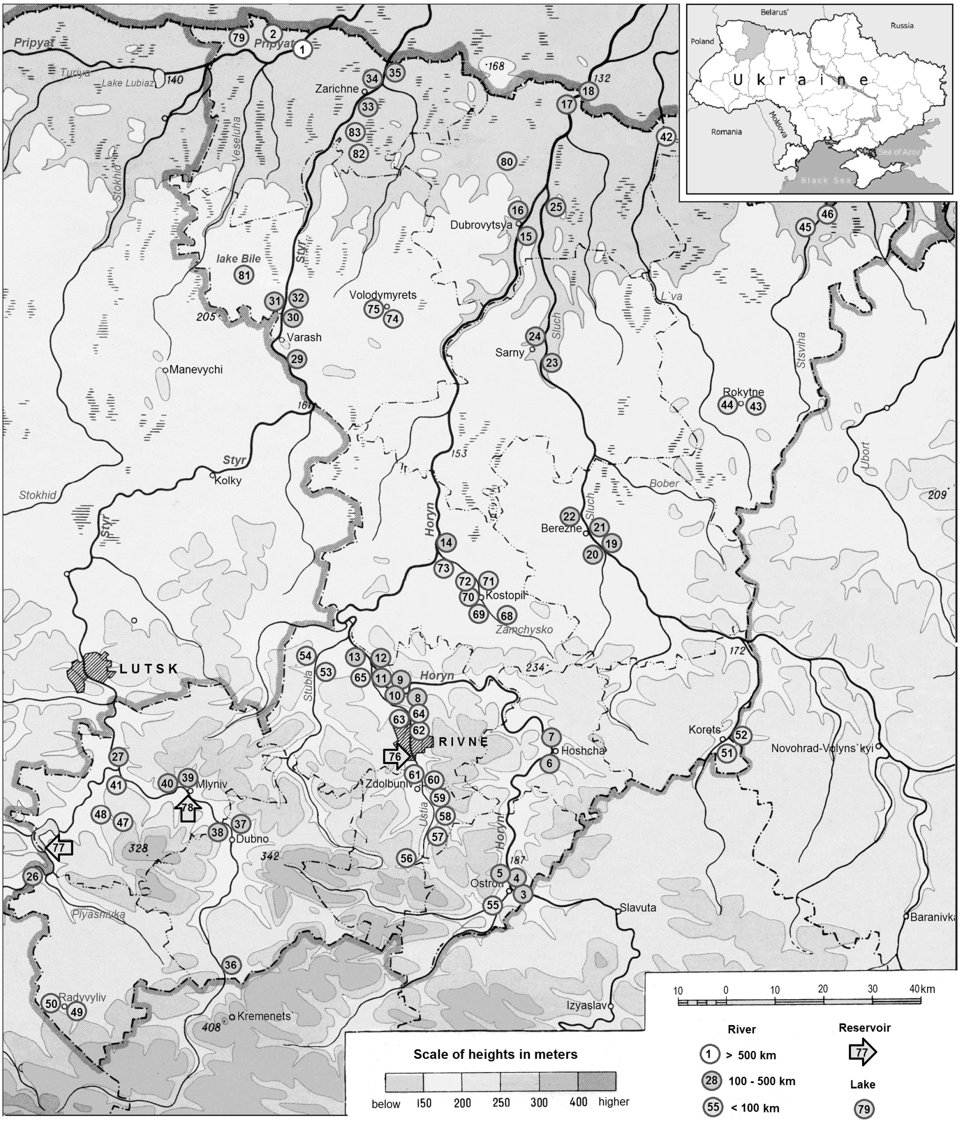

Fig. 1. The Rivne Oblast (region): Control sites on water bodies
Rivers: Pripyat (1), Stohid (2), Horyn (3-18), Sluch (19-25), Styr (26-35), Ikva (36-41), Lva (42), Buniv (43, 44), Stvyha (45), Prostyr (46), Zhabichi (47, 48), Slonivka (49, 50), Korchyk (51, 52), Stubla (53, 54), Vilia (55), Ustia (56-65), Zamchysko (68-73), Berezhanka (74-75). *Reservoirs*: Basiv Kut (76), Khrinnykivske (77), Mlynivske (78). *Lakes*: Nobel (79), Somyne (80), Bile in Volodymyretsky district (81), Bile in Zarichnenskiy district (82), Chorne (83)

The research was carried out mainly within the Styr-Horyn part of the basin. This area was chosen as a representative spatial object to study the problems of degradation of aquatic ecosystem resources in the Pripyat River basin for several reasons. Firstly, the catchments of the right-bank tributaries together make up more than a third of the total basin area. Horyn and Styr are the largest right-bank tributaries of the river, both in length (659 and 494 km, respectively) and in the basin area (27,700 and 12,900 km^2). Secondly, within the study area there are all types of water bodies – reservoirs and streams, artificial and natural, etc. The sizes of the rivers are different: large (Pripyat), medium (Horyn, Ikva, Styr, Sluch, Stvyha, Lva) and small (Ustia, Zamchisko, etc). Thirdly, in aquatic ecosystems there are negative consequences of economic activity, typical for whole 16^{th} ecoregion by WFD (2000) – deterioration of water quality and living conditions of biota.

According to the physical and geographical zoning, the study area is located in four physical and geographical regions: Volyn and Zhytomyr Polissya, which are part of the Polissya province of the mixed forest zone, Volyn Upland and Male (Small) Polissya, which are part of the Western Ukrainian province, forest-steppe zone [2, 6, 7]. Rivers belong to the group of lowland rivers [12]. The lakes are located within Volyn Polissya. According to the natural-agricultural zoning of Ukraine, the area is located within the natural-agricultural Polissya and Forest-Steppe zones. In administrative zoning, it is mainly the territory of Rivne Oblast (region).

Water quality analysis and assessment. The initial data for the implementation of environmental assessment of surface water were the results of monitoring (27 physical and chemical indicators) provided by the analytical control department of the State Department for Environmental Protection in Rivne Oblast. Monitoring data for 2008–2014 were analyzed. Surface water quality indicators (mineralization, pH, content of chlorides, sulfates, ammonium nitrogen, nitrate and nitrite nitrogen, phosphorus phosphates, dissolved oxygen, COD, BOD_5, Fe, Cu, Zn, Mg, Mn, Ca, Ni, total chromium, phenols, petroleum products, etc) were determined in accordance with the current governing normative documents.

Water quality and the aquatic environment state were evaluated according to the environmental assessment of surface water quality by the relevant categories [13] (the aggregation of indicators into indices), the quantitative generalization of which is the integral ecological index (Ie), which was set by three blocks indices according to formula (1):

$$I_e = \frac{I_1 + I_2 + I_3}{3}, \qquad (1),$$

where I_1 – index of indicators of salt composition; I_2 – index of trophic and saprobic indicators (ecological and sanitary); I_3 – index of indicators of specific toxic substances.
The water quality indices were determined by average and the worst values. The procedure for the assessment consisted of three successive stages:

- grouping and processing of initial data;
- determination of classes and categories of surface water quality by individual indicators;
- generalization of water quality assessments by separate blocks with determination of integrated values of water quality categories and classes.

THE RESEARCH RESULTS AND DISCUSSIONS

Insignificant volumes of wastewater from small objects enter *the Pripyat River* within the region; they do not have a significant effect on the salt composition of the water. According to the data of 2008–2014, the river water quality is assessed as category 1^{st} in terms of chloride content and dry residue, as well as category 2^{nd} in terms of sulfate content. The worst values were recorded for the block of trophic and saprobiological indicators – water is polluted with nitrates and nitrites, as well as organic substances (6^{th} category in terms of COD). The deterioration of water quality was also established according to the criteria for the content of specific toxic substances – iron and copper (4-5 categories), zinc and fluorides (3^{rd} category). Thus, the assessment of the Pripyat River showed that the water has belonged to the II quality class (2nd category) for average indicators, and to the III quality class (4th category) for the worst indicators, that is, it is characterized as "clean" or "slightly polluted".

The salt composition of water of *the Horyn River* deteriorated significantly due to wastewater discharges (mainly the content of sulfates). In particular, the content of sulfates, which corresponds to the 2nd quality category, was established at fourteen control sites (Table 1).

Table 1. Assessment of surface water quality of the Horyn River

Site No	I_1		I_2		I_3		I_e		Water quality				Degree of cleanness (pollution)			
									class		category		by class		by category	
	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.
3	1.3	2	3.6	6	3.8	7	2.9	5	II	III	3	5	clean	polluted	fairly clean	moderately polluted
4	1.3	2	3.4	5	4.3	7	3	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
5	1.3	2	4	6	3.6	7	3	5	II	III	3	5	clean	polluted	fairly clean	moderately polluted
6	1.3	2	3.4	5	3.3	5	2.7	4	II	III	3	4	clean	polluted	fairly clean	slightly polluted
7	1.3	2	3.4	6	3	5	2.6	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
8	1	1	3.7	6	2.9	5	2.5	4	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
9	1.3	2	4	7	2.8	5	2.7	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
10	1.3	2	3.2	5	2.9	5	2.5	4	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
11	1.3	2	3.6	7	3	5	2.6	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
12	1	1	3.8	7	3.1	5	2.6	4	II	III	3	4	clean	polluted	fairly clean	slightly polluted
13	1.3	2	4	7	3.1	6	2.8	5	II	III	3	5	clean	polluted	fairly clean	moderately polluted
14	1.3	2	3.9	6	2.9	5	2.7	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
15	1.3	2	3.7	6	3.1	5	2.7	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
16	1.3	2	3.9	6	3.1	5	2.8	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
17	1.3	2	3.6	6	2.8	5	2.6	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
18	1	1	3.8	5	2.8	5	2.5	3.7	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
Mean value	1.2	1.8	3.7	6.0	3.2	5.4	2.7	4.4	II	III	2.9	4.4	clean	polluted	fairly clean	slightly polluted

Note: a. – assessment by average values; w. – assessment by the worst values

The worst indicators in the trophic and saprobiological block (categories 5-7) were the following: phosphates (7th category in four control sites), nitrate nitrogen (6th category in 10 sites), nitrite nitrogen (5th category in 13 sites), COD (5th category in three sites), and BOD_5 (5th category in one control site). The content of phosphates was a critical indicator according to which the water quality of the Horyn River has belonged to 4-7 quality categories. The worst indicators among specific toxic substances (quality categories 5-7) were the following: cadmium (7th category in three control sites), copper (7th category in one site), fluorides (5th category in 14 sites), and zinc (5th category in four sites). The maximum numerical values of I_e index according to the average values (about 3) were established at the sites within the city of Ostroh, in the area of discharge from sewage treatment facilities of the "Vodokanal" communal services. The worst indicators have been in three points (Table 1; sites 3, 5 and 13): on the border with Khmelnytsky region, within the city of Ostroh (0.5 km downstream of the discharge from the treatment facilities), and below the city of Orzhiv (downstream of the discharge of the "ODEK" enterprise storm sewer).

Thus, the water quality of the Horyn River has belonged to the II class (2-3 categories) for average values and II-III classes (3-5 categories) for the worst.

The assessment of the water quality of *the Sluch River* (the right-bank tributary of the Horyn River) showed that in four control sites there have been 2nd quality category in terms of sulfate content, and in one site – chlorides. According to the indicators of the trophic and saprobiological block, the 5-6 categories were established according to the indicators of COD (except for one control site), and BOD_5 (5th category in six sites). Nitrite nitrogen concentration within the 5th category was established at one site. Among toxic substances the maximum 5th category was established on the content of copper in six sites, as well as zinc in one site.

In general, the Sluch river water quality has belonged to the II class (2-3 categories) according to the average values and to the III class (4th category) according to the worst (Table 2).

Table 2. Assessment of surface water quality of the Sluch River

Site No	I_1		I_2		I_3		I_e		Water quality				Degree of cleanness (pollution)			
									class		category		by class		by category	
	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.
19	1.3	2	2.5	5	2.9	5	2.2	4	II	III	2	4	clean	polluted	clean	slightly polluted
20	1.3	2	3.1	6	2.9	5	2.4	4.3	II	III	2	4	clean	polluted	clean	slightly polluted
21	1.3	2	3	5	2.1	5	2.1	4	II	III	2	4	clean	polluted	clean	slightly polluted
22	1.7	2	3.2	5	3	5	2.6	4	II	III	3	4	clean	polluted	fairly clean	slightly polluted
23	1	1	3.2	5	2.25	5	2.15	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
24	1	1	3.1	6	2.6	5	2.2	4	II	III	2	4	clean	polluted	clean	slightly polluted
25	1.3	2	3.3	6	2.75	4	2.5	4	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
Mean value	1.3	1.7	3.1	5.4	2.6	4.9	2.3	4.0	II	III	2.25	4.0	clean	polluted	clean	slightly polluted

Among the salt indicators in most points of *the Styr River* there were without exceedances of environmental standards. Only in the sections located below the runoff of the municipal enterprises of Varash and Zarichne cities (Table 3; sites 31, 33, 34), the salt composition of water deteriorates due to wastewater discharges (2nd category by sulfate content). The worst in the trophic and saprobiological block at all sites were indicators of the 5th category of quality; in the city of Berestechko and below the confluence of the Ikva River – 6th category in terms of nitrate nitrogen content. Critical indicators include COD (5th category at all sites), nitrite nitrogen (5th category at five sites), and BOD_5 (4th category at all sites).

Table 3. Assessment of surface water quality of the Styr River

Site No	I_1		I_2		I_3		I_e		Water quality				Degree of cleanness (pollution)			
									class		category		by class		by category	
	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.
26	1	1	3.2	6	2.4	4	2.2	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
27	1	1	3.1	6	2.3	4	2.1	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
28	1	1	3.3	5	3.1	7	2.5	4.3	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
29	1	1	3.4	5	3.1	6	2.5	4	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
30	1	1	3.3	5	2.7	5	2.3	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
31	1.3	2	3.67	5	2.6	5	2.5	4	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
32	1	1	3.4	5	2	5	2.1	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
33	1.3	2	3.1	5	2.1	5	2.2	4.0	II	III	2	4	clean	polluted	clean	slightly polluted
34	1.3	2	3.2	5	2.4	4	2.3	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
35	1	1	2.7	5	2.4	5	2	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
Mean value	1.1	1.3	3.2	5.2	2.5	5.0	2.3	3.9	II	III	2.2	4,0	clean	polluted	clean	slightly polluted

Among specific toxic substances the highest order of the category was established by the content of copper (4-5 categories) and iron (3-4 categories) at all sites. Among the worst indicators were also fluorides (5th category at two sites) and zinc (4th category at three sites).

Thus, the water of the Styr river was of the II quality class (2-3 categories) by average values and II-III classes (3-4 categories) by the worst indicators, that is, it was characterized as "clean", "fairly clean" and "slightly polluted". The maximum values of the I_e index have established at the sites in the area of the industrial storm sewer discharge of Rivne NPP and the Varash municipal enterprise. Among specific toxic substances the highest order of the category was established by the content of copper (4-5 categories) and iron (3-4 categories) at all observation sites. Among the worst indicators were also fluorides (5th category at two sites) and zinc (4th category at three sites).

Thus, the water of the Styr river was of the II quality class (2-3 categories) by average values and II-III classes (3-4 categories) by the worst indicators, that is, it was characterized as "clean", "fairly clean" and "slightly polluted". The maximum values of the I_e index have established at the sites in the area of the industrial storm sewer discharge of Rivne NPP and the Varash municipal enterprise.

Water quality of *the Ikva River* (the right-bank tributary of the Styr River) has deteriorated due to the increase in the concentration of sulfates (2nd category) in the site, where wastewater from municipal services of Mlyniv settlement is discharged. In other control points of the river, discharges of wastewater from small objects have had no significant effect on salt composition of the water. The results of the river water quality assessment by trophic and saprobiological indicators showed that its waters belong to the 5 – 6 categories. The worst indicators have been: nitrate nitrogen (6th category at three sites), COD (5th category at five sites), nitrites (5th category at four), phosphorus phosphates (5th category at two), and BOD_5 (5th category at one site). Among specific toxic substances, 5-7 categories of the river water quality have been established. The worst indicators have been: fluorides (7th category at one site), copper (5th category at three sites), zinc (5th category at one site). The highest copper content – up to 7th category – was recorded within the village of Bereg in Dubno district (Table 4; site 37). The content of iron and manganese in the water in some control points was within the 4th category. Thus, the water quality of the Ikva River has belonged to the II class (2-3 categories) according to the average values and the III class (4-5 categories) according to the worst indicators.

Table 4. Assessment of surface water quality of the Ikva River

Site No	I_1		I_2		I_3		I_e		Water quality				Degree of cleanness (pollution)			
									class		category		by class		by category	
	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.
36	1	1	3.6	6	3.1	5	2.6	4	II	III	3.0	4	clean	polluted	fairly clean	slightly polluted
37	1	1	2.9	6	3.1	7	2.3	4.7	II	III	2.0	5	clean	polluted	clean	moderatel y polluted
38	1	1	4.2	6	2.5	5	2.6	4	II	III	3.0	4	clean	polluted	fairly clean	slightly polluted
39	1.3	2	3.3	5	2.5	5	2.4	4	II	III	2.0	4	clean	polluted	clean	slightly polluted
40	1.3	2	3.7	5	2.6	5	2.5	4	II	III	2.5	4	clean	polluted	clean – fairly clean	slightly polluted
41	1	1	3.2	5	2.25	5	2.15	3.7	II	III	2.0	4	clean	polluted	clean	slightly polluted
Mean value	1.1	1.3	3.5	5.5	2.7	5.3	2.4	4.1	II	III	2.4	4.2	clean	polluted	clean – fairly clean	slightly polluted

Small rivers. The water of small rivers – tributaries of the Pripyat within the Zarichne district (Stokhid and Prostyr) has belonged to the II quality class in terms of average values and to the III class by the worst. The water of *the Prostir River* within the village of Stari Koni, 1 km below the confluence of the Stubla River, has had the best quality among the studied watercourses (see fig. 1, site 46).

The next in water quality was *the Zhabichi River*. In the control sites upstream and downstream the discharge from the sewage treatment plants of the Demydivka`s communal enterprise, water quality belonged to the II class (2nd category) in terms of average values. According to the worst indicators – up to the II class (3rd category) in the first site and the III class (4th category) in the second site (see fig. 1, sites 47-48).

The water of small rivers in the Horyn River basin has been of different quality. The worst it was in *the Ustia River*, which in half of 10 sites were corresponded to the III class and the 5th category, that is, it was "slightly polluted" and "moderately polluted" according to the worst values (Table 5). In general, along the Ustia River profile, the values of the salt composition indicators were significantly deteriorated due to wastewater discharges. Such water corresponds to 2-3 quality categories for the content of chlorides and sulfates.

Among the trophic and saprobiological block, 5-7 categories were established by the content of nitrogen compounds, phosphates, and COD. In particular, in the sites downstream of the wastewaters of the city of Rivne, the highest, 7th category of quality, was determined by the content of phosphates, and at the mouth – by the content of nitrites.

Table 5. Assessment of surface water quality of the Ustia River

Site No	I_1		I_2		I_3		I_e		Water quality				Degree of cleanness (pollution)			
									class		category		by class		by category	
	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.
56	1.3	2	3.3	6	2.6	5	2.4	4.3	II	III	2	4	clean	polluted	clean	slightly polluted
57	1.3	2	3.7	6	2.88	6	2.6	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
58	1.7	3	3.6	5	2.5	5	2.6	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
59	1	1	3.6	6	1.9	4	2.2	4.3	II	III	2	4	clean	polluted	clean	slightly polluted
60	1.3	2	3.6	6	2.5	5	2.5	4.3	II	III	2-3	4	clean	polluted	clean – fairly clean	slightly polluted
61	1.7	2	4.2	6	2.5	5	2.8	4.3	II	III	3	4	clean	polluted	fairly clean	slightly polluted
62	1.3	2	4.2	6	3.1	6	2.9	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
63	1.7	2	4.6	6	3	6	3.1	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
64	1.7	2	4.6	7	2.5	5	2.9	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
65	1.7	2	4.4	7	3.13	5	3.1	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
Mean value	1.5	2.0	3.98	6.1	2.7	5.2	2.7	4.5	II	III	3	4–5	clean	polluted	fairly clean	slightly polluted - moderately polluted

The nutrient pollution level or trophic state, evaluated by index I_2, the waters of the river was mesotrophic and eutrophic, except for the area below the runoff of the city of Rivne, where the waters were polytrophic. This is the worst trophicity characteristic in the region. Among toxic substances, 4-6 quality categories have been established by the content of copper (4-6 categories in all control sites), fluorides (5th category in two), and zinc (5th category in one).

The water quality of *the Zamchysko River* by the salt components has been assessed as the 1st category. The 5-7 categories were established according to the following indicators: nitrite nitrogen (7th category category in two sites), nitrate nitrogen and phosphate content (7th category in one site). Among specific toxic substances, 6-7 quality categories have been established by indicators of copper content (in all sites, except one) and petroleum products (7th category in two sites). Thus, the water quality of the Zamchysko River has belonged to the II class (3rd category) according to the average values and to the III class (5th category) by the worst values.

The water quality of *the Berezhanka River* has belonged to the II class on average values (3rd category), and to the III class (5th category) by the worst values in both sites (see fig. 1; sites 74-75). The maximum category was set in terms of nitrate and nitrite nitrogen content (7th category), copper and iron (6th category).

The water quality of *the Vilia River* belonged to the II class (2nd category) according to the average and to the III class (4th category) – according to the worst values. The maximum category was established by the concentration of nitrates and COD (5th category); among specific toxic indicators – by the copper content (6th category).

The water quality of *the Korchyk River* corresponded to the II class on average values and to the III class on the worst values. The worst indicator of the salt block was the content of chlorides and sulfates (2nd category). Among trophic and saprobiological indicators the worst have been nitrites content and COD (5th category). In terms of eutrophication, the river was mesotrophic (according to average values) and eutrophic (according to the worst values). Among toxic substances, the 6th category of river water quality was established by the copper content.

To summarize, predictable deterioration in water quality was observed in rivers below the discharges of industrial and communal enterprises, within cities and other settlements (for the Horyn River – below treatment facilities of PJSC "Rivneazot" and discharge of drainage water from the phosphogypsum dump, below the settlement of Orzhiv, below the discharge of the city of Dubrovytsia; for the Styr River – the areas of discharge of industrial storm sewer of Rivne NPP and from the treatment facilities of Varash municipal enterprise etc.) The main source of pollution of the rivers is wastewater from cities and towns. In addition, there are a large number of diffuse sources of pollution: stormwater runoff from urbanized areas, surface runoff from agricultural land, farms and livestock complexes, summer livestock camps, etc.

However, in the areas of rivers below discharges from sewage treatment plants of public utilities, a decrease in the content of heavy metals (including copper) was quite often observed, compared to the points above discharges. Such a phenomenon, for example, was recorded for the rivers Zhabichi within Demydivka, Horyn within Ostroh, Sluch within Mokvyn, etc. This can be explained by the well-known fact about the ability of heavy metals to complexation with organic substances, which are found in excess in the wastewater of municipal enterprises.

Lakes and reservoirs. The water quality of *Lakes Chorne* and *Bile* (in Zarichne district) is characterized by the II quality class by average values (2nd category) and the III class – by the worst values (categories 4-5) (Table 6). The worst indicators were pH (categories 6–7), ammonium nitrogen (6th category), iron and copper.

Table 6. Water quality of lakes and reservoirs in the Rivne region

Water bodies	I_1		I_2		I_3		I_e		Water quality				Degree of cleanness (pollution)			
									class		category		by class		by category	
	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.	a.	w.
lakes																
Nobel	2.3	5	3.7	6	2.4	4	2.8	5	II	III	3	5	clean	polluted	fairly clean	moderately polluted
Somyne	1.7	2	3.5	7	5	5	3.4	4.7	II	III	3	5	clean	polluted	fairly clean	moderately polluted
Bile*	1	1	2	5	2.1	4	1.7	3.3	II	II	2	3	clean	clean	clean	fairly clean
Bile**	1.3	2	2.5	6	1.7	3	1.8	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
Chorne	1	1	3.7	7	2.3	6	2.3	4.7	II	III	2	5	clean	polluted	clean	moderately polluted
Reservoirs																
Basiv Kut	1.3	2	3	5	2.3	4	2.2	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
Mlynivske	1	1	4.2	6	-	-	-	-	-	-	-	-	-	-	-	-
Khrinnitske	1	1	3.3	6	2.3	4	2.2	3.7	II	III	2	4	clean	polluted	clean	slightly polluted
Mean value	1.3	1.9	3.2	6.0	2.6	4.3	2.3	4.1	II	III	2	4	clean	polluted	clean	slightly polluted

*the lake is in the Volodymyrets district, ** in the Zarichne district

Lake Bile (in the Volodymyrets district) water quality has belonged to the II quality class (2nd category by average values and 3rd category for the worst values). This is the best water quality in Rivne region according to the ecological index I_e. The worst indicators have been COD (5th category), copper, and iron (4th category).

The water quality of *Lake Nobel* has belonged to the II class (3rd category) by average values, and to the III class (5th category) by the worst values. The worst criteria have been: the salt block – sulfates (3rd category); trophic and saprobiological block – COD and nitrate nitrogen (6th category); block of toxic substances – fluorides, copper, and iron (4th category).

Lake Somyne has had water quality of the II class (3rd category) by the average values and III class (5th category) by the worst. The content of chlorides and sulphates was assessed as 2nd category. The worst indicators of the trophic and saprobiological block – COD (7th category), among toxic substances – iron (5th category).

The water of *Khrinnitske* and *Basiv Kut* reservoirs has belonged to the II quality class in terms of average (2nd category), and to the III class by the worst values (4th category). In Khrinnitske reservoir the worst indicators were the content of nitrate nitrogen and COD (6 and 5 categories, respectively). The content of copper, zinc and iron has been at the level of the 4th quality category. Nitrite nitrogen has been a critical criterion for the Basiv Kut reservoir (5th category). Among the toxic indicators, copper and iron have had the worst values (4th category).

The water quality of *Mlyniv Reservoir* was established by the tropho-saprobiological block – quality class III, category 4th; the worst indicators – nitrite and nitrate nitrogen (6thcategory).

Thus, according to the average values of the salt block indicators, the surface waters of the region belonged to the I-II quality classes. The assessment by worst values showed that the surface waters are described by the spectrum of I-II-III quality classes (46% – 53% – 1% of sites, respectively). In particular, the worst category was established by sulfates content in 31 control sites, chlorides – in three sites on the Ustia River, sulfates and chlorides – in eight sites.

The study of water quality according to trophic and saprobiological criteria showed that the surface waters are related to the II-III classes by average values, and to the III-IV-V classes according to the worst. The worst indicators (7th category) were following: phosphate phosphorus (Horyn, Ustia, Zamchysko), nitrite nitrogen (Ustia, Zamchysko, Berezhanka), nitrate nitrogen (Slonivka, Berezhanka), COD (Lake Somyne), and pH (Lake Chorne). Since the trophicity (the predominant type) can be established by the trophic and saprobiological indicators (index I_2), it is allowed to conclude that about a third of the surface waters are eutrophic (37% of sites), while the rest water bodies have the more threatening trend (fig.2).

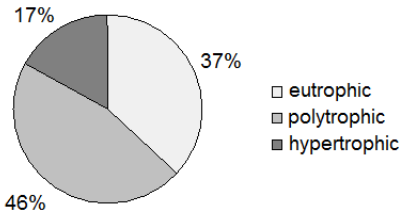

Fig. 2. Spectrum of trophicity categories (predominant type) of surface waters in the Pripyat River basin (% of control sites)

This is a regional illustration of global problem of surface waters eutrophication, which is accelerating as a result of economic activity. Under the greatest risk of eutrophication – the Horyn River in the area of drainage water discharge from the territory of the phosphogypsum dump of PJSC "Rivneazot", and also separate parts of rivers Sluch, Ustia, and Zamchysko.

According to the criteria for the content of specific toxic substances, the surface water quality of Rivne region is described II-III classes by average values, and II–III–IV–V classes by the worst values (1%–65%–21%–13% control sites). The worst indicators (7th category) were concentration of copper (Horyn, Styr, Slonivka, Zamchysko Rivers), fluorides (Horyn, Styr, Ikva), petroleum products (Horyn, Zamchysko, Buniv), and zinc (the Buniv River).

Thus, the ecological assessment of water quality according to the ecological index I_e has showed that the water bodies of the region belonged to the II quality class in terms of average values, that is, they are characterized as "clean" and "fairly clean". According to the worst indicators, the surface waters have belonged to the II-IV classes, and are characterized by the range of assessments "fairly clean" – "slightly polluted" – "moderately polluted" (Table 7).

Table 7. Assessment of surface water quality of the Pripyat River basin according to the integral ecological index (I_e) by the worst values

Water quality class	Degree of cleanness (by class)	Water quality category	Degree of cleanness (by category)	Number of sites / %	Water bodies (site)
II–III	clean-polluted	3	fairly clean	2 / 2.4	Zhabichi River (upstream the discharge from the treatment plant of Demydivka settlement) Bile Lake in Volodymyrets District
		4	slightly polluted	56 / 68.3	Rivers: Pripyat, Stokhid, Sluch, Styr, Prostyr, Stubelka, Viliya, Putylivka, Zhabichi (downstream the discharge from the treatment plant of Demydivka settlement); Khrinnitske reservoir, Bile Lake in Zarichne district
		5	moderately polluted	24 / 29.3	Rivers: Horyn, Ustia, Slonivka, Buniv, Ikva, Zamchysko, Berezhanka; Lakes: Nobel, Somyne, Chorne

Analysis of the ecological indices of the rivers of the region (fig. 3) makes it possible to distinguish three stages in the quality changes of the surface waters [5]: 1 – deterioration, from 1964 to 1990 (I_e from 2.5-3.3 to 3.1-3.3 by average values, from 3.0-3.7 to 3.6-4.3 by the worst); 2 – improvement, from 1990 to 2000 (I_e to 2.3-2.8 by average values, 2.6-2.9 by the worst); 3 – stabilization and decrease in the water quality of some rivers by the worst values, after 2000 (I_e fluctuations 2.1-2.6 by average, 2.4-3.5 by the worst). Such dynamics of surface water quality in the region could be explained by economic reasons, in particular, by a decrease in industrial production in the 90s of the XX century, as well as by a decrease in the water content of rivers at the beginning of the XXI century, due to the growing aridity of the climate.

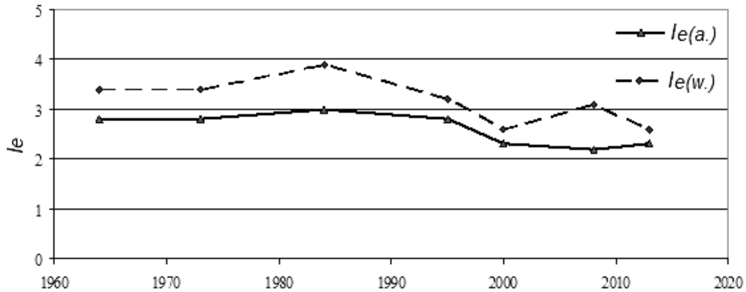

Fig. 3. The change in the quality of surface waters of the Styr River by I_e index: *Ie(a.)* – average values, *Ie(w.)* – the worst values

CONCLUSION

The assessment of surface water quality of the Pripyat River basin (the area of right-bank tributaries of the middle reaches) according to the I_e index has showed that the water bodies belonged to the II quality class in terms of average values and are characterized as "clean" and "clean enough". According to the worst values, the water bodies belonged to the II-IV quality classes and are characterized as “fairly clean” – “slightly polluted” – “moderately polluted”.

Most often, the 7th category of water quality (very dirty) was set by the content of phosphates, less often – nitrogen compounds. More than a third (37% of control points) of the region's surface waters have been eutrophic, for the rest the trend has been even more threatening: polytrophic – 46%, hypertrophic – 17%. The worst criterion among the block of specific toxic substances (7th category) has been the high concentration of copper. The Ustia River water below the runoff of the city of Rivne has corresponded to IV-V classes ie was "dirty" and "very dirty", with a high content of phosphates, nitrogen compounds, copper, manganese, and zinc.

The analysis of ecological indexes of the region's rivers has shown three periods of changes in the quality of surface waters, which caused by economic and climate reasons: 1 – deterioration, from 1964 to 1990; 2 – improvement, from 1990 to 2000; 3 – stabilization and decrease of water quality of some rivers by the worst indicators after 2000.

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PHENOMENON OF THE ELECTRORETENTION AS MOTIVE FORCES OF CONCERTED ACTION OF ENZYMES ON CELLAR MEMBRANES

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ABSTRACT

Light microscope observation of the electroretention of microorganisms and experiments with enzymes immobilization on collectors in the electric field, give the reason to foresee the determinative role of the electroretention in the concerted action of enzyme systems in any living cells owing to the transmembrane transport of ions, which produce inhomogeneous electric field, polarize of enzymes molecules and force them to pulsatile move. All these circumstances promote enzyme mutual contacts and guarantee coordinated function of biological conveyor with transformation suitable substrates.

Key words: electroretention, immobilization of enzymes, the functioning of enzymes оп membranes.

INTRODUCTION

February 23 1972 a group of researchers Institute of Colloid and Water Chemistry of National Academy of Sciences of-Ukraine (Gvozdyak P.I., Chekhovskaya T.P., Grebenyuk V.D., Koshechkina L.P.) aceidently revealed an incredibly interesting phenomenon, which was named “electroretention” [l].

The essence of the electroretention is that granular, porous or fibrous dielectrics and second-class conductors (collectors, charges) obtain from the water, flowing through them, and accumulate dispersed, colloidal and liquefied in water charged substances or the ones that are polarized (alive and dead microorganisms cells, their detritus, viruses, proteins, nucleic acids, other biopolymers, clay minerals, pigments, dyes and some other organics), after de-electrifying they are separated from the collector, slurried and easily washed with flowing water; the subsequent electric field superposition on the collector restrains the indicated objects from the flowing water and it is endless [2-7].

The electroretention phenomenon, its application part called ”electrofiltration" in particular [8, 9] has become the object of several theses [10-14] and is described in the doctoral thesis in details [15].

Interestingly, at the electroretention on granular silica gel as the collector of known among biologists "wonderful bacillus" – bacterium *Serratia marcescens* – the present red pigment prodigiosin came out of bacterial cells and was sorbed on silica gel, painting it in brightly purple colour [16]. We haven't established the mechanism of this phenomenon.

Incidentally, in almost a decade after our publications concerning enzyme electroretention, a famous Japanese enzymologist, the professor of Tokyo University Shintaro Furusaki published an article about "the new method of enzyme immobilization by the Coulomb force" [20] without reference to our works. As it was found out from our private correspondence

Professor Furusaki not knowing about our publications in the leading scientific magazines of the Soviet Union ("Doklady Akademii nauk SSSR", ”Mikrobiologiya", "Prikladnaya Biohimiya i Mikrobiologiya") rediscovered the electroretention by himself. Soon Tokyo University officially notified us of embodiment of Institute of Colloid and Water Chemistry of National Academy of Sciences of Ukraine in the list of "the best 500 world laboratories", pointing out that "Professor Pilipenko A. heads the institute, and Professor Gvozdyak and others work in it", that surprised and even amused the ones who were present at the academic council meeting of the Institute where this information was announced.

The specialists of colloid chemistry and electrochemistry have had many various. sometimes enough original, but inadequate, speculative explanations of the electroretention phenomenon.

METHODS AND EXPERIMENTAL PROCEDURES

We've decided to visualize the process of microorganisms cells removal from the water flow suspension and their delay on the collector grains under the influence of the electric field. We've produced a special chamber for this purpose [21] Figure 1.

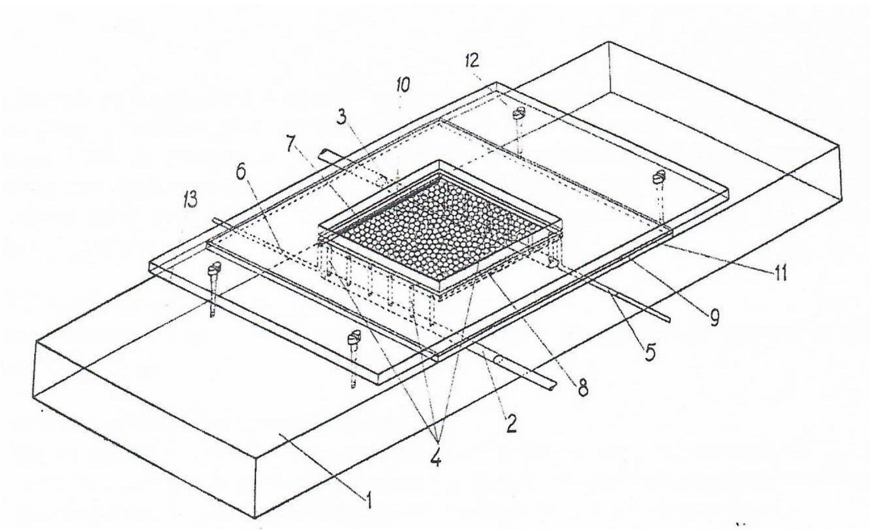

Fig. l. The chamber for observing the electroretention of microorganisms

75 x 28 x 4 mm organic glass plate served the basis of the chamber. In the plate side walls the canals 2 and 3 were drilled opposite each other. They reached 3/4 of its width with an output in the form of thin orifices 4 оп the upper plane. These canals with orifices are assigned to suspension's inlet and drain. The rods 7 and 8, which served as electrodes, were put through the orifices 5 and 6, which also come to the surface plate. The frame 9 made of thin (0.6 mm) elastic rubber sheet was put on the top of the plate. The 15 x 15 x 0.6 mm chamber formed was filled with the layer of spherical silica gel grains 10, 0.5 mm in diameter, and it was covered with the coating small glass 11, pressed to the rubber 9 by the thin plexiglass frame 13 by means of the screws 12. The chamber was placed оп the microscope stage, the suspension flowing was provided optional from the right to the left or from the left to the right; and the behavior of microorganisms cells during different electric field strengths on the electrodes was being observed.

THE RESEARCH RESULTS AND DISCUSSIONS

The experiments were conducted with the suspensions of different microorganisms cells in distilled water. Silica gel and yeast were painted with fuchsine and methylene blue for better Visual clarity. The observations were held in the plane passing through the filler balls diameter.

Only individual cells are adsorbed on the surface of silica gel during the suspension flow through the chamber without the superposition of the electric field, and the principal amount of microorganisms is removed by the flow of the liquid (Figure 2a). Switching on the current puts the microbial cells in motion, different from the direction of the suspension flow.

This movement is not very intense, more or less well-regulated and directed towards the anode at low total electric field strength (about 5 V/cm). The cells are attracted to the surface of silica gel grains, but their especially large number is accumulated in the places of contact between the grains. On the side of the silica gel surface, facing the cathode, numerous chains of microbial cells appear. And if, for example, in the case of *Saccharomyces cerevisiae* the cell number in the chain is 3-7 (Figure 2b), there are twenty and more individuals in each of them in the case of *Bacillus subtilis*. Hardly observable circle-vise movement of cells is observed in the space between the silica gel grains, which intensifies with the increase of electric field strength (Figure 2c).

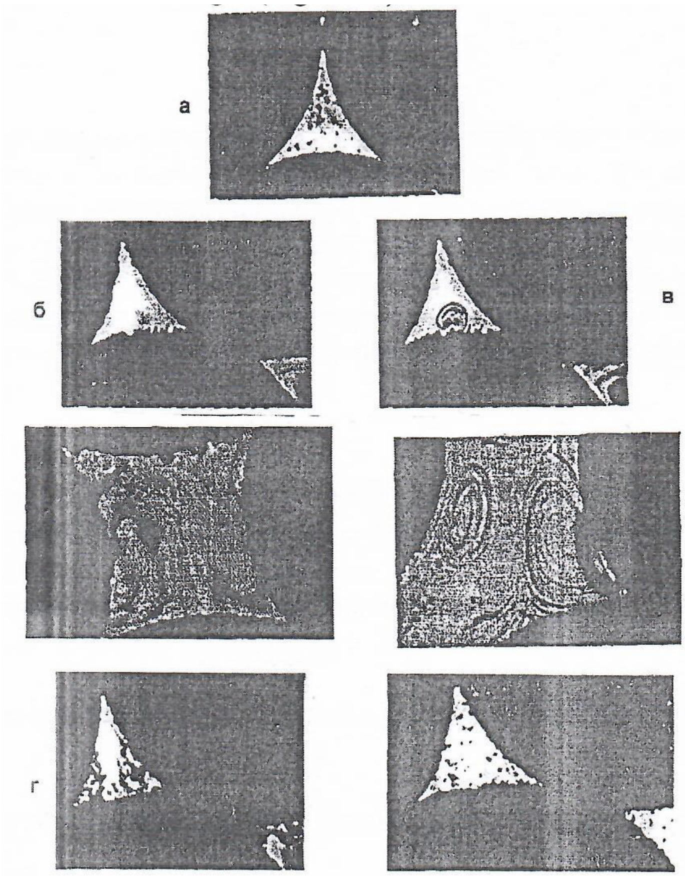

Fig. 2. The behavior of the yeast cells during the suspension movement between the silica gel grains at the electric field strength (V/cm): a – 0; b – 5; c – 20; d – 150; e – after switching off the current

In larger volumes, created by 4-5 grains of silica gel, two or three centers can be observed around which microorganism cells revolve. (Figure 2c). It is characteristic that, when the cells move clockwise around one center, around its nearby one they move counterclockwise. Termination or suspension flow or its slow change to the opposite does not affect the direction of microorganisms rotation, but the change of the polarity on the electrodes results in an immediate change of direction of cell rotation to the opposite one. With further increase of the electric field intensity (about 70-200 V/cm), microorganisms cells accumulate mainly in the joints of grains of silica gel (Figure 2 d), their circular motion is suppressed, and in the intergranular space intense translational movement towards the anode dominates.

After switching off the current, microorganisms cells involved in rotational motion and the 1naj ority of cells that have accumulated on the surface of silica gel are captured by the fluid flow (Figure 2e). Herein, chain units and cells conglomerates immediately fall apart.

Electrostatic interaction of cells with the materials polarized by field obviously plays an important role in the implementation of the effect of microorganisms' retention. To confirm the existence of this interaction direct observation of the behavior of microbial cells in the presence of particles of different materials in an electric field was conducted [22, 23]. We used a very simple installation, the scheme of which is presented in Figure 3. Perfilev's plane- parallel glass capillary [24] was connected to glass tubes 2 With two pieces of thin rubber hose 3. The box was filled with the suspension of microorganisms cells mixed with particles of the test material, and using a special holder fastened to the microscope stage. Electrodes 4 and 5 were placed in glass tubes and the specimen was Viewed under a microscope under different modes of electric power. Bacillus subtilis cells' behaviour 21 (caprolactam and hexamethylenediamine destructor) in the presence of particles of clay minerals (montmorillonite, kaolin, vermiculite, polygorskite), subsoil, sand, silica gel (sorts KSM-2,5 and KSM-S), aerosil A-175, glass (including quartz), asbestos, ion exchange resins (AB-I7 and KU-2), polyurethane, teflon, graphite, activated carbon, iron, copper and such fibers as cellulose 7 cotton, wool, silk, capron, nylon and some others under the influence of constant electric current was studied.

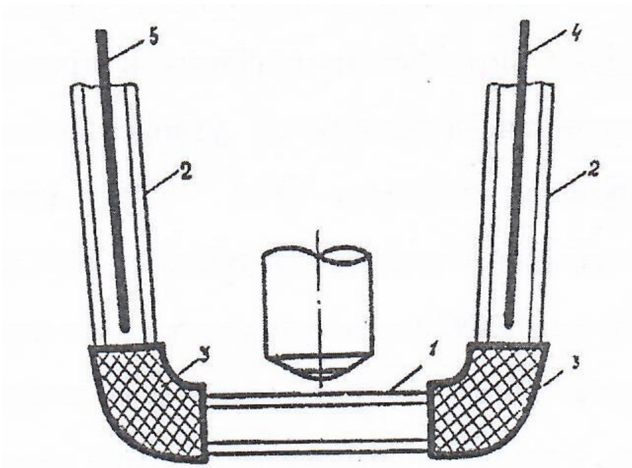

Fig. 3. The chamber for the study of the microorganisms cells behaviour in the electric field in the presence of separate parts of various materials (1 – Perfilev's capillary; 2 – glass tubes; 3 – connecting hoses; 4 and 5 – electrodes).

The interaction of microbial cells with different materials in the direct current electric field is determined by the nature of this material. Thus, for the same values of the electric field intensity and the same suspension of microorganisms, a large number of cells is accumulated on the particles of anionite, clay minerals, aerosil, cation exchange resin, ion-exchange fibers, silk.

The first-class conductors (coal, metals) do not interact absolutely with the microbial cells, which move towards the anode in the constant electric field, avoiding and flowing past these particles. The rest of the investigated materials mediates.

Figure 4 presents the photographs, which illustrate the behavior of the one-day culture cells *Bacillus subtilis* in the presence of the montmorillonite clay mineral particles. In normal conditions (without the electric field superposition) only some cells contact with the clay surface (Figure 4a): the mineral particle has the minus charge similar to the cells, and the suspension is prepared with distilled water which does not contain a fair number of cations that would contribute to adsorbation. A separate mineral particle in a capillary can not be a barrier to microbial cells and they pass it easily in motion of the suspension towards the particle (which can be easily achieved by means of the liquid level change in one of the glass tubes). However, it is enough to apply the direct current electric field to the system, and the cells collect in large numbers on the side of the clay mineral surface, facing the cathode, and are strongly attracted to it (Figure 4b). After switching off the field the bacterial cells leave the clay, forming the uniform suspension. The subsequent electric field superposition leads to the cells accumulation on the particle; if the polarity of electrodes changes, all microbial cells are strongly repelled from this part of the mineral surface, and the others are attracted to the opposite side (Figure 4c).

The differences in the interaction of the microorganisms cells with the surface of various materials in the electric field are determined not only by the nature of these materials, but also by their condition, hydrophilic behaviour in particular. This can be demonstrated through the example of clay minerals, hydrophilic behaviour of which decreases with the increase of baking temperature.

We conducted the experiments with natural montmorillonite of Cherkasy deposit. It is known that at a temperature of 130-140 °C montmorillonite loses sorption associated water (inverse process); at a temperature of 550-575 °C irreversible dehydration of the mineral arises – it gets rid of crystal (structural) water; at a temperature of 850 °C mineral crystallization structure changes, albite and then spine] and other high-temperature crystal phases appear. In this series of experiments the minerals heated to 100-1000 °C and cooled with muffle were used. The baked montmorillonite was split up, the fractions with 30-40 microns particles were selected and mixed with the suspension of microorganisms in distilled water. Intact daily cultures *Saccharomyces cerevisia*e, grown on wort agar-agar (4.0 x 11.0 microns oval cells), and *Bacillus subtilis*, grown on meat- and-peptone agar (MPA) (1,5-3,0 x 0,5-0,8 microns sticks) were used. The concentration of the microorganisms in the suspension was 106-108 cells/ml The same suspension of the microorganisms was used in each series of experiments to compare the intensity of the interaction of the microbial cells with the separate particles of clay tractable to varying temperature processing; more or less the same size particles of montmorillonite were chosen for monitoring. The rectified diode current was conveyed on the electrodes over the same period of time. The picture was recorded on film, the polarity changing was realized and the field of vision was photographed within the given period of time. The electric field strength 15-25 V/cm was created in the chamber.

The relatively large and massive particles of montmorillonite with such intensity of the field didn't move out of location, and the cells rapidly displaced towards the anode. However, as soon as they approached the polarized particle of clay, they were immediately attracted to the side surface, facing the cathode, they were amassed on it and formed many chain aggregates and accumulations. Figure 4 presents the photographs recording the result of the cells Bacillus subtilis two-wave interaction with the particles of montmorillonite without burning and varying degrees (temperature) of burning, in the electric field, the intensity of which was 25 V/cm.

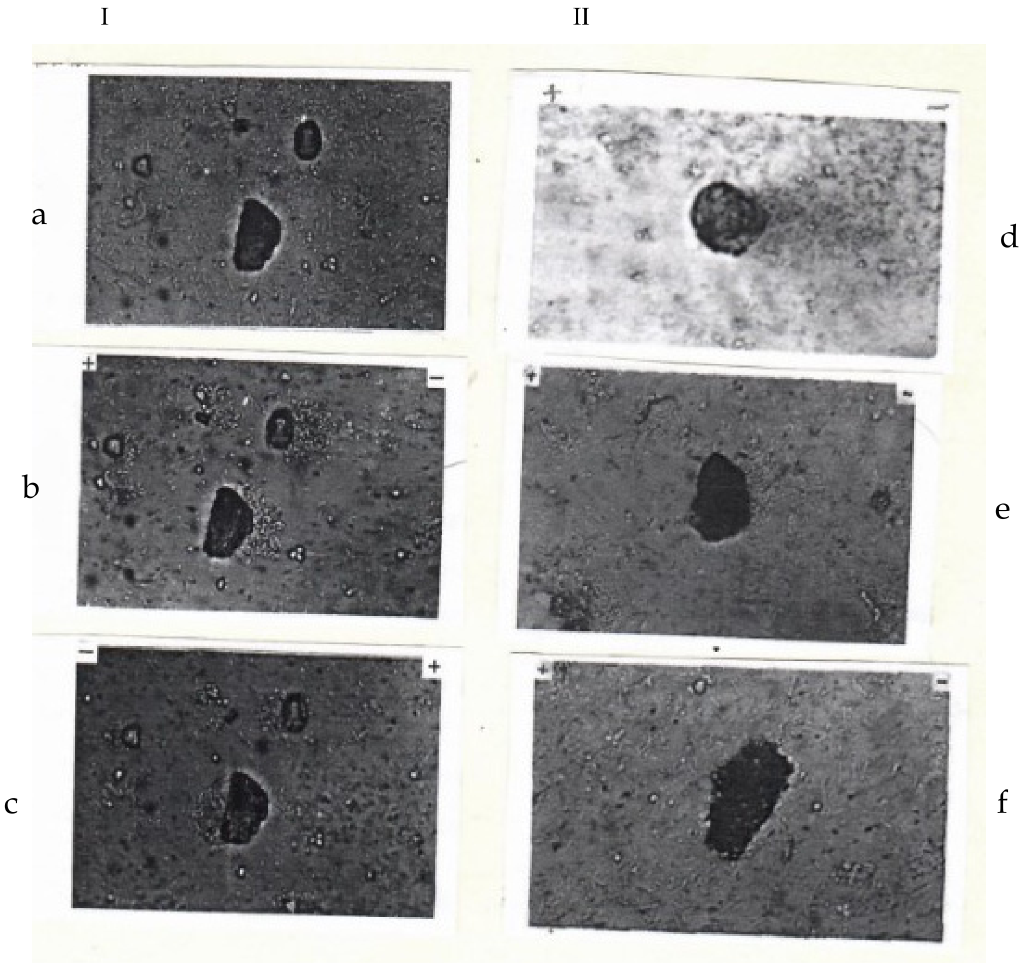

Fig. 4. *Bacillus subtilis* cells behaviour in the presence of particles of clay mineral montmorillonite: I – without superposition of the electric field (a), in the electric field of direct current (b) and after the change of polarity on the electrodes (c); II in the electric field of unbaked montmorillonite (d); after baking clay at 500 °C (e); and after baking clay at 800 °C (f).

Studies have shown that untreated clay mineral particles and samples burned at temperatures below 500-600 °C, with the electric field of direct current rapidly accumulate microbial cells on its surface drawn to the cathode. Changing the polarity of the electrodes leads to a sharp mutual repulsion of the clay particles and microorganisms cells. At this point, with a significant clumping of microbial cells on the surface of the mineral, which can be achieved by increasing time of application of voltage or applying more thick suspension, a sharp shift of clay particles in the opposite direction to the cells' movement is observed. The same kind of repulsive forces act between individual microorganisms cells during polarity inversion. After current cut-off, cells in course of time evenly distribute throughout the volume of the camera again, without forming conglomerates or clusters.

This behaviour of clay particles and microorganisms cells suggests an important role of double electric layer (DEL) in their polarization. It is known that clay mineral particles and microbial cells have some double electric layers in water, the outer cover of which is presented by positively charged ions (Figure 5a). This fact prevents microbial cells from being adsorbed rapidly on the surface of natural clay particle. Superposition of the DC electric field leads to a DEL shift, polarization of particles, causing the cells to be pulled to particles at close distance (Figure 5b). When the electric field is turned off, double electric layers of mineral particles and microorganisms revert to their original “normal" position and overlap (Figure 5c) and being like~charged, cause a sharp mutual repulsion of particles and cells from each other (Figure 5d).

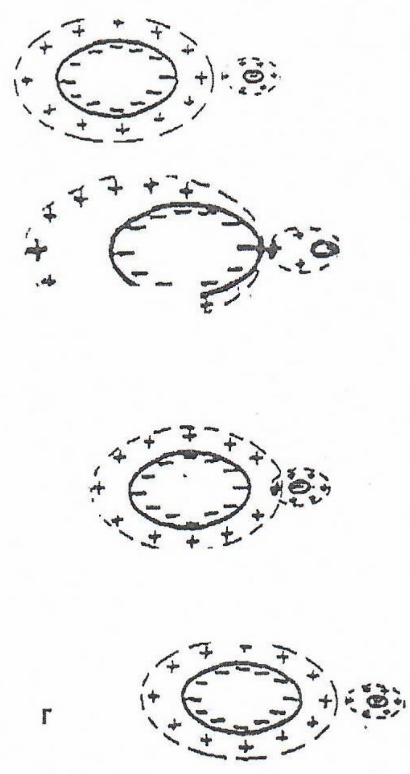

Fig. 5. Scheme of interaction of microbial cell with a clay mineral particle in aqueous suspension – a; with superposition of the electric field – b; after the electric field is turned off – c and d

Thus, the effect of electroretention is apparently connected with polarization of substances in electrical field, charge redistribution, electrostatic, dipole-dipole interaction of materials (collectors) and microbial cells that are known to have significant dipole moment in aquatic environment. This interaction in the first place provides retention of disperse particles by different grainy, porous and fibrous materials in an electric field.

Processes of electroretention of microbial cells, observed directly through a light microscope, can serve as a model of the processes which are still impossible to be seen experimentally: it is, in particular, the immobilization of enzymes on collectors, placed in an electric field.

Cotton wool or sheep wool degreased with chloroform were used as an enzyme collector. Through this filling polarized by the DC electric field, the following solutions were passed: crystalline bacterial amylase (Daiwa Kasei K.K.), purified amylolytic enzyme preparation from the fungus *Aspergillus awamori* (Ukrainian Research Institute for Food Industry, Kharkiv) Amilosubtilin HZh-l (Vilnius plant of enzyme preparations) or *Bacillus subtilis* cell-free extract

21 containing hexamethylenediamine deaminase (HMD) – toxic synthetic substance contained in anide polyamide fiber production wastewater.

Through the filling, with the enzyme fixed on it on the principle of electroretention, the solution of corresponding substrate in distilled water was passed – 1% solution of pasted water – soluble potato starch or 0.1% solution of the HMD.

It was shown that crystalline and technical amylase held by the polarized collector, hydrolyse starch to dextrin, which is not iodophilic, as well as to maltose and glucose. The experiments lasted up to 12 weeks without significant loss of activity of enzymes.

Enzyme systems with *Bacillus subtilis* immobilized in the electric field decomposed HMD almost completely. The experiment lasted for 2 weeks [25, 26].

Thus, enzymes held in an electric field perform appropriate conversions of substrates. It should be noted that enzymes are washed off by the flow of liquid from the volume of filling when the electric field is turned off. However, they do not lose their catalytic properties and can be re-immobilized.

Finding of the fact of enzymes' activity retain in their electroretention opens the prospect for the use of this phenomenon in the immobilization of enzymes in biotechnology as well as in the development of methods for purification and isolation of enzymes from biological mixtures.

Fixing enzymes by the type of electroretention has advantages over other types of immobilization. Thus, for its implementation there is no need in specially prepared collectors and any reagents; both pure crystalline and technical preparations, even cell-free extracts can be sources suitable for fixing enzymes; enzymes can be easily removed from the collector (it is enough to turn off the electric field and flush the system with water) and then use it to secure the same or other enzymes; there is a possibility to immobilize the complex of enzymes or the mixture of various microbial cultures and enzymes; the electroretention minimizes the danger of microbial damage of the immobilized enzymes.

The fact that the system should be kept energized all the time is the essential restriction and disadvantage of the enzyme electroimmobilization, and this complicates the work when the substrate or the resultant is very fluent in the electric field, or when the high ionic strength medium is indispensable for an enzymatic reaction.

The described enzyme immobilization is obviously similar to the electroretention of microorganisms; and it is realized through the electrostatic and dipole-dipole interactions between the polarized particles of collector and protein molecules, which bear an appropriate charge and, as it is known, have a large dipole moment in the electric field. For the reason that collector material has the dielectric permittivity different from liquid and is polarized, the electric field in the volume of the processing chamber is strongly heterogeneous with numerous potential gradients. This creates conditions for dielectrophoretic mobility of protein dipoles in the layers of greater field intensity, and the enzymes are carried to the collector surface by means of electrophoresis and dielectrophoresis. After switching off the electric field the dipole-dipole interaction disappears and the protein is washed out from the collector.

It is commonly known that in any living cell enzymes are united on membranes in the assemblies of clear spatial structure and fixation, moreover all the enzymes of the assembly interface in space and time, realizing the transformation of compounds gradually, by stage as on the conveyer: the product of one enzymatic stage serves as the substrate for the next one. Some enzymes of such a conveyor are mounted in the membrane, permeate it; being fixed in it they can not move rapidly in the membrane, while others, which are placed on the membrane, can move laterally (of course, within certain limits) on its surface.

In our opinion it is the processes, described in the electroretention phenomenon, that provide the mechanics of movement and coordinated interaction of enzymes in their assemblies on (in) the membrane: it is the inhomogeneous electric field of cations' point charges, that pass through the membrane under the influence of transmembrane potential, that forces the enzymes, localized in the membranes, to be polarized, forming temporary dipoles, and the enzymes, placed on the membrane, not only to be polarized but also to move towards more intensive electrical field and thus to come into direct physical contact with the relevant neighbours of the enzymatic assembly (Figure 6), during which the transmission of chemical compounds, the product of the previous enzyme bioconveyor as the substrate for the next enzyme, arises, etc. After the disappearance of the electric field as a result of ionic hydration (for example K^+) or its neutralization by counter ion (for example Cl^-) the enzyme molecules get rid of the dipole state, restore their normal double electric layer (or hydration shell). This leads to their rapping, disjunction, resetting on the membrane; the enzymes realize their inherent transformations of chemical compounds and wait for the appearance of the next inhomogeneous electric field determined by the appearance of another dehydrated ("bare") ion the inside of the membrane, that leads afresh to the dipole formations on the enzymes and provides movement and physical contact between them for a harmonious transmission of the intermediate products of another enzymatic act.

On exit to the surface of the membrane (it is no matter from which side - intracellular or external) this ion creates a three-dimensional inhomogeneous electric field which causes polarization, interaction, movement and contact between the enzymes, set on/in the membrane around the ion channel, that is one and the same ion can "serve" not only one but several enzyme assemblies, exposed from every side by the ion channel.

Section Plan

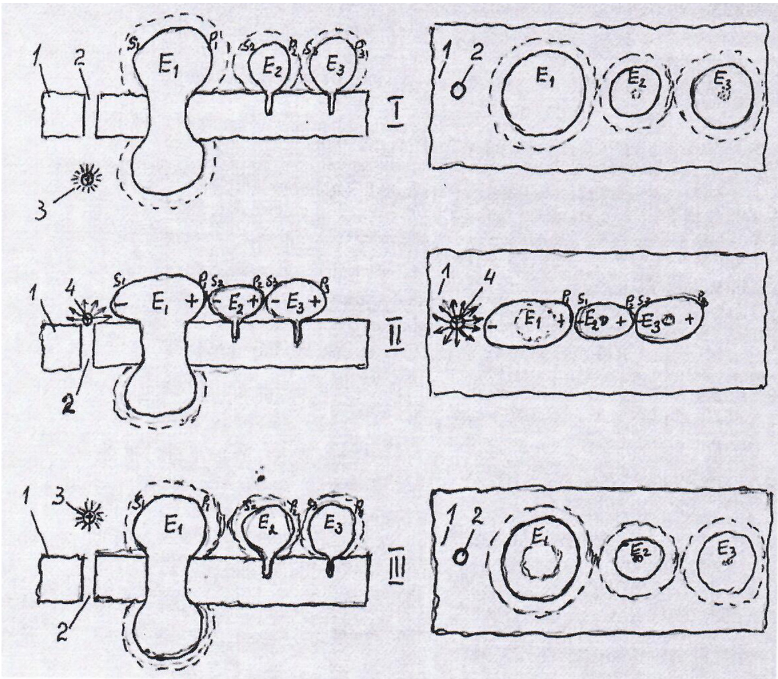

Fig. 6. The fragmentary scheme of functioning of the enzyme assembly on a living cell membrane on the principle of the electroretention. 1 – membrane; 2 – ion channel; 3 – hydrated (neutralized) cation; 4 – "bare" cation; E_1, E_2, E_3 – enzyme assembly; S, P – substrates and products of relevant enzymatic reactions; $P_1 = S_2$, $P_2 = S_3$. I, III – situation without the inhomogeneous electric field; II – situation with the inhomogeneous electric field

CONCLUSION

Incidentally, the proposed hypothesis also explains why the molecules of enzymatic proteins are much larger than it is necessary for the realization of purely enzymatic reactions: the large size of the molecules of enzymatic proteins creates the possibility for its greater polarization, the formation of more powerful dipole moment, which is so indispensible for transition in the inhomogeneous electric field.

Thus, enzymatic reactions in a cell are clearly organized, controlled and determined by the ion transit through the membrane. Substrates are the products of multi-layered enzymatic reactions, which are transferred from one enzyme to another upon their direct contact, realized on the principle of the electroretention phenomena.

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WATER POLLUTION BY SPECIAL WASTE

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ABSTRACT

The environmental impact of special waste was determined using bioindication method. The results show that even small concentrations (1-2%) of shampoos in the water cause total loss of zooplankton and phytoplankton and most of bacterioplankton, indicating the risk of shampoos use. To assess contaminants leaching from waste to water, landfill simulation reactors were used to simulate conditions over several decades. The metals' weight in the input and output waste was compared. The lowest leaching rate was found for lead, while the highest was found for cadmium and chromium. Besides, it was confirmed that the degree of leaching depends on the humidity and organic matter in the landfill: the higher the organic matter, the more heavy metals are leached from the waste. Besides, the system was developed allowing to control light scattering characteristics for environmental monitoring of natural water-disperse media, measuring of brightness at different observation angles under deep-regime conditions, building spatial scattering indicatrix, which makes it possible to determine the ecological state of the water object and the nature of pollution processes.

Keywords: special waste, shampoo, hazardous household waste, bioindication, heavy metals, leaching, water, pollution, water monitoring

INTRODUCTION

Environmental pollution by waste is one of the key environmental challenges. The increase of the world's population and technological progress cause an increase in not only waste amount but also its diversity. To a large extent, this also applies to so-called special waste – the waste requiring special treatment other than household waste. Special waste usually include hazardous household waste (batteries, fluorescent lamps, medical waste, residues of liquids used at households – paints, varnishes, cosmetics, etc.), as well as waste electrical and electronic equipment.

This study evaluates the impact of special waste on water environment by bioindication method using shampoos as a case study. The growing use of shampoos containing dangerous components poses a danger to human health and the environment. Numerous studies confirm this. According to [1], more than 13000 substances may not be used in cosmetic products, and around 250 compounds may be used only under certain conditions. In the studies [2–4], the presence of dangerous ingredients in shampoos in quantities posing a risk was investigated. Besides, under certain circumstances, shampoo components not having significant toxicity can be transformed to more dangerous compounds. For example, Regueiro et al. [5] investigated the possibility of converting triclosan to toxic chlorophenols, dioxins or methyltriclosan. The largest study was conducted by the authors [6], which analyzed about 500 cosmetic products. The results indicate a significant risk to the environment: the predicted concentrations of many chemical compounds contained in cosmetic products (benzophenone, diethylphthalate, butylparaben, triclosan and others) exceed the limits for surface water. Similar results were obtained in [1] as well. There are studies of the environmental impact of cosmetics by various methods, including the method of bioindication [7–9], which show the negative impact of cosmetics on living organisms. The advantage of the bioindication method is that it shows the effect of various substances directly on the life and development of organisms. The quality of the environment should be assessed not only by concentrations of pollutants, but also by the final effect: the presence or absence of toxic effects on living organisms. Different organisms are used for ecological research by the bioindication method: Cladocera – to study the effects of detergents [10], Chlorella algae – to study the influence of hazardous components entering the water [11], microorganisms Daphnia and algae Ulva lactuca – to study the effects of certain species of surfactants [12–14], diatoms and other algae were used [15] to assess the overall pollution of water bodies. The study [13,16] also prove the toxic effect of surfactants on phytoplankton.

Besides, heavy metals are known to be one of the main pollutants in special waste. According to rough estimates, decomposition of electronic waste annually produces more than 40 kg of mercury, 160 kg of cadmium, 260 tons of manganese compounds, and 400 tons of other metal compounds entering the aquatic environment. Moreover, these metals can undergo various uncontrolled reactions in aggressive landfill environment followed by unpredictable formation of hazardous chemicals. Therefore, to assess the environmental risk of aquatic environments pollution by special waste, the degree of heavy metals leaching from waste was estimated using batteries as case study.

Water pollution control is also important. There are many papers [17–19] dedicated to the identification of the most significant polluting substances and to the development of high-quality devices for measuring their concentration in the aquatic environment. The relevance of such research is evident because these devices could help to control a huge amount of substances that are dangerous for the environment. The need for such approach is also due to the fact that each year the number and location of pollution sources varies. This leads to decreasing of surface and underground water quality. Therefore, there is a need for in-time detection and evaluation of new sources of pollution. To ensure proper environmental control of water quality, it is necessary to measure the pollution parameters and to have criteria for making decisions about environmental pollution by this parameter.

METHODS AND EXPERIMENTAL PROCEDURES

To study the effect of dangerous components of cosmetics on living organisms in water environment, the bioindication method proposed in [20] was used. It is based on determining the change in the intensity of algae reproduction under the influence of toxic substances contained in the aquatic environment. Short-term biotesting (96 hours) allows to determine the presence of acute toxic effects on algae, and long-term biotesting (14 days) indicates the presence of chronic toxic effects. In the environmental analysis, the detection of chronic effects is more relevant, as the constant presence of pollution leads to constant exposure. Therefore, a 14-day study was conducted. Chlorella unicellular algae was used a testing object. For the cultivation of Chlorella, 1.5 liters of pond water was sampled and provided with a nutrient medium (KNO_3 – 0,025 g/l, $MgSO_4 \cdot 7H_2O$ – 0,025 g/l, KH_2PO_4 – 0,025 g/l, K_2CO_3 – 0,0345 g/l, $Ca(NO_3)_2$ – 0,1 g/l). 10 samples were prepared from the test water with adding 5 shampoos in different concenrations (1 ml and 2 ml per 150 ml of water) and 1 control sample did not contain any shampoo. The samples were stored in a lighted place for 14 days. Afterwards, a visual examination of the samples was performed using Biolam P-16 microscope (magnification 400 times).

To assess heavy metals leaching, mixed household waste was used. Approximately 3 m^3 of waste was manually separated into 11 fractions: metal, glass, hazardous waste, rubber, wood, food waste, paper, plastic, textile, construction waste, and residual waste. The condition of the three waste fractions listed first were not conducive to proper measurement. The metal fraction contained only steel and aluminum cans and any heavy metals inside the inert glass were mostly immobilized. Heavy metals in these fractions are therefore considered to be negligible, relative to the other fractions. The fraction of hazardous waste was represented by batteries and the metals content was calculated using literature data and masses of batteries found in municipal waste. The concentrations of 4 selected heavy metals (lead, cadmium, nickel, chromium) and of total organic carbon (TOC) were measured in each fraction by graphite furnace atomic absorption spectrometer (ZEEnit 600, ANALYTIK Jena AG) and TOC-L Analyzer (Shimadzu), respectively. The ability of heavy metals to leach from waste was estimated in the following manner. Two different mixtures of the separated waste fractions (see above), were prepared with the following compositions:

(1) Metals – 3%, rubber – 3%, wood – 3%, glass – 8%, food – 20%, paper – 30%, plastic – 10%, textile – 7%, hazardous waste – 1%, construction materials – 6%, residual waste – 9% (total weight 33 kg).

(2) Metals – 2%, rubber – 2%, wood – 6%, glass – 8%, food – 48%, paper – 10%, plastic – 6%, textile – 6%, hazardous waste – 1%, construction materials – 6%, residual waste – 5% (total weight 40 kg).

These waste mixtures were loaded into 2 landfill simulation reactors (LSR) for 3 months to simulate landfill conditions in an accelerated regime. The bottom of the reactors was covered by a 10 cm layer of boulders followed by a layer of tissue to filter the leachate. The waste mixture was then placed followed by more tissue and another layer of boulders to press the waste. To reproduce landfill conditions, the waste in the reactors was compressed, and a constant 37°C temperature was maintained in the reactors by a special isolation cover with heating pipes. Besides, to provide a natural humidity (average in European countries: 650 mm/year), fresh water was added daily to the reactors. With internal reactor diameter of 40 cm and cross-section area of 0.126 m^2, it was necessary to add (650 L × 0.126 m^2) / 1 m^2 = 82 L of water per year or 1.6 L per week. After 3 months, the concentrations of heavy metals and total organic carbon were measured in the output waste.

For the purpose of investigating the possibilities of pollution (incl. by special waste) control, a series of experiments using the automated control system under investigation were carried out in order to obtain the brightness bodies of water-dispersed media with different particle size of the disperse phase. The experiment involved both natural and artificial model environments.

THE RESEARCH RESULTS AND DISCUSSIONS

Impact of special waste on living organisms in water: case study of shampoos

The following 5 types of shampoos were analyzed to assess the effect on living organisms in water environment:

Shampoo No.1: Aqua, Cetearyl Alcohol, Quaternium-87, Propylene Glycol, Panthenol, Niacinamide, Prunus Armeniaca Kernel Oil, Isopropyl Myristate, Distearoylethyl Hydroxyethylmonium Methosulfate, Sodium Benzoate, Citric Acid, Stearamidopropyl Dimethylamine, Ceteareth-20, Glyceryl Stearate, Parfum, Hexyl Salicylate, Benzyl Salicylate, Hexyl Cinnamal, Linalool, Limonene.

Shampoo No.2: Aqua, Sodium Laureth Sulfate, Disodium, Cocoamphodiacetate, Sodium Chloride, Laureth-2, Peg-12, Dimethicone, Citric Acid, Peg-7 Glyceryl Cocoate, Sodium Benzoate, Propylene Glycol, Peg-40 Hydrogenated, Castor Oil, Polyquaternium-10, Peg-55 Propylene Glycol Oleate, Parfum, Salicylic Acid, Niacinamide, Panthenol, Macadamia

Ternifolia Seed Oil, Peg-14M, Hexyl Cinnamal, Butylphenyl Methylpropional, Benzyl Salicylate, Linalool, Limonene, CL 15985, CL 47005.

Shampoo No.3: Aqua, Cichorium Intybus, Sodium Laureth Sulfate, Sodium C12-13 Pareth Sulfate, Cocamidopropyl Betaine, Sodium Chloride, Glycerin, Dimethiconol, Parfum, Glycol Distearete, Carbomer, Sodium Hidroxide, Guar Hidroxypropyltrimonium Chloride, Sodium Laureth Sulfate, Gluconolactone, Trehalose, Adipic Acid, Sodiumcyibenzennesulfonate, PPG-12 Sulfate, Amodimethicone, DMDM Hydantoin, TEA, Citric Acid, Disodium EDTA, Peg-45M, Mica, Sodium Benzoate, TEA- Sulfate, Cetrimonium Chloride, Benzil Alcohol, Benzil Salicylate, Linalool, CL 15985, CL 19140, CL 77891.

Shampoo No.4: Aqua, Sodium Laureth Sulfate, Sodium Chloride, Sodium Benzoate, Glycerin, Cocamidopropyl Betaine, Sodium Xylenesulfonate, Cocamide MEA, Sodium Citrate / Citric Acid, Parfum, Dimethiconol, Cassia Hydroxypropyltrimonium Chloride, TEA-Dodecylbenzenesulfonate, Disodium EDTA, Sodium Oxide, Laureth-23, Dodecylbenzene Sulfonic Acid, Benzil Salicylate, Panthenol, Panthenyl Ethyl Ether, Hexyl Cinnamal. Hydroxyisohexyl, Linalool, Magnesium Nitrate, Argania Oil, Methylchloroisothiazolinone, Magnesium Chloride.

Shampoo No.5: Aqua, Glycerin, Cetyl Alcohol, Amodimethicone, CL 77891/Titanium Dioxide, Mica, Hidroxyethylcellulose, Stearyl Alcohol, Arginine, Behentrimoniun Chloride, Trideceth-6, Chlorhexidine Digluconate, Benzil Benzoate, Benzil Alcohol, Linalool, Isopropyl Alcohol, Hidroxyethylmonium Methosulfate, Myristyl Alcohol, Cetyl esters, Cetearyl Alcohol, Cetrimonium Chloride, Citric Acid, Parfum, Coumarin, Hexyl Cinnamal, Glyceryl Oleate, Glyceryl Linolenate.

The characteristics of water samples with algae are given in the Table 1.

Table 1. Characteristics of samples for biotesting

No. of sample	Volume, ml	Shampoo added	Volume of shampoo, ml
1a	150	No.1	1
1b	150	No.1	2
2a	150	No.2	1
2b	150	No.2	2
3a	150	No.3	1
3b	150	No.3	2
4a	150	No.4	1
4b	150	No.4	2
5a	150	No.5	1
5b	150	No.6	2
6	150	control sample	0

The results of visual analysis of the samples with a microscope after 14 days (Table 2) show that zooplankton has died in all the samples (except the control).

Another study with use Daphnia magna Straus [9] showed 100% mortality of living organisms in 5–47 minutes after adding the shampoo. However, the concentration of shampoo in the samples in that study was higher (5%). Bacterioplankton was still alive only in samples 2a, 4b, 5a, 5b and 6 (respectively shampoos No. 2, 4, 5 and control sample), and phytoplankton – in samples 2a, 5a, 5b and 6 (respectively shampoos No. 2, 5 and control sample). Therefore, most of the bacterio- and phytoplankton have died. Though zooplankton is less resistant to shampoos.

Table 2. Results of visual analysis of the samples

No. of sample	Description	Presence of zooplankton	Presence of phyto-plankton	Presence of bacterio-plankton	Presence of small colloidal particles
1a	small colloidal particles, absence of bacterioplankton	-	-	-	+
1b	small colloidal particles, absence of bacterioplankton	-	-	-	+
2a	partially damaged phytoplankton cells, phytoplankton became 5-10 mm mucus clots with rare (10-15%) partially damaged phytoplankton cells, presence of bacterioplankton	-	15%	+	+
2b	completely destroyed phytoplankton cells, absence of bacterioplankton	-	-	-	+
3a	small colloidal particles, absence of bacterioplankton	-	-	-	+
3b	small colloidal particles, absence of bacterioplankton	-	-	-	+
4a	small colloidal particles, absence of bacterioplankton	-	-	-	+
4b	small colloidal particles, completely destroyed phytoplankton cells, presence of bacterioplankton	-	-	+	+
5a	completely destroyed phytoplankton cells, small colloidal particles and bacterioplankton	-	5%	+	+
5b	partially damaged phytoplankton cells, small colloidal particles and bacterioplankton	-	30%	+	+
6	undamaged cells of phytoplankton and zooplankton, presence of bacterioplankton	+	+	+	+

It is worth noting a clear correlation between the death of phyto- and bacterioplankton. That is, all the samples (except sample 4b) with phytoplankton survived had bacterioplankton alive as well. Comparing the effects of different amounts of shampoos added, it can be concluded that in some cases the content of shampoos significantly affected the survival rate of plankton. Microorganisms in the samples 2a and 2b (shampoo No.2) reacted differently to different concentrations of the same shampoo. In the sample 2a, where the shampoo content was twice lower than in sample 2b, bacterioplankton and partly phytoplankton have survived. In turn, all living organisms have died in the sample 2b. A similar result was obtained for pairs of samples 1a – 1b, 3a – 3b, and 5a – 5b. Difference in the pair of samples 4a – 4b may indicate that the content of the shampoo about 1% (2 ml of shampoo per 150 ml of water) was the threshold for the survival of bacterioplankton (bacterioplankton has died in the sample 4b). In the remaining samples, the microorganisms have died regardless of shampoo content. This indicates a significant negative impact of small shampoo concentrations on living organisms. This is also confirmed by another study [14] of surfactants, which are the main potential danger in shampoos. The authors found some surfactants to be toxic at 2.5–3 mg/l concentration, which roughly corresponds to the concentration in our study.

The results show that most phytoplankton have survived in the sample 5b. One can assume this is due to the absence of many potentially dangerous ingredients (e.g., SLS/SLES, Cocamidopropyl Betaine, Propylene Glycol) in the shampoo No.5 (unlike other samples). Previous studies using unicellular green algae [16] confirm this assumption to some extent: the effect of SLES on test organisms was one of the largest. 2–3 mg/l of SLES caused 100% death of test organisms (Scenedesmus subspicatus algae). However, it certainly needs more research.

Water contamination by heavy metals leaching from municipal waste

To assess metals leaching from waste to water, one should measure metal concentration in the input waste. Since all waste fractions were mixed and partially decomposed at the end of the experiment, it was impossible to measure the residual concentrations of heavy metals and TOC in each fraction separately. Therefore, the input and residual weight of each heavy metal and TOC in the waste mixtures were compared (see Tables 3 and 4).

Table 3. Heavy metals in municipal waste fractions, μg/kg

Waste fraction	Pb	Cd	Ni	Cr
Plastic	40.1	0.8	–*	38.6
Textile	10.2	0.3	–*	14.0
Rubber	170	6.4	–*	1228
Wood	10.6	0.2	–*	167
Paper	7.7	0.1	–*	9.4
Construction material	6.9	0.1	–*	10.5
Food waste	4.0	–*	–*	7.0
Hazardous waste	13950**	228220**	661220**	50550**
Residual waste	19.9	0.2	–*	49.3
Mean in MSW1	226	3330	9646	819
Mean in MSW2	248	3762	10899	908

*below the detection limit

**calculated

If comparing the landfill simulation reactors used, there was a trend for all heavy metals and TOC to be leached more in LSR2. This is probably caused by higher waste humidity in LSR2 due to significantly higher content of organic (food) waste. It is known that metals are leached from the waste in a soluble form that can be ensured by moisture [21]. Besides, high content of organic waste in LSR2 has evidently contributed to lowering the pH. Average pH of the leachate was 5.5 and 5.8, respectively for LSR1 and LSR2. A low pH increases metals solubility and hence leaching [22]. The difference between the reactors in metals leaching was approximately the same, while the difference between TOC leaching was much more. This finding also relates to the content of organic waste since its decomposition is the main reason of TOC leaching. Therefore, food waste is likely to be the main source of mobile organic compounds. That explains increased metals leaching in LSR2 taking into account more food waste in that reactor. There were 76 and 265 mg/kg of TOC leached in LSR1 and LSR2, respectively. These data are consistent with previous study (120 mg/kg) [23].

Table 4. Weights of heavy metals and total organic carbon

Parameter	LSR1			LSR2		
	Input weight (mg)	Input weight excl. batteries (mg)	Residual weight, mg (%)	Input weight (mg)	Input weight excl. batteries (mg)	Residual weight, mg (%)
Pb	5.1	0.5	3.5 (69%)	6	0.4	3.4 (57%)
Cd	75.3	0.01	2.7 (3.6%)	91.3	0.01	1.8 (2%)
Ni	218.2	0	0.7 (0.3%)	264.5	0	0.5 (0.2%)
Cr	18.5	1.8	3.3 (18%)	22	1.8	2.5 (11.5%)
TOC	11.3	–	9.5 (85%)	13.9	–	7.5 (54%)

In 12 weeks, several decades of real landfill were simulated under an accelerated water regime [24]. The lowest leaching rate was noticed for lead. That can be explained by low solubility of many lead compounds even in an aggressive environment. Widespread lead compounds in household waste including oxides, sulfates, sulfides, and organometallic compounds are insoluble in water and, according to authors [25] can hydrolyze and become soluble only when pH > 6. Prechthai [26] has defined that 80% of lead in household waste is insoluble, which was proved by Yanful et al. [27] indicating insoluble carbonate as the most widespread lead compound in the waste. Besides, as described in previous section, most of the lead was found in the batteries (in the form of insoluble oxides and sulfates), as well as in the rubber and plastic slowly degrading in landfills. Therefore, even lower lead leaching could be expected. Theoretically, lead can be leached by dissolving its compounds in an acidic environment to form soluble lead acetate or nitrate. The higher amount of organic matter in LSR2 creates a more acidic environment and thus more favorable conditions for leaching of lead and other metals. For example, Janz [21] reported lead mobilization by organic chelate complexes. Lincoln et al. [28] have measured the highest concentration of lead in the leachate in comparison to other heavy metals when simulating their leaching from WEEE. On the other hand, Aucott et al. [29] have investigated that organic compounds have a high sorption capacity for lead, and can bind it retaining in the waste body. Also, lead leaching from municipal waste was the lowest among heavy metals studied by Qu et al. [30].

Much more chromium and cadmium were leached. First, more chromium compounds are water-soluble (for example, chromium sulfates and dichromates contained in some waste fractions) and hence can easily be leached. Secondly, other authors [26,31] consider chromium as a metal with one of the largest exchange form that can be easily leached. Since much of chromium was found in rubber, it probably remained unleached due to inertia of rubber (almost half of the total residual mass of chromium was initially in the rubber). This allows for the assumption that most chromium contained in hazardous waste (batteries) was leached. Less chromium was leached in another study [21]. The author explains this fact by the reduction of chromium (VI) to chromium (III) in acidic environment and subsequent immobilization to a low-soluble chromium oxide $Cr(OH)_3$ and chromium-organic complexes.

The high leaching of cadmium can be explained by the interaction of cadmium hydroxide (the main cadmium form in batteries known to be the main source of this metal in household waste) with acids and the formation of soluble cadmium salts. It is also known that cadmium intensively forms metal-organic compounds through binding with organic matter [25]. Afterwards, cadmium metal-organic compounds can be easily leached. Also, chloride complexes may have some influence. Among the heavy metals, according to the study [25], mobile chloride complexes of cadmium are most likely to be formed. As the potential source of chlorides in municipal waste, one may consider food waste and some types of plastic (PVC). It can be concluded that most cadmium (more than 95%) was leached from batteries as it was supposed for chromium. In another study [21], cadmium leaching from the waste was lower due to the formation of low-soluble cadmium sulfides and their subsequent sorption by solids. Cadmium may also be bound with manganese (iron) oxide or carbonates as shown in [26].

The change in the nickel content cannot be clearly interpreted. On the one hand, the residual nickel content was very low. This could mean that all the nickel was leached. For example, den Boer [32] has found nickel having the largest share of mobile forms among heavy metals in waste. Considering batteries as the only source of nickel found in municipal waste, we can conclude that all nickel was leached. On the other hand, an error might have occurred as Ni was only present in batteries and those might not have been included in the sample which was taken after leaching (nugget effect). The latter is confirmed by the insolubility of nickel compounds in batteries (nickelates, nickel oxides and hydroxides). However, these compounds can be converted in soluble nickel sulfate or chloride and leached under favorable conditions – acid environment and sufficient moisture content. Taking into account the measurements made, it is difficult to define whether such conditions have occurred. The hypothesis of nickel non-leaching is also evidenced by the fact that only 5% of nickel compounds in natural environments exist in soluble forms [25]. Besides, some studies [21,33] have shown that 99% of metals, including nickel and mercury, are not leached from waste containing e-waste, including batteries. However, leaching ability was determined by metals contained in the leachate. In fact, some amount of metals was released from the waste, but sorption processes did not allow metals to be leached by liquid.

A high importance for heavy metals leaching may have sulfur compounds contained in municipal waste, first of all in organic waste, plastic, and paper. Due to the short experimental period in the current lab-scale study, only the first acid phase in real landfill was simulated, when most sulfur is known [21] to be in the form of sulfates. The solubility of cadmium, chromium, and nickel sulfates and the insolubility of lead sulfate confirm accordingly high (for Cd, Cr, Ni) and low (for Pb) metals leaching.

If not considering the batteries, the concentrations of metals (except nickel) in the output waste were higher compared to those in the input waste. This may be explained by low metals leaching from the waste and by waste mass reduction due to the decomposition and leaching of organic matter, which is confirmed by other studies [34]. Another reason might be the binding of heavy metals leached from batteries in, for example, aluminosilicate complexes as reported by Qu et al. [30].

The heavy metals concentrations measured in the output waste after 12-week simulation (Pb: 0.13–0.16 mg/kg, Cd: 0.09–0.10 mg/kg, Ni: 0.03 mg/kg, Cr: 0.12–0.13 mg/kg) were significantly lower in comparison to those in the waste from real landfills. For example, in Greece metals content ranged from 5 (for Cd) to 50 (for Cr) mg/kg [35], and in Austria – from 50 (for Cr) to 350 (for Pb) mg/kg [36]. It should be noted that waste was sampled in the old landfills. Thus, there was more time for heavy metals to be enriched in waste body.

Heavy metals are known to be leached from landfills for hundreds of years, especially if they are bound within a mineral phase [37]. Therefore, if landfill is still in operation or after-closure procedures would not take place, and leachate is continuously generated, then heavy metals cause a long-term environmental risk.

Experimental studies of impurities in aqueous disperse media

A series of experiments using the automated control system were carried out in order to obtain the brightness bodies of water-dispersed media with different particle size of the disperse phase. The experiment involved both natural and artificial model environments.

According to the task the turbid media (milk, rosin and soap solutions) were used. They have absorption coefficient negligible in comparison with the scattering coefficient. Also the model disperse artificial (polychlorinated vinyl latex) and natural (phytolatex of Rewultex type) media were used. The following particle sizes were used: 0.0087 μm, 0.0875 μm, 0.55 μm, 0.875 μm and 5.255 μm.

The milk medium was prepared by mixing the appropriate amount of natural milk with water. In this case, the concentration of the solution from 0.05 to 5% was applied so that the conditions of the deep regime were most effectively implemented. To obtain a rosin medium, a saturated solution of rosin in alcohol was prepared. The two parts of this solution were mixed with one part of the alcohol, and then diluted with distilled water. The resulting rosin "milk" was mixed in the right amount with tap water. This method of preparation prevents coagulation of the rosin. When considering the rosin medium under a microscope, a large number of Brownian particles, as well as particles of irregular shape with different diameters were observed.

The soap medium belonging to colloidal media was prepared by dissolving soap in hot distilled water. The resulting solution was diluted with warm bidistilled water to the desired concentration, and then the medium was cooled to air temperature. PVC latex and phytolatex of Rewultex type were prepared according to the methods developed by the State Research Institute "Elastik" of the National Academy of Sciences of Ukraine.

The irradiation was carried out on the most characteristic wavelengths for the visible range: 450, 550 and 650 ηm. The received experimental bodies of brightness for a wavelength of 550 ηm are presented in Fig. 1.

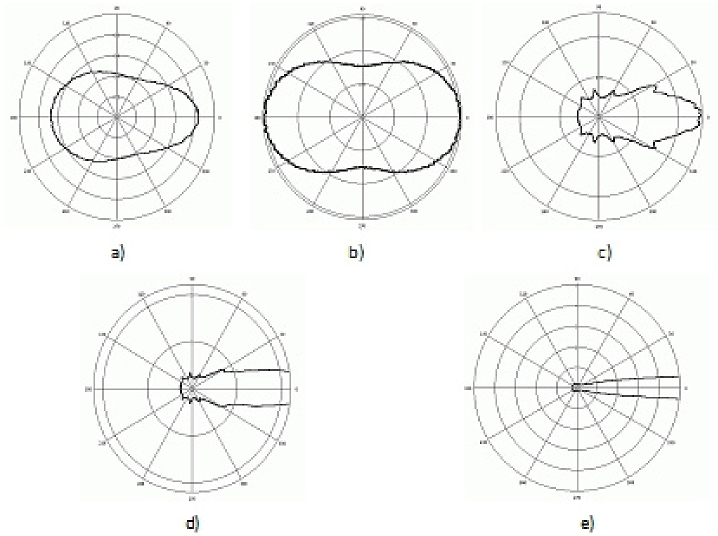

Fig. 1. Body of brightness (scattering indicatrix) of dispersed media based on PCV-latex with different sizes of dispersed particles:
a) 0.0087 μm, b) 0.0875 μm, c) 0.55 μm, d) 0.875 μm, e) 5.255 μm

According to Fig. 1, as the particle size increases the brightness body gradually shifts and extends toward the dissemination of the radiation flux. In addition, for the case of the equality of the particles size and wavelengths of the incident light, sharply expressed diffraction and interference extremes are observed. This is particularly for the angles of 30˚, 60˚, 100˚ and 135˚, which coincides with the theoretically predictable mathematical models [38].

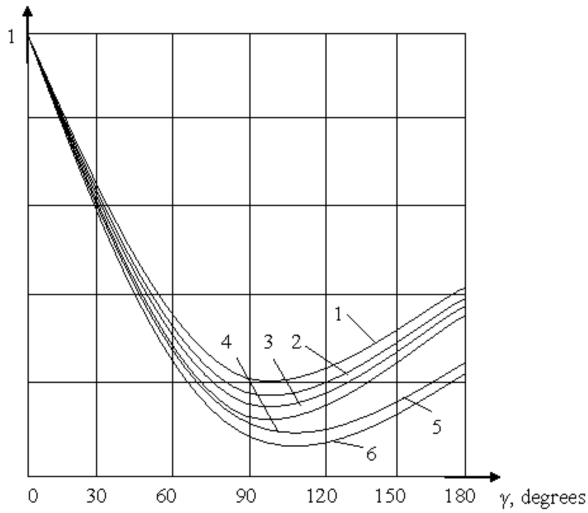

Fig. 2. Scattering indicatrix of dispersed media: 1 – seawater; 2 – river water; 3 – soap water; 4 – rosin milk; 5 – phytolatex of Rewultex type; 6 – aqueous solution of natural milk.

On the basis of investigations of selected model environments indicatrix using the developed automated system, it has been proved that the patterns of radiation dissemination in the model environments are to a large extent adequate to real natural objects such as lake, sea, etc. (Fig. 2).

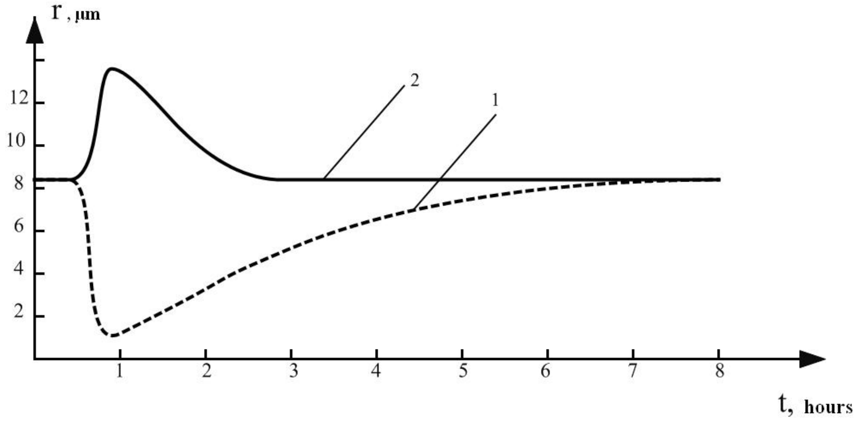

Fig. 3. Changes of contaminant particles size (rc) in polluted water with different dispersion of pollution: 1 – rc < r of water particles; 2 – rc > r of water particles

According to the results of experimental studies, as shown in Fig. 3, it was established that depending on the size of the contaminant particles, the average particle size of the water-dispersed medium also changes. That is, in order to establish the fact of pollution at the certain time and to predict the dispersal composition of the pollutant, it is sufficient to know the disperse composition of the water environment before the pollution and to determine the average particle size of the contaminated water-dispersed medium.

On the basis of the observations results (Fig. 4), one can also concludes that the scattering indicatrix and brightness body for contaminated water-dispersed media extend with the increase of contaminant particles size. After some time after the beginning of the pollution, the pollutants start to interact with the water-dispersed medium. There are a number of physico-chemical processes of transformation, in particular, coagulation, sedimentation, etc., resulting in the changes of initial water-disperse medium dispersal composition.

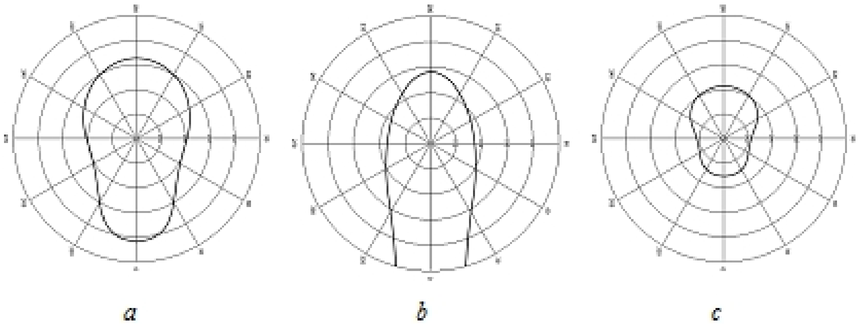

Fig. 4. Changing the scattering indicatrix: a – prior to contamination; b – after contamination with the $r_1 > r_2$; c – after contamination with $r_1 < r_2$, where r_1 is the average particle size of the contaminated water-dispersed medium, r_2 is the average particle size of the water-dispersed medium prior to contamination.

CONCLUSION

A study shows a significant environmental impact of special waste on living organisms in water environment using shampoos as case study. Even small (1–2%) impurities of shampoos in water cause total death of zooplankton and most of the phyto- and bacterioplankton within 14 days. Comparison of the shampoos of different composition suggests that the algae Chlorella can be most affected by surfactants SLS/SLES, Cocamidopropyl Betaine, Propylene Glycol. Some research results indicate that 1% shampoo content in water leads to total death of living organisms in most cases.

Assessment of water contamination using simulation of real landfill conditions shows higher leaching of all metals from waste fractions with a higher content of organic matter. Lead has the lowest leaching rate, which can be explained by the low solubility of its compounds. High cadmium and chromium leaching rates indicate a significant potential risk of their mobile compounds being released into the environment. Therefore, knowledge of short and long-term leaching behaviors of heavy metals may prevent contamination of the water environment or at least better assess its environmental impact when landfills are closed.

Regarding the water pollution control, the main indicators are scattering indicatrix and brightness body, which are extended with the increase of contaminant particles size for contaminated water-dispersed media. Therefore, in order to prove the fact of pollution at the certain time and to predict the dispersal composition of the pollutant, it is sufficient to know the disperse composition of the water environment before the pollution and to determine the average particle size of the contaminated water-dispersed medium.

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INFLUENCE OF WASTE WATER DISCHARGE ON NITRIFICATION PROCESSES IN NATURAL WATER BASIN

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ABSTRACT

Nitrification activity determines the activity of «self-purification» of natural water basins from the nitrogen compounds The data of regular monitoring of the concentration of nitrogen-containing compounds and indicators of nitrification in the river Udy (in areas of 500 m before to the discharge of treated wastewater of Kharkov and 500 m after the discharge downstream) and in wastewater have been analyzed. Special laboratory experiments determined the chemical and biological kinetic constants of nitrification in the water column and biochemical characteristics of nitrification in the bottom sediments in these areas, as well as on sections of the river Siv.Donets (500 m before the wastewater discharge of the Zmiiv Paper Mill and 500 m after the discharge downstream)**.** It is shown that the rate of nitrification in the water column in the River Udy doubles in the area after the discharge of treated wastewater in Kharkiv compared to the area before the discharge. It is likely that the discharge of deeply treated wastewater from treatment plants that carry out biological treatment with nitrification, is accompanied by a certain removal of nitrifying bacteria and increases the activity of nitrification processes in the water column of the natural reservoir downstream. On the contrary, the discharge of low-treated wastewater from the Zmiiv Paper Mill in the river Siv.Donets inhibits nitrification (hence the activity of "self-purification of the river" from nitrogen compounds) in the river by 59% due to the high residual content of organic pollutants.

Keywords: nitrification1, natural water reservoirs2, wastewater3, environmental safety4, nitrites5.

INTRODUCTION

The ammonia nitrogen treatment of sewage is an important environmental and technological problem, a solution of which is necessary both for the discharge of wastewater into natural reservoirs [1] and for the introduction of closed water systems [2]. For such purification adsorption [3], reagent [4] technologies and biotechnology nitrification are used.

Nitrification is two unique reactions of nitrogen cycle in the biosphere which conducted by hemolytoavotrophic nitrification bacteria [5, 6]. Ammonia oxidation bacteria (nitrificators of the 1^{st} stage) make the first stage of nitrification by oxidizing ammonia to nitrite and nitrite oxidizing bacteria (nitrificators of the 2^{nd}stage) make the second stage of nitrification by oxidizing nitrite to nitrate [7].

Nitrification activity determines the activity of «self-purification» of natural water basins from the nitrogen compounds [8-10], what is more ecologically safe via the speed equality of the both stages of nitrification. In some areas of the water basins the rate of the 2^{nd}stage of nitrification is lower than the one of first stage what causes nitrite accumulation [11]. Low nitrite concentration maintenance in water systems is a serious problem because nitrite is very toxic substance [12, 13].

Ability of nitrifying microorganisms to oxidize $N\text{-}NH_4$ and $N\text{-}NO_2$ was widely used in the biological treatment of wastewaters [1, 14, 15]. Biological nitrification as a wide scale biotechnology used as a final stage of wastewater treatment when treated water which contains nitrates can be discharged into the water basin and in the modern technologies for the deep treating from nitrogen compounds as intermediate stage when it is composed with denitrification [16, 17]. Modern schemes of municipal wastewaters treatment use recycles of sludge liquid in the two-, three-, four- and five-stage processes which allow not only remove nitrogen compounds, but also another biogenic elements [18]. In practice of municipal wastewater treatment one-sludge systems usually used which must conduct chemoorganotrophic and chemoautotrophic (mainly chemosynthesis of nitrification bacteria) microbiological processes [1, 19].

Biological wastewater treatment plants are potential sources of biogenic elements and also microorganisms (included nitrification bacteria) for the rivers in which carried out wastewaters discharge. Species and activity of microorganisms from the wastewaters from the wastewater treatment plants can differ from the ones which was found in a river upstream and can change river ecological functioning [20]. Hence, wastewaters from the wastewater treatment plants can change nitrification and nitrification bacteria concentration in natural water basin. Particularly dangerous in this sense is the discharge into the natural reservoirs of insufficiently purified landfill filtration. The concentration of ammonium ions in them is ten times higher than that concentration in urban wastewater [21]. And though throughout the last decade wastewater treatment processes were essentially improved discharge of the treated wastewaters can lead to increasing of ammonia and nitrifying bacteria concentrations in river systems and, as a result, to change nitrification kinetic and nitrite dynamics in a water system area [11, 22].

The aim of the work is determination of nitrification process activity in the river Udy and the river Siv.Donets before and after treated wastewaters discharge.

METHODS AND EXPERIMENTAL PROCEDURES

Objects of experimental investigations:

– The water and bottom sediments from the river Udy in the area 500 m before and 500 m after the treated municipal wastewaters discharge;

– Wastewater and active sludge of aeration tanks from the Municipal wastewater treatment plant №2, which conduct discharging into the river Udy;

– The water and bottom sediments from the river Siv.Donets in the area 500 m before and 500 m after the Zmiiv Paper Mill wastewaters discharge;

– Wastewater of the Zmiiv Paper Mill

Previous investigations of nitrification process evidence in the river Udy within the area of the treated municipal wastewaters discharge were executed by the multiyear data analysis of every day nitrogen compounds concentration control in the areas of investigation. Chemical and biological constants determination in natural water basin was implementing on the basis of laboratory experiment results which have been done according to the method [13]. For the experiment the water from the river Udy and the river Siv.Donets in the area 500 m before and 500 m after the wastewaters discharge have been taken. In the day of taking samples in water concentrations of mineral nitrogen compounds (N-NH_4, N-NO_2, N-NO_3) and organic nitrogen were determined. Every sample (2.5 dm^3each) was incubated without adding any reagents during 20-31 days in a dark place and a temperature 19ºC in not tightly closed bottle to provide oxygen income. At certain intervals samples of water from the each bottle were taken to determinate the nitrogen compounds concentration.

Chemical constants of ammonification and both stages of nitrification were determined based on the experimental data via the formulas listed in [13] and designed mathematic program (C++ programming language and Qt framework). Biokinetic constants value (Michaelis constant – K_S, and the maximum rate of the biochemical reaction) were determined via the data by linearization method of Wolker Shmidt [23].

Nitrification capability and rate of nitrification in bottom sediments from the river Udy (in the area 500 m before and 500 m after the treated municipal wastewaters discharge) were determined via the biochemical method [24] according to enzyme activity which catalyzes hemolitotrophic ammonia oxidation (hydroxylamine oxidoreductase). The concentrations of nitrification bacteria were determined by microbiological methods of limit dilutions [25].

Hydrochemical analysis of water environments (N-NH_4 – colorimetrically adding Nessler reagent; N-NO_2 – colorimetrically adding α-naphthilamine, N-NO_3 – colorimetrically adding sodium salicylate, N_{org} titrometrically after wet mineralization, pH – electrometrically, COD – arbitration method adding potassium dichromate) was conducted via standard methods according to Ukraine standards demands [26]. Statistical processing of data was conducted via computer program Microsoft Excel.

THE RESEARCH RESULTS AND DISCUSSIONS

NITRIFICATION ACTIVITY EVALUATION IN THE WATER OF THE RIVER UDY IN THE AREA 500 M BEFORE ANG 500 M AFTER THE TREATED MUNICIPAL WASTEWATERS DISCHARGE ACCORDING TO REGULAR CONTROL DATA

Nitrogen compounds concentration in the river Udy (daily water consumption is 950 000 m^3) in the area 500 m before and 500 m after the treated municipal wastewaters discharge presented in Fig. 1.

It's shown that in 5 years dynamics N-NH_4 concentration after the treated wastewaters discharge in the river Udy mainly decreases. At that time N-NO_2 and N-NO_3 concentrations constantly increase, which testifies that nitrification activity in the river Udy after the wastewaters discharge is increasing.

This conclusion was confirmed by the calculation of the nitrification index (I_{nitrif}) within the period of investigation (2014-2017) in the area before and after the treated wastewaters discharge (Fig. 2). Water nitrification index (I_{nitrif}) was determined via the formula 1 recommended by the scientific literature [8]:

$$I_{\text{нітр}} = C_{NO_3}/(C_{NO_3} + C_{NH_4} + C_{NO_2}), \quad (1)$$

where C_{NO_3}, C_{NH_4}, C_{NO_2}–N-NO_3, N-NH_4 and N-NO_2 concentrations.

As it is shown nitrification index from 2015 till 2017 at the area after the treated wastewaters discharge is 5-13% higher then this index in the area before the discharge.

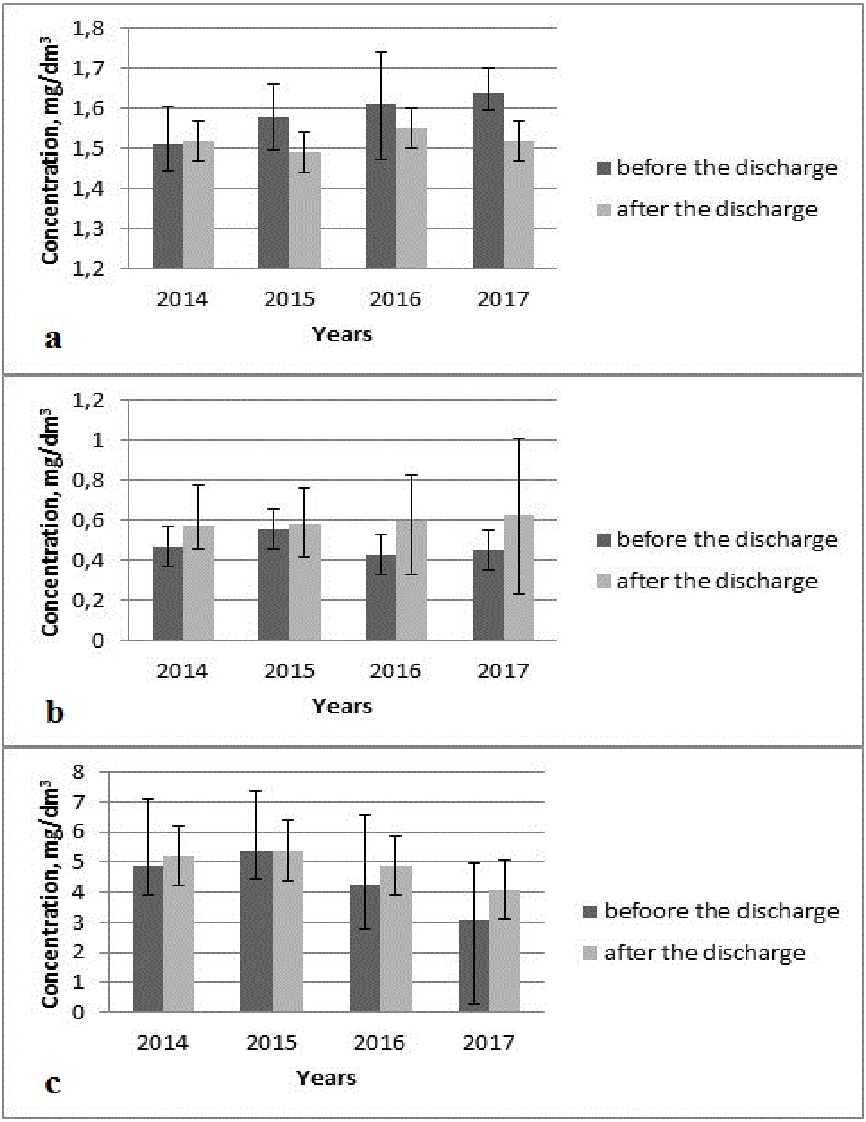


Fig. 1. Average annual concentration dynamics of $N\text{-}NH_4$ (a), $N\text{-}NO_3$ (b) and $N\text{-}NO_2$ (c) in the river Udy before and after the treated wastewaters discharge

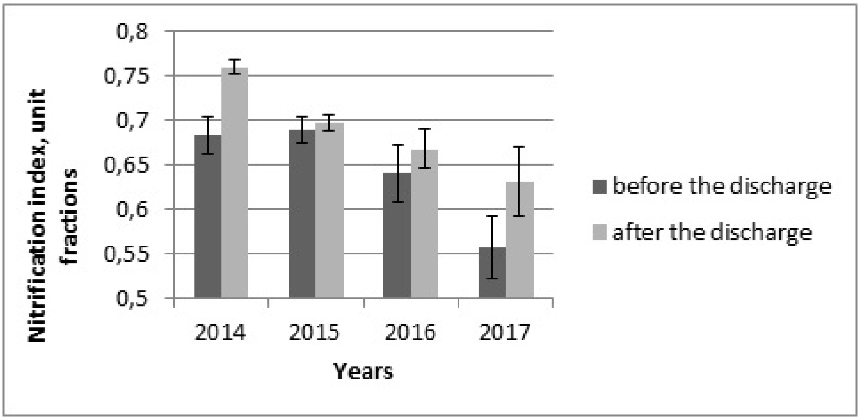


Fig. 2. Average annual dynamics of the nitrification index (2014-2017) in the river Udy before and after the treated wastewaters discharge

DETERMINATION OF NITRIFICATION KINETIC CHARACTERISTICS IN THE RIVER UDY BEFORE AND AFTER WASTEWATERS DISCHARGE

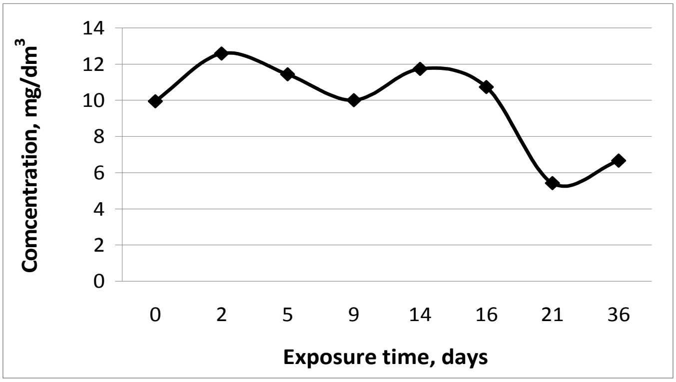
Determination of nitrification kinetic characteristics in the river Udy before and after the treated wastewaters discharge was implemented in October in the period of death and destruction of hydrobionts and aquatic plants biomass after summer vegetation and therefore high concentration of organic and nitrogen compounds in water.

According to experiment results (Fig. 3), N-NH_4 concentration during the exposition in initially increases (due to free ammonia and ammonification reactions [9, 13]. But then it fell steadily, more over in the area after the treated wastewaters discharge more intensive than in the area before the discharge.

The sequence of biochemical transformations of nitrogen compounds studied in laboratory experiments can be represented as follows (2):

$$N_{org} \overset{k_1}{\rightarrow} NH_4^+ \overset{k_2}{\rightarrow} NO_2^- \overset{k_3}{\rightarrow} NO_3^+, \quad (2)$$

where k_1 – ammonification rate constant, k_2 –nitrification 1st stage rate constant, k_3 – nitrification 2nd stage rate constant.



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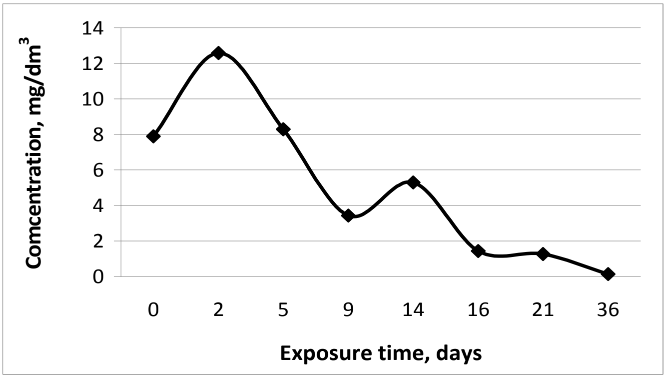

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Fig. 3. Dynamics of the concentration of N-NH_4 in water from the river Udy, sampled 500 m before (a) and 500 m after (b) of thetreated wastewaters discharge, in the exposure process

For the determination of ammonification and nitrification (1^{st} stage) rate constants was used method [13], which implies that these reactions are sequential and have the first order. This system includes two equations (3, 4) and looks like this:

$$[N_{\boldsymbol{N-NH_4}}]_{max} - [N_{\boldsymbol{N-NH_4}}]_0 = [N_{\boldsymbol{org}}]_0(\frac{k_2}{k_1})^{\frac{k_2}{k_1-k_2}} , \quad (3)$$

$$t_{max} = \frac{\ln\frac{k_2}{k_1}}{k_2-k_1}, \quad (4)$$

where $[N_{org}]_0$– initial organic nitrogen concentration, mg/dm^3; $[N_{N-NH_4}]_{max}$ – maximum N-NH_4 concentration, mg/dm^3; $[N_{N-NH_4}]_0$ – initial N-NH_4 concentration, mg/dm^3; t_{max} – time of N-NH_4 maximum concentration reaching, days.

2^{nd}stage of nitrification rate constant determination was conducting (equation 5):

$$\left[NO_2^-\right]_{max} - \left[NO_2^-\right]_0 = k_1 k_2 \left[N_{org}\right]_0 \left[\frac{e^{k_1 t}}{(k_1 - k_2)(k_3 - k_1)} \frac{e^{k_2 t}}{(k_1 - k_2)(k_3 - k_2)} \right], \quad (5)$$

where $\left[NO_2^-\right]_{max}$ – maximum N-NO$_2$ concentration, mg/dm^3; $\left[NO_2^-\right]_0$ – initial N-NO$_2$ concentration, mg/dm^3; t – time of N-NO$_2$ maximum concentration reaching, days.

As it is shown in Table 1, the value of k_1 (ammonification rate constant) is the same in the both areas of investigation. In that time k_2 and k_3 in the area after the discharge of the treated wastewaters are slightly higher compared with the area before the discharge. This means that nitrification activity enhances after the treated wastewaters discharge. In water samples before and after the treated wastewaters discharge k_2 is several times higher than k_1, and k_3 far exceeds k_2, which allows to assume that nitrites accumulation probability in the river is minimal. In general, values of k_1, k_2 and k_3 (determined in experiments) correspond with data from the investigations of north natural water basins (presented in scientific literature) [13].

Table 1. Nitrification and ammonification kinetic characteristics in the water of the river Udy in the area 500 m before and 500 m after the treated municipal wastewaters discharge

Water basin	Ammonification and nitrification 1st and 2nd stages rate constants (k_1, k_2, k_3), day^{-1}		
	k_1	k_2	k_3
The river Udy (500 m before the discharge)	0.22	0.9	1.3
The river Udy (500 m after the discharge)	0.22	1.0	1.4

Calculated value of biokinetic constants is presented in Table 2. According to determined rate of nitrification is possible to calculate nitrifying bacteria (ammonia oxidizing bacteria) concentration (kinetic determination) (Table 2) based on the data [27]: NH_3 oxidizing rate by one cell of ammonia oxidizing bacteria reaches 484 *f*mol NH_3/h. The obtained results (taking into account the concentration of N-NH$_4$ in the used aqueous media) are consistent with those ones of other researchers [27]**.**

Biokinetic indicators calculation (Table 2) showed that received data is corresponding with data of other natural water basins and wastewater treatment plants [13]. Before the treated wastewaters discharge K_s is ten times higher than after the discharge. It indicates the essentially lower affinity of nitrification enzymes to ammonium nitrogenin the area before the discharge.

Table 2. Biokinetic nitrification indexes in the river Udy and 1st stage of nitrification bacteria concentration in water basin environment in areas before and after the treated wastewaters discharge

Nitrifying microboicenoses	K_S, mg/dm^3	V_{max} of 1st stage nitrification, mg N-NH$_4$/(dm^{3}day)	Concentration of 1st stage nitrifying bacteria, cells/cm^3
The river Udy (500 m before the discharge)	1.7	0.48	$2.9 \cdot 10^3$
The river Udy (500 m after the discharge)	0.17	1.29	$7.9 \cdot 10^3$

Nitrification rate in the area after the treated wastewaters discharge is more than double exceeds this value before the discharge. So the deep treated wastewaters discharge promotes increasing of nitrification ability of water environment in the river Udy. Such phenomenon in the area after the treated wastewaters discharge in the river was noted by foreign scientific experts [22].

DETERMINATION OF NITRIFYING ABILITY OF BOTTOM SEDIMENTS IN THE RIVER UDY IN THE AREA BEFORE AND AFTER THE WASTEWATERS DISCHARGE

According to data from the scientific literature [13] main input in the natural water basins nitrification make the activity of nitrifying bacteria immobilized in the top layer of bottom sediments. Nitrifying ability in bottom sediments determination results according to biochemical analysis data is shown in Table 3.

Table 3. Biochemical characteristics of bottom sediments from the river Udy

Bottom sediments	Activity of hydroxylamine oxidoreductase, μg formazan/($g_{dry\ substance}$·min)	1^{st} stage nitrification rate, mgN-NH_4/ ($g_{dry\ substance}$·h)
Before the wastewater discharge	3.1	0.03
after the wastewater discharge	3.2	0.03
Active sludge (Brion et al. 2000)	22-50	0.35-0.77

As received data shows, hydroxylamine oxidoreductase enzyme activity in bottom sediments before and after the discharge have the same order of values and, consequently, the rate of nitrification in this bottom sediments is almost the same.

Thereby, nitrification activity increasing in the river Udy which was determined (according to multiyear regular control data of nitrogen compounds, nitrification index) in the area before and after the wastewaters discharge is because of wastewaters discharge intensify influence on the indexes in water (not on the nitrification indictors in bottom sediments). The such conclusion confirms data of French scientists, which was got during the investigation of nitrification in the river Seine [22].

INDICATORS OF NITRIFYING ABILITY DETERMINATION IN ACTIVE SLUDGE FROM THE MUNICIPAL WASTEWATER TREATMENT PLANT №2 WHICH DISCHARGE WASTEWATERS IN THE RIVER UDY

Data on the composition of the treating urban wastewater are presented in Table 4.

N-NH_4 concentration after the treatment essentially decreases (up to 92,5 %). In that time nitrite and nitrate concentrations increasing which are an obvious characteristic, firstly, of the deep wastewaters treatment and, secondly, of passing the full nitrification process (1^{st} and 2^{nd} stages) (Table 4).

Data of straight microbiological nitrification bacteria concentration determination in active sludge of biological waste water treatment plant and its nitrifying activity are presented in Table 5.

Table 4. The composition of wastewater at municipal sewage treatment plants № 2 Kharkiv

№	Indexes	Concentration, mg/dm^3	
		incoming	treated
1	BOD_5	240	15
2	$N\text{-}NH_4$	30	2.3
3	Mineralization	600	610
4	Suspended solids	220	15
5	SO_4^{2-}	218	235
6	Cl^-	117	120
7	COD	395	80
8	Fe_{tot}	1.3	0.42
9	Cu^{2+}	0.028	0.013
10	Cr^{+6}	0.024	0.013
11	Petroleum products	2.7	0.35
12	PO_4^{3-}	15.1	2.1
13	Synthetic surfactants	0.12	0.038
14	NO_3^{--}	1.2	14.5
15	NO_2^-	0.33	0.43

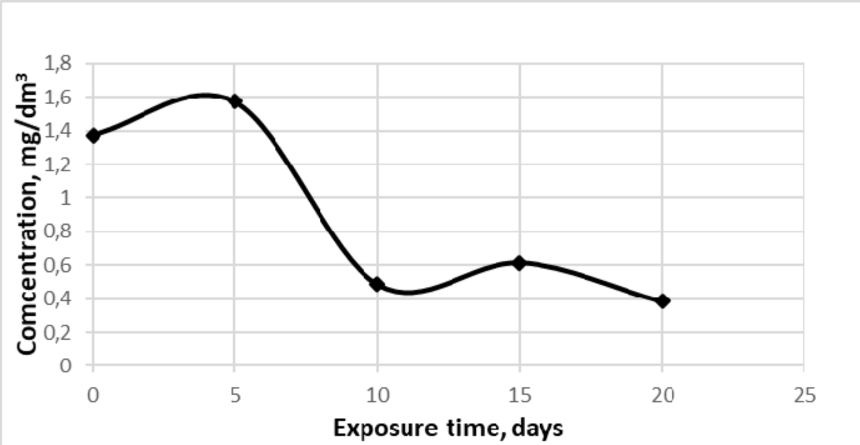
Table 5. Microbiological characteristics of the nitrifying ability of active sludge from the municipal wastewater treatment plant №2

Sludge samples	COD, mg/dm^3	Concentration N-NH_4, mg/dm^3	Concentration of 1st stage nitrifying bacteria, cells/g $_{ashless\ sludge}$
Beginning of aeration tank-displacer	110-160	16,7-19,1	10^6-10^7
Ending of aeration tank-displacer	30-52	1,8-2,3	10^6-10^8

As the presented data show, nitrification bacteria concentration in active sludge from wastewater treatment plant in the ending of aeration tank-displacer increases as a result of passing nitrification in this zone and reaches 10^6-10^8 cells/g $_{ashless\ sludge}$. Everyday emission of nitrification bacteria from the wastewater treatment plant into the river Udy can reach 2,7·(10^{15} - 10^{17}) cell/day, taking in account suspended meter concentration in wastewaters when discharging (≤ 15 mg/dm^3) and the discharge volume (180 ths. m^3/day).

DETERMINATION OF THE IMPACT OF WASTEWATER DISCHARGE OF ZMIIV PAPER MILL IN THE RIVER SIV.DONETS ON THE ACTIVITY OF NITRIFICATION IN THIS RESERVOIR

The volume of wastewater discharge from sewage treatment plants at the Zmiiv paper Mill is 2,400 m^3 / day. The results of the laboratory study of the dynamics of N-NH_4 concentration in the water from the river Siv.Donets on the area of 500 m before and 500 m after the discharge of wastewater from the Zmiiv paper Mill are presented in Fig. 5.



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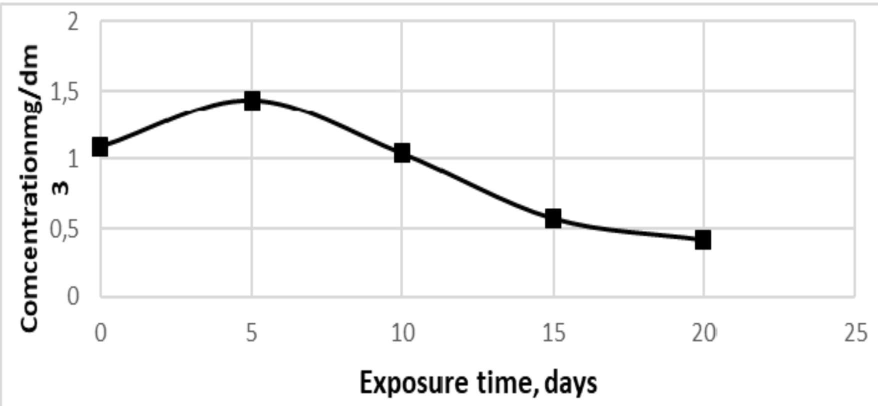

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Fig. 5. Dynamics of the concentration of N-NH_4 in water from the river Siv.Donets, sampled 500 m before (a) and 500 m after (b) of thetreated wastewaters discharge, in the exposure process

As you can see from the dynamic of N-NH_4 concentration the process of nitrification of ammonium compounds took place more actively in the water of the river Siv. Donets on the site before the sewage discharge of Zmiiv paper mill.

The results of calculations of biokinetic constant of nitrification activity at the site are presented in table. 6. Calculation of the rate of nitrification in the water of the river Siv.Donets in the area of Zmiiv showed that the discharge of insufficiently treated wastewater of the Zmiiv paper mill in the river Siv.Donets significantly (approximately 59%) suppresses the rate of nitrification in the reservoir.

To determine the factors of negative impact of wastewater on nitrification in the river Siv. Donets performed water analysis before and after discharge and analysis of wastewater itself. The results of hydrochemical studies are presented in table. 7. As can be seen, after the discharge of the Zmiiv paper mill wastewater into the river water, the salt content increases significantly (by about 40%).

Table 6. Biokinetic nitrification index in the river Siv.Donets, and 1st stage of nitrification bacteria concentration in water basin environment in areas before and after the treated wastewaters discharge

Nitrifying microboicenoses	V_{max} of 1st stage nitrification, mgN-NH_4/(dm^3day)	Concentration of 1st stage nitrifying bacteria, cells/cm^3
The river Siv.Donez (500 m before the wastewater discharge by the Zmiiv paper mill	0.22	$1.3 \cdot 10^6$
The river Siv.Donez (500 m after the wastewater discharge by the Zmiiv paper mill	0.09	$5.2 \cdot 10^5$

Table 7 – Indicators of water quality in a natural reservoir (the river Siv.Donets) and wastewater of Zmiiv paper mill

Water basin	Indexes			
	N-NH_4, mg/dm^3	N-NO_2, mg/dm^3	Mineralization mg/dm^3	COD, mg/dm^3
The river Siv.Donez (500 m before the wastewater discharge by the Zmiiv paper Mill	1.37	0.19	323	10
Wastewater of Zmiiv paper mill	1.31	0	619	424
The river Siv.Donez (500 m after the wastewater discharge by the Zmiiy paper mill	1.09	0.21	451	20

The concentration of organic matter (COD) in the wastewater of the Zmiiv paper mill had high concentrations, which were unacceptable for the discharge of such wastewater into natural reservoirs. Thus, when discharging untreated wastewater with a high content of inorganic (salt) and organic compounds, nitrification in a natural reservoir is significantly inhibited, and, consequently, the "self-purification" of the reservoir as a whole.

CONCLUSION

1. According to multiyear monitoring (nitrogen compounds concentration, pH of the water and the nitrification index) the treatment wastewaters discharge from the wastewater treatment plant (which conduct deep biological treatment with nitrification) increases the nitrification activity in natural water basins and, as a result, «self-cleaning» activity of the basins from ammonium nitrogen of autochthonous and allochthonous origin.

2. The determination of the rate constants of the I and II phases of nitrification in laboratory experiments showed that the constants of the rates of nitrification of the I and II phases in the area after discharge of treated wastewater are somewhat higher than at the site before discharge. Moreover, the rate constant of nitrification of phase II significantly exceeds the rate constant of nitrification of phase I in water samples before and after discharge of treated wastewater. This allows us to predict the minimum probability of nitrite accumulation in the river.
3. Calculations of biokinetic nitrification constants have shown that the rate of nitrification in the area after sewage discharge exceeds this figure before discharge more than twice. Michaelis constant in the river water before discharge is about an order of magnitude higher than after discharge. This indicates a greater affinity of nitrification enzymes to ammonium nitrogen in the area after discharge, and probably changes in the species composition of the nitrifying microbiocenosis in the river Udy water.
4. Sewage discharge of Zmiiv paper mill inhibits nitrification in the river Siv.Donets by 59%. The most probable reason for the inhibitory effect of wastewater from the Zmiiv Paper Mill on nitrification in the river Siv.Donets River is the extremely high concentration of organic pollutants (COD).
5. Discharge of wastewater from Kharkiv treatment plants, which carry out deep biological treatment with nitrification, increases the activity of nitrification processes in the river Uda, and, consequently, the activity of "self-treatment" of this reservoir from ammonium nitrogen of autochthonous and allochthonous origin. Everyday emission of nitrification bacteria from the wastewater treatment plant into the Udy river can reach 2.7 (10^{15} - 10^{17}) cell / day.

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CONCENTRATION OF ACIDIC INDUSTRIAL WASTEWATER BY ELECTRODIALYSIS

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ABSTRACT

On an industrial electrodialysis apparatus equipped with industrial membranes MK-40 and MA-40, at different hydraulic and electrical operating modes of the apparatus, the possibility of maximum concentration of the residual acid HCI present in the H-cation washings was investigated. It has been shown that when the ratio of the flow rate of the initial solution in the dialysate and concentration sections is 13: 1 and the voltage on the apparatus is 180-200 V, it is possible to concentrate hydrochloric acid up to 5% and return it to the production cycle for regeneration of the cation exchanger. At the same time, the residual concentration of hydrochloric acid in the dialysate is 0.05%, which significantly reduces the consumption of alkali, which is currently used to neutralize acidic industrial wastewater.

Key words: electrodialysis, ion-exchange membranes, waste water, ion exchangers.

INTRODUCTION

Wastewater, including acidic industrial waters, have a negative impact on the environment, especially on its water basin, drainage and sewerage systems. Liquid solutions, the pH of which goes beyond pH 6.5-8.5, are excessively (physiologically and technically) active and usually, before discharge, are subject to additional treatment. Pretreatment and purification of acidic effluents should be carried out at enterprises of the chemical, textile and light, pharmaceutical, ferrous and non-ferrous metallurgy, oil and gas and hydrocarbon industries [1-3].

There are two main methods for treating acidic effluents - neutralization and dilution of the solution to acceptable pH values. When diluted with water, undesirable acidic compounds do not actually disappear, but only diluted with water and carried away by the liquid flow through the drain pipes [4-6,8]. Gradually, this weak acid solution will react with the surrounding aquatic environment to form compounds, some of which can pose a significant environmental hazard; it is also possible to purify acidic effluents by coating the inner walls of the discharge lines with a salt or corrosive coating, however, when using this method, the service life of the discharge system is significantly reduced [7-9].

In the chemical neutralization of acidic effluents, the pH of liquids is adjusted by adding alkali, using various methods of dosing the reagent; it was found that the use of dispensers for this purpose is unprofitable and creates great inconveniences in the work [1, 5, 10-15]. Neutral waters, in the case of increased salinity and their large volumes, pose an ecological threat to the environment. So, thermal and nuclear power plants annually throw 780-800 thousand tons of salt [6, 14, 16].

At some enterprises, attention is paid to the maximum possible extraction of pollutants from wastewater resulting from the loss of raw materials or products for their subsequent use [17, 18].

One of the possible methods for the regeneration of acidic wastewater is membrane methods, in particular electrodialysis. Electrodialysis is a membrane separation process in which ions of a solute are transported across a membrane by an electric field [7, 8, 19-21]. The driving force of the process is the electric potential gradient. Under the action of an electric field, cations move towards the negative electrode (cathode). Anions move towards a positively charged electrode (anode) [22, 26, 28]. By using cation-exchange or anion-exchange membranes, electrodialysis can be used to increase or decrease the concentration of the electrolyte solution. The matrix of the anion exchange membrane has cationic groups [23-25, 27, 29]. The charge of cations is neutralized by the charge of mobile anions in the pores of the membrane. Anions of the electrolyte solution can be incorporated into the membrane matrix and replace the anions initially present in it. The penetration of cations into the membrane is prevented by the repulsive forces of cations fixed in the membrane matrix. Cation-exchange membranes containing fixed anionic groups act in a similar way. In a multi-chamber electrodialyzer, a certain number of cation-exchange and anion-exchange membranes alternate (their number is determined by the capacity of the apparatus), located between two platinum electrodes (Figure 1).

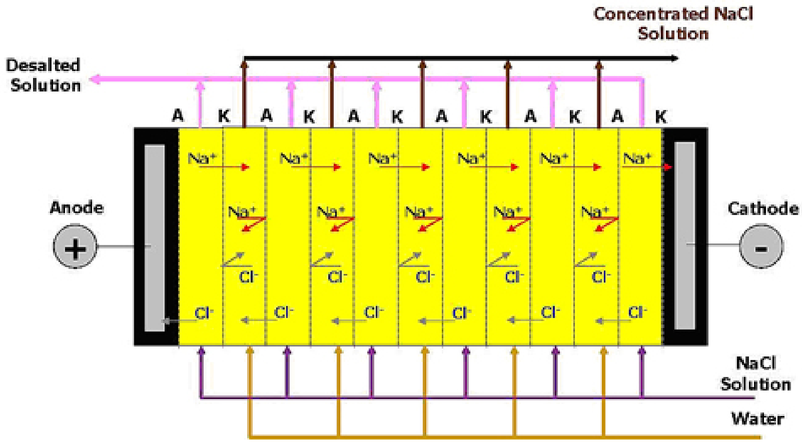

Fig. 1. Electrodialysis (membrane electrolysis) process: A – anion exchange membranes, K – cation exchange membranes.

The electric current carries cations from the initial solution into the concentrate stream through the cation-exchange membrane located on the cathode side. Cations are retained in this flow by an anion-exchange membrane from the cathode side. The direction of movement of the anions is opposite. They are transferred to the concentrate stream through an anion exchange membrane. On the anode side, anions are retained in the concentrate flow by a cation-exchange membrane. Thus, the overall result of the process is to increase the concentration of ions in one of the alternating chambers while decreasing their concentration in other chambers [30-32]. The electrolysis process takes place on the electrodes. In a multi-chamber apparatus, unproductive energy costs are inevitable due to this process, they are distributed over a large number of chambers, therefore, per unit of production, these costs are minimized [33-36].

Electrodialysis is an environmentally friendly and low-energy-consuming technological process. With its use, the processes of desalination and concentration of solutions are successfully carried out, as well as the production of drinking water from salt waters. Electrodialysis is also used for pretreatment of water for thermal power plants [37,38,40-42].
An important direction of using electrodialysis plants is wastewater treatment. Electrodialysis is used for desalting wastewater from galvanic industries (galvanic effluents) [39,43-45]. Also, membrane electrolysis is used to concentrate wastewater containing valuable components (for example, precious metals), before the subsequent extraction of these components. One of the possible methods for the regeneration of spent pickling solutions is electrolysis using ion-exchange membranes, while the process schemes can be different. Some electrodialysis schemes were tested for the regeneration of spent solutions after etching steels in hydrochloric acid, characterized by a low HCl content (1-4%) and a high FeCl2 content (18-27%). The problem of regeneration by concentrating pure HCl practically free of iron from spent pickling solutions has been solved [9, 46-52].
Enterprises that consume large volumes of water have certain requirements for water. Many of them have special water treatment systems [53-58]. One of the stages in these systems is water softening, which is carried out using ion exchangers. The process of water softening by the method of H-cationization (cation exchanger H-form) is intended to remove cations and replace them with hydrogen ions. After depletion of the cation exchanger, it is regenerated with a 0.6 - 1.5% solution of H_2SO_4 or 2.0 - 6.0% HCI solution followed by washing. When choosing an acid to restore the working capacity of the cation exchanger, preference is given to hydrochloric acid, which avoids the "gypsum" of the ion exchanger - the precipitation of calcium salts in the resin layer in the case of using an H_2SO_4 solution for regeneration [59-63].
The residual concentration of hydrochloric acid in the wash water after regeneration of the cation exchanger (H-cationization) is approximately 1% [10, 64-69].
The purpose of this work is to study the possibility of maximum concentration and return to the technological cycle of residual acid from the H-cationization wash water using the electrodialysis method.

METHODS AND MATERIALS

The work on studying the possibility of maximum concentration of the residual acid of the H-cationation wash water, in order to return HCI to the technological cycle, was carried out on a press-type filter electrodialysis apparatus. A membrane stack, located between two platinized titanium electrodes, was assembled by series MK-40 and MA-40 monopolar membranes. The membranes are mass-manufactured at JSC Shchekinoazot (Russia). The MK-40 cation-exchange membrane was made of the KU-2 (2/3) strongly acidic cation exchanger composition containing sulfo groups and polyethylene, the MA-40 anion-exchange membrane was made of the EDE-10 P anion exchanger composition containing quaternary ammonium bases (20%), secondary amines and polyethylene. Sheme of the process for adjusting the pH of technological solutions is shown in Figure 2.

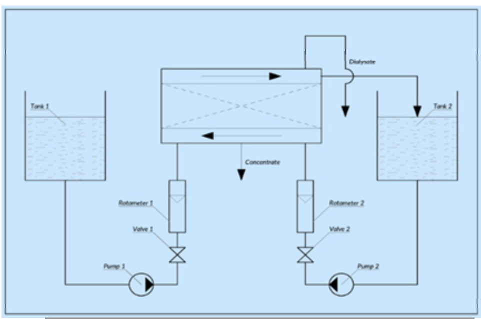

Fig. 2. Sheme of the process for adjusting the pH of technological solutions

Consequently, in the apparatus, the desalination (dialysate) and acid concentration sections were sequentially created. The number of membranes of the same name and the working area, respectively, were 200 pieces and 32.8 m^2.
The Cl^- ion content was determined by the argentometric method in the presence of the K_2CrO_4 indicator. The concentration of alkali and acid was determined by acid-base titration in the presence of the phenolphthalein indicator.
As a working solution, wash water was used, after H-cationization, containing a residual concentration of HCI up to 1%. The electrodialysis process of acid concentration, based on the productivity of the apparatus (660 l / h), was studied in the following hydraulic modes:

- ✓ mode 1 - the flow rate of the initial solution in the dialysate and concentration sections was the same - 330 l/h;
- ✓ mode 2 - the flow rate of the initial solution in dialysate sections was 660 l/h, in brine sections – 400 l/h;
- ✓ mode 3 - the flow rate of the original solution in dialysate sections was 660 l/h, in brine sections - 50 l/h
- ✓ mode 4 - the flow rate of the original solution in the dialysate sections is 660 l/h, and in the brine sections - the solution was not supplied.

For each hydraulic mode, by changing the value of the applied voltage to the apparatus, the optimal electrical parameters of the process were set and the following process indicators were calculated on their basis: desalination depth - (β(d)), degree of concentration - (β(c)), current efficiency (ή), operating capacity (Q) and energy consumption (W) per process.

RESULTS AND DISCUSSION

On an industrial electrodialysis apparatus, the membrane package of which was assembled only with monopolar membranes MK-40 and MA-40, an experiment was carried out to study the possibility of maximizing the concentration of residual acid HCI in wash water after H-cationization (regeneration) of the KU-2-8 cation exchanger. This cation exchanger is used in many water treatment systems for water softening. Regeneration of cation exchangers is carried out with solutions of hydrochloric (2-6%) or sulfuric (0.6-1.5%) acids. When using hydrochloric acid, its residual concentration in the wash water is approximately 1%.
The electrodialysis process of acid concentration was studied depending on the applied voltage, at different hydraulic operating modes of the apparatus. The data obtained are shown in Figures 3-7.
As can be seen from Fig. 3 and Fig. 4 (mode 1), when the source water is supplied to the dialysate and concentration sections with a ratio of 1:1, even at a voltage of 50 V, the acid concentration in the concentration section increases from 9 to 16 g/L.

However, as can be seen from Fig. 3, under the conditions of this mode, a further increase in voltage practically does not cause a change in the concentration of acid in the concentration sections.
The process proceeds similarly in the case of hydraulic flows of solutions in sections of the apparatus with a ratio of 3:2 (mode 2). When a voltage of 160 V was applied to the installation, the concentration of hydrochloric acid in the concentration sections increased to 20 g/L and the subsequent increase in voltage only increased the desalination depth, which is clearly shown by the curves in Figure 5.

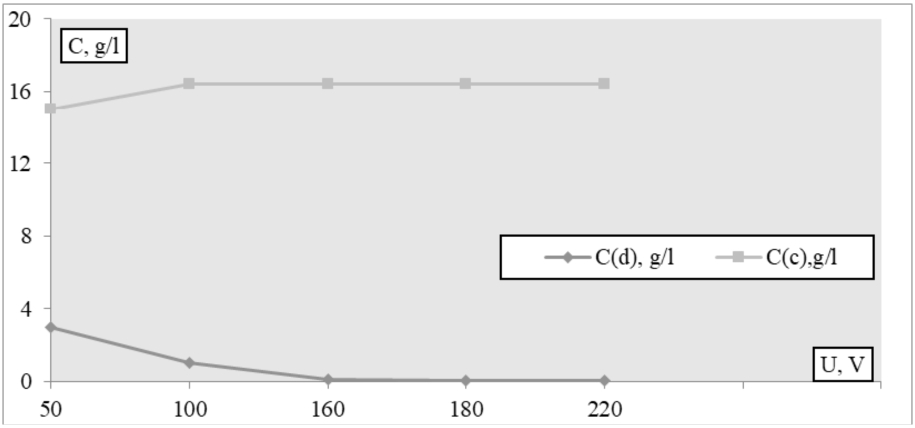

Fig. 3. Curves of changes in the concentration of HCI in the brine C (s) and dialysate C (e) sections depending on the applied voltage to the device (mode 1)

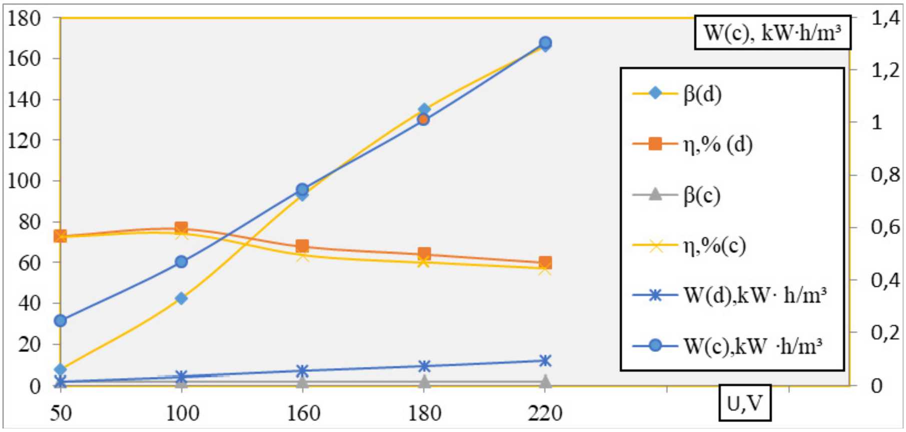

Fig. 4. Curves of the process parameters changes depending on the voltage value (mode1).

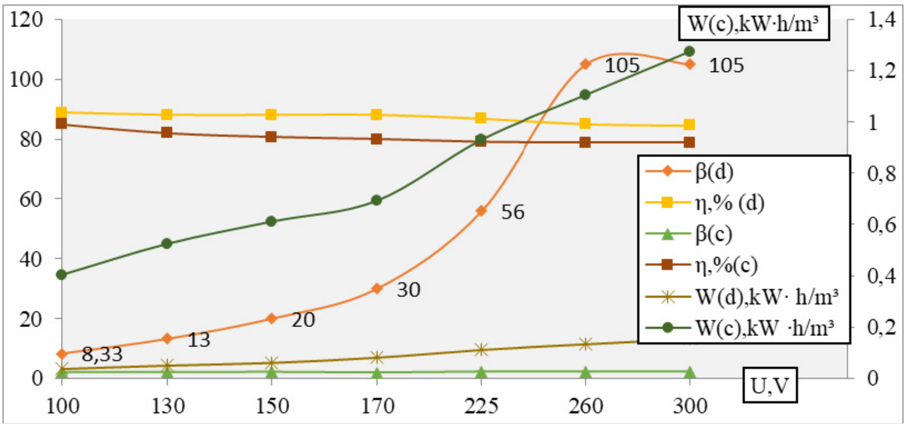

Fig. 5. Dependence of process parameters on voltage (mode 2).

In the case of hydraulic flows with a ratio of 13:1 (mode 3), after applying a voltage of 200 V to the installation, the concentration of hydrochloric acid in the concentration section was 50 g/l. At the same time, in this mode, there was a decrease in the depth of desalination compared to the above modes, but it still remained quite high. The concentration of hydrochloric acid, at the above voltage value, in the dialysate section was 0.6 g/l. Fig. 6 shows the dependence of process parameters on voltage value (mode 3).

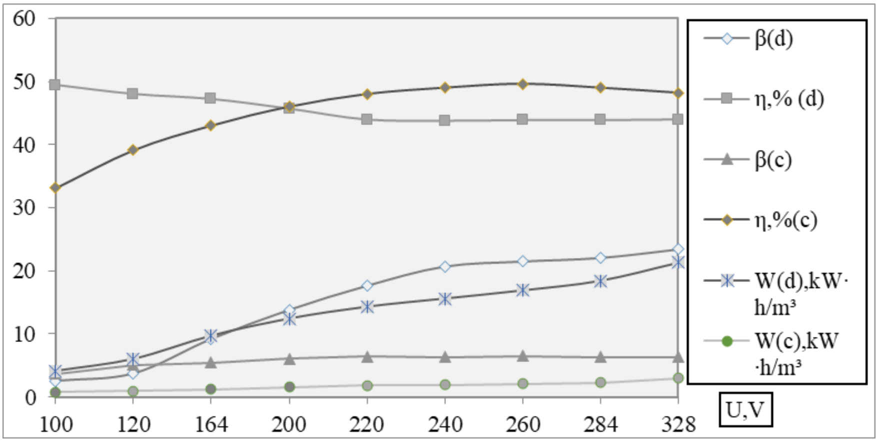

Fig. 6. The dependence of the process parameters on voltage value (mode3)

During the hydraulic mode, when the initial solution was not supplied to the concentration section (mode 4, Fig. 7), applying a voltage of 150-160 V to the device made it possible to achieve high levels of the degree of concentration of hydrochloric acid. But under these conditions, an acceptable desalination depth could not be achieved in the dialysate section, and the increased voltage rendered the process virtually ineffective. This is easily explained by the presence of a high concentration gradient between the concentration and dialysate sections.

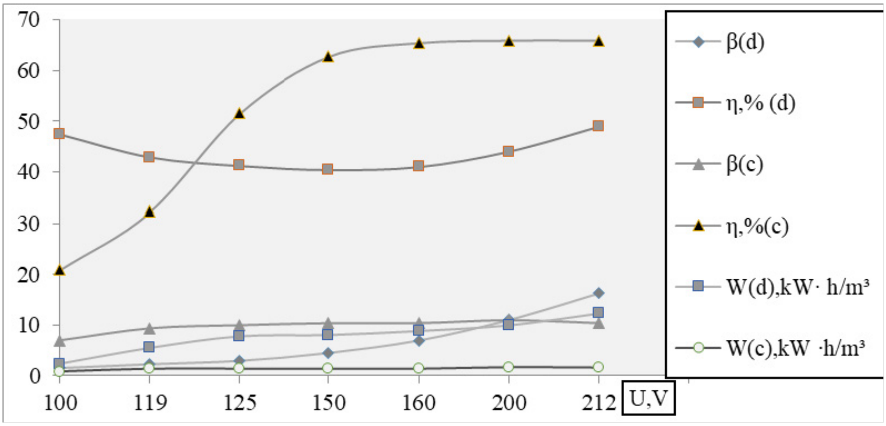

Fig. 7. The dependence of the process parameters on voltage value (mode 4)

Thus, the most effective method for concentrating hydrochloric acid of all the studied hydraulic modes is mode 3 - with a ratio of solution flow in dialysate and concentration sections of 13:1. Under the aforementioned operating conditions, when a voltage of 180-200 V is applied to the installation, hydrochloric acid can be concentrated up to 5 %, which is quite enough for the regeneration of the cation exchanger.

Under the abovementioned operating conditions, when applying a voltage of 180-200 V to the installation, hydrochloric acid can be concentrated up to 5%, which is quite enough for the regeneration of cation exchanger. At the same time, the residual concentration of hydrochloric acid in the dialysate is 0.05%, which significantly reduces the consumption of alkali that is currently used to neutralize industrial wastewater.

It is shown that when applying the sorption method for water softening in the water treatment system, it is recommended to concentrate the residual acid present in the wastewater by the electrodialysis method and return it to the process cycle, which makes the sorption method for water softening more environmentally friendly and economical.

It was found that at high concentration gradients between the concentration and desalination sections, the required level of desalination is not achieved in the dialysate chamber, and the voltage increase is practically ineffective.

CONCLUSIONS

When using the sorption method to soften water, it is recommended to concentrate the residual acid present in the washing water after H-cationization by the electrodialysis method.

It is shown that the most effective method for concentrating hydrochloric acid of all the studied hydraulic modes is mode 3 — with a ratio of solution flow in dialysate and concentration sections of 13: 1. It has been established that under the abovementioned operating conditions, when a voltage of 180-200 V is applied to the installation, it is possible to concentrate hydrochloric acid up to 5% and return it to the process cycle for the regeneration of cation exchanger. It is shown that in this mode, the residual concentration of hydrochloric acid in the dialysate is 0.05%, which significantly reduces the consumption of alkali that is currently used to neutralize industrial wastewater.

The data obtained in this work can be used to concentrate rinsing water of H-cationization by electrodialysis.

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EXPRESS MONITORING OF SURFACE WATERS QUALITY AND MODELING OF CHANGES IN THE ECOLOGICAL STATE OF RECREATIONAL AREAS CAUSED BY VEHICLE EXHAUST EMISSIONS

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ABSTRACT

Vehicle emissions have a significant impact on the state of all components of the environment and are harmful to human health. The danger of exhaust gases emissions is exacerbated by the fact that they, spreading over long distances, are concentrated in the surface layer of residential areas, on sidewalks, public transport stops and recreational areas. So, monitoring changes in the ecological state of environmental components influenced by the transport infrastructure is an important task. In the study, attention was focused on the methods of express monitoring of the quality of the environment components. Since it is difficult to control the impact of all pollutants in the ecological monitoring system, such indicators as electrical conductivity, hydrogen index pH and optical properties of natural solutions have been chosen. These characteristics are sensitive to the complex effects of many factors and can be easily measured. Densimetry, viscometry and stalagmometry methods were also used during the implementation of the full environmental express monitoring program. The computational experiment on the determination of the pollution level of studied areas was carried out using mathematical modeling and the MathCad software environment.

Keywords: recreational area, water pollution, air pollution, modeling of air pollution, urbanization problems

INTRODUCTION

It is well known that mobile pollution sources (mainly vehicles) have a very significant and sometimes even decisive impact on the state of the environment contaminating it by harmful substances, which also include greenhouse gases, containing in the emissions from internal combustion engines. Among the main air pollutants there are nitrogen oxides N_2O, NO, N_2O_4, NO_2, N_2O_5 (less often), sulfur compounds SO_2, SF_6, etc., carbon oxides CO and CO_2, hydrocarbons of various composition C_xH_y, including polycyclic, polyaromatic, etc., aldehydes, fine dust and soot particles (particulate matter) PM_{10} and $PM_{2,5}$ (so-called "black carbon"). It is also important that the emissions of toxicants with the exhaust gases of engines occur in the respiratory zone of humans, especially children. Experts have discovered that almost 20 % of vehicle emissions remain near the roads [1], and the negative impact can be determined at a distance of up to 2 km from the road, extending to a height of 300 m [2].

Among the total volume of harmful substances emitted into the atmosphere during the vehicle operation there are not only exhaust gases ingredients, but also crankcase gases, products of evaporation from the car's power system, in particular, volatile hydrocarbons, etc [2]. However, the most dangerous pollution of urban and suburban areas caused by vehicles is due to the emissions of harmful ingredients containing in their exhaust gases. The danger of these emissions is exacerbated by the fact that they, spreading over long distances, are concentrated in the surface layer of residential areas, where there is a significant population density with private vehicles; on sidewalks, public transport stops, even in areas intended for human recreation (park areas and squares, areas near water bodies, playgrounds, etc.).

The level of air pollution and contamination of the adjacent to the roads territories (including recreational areas) largely depends on the traffic density, the number of lanes, the terrain of the road and surrounding areas, the fuel used, the condition of the road surface, the technical condition of cars and their speed, the share of trucks, climatic conditions, etc. [1]. The maximum volumes of harmful emissions from exhaust gases are observed during engine operation in idle mode, during traffic jams, at the moment of starting or stopping of the car. The supply of the engine with poor quality fuel or the operation of an unregulated engine also causes a significant increase in the exhaust gases volume and toxicity.

Thus, monitoring changes in the ecological state of water, air, soil, etc. mediums influenced by the transport infrastructure is an important component of the state environmental monitoring system. And given the complexity of the organization of the environmental monitoring in the technogenically disturbed ecosystems [3], in our study, we focus attention on methods of express monitoring of the quality of the studied components of the environment combining them with the methods of mathematical modeling.

METHODS AND EXPERIMENTAL PROCEDURES

Changes in the ecological state of urban water bodies and soils were studied by analyzing samples taken in spring, summer and autumn. During the research, the results obtained on the pollution of the components of the environment were compared with the background values determined in the least contaminated areas. The background values are the average values of concentrations of harmful substances determined from the samples taken in the eco-friendly area near the Irpin River (Kyiv region, Ukraine) at a distance of 200–250 m from the highway, as well as in the water body (lake) located there.PhD

According to the preliminary analysis of cartographic information, scientific literature and by processing the data of field observations of traffic flows, zoning of recreational areas adjacent to the highways was carried out according to the level of pollution by certain toxicants. Observation points that most representatively characterize their ecological state were selected.

Sampling sites were recorded using a GPS navigator and marked on a map. The capacity of traffic flows was studied on weekdays, weekends and holidays, as well as at different time periods and different seasons. The calculation method described in [4–6] was used to evaluate the volumes of emissions of specific pollutants from vehicle exhaust gases.

To obtain actual data on the potential pollution of urban water bodies and recreational areas near them, as well as to establish the level of their environmental safety, a set of physicochemical methods of analysis was used, namely:

– potentiometric (for measuring the acidity of solutions – hydrogen index pH);

– conductometric (for measuring the electrical conductivity of solutions) and

– optical (in particular, refractometry) research methods, which require special equipment but are quite sensitive and do not require much time for analysis; this is especially important because the detected fact of changes in the ecological state of the studied object (water body, soil cover, precipitation, etc.) allows making quick management decisions and prevent further pollution problems.

Densimetry (determination of solution density by pycnometric method), viscosimetry (determination of viscosity by Ostwald viscometer) and stalagmometry (determination of surface tension by stalagmometer) methods were also used when the full program of ecological express monitoring was implemented. For the surface waters, organoleptic parameters were also studied.

For the modeling of the dispersion of toxicants in the environment, the orography of the territories was studied and field observations of traffic flows moving along the roads near the studied recreational areas and water bodies were carried out.

THE RESEARCH RESULTS AND DISCUSSIONS

1. Conductometric study of surface water quality. In natural waters, including lakes located within recreational areas, the migration of chemical elements is quite intense. At the same time, as a rule, a change of qualitative and quantitative content of natural waters (their metamorphization) is observed. In addition, in water, bottom sediments, organs and tissues of aquatic plants and animals the compounds of chlorine, sulfur, sodium, calcium, magnesium, heavy metals, etc. can accumulate in large quantities. That, in turn, has a harmful effect on the vital functions of organisms and human health. Particularly dangerous is the pollution of recreational areas, where adults and children spend a long time without even realizing the potential danger. Such territories, as a rule, are subject to complex contamination – water quality deterioration, pollution of atmospheric air, soil cover, vegetation, fauna, etc.

Natural water systems usually contain solutions of weak and strong electrolytes. Their mineral basis consists of ions of sodium Na^+, potassium K^+, calcium Ca^{2+}, magnesium Mg^{2+}, quite often also iron Fe^{2+}, as well as sulfate- SO_4^{2-}, chloride- Cl^- and bicarbonate-ions HCO_3^- etc. The presence of these ions determines the electrical conductivity of natural solutions, including groundwater.

The presence of other ions, in particular, iron Fe^{3+}, aluminum Al^{3+} and their complex compounds, as well as ions NH_4^+, NO_2^-, NO_3^-, HPO_4^{2-}, H_2PO_4 and ions of some organic compounds has almost no effect on the conductivity of natural systems because they rarely can be found in them in significant quantities. As for H^+ and OH^- ions, for example, in natural water with pH = 5–9 their content is insignificant, and, consequently, the share of their influence on the electrical conductivity of solutions does not exceed 0.1–0.2 % [7].

It is known that electrical conductivity (specific conductivity χ, μS/cm) characterizes the ability of solutions to conduct electric current and can serve as a characteristic of the total salt content (mineralization) in aqueous solution (water body, soil extract, etc.) at a certain fixed temperature [8, 9].

According to [8], the value of the specific electrical conductivity of the solution is proportional to its total mineralization with a coefficient of proportionality of 0.55–0.75. In our study to assess the salinity of the natural system a proportionality factor of 0.65 was used:

$$\text{Salt content in the solution} = \chi(\text{solution})\cdot 0.65, \tag{1}$$

where χ(solution) is the specific electrical conductivity of the sample of water, soil solution, precipitation, etc., μS/cm; "salt content" – the content of dissolved salts in the sample, mg/dm^3.

Thus, the specific conductivity serves as an indicator of the total mineralization (salt content) in aqueous solution, and its changes allow to make conclusions about the ingress, accumulation, or, conversely, a decrease in the concentration of dissolved electrolytes in water. However, due to coagulation and sedimentation processes, as well as due to secondary chemical and physicochemical transformations of pollutants, the specific conductivity of water samples may decrease significantly, which will provide false information about the reduction of soluble electrolytes in the aquatic environment and, consequently, about the reduction of water contamination levels. However, the sediments formed as a result of such transformations and coagulated substances will be accumulated in the bottom sediments, vegetation, tissues of various organisms, etc., which also poses a certain threat to aquatic life and human beings.

The specific electrical conductivity of solutions (water samples, soil extracts, precipitation, etc.) was measured using an alternating current conductometer (bridge), which was calibrated according to standard solutions of potassium chloride KCl with a known specific electrical conductivity. A glass conductometric cell with soldered platinum electrodes was used in the study; the number of measurements for each sample was n = 5.

To establish the impact of emissions of traffic flows, water (soil) samples were taken at 5 observation points, if possible, at approximately the same distance from the highway in accordance with [10]. The reference was a sample of water from a natural reservoir (lake), located in forestry at a distance of 200–250 m from the highway. Statistical processing of experimental data was performed according to the methodology of [11] and [12]; the relative error of the experiment did not exceed 2 %.

The results on the indicator of specific electrical conductivity of water samples of the studied water body – Raiduzhne Lake (Kyiv, Ukraine) at different seasons are presented in Fig. 1. During the observations (2018–2019), sharp changes in the specific electrical conductivity of samples of the studied object was observed only twice (deviation was up to 30 % of the average value), which is due, in our opinion, to the possible ingress of household waste and electrolytes from the nearby cafes into the lake. The change in the electrical conductivity of water samples was not critical.

As can be seen from the data of Fig. 1, at the beginning of summer the influence of electrolyte contaminants is minimal, while after the snow melts (March-April) and in autumn the studied water body is heavily polluted. In addition, the results of measurements (calculations) of electrical conductivity in April are much lower than in March, which can be explained by salt-contaminated runoff of meltwater due to the use of anti-icing agents by utilities in winter.

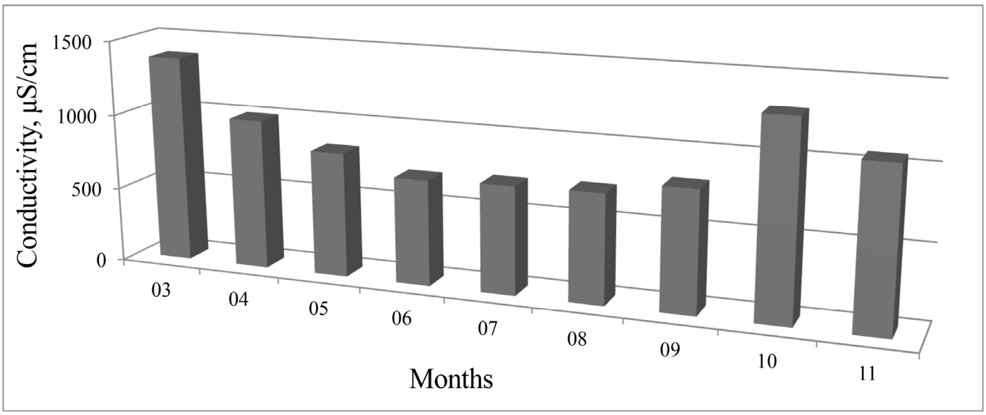


Fig. 1. The dynamics of specific electrical conductivity (average values) of water samples (Raiduzhne Lake, Kyiv, Ukraine) at different seasons.

The specific electrical conductivity in October is almost 2 times higher than in June. This can be explained by weather conditions (fog, temperature inversions, etc.), changes in meteorological conditions (wind direction and wind speed), as well as active recreation of people during the spring and summer months. In November, the electrical conductivity of water samples decreases significantly, probably due to frequent rains (water dilution of the reservoir) and cooling, which, in turn, reduces the number of vacationers in nature.

Thus, the study of changes in the specific conductivity of solutions (media) over time (especially the determination of sudden changes) makes it possible to establish the fact of entry into the water body (soil, precipitation, etc.) of electrolytes, to conclude about their accumulation or, conversely, neutralization, deposition, etc., as any significant changes in the electrical conductivity of the environment promptly signal about the potential contamination of the water body, soil cover, precipitation, etc.

After establishing the fact of contamination of a certain component of the environment with electrolyte compounds, we recommend applying analytical methods to identify contaminants, as well as determine the content of individual chemical elements, which will allow, firstly, to establish the source or sources of pollution; secondly, to locate the contaminated area and thirdly, to prevent the appearance of an emergency situation and increasing the risk to human health, to develop appropriate management measures.

2. Potentiometric method of aquatic ecosystems investigation. One of the important indicators that affect the chemical, physicochemical and biochemical processes in natural ecosystems is the hydrogen index pH. Depending on its values, not only the speed but even the direction of processes can change, while the toxicity of substances and activity or stability of the environment can decrease or increase. The pH of the solutions is determined either approximately by colorimetric (indicator) method, or more precisely – using the method of potentiometry. The pH of the natural environment indirectly characterizes its chemical composition.

The potentiometric method is based on the use of so-called indicator electrodes, the electrode potential of which directly depends on the concentration of H^+ hydrogen ions in the studied solution, and reference electrodes, the electrode potential of which is known and does not depend on the concentration of H^+ or OH^- ions.

Therefore, the potential of the indicator electrode is determined by measuring the electromotive force of the galvanic cell, which consists of the test electrode, the potential of which is unknown and depends on the concentration of H^+ ions, and the reference electrode, whose potential is known. A silver chloride electrode was used as a reference electrode in the study; a glass electrode was used as an indicator electrode. Before use, the instrument was calibrated using buffer solutions with known pH values; the effect of temperature on the electromotive force of the galvanic cell was compensated by a thermal compensator built into the device.

It is known that the pH of natural surface waters, as a rule, varies within 6.5–8.5 units; whereas groundwater and soil solutions may have higher pH values. Therefore, by the pH value the aqueous solutions are usually divided into:

– strongly acidic (pH < 3);

– acidic (pH = 3–5);

– weakly acidic (pH = 5–6.5);

– neutral (pH = 6.5–7.5);

– slightly alkaline (pH = 7.5–8.5);

– alkaline (pH = 8.5–9.5) and

– strongly alkaline (pH > 9).

However, most natural waters usually have a neutral or slightly acidic reaction. Moreover, the pH of natural water in each specific water body is almost constant, due to the action of the main natural buffer system – "aqueous solution of carbon dioxide – bicarbonates".

Therefore, the active concentration of H^+ ions, more precisely, H_3O^+ ions in the aqueous medium is determined by its chemical composition, the concentration of substances that got into it, as well as the quantitative ratio of concentrations of carboxylic acid H_2CO_3 and anions of its acid residues HCO_3^-, CO_3^{2-} due to the following processes:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}.$$

So, for surface waters that contain small amounts of dissolved carbon dioxide CO_2, the reaction of the medium is likely to be alkaline or slightly alkaline.

Thus, in the case of detection during the express analysis of significant changes in the pH of water and soil samples, precipitation, etc., it can be concluded that it got contaminants from industrial or domestic effluents or, for example, wet or dry deposition (sedimentation) of engine exhaust gases components.

However, it is known that many metals, including heavy ones, are able to form amphoteric oxides and hydroxides (for example, lead, stanum, aluminum, zinc, etc.). Therefore, even when the acidity of the medium is shifted to the alkaline side, it will not become safer in the ecological sense, because the feature of amphoteric compounds is the ability to react both with acids (acidic substances) and bases (basic substances).

When assessing the impact of chemical compounds on ecosystems and water bodies, it is necessary to take into account possible hydrolytic processes, which, in turn, can change the reaction of the environment, in particular, due to the hydrolysis of salts. For example, $FeSO_4$ is gradually hydrolyzed in an aqueous medium, changing its pH to acidic, even if the hydrolysis occurs only in the first stage:

$$FeSO_4 \rightarrow Fe^{2+} + SO_4^{2-} ,$$

$$Fe^{2+} + HOH \leftrightarrow FeOH^+ + H^+ ,$$

(pH < 7, the environment is acidic).

Insoluble forms of chemical elements are also not completely safe, because in the form of fine dust and due to adsorption on dust particles and soot can not only get into living organisms (for example, human respiratory system, higher animals, etc.), but also can be transferred over long distances, to form local areas of secondary emergency pollution and then under the new environmental conditions they can turn into water-soluble, mobile forms.

With repeated or prolonged action, especially at elevated temperatures, natural water also ceases to be only a solvent and/or mechanical carrier of harmful substances and becomes an active chemical agent. At the same time, there are secondary physicochemical, chemical and biochemical transformations of pollutants with its participation, which, in turn, can lead to a significant increase in chemical mobility of certain chemical elements and increase the concentration of their migration-capable forms in surface and groundwater, soil solutions, etc. In particular, when heavy metal compounds interact with water, the concentration of their mobile acid- and water-soluble forms can increase 2–6 times compared to their initial concentration [13].

Contaminated precipitation and groundwater, as well as the ingress of toxicants into water bodies in concentrations that are above the maximum permissible concentrations, significantly increases the potential biotoxicity of vehicle exhaust gases components; contributes to the conversion of immobilized metal compounds in a mobile and migratory state. Thus, technogenic pollution of territories adjacent to highways and recreational areas, including lakes, rivers, reservoirs, etc., significantly increases the environmental hazards and risks to human health.

The highest solubility, and, consequently, bioavailability, is inherent for the compounds of strontium, cadmium, cobalt, copper and nickel. As for the compounds of manganese, chromium, lead and iron, they are usually strongly bound to the insoluble part of the "mineral matrix" of rocks and therefore are leached from the soil in small quantities.

Changes in the pH of water in nature can also be associated with the processes of photosynthesis, in particular, due to the consumption of carbon dioxide by aquatic vegetation. Soil humic acids are also a natural source of hydrogen ions.

Thus, a potentiometric study of surface water samples, soil extracts and precipitation in the studied territories (in particular, recreational areas) was conducted in the warm and cold seasons. The results of measuring the acidity of soil extracts on the example of the recreational area of people near Raiduzhne Lake (Kyiv, Ukraine) are presented in Fig. 2 [14]. In addition, changes in the acidity, as well as the content of chloride ions Cl^- (acid-salt contamination) in snow and rain samples were studied according to the method presented in [15].

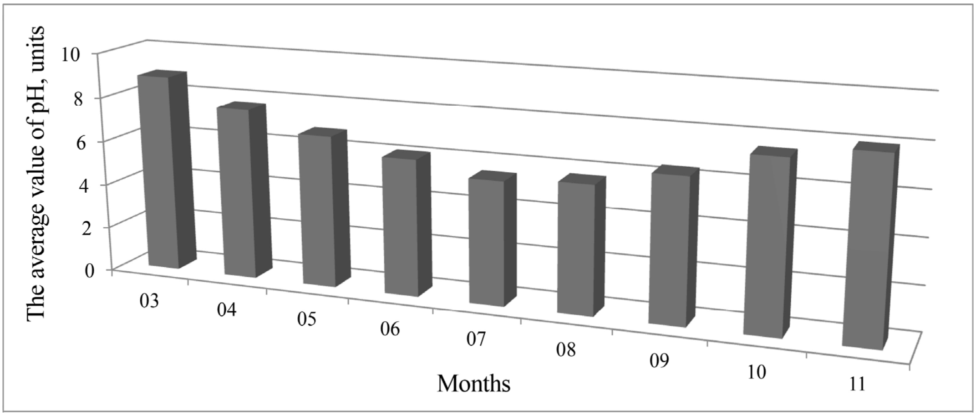


Fig. 2. PH dynamics of samples of water soil extracts (average values) in the recreational area near Raiduzhne Lake (Kyiv, Ukraine).

According to Fig. 2, in the summer, the pH values of the samples are slightly lower than in the cold season (early spring). That is, in the warm season, the acidity of soil solutions increases. As was shown in [15], this may be due to the fact that in winter utilities perform so-called rotary transshipment of contaminated snow and also actively use salt anti-ice mixtures, which, penetrating the soil in the spring with meltwater, change the pH of the environment.

Analysis of the pH of samples of water soil extracts in the studied recreational areas also showed that the lowest values of the hydrogen index pH are observed at a distance of up to 15 m from the center of the road. The difference between the pH values of the water body and the extracts from the soil (at a distance of 5 m from the road) is 0.5–1.7 pH units. However, such changes in acidity cannot be considered regular, because the formation of soil and water pH is significantly (but differently) affected by greenery. In particular, the presence of a "green screen" (for example, grass, shrubs, trees, etc.) can greatly change the pH, even with the same traffic load on the territory.

So, the potentiometric method is very sensitive to certain contaminants penetrating the components of the environment, but it cannot provide complete information on changes in the ecological state of water bodies, soils, etc. In our opinion, potentiometric measurements must be combined with conductometric studies, as well as with measurements of optical density and refractive index of the investigated solutions (optical research methods).

3. Refractometry, optical methods of analysis. Refractometry is one of the optical methods of analysis of natural and artificial systems that is based on the phenomenon of polarization of molecules of matter under the action of light radiation. The refractometric method of analysis is based on the phenomenon of refraction of light during the transition from one medium to another (refraction, which is a measure of electronic polarizability of atoms, molecules, ions) and involves measuring the refractive index of the medium [16].

In the study, the method of refractometry was proposed as a method by which researchers can, firstly, identify a substance, and secondly, quickly obtain information about the sudden contamination of the aquatic environment with electrolytes, organic matter, etc., develop and implement management decisions. Quantitative determination of impurity concentrations by refractometry method was not performed.

Among other optical methods for the analysis of suspensions, emulsions and other opaque media methods of nephelometry and turbidimetry are usually used. Both methods involve the interaction of light radiation with colloidal particles of suspensions (emulsions). In particular, the nephelometric method for determining the concentration of a substance is based on measuring the intensity of light reflected or dispersed by colloidal particles of an uncolored suspension (emulsion) in a direction perpendicular to the direction of the primary bundle. Turbidimetric method is based on the measurement of the intensity of light absorbed by the studied medium – uncolored suspension (the source and receiver of radiation are on the same line).

Measurement of the refractive index of the studied water samples was performed at a temperature of $20 \pm 0{,}1\ ^{o}C$ and the wavelength of the sodium gas D-spectrum line of 589.3 nm. The measurements were repeated 5 times until the measurement results coincided. Each time a fresh drop of the test sample was added to the prism of the refractometer. The arithmetic mean value of parallel measurements of the refractive index was determined. The measurement accuracy was not less than $\pm 2 \cdot 10^{-4}$.

The presence of diluted direct "oil–water" type emulsions in the studied water bodies, as well as the fact of formation of suspensions due to the ingress of dust contaminants into water bodies, were found out in the study.

It is known that some salts, such as aluminum sulfide, entering the aqueous medium, can almost completely hydrolyze forming sediment of metal hydroxide:

$$Al_2S_3 + H_2O \leftrightarrow Al(OH)_3\downarrow + 3H_2S\uparrow.$$

Thus, the complex application of such physicochemical methods of analysis as conductometry, potentiometry and refractometry (in some cases the methods of densimetry – measuring the density of the solution by pycnometric method, viscosimetry – measuring the viscosity of the medium with an Ostwald viscometer, stalagmometry – measuring surface tension with a stalagmometer were used), helps to obtain quick information on changes (in particular, deterioration) of the ecological state of the studied water body, the territory of the recreational area, etc., as well as to conclude on the potential pollution sources (domestic or industrial effluents, emissions from vehicles, etc.), pollution intensity and possible health consequences for people who rest in a polluted area or swim in polluted water.

Therefore, although the listed instrumental methods require special equipment, they do not require much time for analysis, are quite simple and need small amounts of solution. For example, the portable optical refractometer Kelilong RHS-28ATC can be easily used to determine the salt content in water, as its scale is graduated both to measure the density in kg/dm^3 and to measure the salinity of aqueous solutions in ‰.

4. Transformation of chemicals in the components of the environment, their sedimentation in surface waters and recreational areas. Harmful substances can enter the pedosphere and water bodies in different ways and different physical states, in particular, from atmospheric air (various aerosols – both coarse and fine), with precipitation and groundwater, using anti-icing agents in winter, etc. Nitric and sulfuric acids, sulfates, nitrates and other toxicants get to water bodies with precipitation (rain and snow). As a result, there is not only pollution of water bodies and soils but also changes in their acidity and salt composition.

Further, some of the possible chemical and physicochemical transformations of toxic emissions of vehicles in the natural environment are considered in more detail.

In particular, in humid air nitrogen dioxide NO_2 reacts with the aerosol of NaCl, which is always present in it (especially after it was used as an anti-ice agent in the form of a sand-salt mixture), with the formation of sodium nitrate $NaNO_3$ and strong hydrochloric acid HCl, which is extremely harmful to the environment. This process occurs in two stages, and the first stage of the process takes place with the formation of an even stronger pollutant – nitric acid:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The second stage of the process is the sorption of nitric acid vapors by particles of sodium chloride with the release of HCl:

$$HNO_3 + NaCl = NaNO_3 + HCl.$$

Carbon dioxide CO_2 dissolves during interaction with rain or humid air with the formation of a weak carboxylic acid H_2CO_3 ($CO_2 \cdot H_2O$), while carbon monoxide CO retains its molecular form.

Sulfur dioxide SO_2, which is usually present in the vehicle exhausts, is capable of photochemical (or by another mechanism) oxidation to sulfur trioxide SO_3, the interaction of which with water leads to the formation of strong sulfuric acid H_2SO_4. In this case, if, for example, in the air, there is ammonia NH_3 (that is a very harmful substance to the environment and human health), it can somewhat neutralize the harmful effects of sulfuric acid due to the formation of solid ammonium sulfate $(NH_4)_2SO_4$.

The end products of the transformation of sulfur dioxide SO_2 in the environment can also be sodium sulfate Na_2SO_4, which is formed by the interaction of droplets of sulfuric acid with aerosol sodium chloride NaCl, and hydrochloric acid HCl:

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl.$$

A similar interaction is known also for carbonates.

5. Dispersion of pollutants in atmospheric air, their sedimentation in surface waters and recreational areas. According to the Borys Sreznevsky Central Geophysical Observatory, water bodies and soils of Ukraine and its capital Kyiv are polluted mainly with compounds of nitrogen, phosphorus, heavy metals, as well as petroleum products, phenols, sulfates, surfactants, etc. The authors of [17] found a correlation between the content of nitrates in rainwater and the content of nitrogen dioxide NO_2 in the air of cities. NO_2 is one of the main ingredients of vehicle exhausts. The emissions of this harmful pollutant (together with the emissions of fine soot particles) are the main environmental threat from functioning diesel engines.

In Fig. 3 an example of typical water bodies of Kyiv, which are exposed to harmful effects of emissions from traffic flows of the international highway E 40 [18] – Pond № 15 (Fig. 3a) and Pond № 14 (Fig. 3b) are shown. As can be seen from Fig. 3, near these ponds there are recreational areas, "open" cafes, boat and catamaran rentals, and even some facilities of the transport infrastructure (for the Google Maps design Snazzy Maps tool was used).

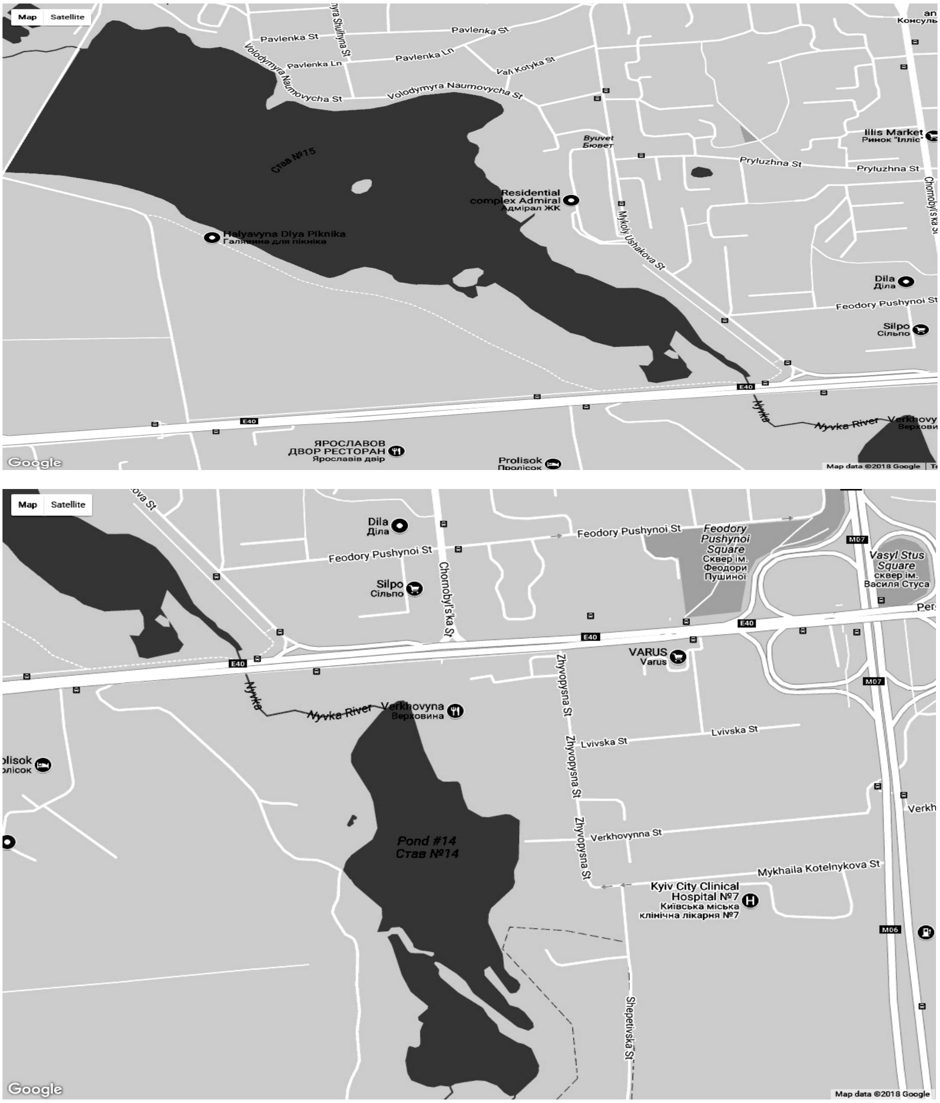


Fig. 3. Examples of water bodies, the ecological state of which was assessed in the research: a – Pond № 15; b – Pond № 14 (Kyiv, Ukraine).

It should be noted that the determination of the characteristics of the dispersion of toxicants in the environment is especially important in the case when water bodies (natural or artificial reservoirs, rivers, etc.) are located near the emission sources. This is due to the fact that penetrating the aquatic environment, pollutants not only interact more actively with each other and with substances dissolved in water but also are able to be absorbed by living organisms, accumulate in their organs in dangerous doses. In particular, this problem is extremely relevant for the capital of Ukraine, as the city of Kyiv is a place of significant concentration of water bodies, which are actively used by the population for recreation (Fig. 4).

The authors of [19] proved that the dynamics of concentrations of harmful impurities in the surface air and the pedosphere and water bodies is significantly influenced not only by the characteristics of traffic flows moving along the highways, but also by the wind regime, the conditions of leaching of harmful substances by precipitation, dry deposition, etc.

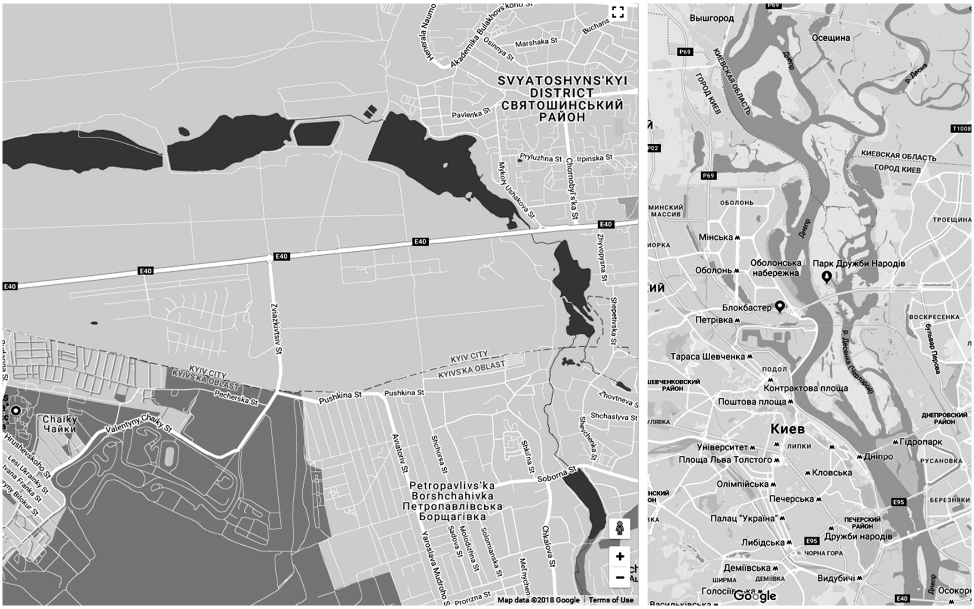


Fig. 4. Water bodies of Kyiv city (Ukraine), which are exposed to the influence of intensive vehicle emissions.

It was established that the wind speed of 0–1 m/s is dangerous in terms of the dispersion of impurities originated from the low emission sources (in particular, road transport), while the wind speed of 3–6 m/s is dangerous in terms of the dispersion of pollutants from the emissions of industrial enterprises with high pipes. In [20] the ways of distribution of air masses and gaseous impurities from vehicle emissions moving in a stream on a regulated section of the highway are shown.

Numerous studies have shown that the real process of toxicants dispersion is conditioned by peculiarities of their emission, vertical and horizontal transfer taking into account the turbulent nature of their movement. Dispersion of harmful impurities in the air occurs due to convective transfer of air masses (in particular, in the direction of the average wind); due to diffusion processes associated with the concentration gradient of a particular toxicant; as well as turbulent diffusion processes due to mixing air flows in all directions.

Thus, the processes of dispersion and local concentration of harmful substances in the air are significantly influenced by:

– physical and chemical properties of the harmful impurity, its natural toxicity and reaction activity;

– the ability of the impurity to form water- and acid-soluble mobile forms;

– wind direction and speed;

– terrain, geochemical features of the territory, proximity to water bodies, etc.;

– climatic and meteorological conditions of pollutant transfer;

– diversity of flora and fauna;

– intensity and qualitative characteristics of traffic (in particular, the structure of the traffic flow);

– the presence, proximity and type of other sources of pollution, class and chemical properties, hazard indicators of associated pollutants, their concentration and dispersion conditions;

– sedimentation conditions (dry or wet), secondary transfer conditions, etc.

The level of threat of air pollution to human health, and, consequently, the level of environmental hazard, is determined by the maximum concentration of the toxicant, which is calculated in the most threatening weather conditions – in the warmest month and at calm wind speeds.

In mathematical modeling of the dispersion of impurities and the study of the processes of their turbulent diffusion, as a rule, two main approaches are used. The first approach is to solve the turbulent diffusion equation with constant diffusion coefficients determined on the basis of Fick's law; and the second approach is to establish the concentrations of the toxicant according to the formulas obtained using statistical methods. The latter method uses the normal Gaussian distribution law to obtain the concentration fields of impurities near the source of contamination.

In order to build spatial models of the dispersion fields (concentration fields) of toxicants, which are ingredients of vehicle emissions, spatial-temporal investigations of the intensity and composition of traffic flows were conducted on the Kyiv roads adjacent to recreational areas. To collect the observation data (number of vehicles on the road section for a certain time, mode of their movement, etc.) video recording, online services of road webcams, etc. were used. Field observations of traffic flows were carried out at different seasons (warm, cold) on days when there was no precipitation and in the absence of traffic jams.

The intensity of the traffic flow N_{TF} was determined by the number of vehicles passing through the intersection of the studied section of the road for 20 minutes. Traffic flow density ρ_{TF} was calculated by the number of vehicles that were present in the studied area at a certain point in time. This indicator was also used to determine road congestion. The composition of the flow was characterized by the ratio of vehicles of a certain type – cars, buses, minibuses, trucks, etc.; the share of diesel vehicles in the flow was also determined.

To model concentrations fields of impurities in surface airspace in the recreational areas adjacent to the roads, in addition to the main characteristics of the traffic flow, the following ones were determined:

– geographical location of the road section (Google Maps and GPS software products were used);

– the length of the section L (with fixation of streets crossing it if they were present);

– width of the sidewalks b_{sw} (if available), the width of protective "green" strip (if available), vegetation on it (if available), etc.;

– width of the roadway b, the presence of a longitudinal slope;

– the number of lanes in each direction of the road;

– the average flow velocity v_{TF};

– distance to the nearest buildings, density and peculiarities of the urban planning;

– weather and meteorological conditions;

– roughness of the underlying surface, the presence of water bodies nearby.

Methods described in [21] and [22] were used to build models of dispersion of toxicants. The result of the calculation of surface concentrations of impurities is given in the multiplicity of exceeding their maximum permissible single concentration ($MPC_{m.s.}$), and the fields of pollutants dispersion are a function of three parameters in the case of a stationary process. In this case, the mathematical model of the variance of a certain impurity has the form of a system of differential equations in partial derivatives, and to solve it certain boundary conditions need to be set.

Thus, the flare approximation model, which is the solution of the semi-empirical turbulent diffusion equation, was implemented in the MathCad software environment and based on it, the concentration fields of harmful substances that are the main ingredients of vehicle exhausts were visualized.

A computer program was created in collaboration with an IT specialist in the C++ programming language to calculate the turbulent diffusion coefficients of light (for example, CO and NO_x) and heavy (in particular PM_{10}) impurities at different temperatures.

For each of the studied recreational areas, the most dangerous wind directions and speeds, which have the strongest impact on the ecological state of the air, water bodies, etc., and have a negative impact on human health were determined by a computational experiment.

In Fig. 6 the examples of PM_{10}, NO_x and CO dispersion fields with the established most dangerous direction of the average wind and wind speed of 5 m/s on the territory near the recreational area with ponds № 14 and № 15 (Fig. 5, Kyiv, Ukraine) are shown. In the calculations, it was assumed that the PM_{10} dispersion (with a particle size $\leq$ 10 μm) obeys the laws that are typical for the dispersion of gaseous substances, while for larger particles, these laws change significantly [23].

In Fig. 7 the results of modeling the pollution of the surface air layer with nitrogen oxides NO_x (in terms of NO_2) at the most unfavorable for the studied water bodies and adjacent territories directions and average wind speed are shown (except shown in Fig. 6). As can be seen from the figures, the studied water bodies are exposed to significant technogenic load from vehicle emissions caused by transport flows located closely to them.

For the obtained models of dispersion of pollutants on the basis of the analysis of literature data, the following gradation of surface air pollution levels was proposed (without taking into account the synergistic effects of environmental pollution by several harmful substances; the geometric features of the road also have not been considered) [24]:

– environmentally hazardous medium (very high pollution level) – in the case when the multiplicity of exceeding the pollutant $MPC_{m.s.}$ is more than 8.0 $MPC_{m.s.}$;

– high level of pollution – in the case when the multiplicity of exceeding the pollutant maximum permissible concentration is 4.4–8.0 $MPC_{m.s.}$;

– the average level of pollution – can be observed when a multiplicity of exceeding the impurity maximum permissible concentration is 2.0–4.4 $MPC_{m.s.}$;

– bellow average pollution level can be observed when a multiplicity of exceeding the maximum permissible concentration of the harmful substance is 1.1–1.9 $MPC_{m.s.}$;

– ecologically safe low pollution level – can be observed under conditions when there is no excess of $MPC_{m.s.}$ for the contaminant.

As can be seen from the figures, in the studied areas located near the water bodies, among the harmful impurities, the largest exceedance of the maximum permissible concentration $MPC_{m.s.}$ is observed for nitrogen oxides – about 3.8 times. Such excess of the $MPC_{m.s.}$ is extremely dangerous, because, according to scientists [25, 26], increasing the content of nitrogen dioxide NO_2 in the air of the city by 10 % leads to an increase in the morbidity of the population by 0.25–0.35 %.

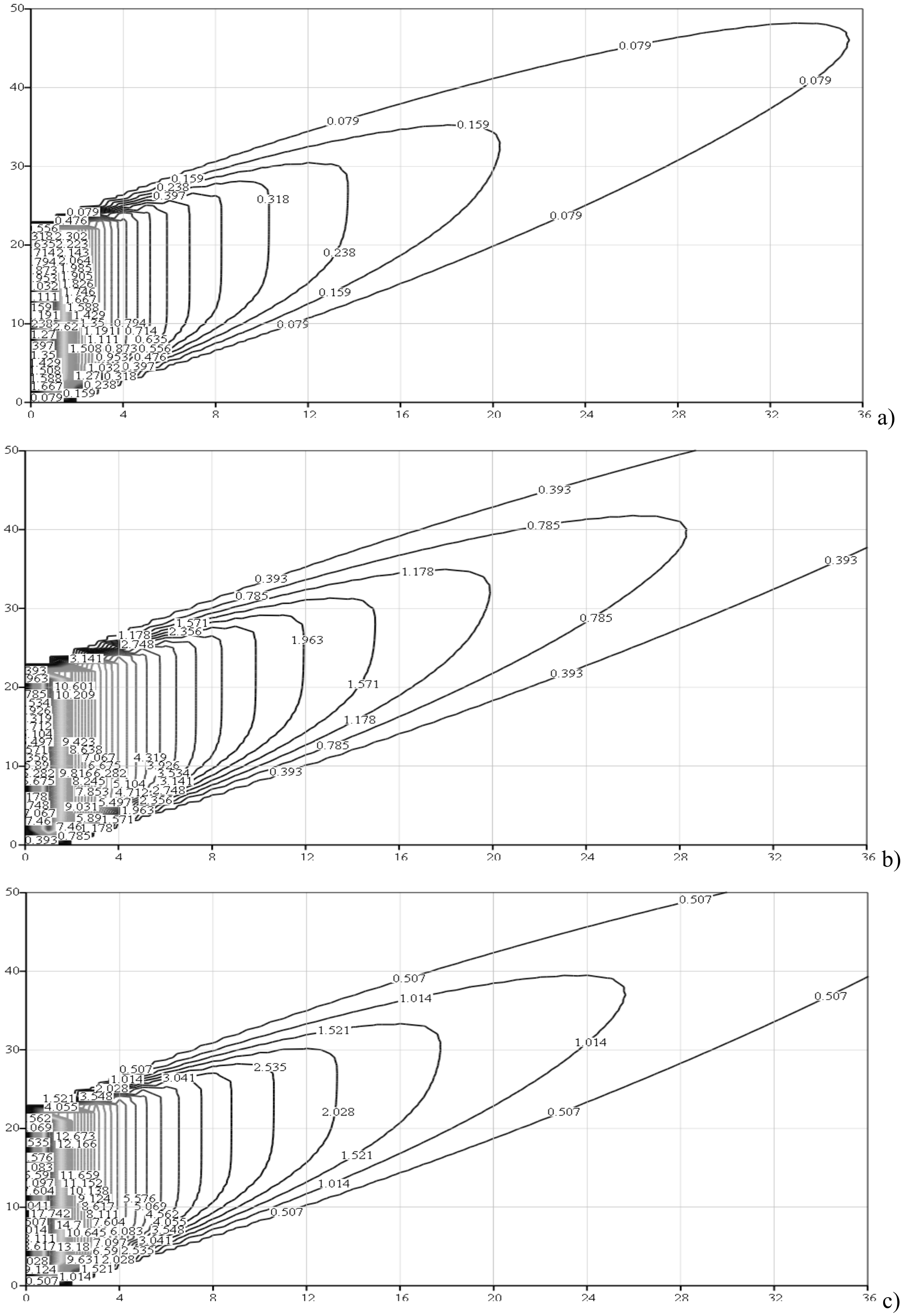
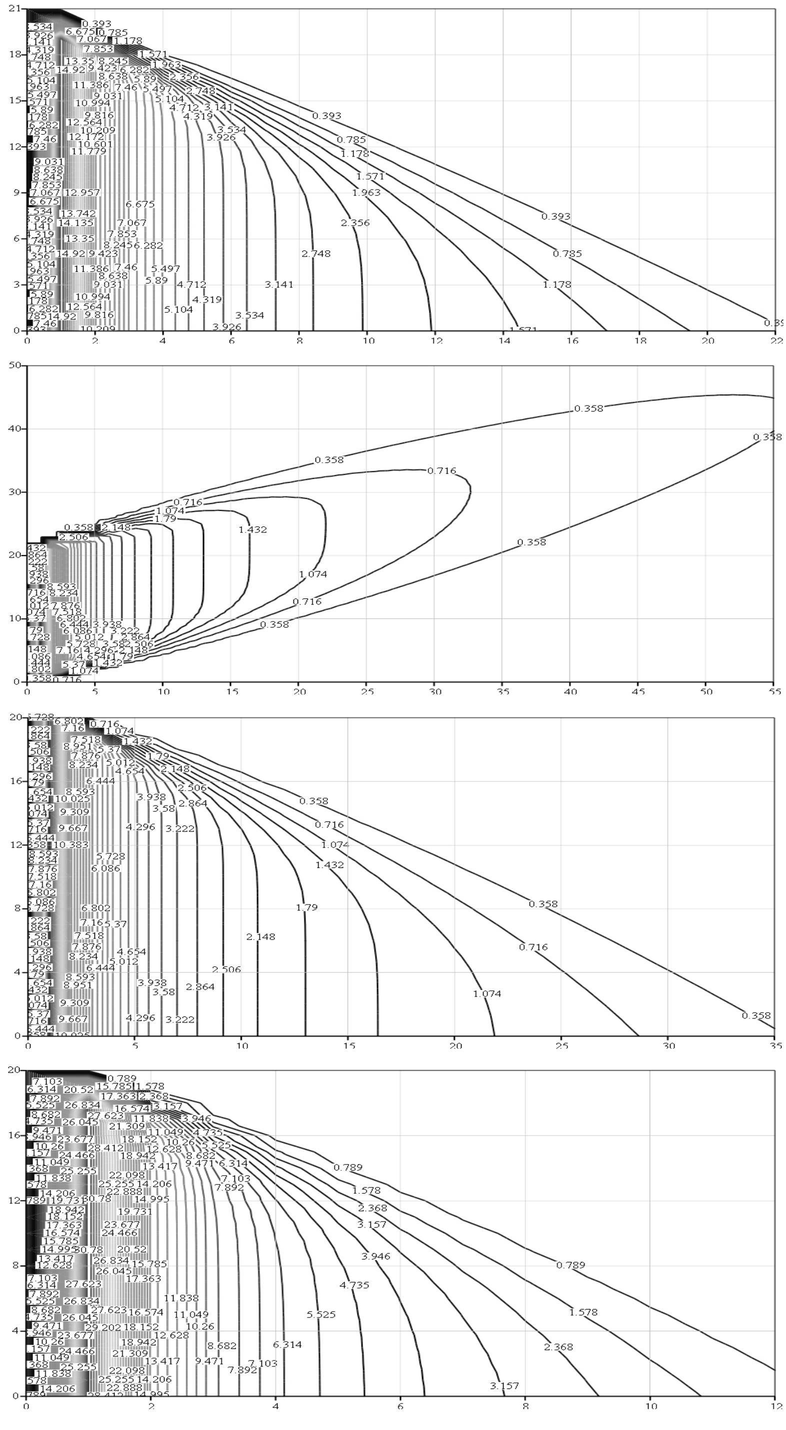


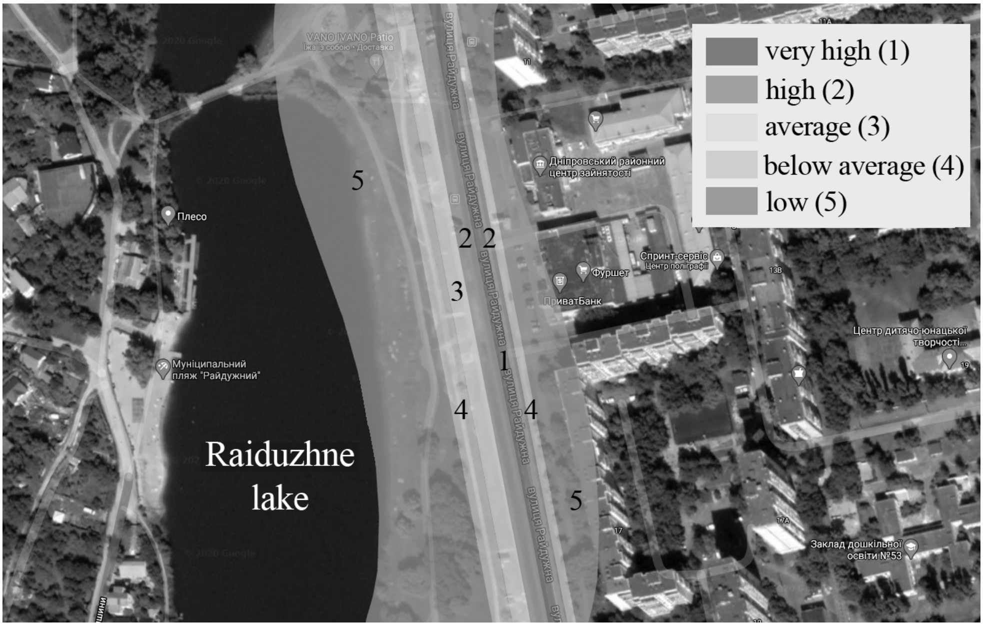
Fig. 5. The results of modeling the dispersion fields of pollutants in the studied recreational areas near the Pond № 15 (Kyiv, Ukraine) with the most dangerous western wind at a speed of 5 m/s: a) PM_{10}; b) NO_x; c) CO.



a) b) c) d)

Fig. 6. Results of modeling of dispersion fields of nitrogen oxides (in terms of NO_2) near water bodies in Kyiv city (Ukraine) at unfavorable directions and average wind speeds of 5 m/s: a) Pond № 15, eastern wind; b) Pond № 14, western wind; c) Pond № 14, eastern wind; d) Pond № 14, northern wind.

In Fig. 7 and Fig. 8 the maps representing ecological danger levels are given on the example of recreational areas located near Raiduzhne Lake, Nyvky Park (with lakes) and ponds № 14 and № 15 (Kyiv, Ukraine).

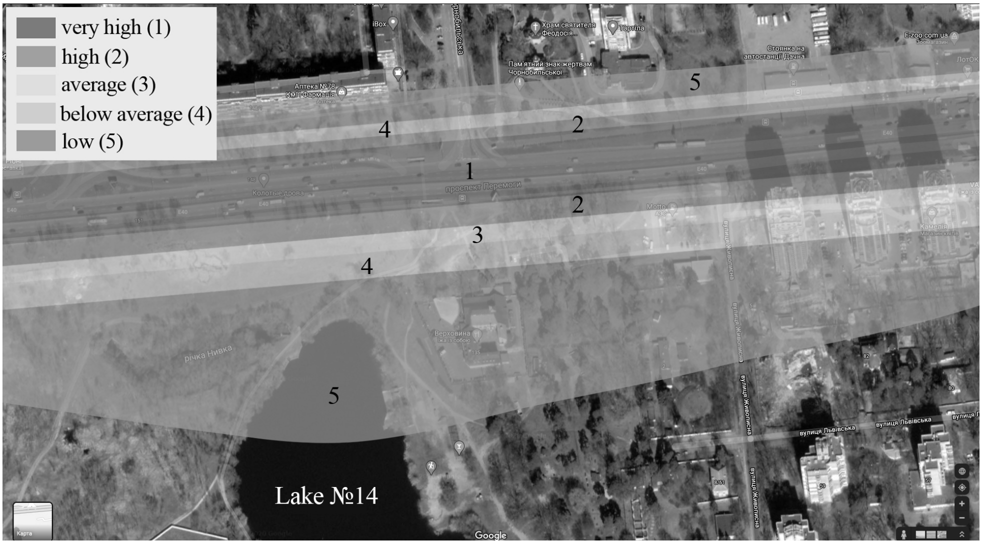


a)

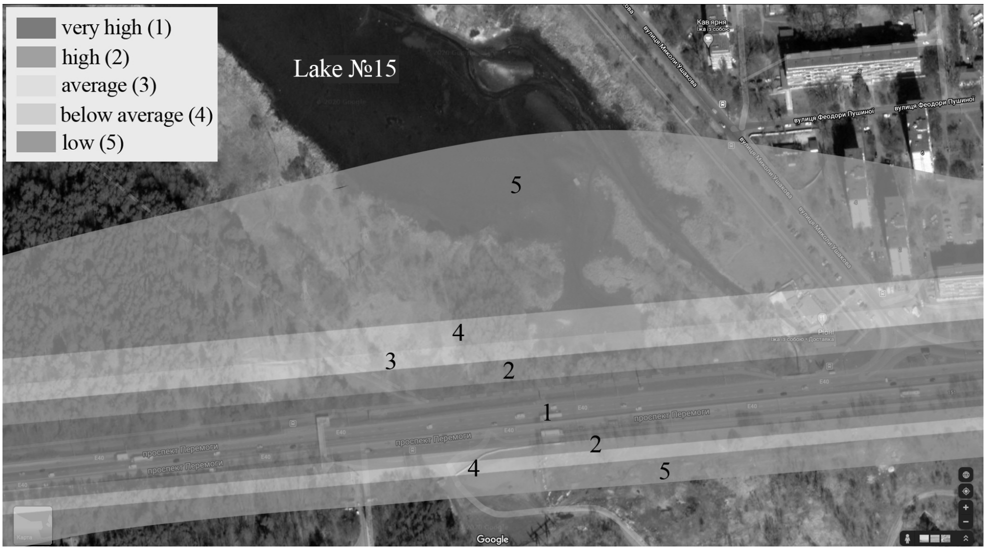
b)

Fig. 7. Maps representing ecological danger levels of recreational areas located near a) Raiduzhne Lake and b) Nyvky Park (Kyiv, Ukraine).

Thus, field studies of road conditions (traffic intensity and density, distribution of vehicles by type and fuel used) on the Kyiv roads located closely to the recreational areas, water bodies, etc. allowed (using the MathCad software) to create spatial mathematical models and predict pollutant spreading analyzing dispersion fields of harmful substances originated from vehicle exhaust gases, determine the conditions of their distribution and local hazardous concentration. Based on a computational experiment, a set of unfavorable meteorological conditions for the studied recreational areas and water bodies, in particular, wind direction and speed, were determined. An environmentally acceptable (safe) distance from the road where there is no exceeding of the maximum permissible concentration $MPC_{m.s.}$ for any pollutant was established.



a)



b)

Fig. 8. Maps representing ecological danger levels of recreational areas located near ponds a) № 14 and b) № 15 (Kyiv, Ukraine).

CONCLUSION

So, the problem of assessing the levels of environmental safety and the development of measures to minimize the risk to human health is of particular importance for urban recreational areas (parks, areas near natural and artificial water bodies, etc.). These territories are not always specially organized by authorities, many of them arise spontaneously, unorganized, but this does not diminish the importance of the problem of ensuring their environmental safety.

Thus, improving the system of ecological monitoring of urban territories, especially those of recreational purpose, is an urgent scientific and practical task. The results of the research on the changes in their ecological state will allow to reasonably determine the risk levels to human health, find out causes of degradation of the natural and urban environment, etc., as well as to make accurate forecasts of the safety of recreational areas.

However, since it is quite difficult to control the impact of all pollutants in the ecological monitoring system, such indicators as electrical conductivity, hydrogen index pH and optical properties of natural solutions (only for analysis of water samples) have been chosen to assess the environmental safety of the studied water bodies and urban recreational areas located nearby roadways, as well as to study changes in surface water and soil quality indicators. These characteristics are sensitive to the complex effects of many factors, easily measured even with the help of portable devices.

Densimetry, viscometry and stalagmometry methods were also used during the implementation of the full environmental express monitoring program. For the surface waters, organoleptic parameters were also studied. For the purposes of modeling the dispersion of toxicants in the environment, the orography of the territories was studied; field observations of traffic flows moving along the roads near the studied recreational areas were carried out.

The computational experiment on the determination of the level of pollution of the air surface layer and territories adjacent to the roadways, including water bodies, with such components of vehicle exhausts as nitrogen and carbon oxides, fine dust (particulate matter) was carried out using mathematical modeling and the differential equation of turbulent diffusion in different weather conditions.

The laboratory-analytical method (qualitative and quantitative analysis) was used to determine the content of chemical elements and the concentration of ions in water samples and soil extracts. Particular attention was paid to the presence and content in the studied samples of heavy metal compounds, as well as sulfate- SO_4^{2-} and chloride-ions Cl^-.

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USE (EXPLOITATION) OF DUAL (DOUBLE) WATER SUPPLY SYSTEMS AS A WAY TO RATIONALIZE THE USING OF DRINKING WATER

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ABSTRACT

The authors have studied one of the most actual problems of today - the problem of reducing the amount of fresh water and deteriorating of its quality. The world scientific community considers the water crisis to be one of the 5 most important global risks for the next ten years, so studying the issue of streamlining the structure of drinking water is appropriate and timely. The authors have found that the share of water consumption from the water supply network to meet drinking needs is on average only 15%, everything else is used for domestic and technical purposes. It was found that in some cities the daily use of drinking water exceeds the physiological needs of the human body more than 200 times. The authors work on solving an urgent practical problem - finding new approaches to improving the environmental safety of drinking water supply systems in order to rationalize the use of fresh water. The authors have analyzed the international experience of dual (double) drinking water supply systems as an alternative approach. It is established that the use of dual water supply systems has proven and economic efficiency.

Keywords: environmental safety, fresh water, drinking water supply, drinking water, dual (double) systems.

INTRODUCTION

The degradation of the aquatic environment and depletion of water resources are among the most acute problems today. Due to its unique properties, water, much more than other natural resources, affects the development and formation of human civilization. It is of key importance in the formation and maintenance of life on Earth, it is the basic biological substance of which living organisms are composed and without which they cannot exist.

The problem of rational use of fresh water and increasing the level of ecological safety of drinking water supply is the most pressing among today's problems. According to UNESCO (World Water Resources and their use), the world's water resources are distributed as follows: 97.5% - of the sea and oceans; 2.5% - fresh water; arctic ice and glaciers of mountainous areas -

68.7%; ground fresh water - 29.9%; 1.14% - swamps, permafrost [18]. In figure 1 it is showed the distribution of available world freshwater reserves on the continents.

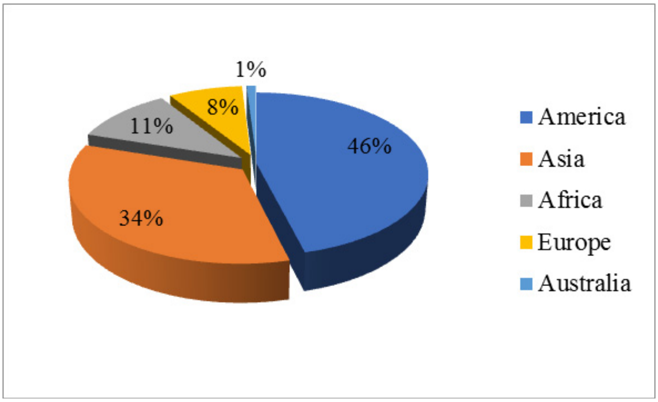

Fig. 1. World freshwater reserves on the continents [17]

The world's water supply is three-quarters of the globe, which is permanently covered by water, although it should be noted that only a small part of water resources is a source of water supply. Sources of fresh water are rivers, lakes, reservoirs. They are 0.09 million km^3 of the total volume of water on Earth 1386 million km^3. Given these facts, we can say that in the near future, fresh water may belong to non-renewable natural resources [17].

According to The United Nations World Water Development Report, in 2019, three out of ten people in the world are denied access to quality drinking water [13].

The World Wildlife Fund's 2020 Review of the State of the Environment and Risks for Humans identifies the water crisis as one of the 5 most important global risks for the next ten years [13].

In the World Bank reports and documents [9] it is indicared that clean water is one of the key factors in economic development, and deteriorating water quality slows economic growth, well-being, negatively affects human health and leads to increased poverty.

The issues of water conservation are among the priority areas of the ecological vector of human development. This is confirmed by the fact that among the 17 Sustainable Development Goals (SDGs) of mankind, a special place is occupied by those related to the issues of rational water use and safety for consumers, namely:

- goal № 6 Clean water and sanitation - ensuring the availability and rational use of resources and sanitation for all consumers;

- goal № 14 Life bellow water - Conservation and sustainable use of oceans, seas and marine resources for sustainable development.

Among the tasks listed in goal № 6, we want to highlight the following: 6.1. "By 2030, ensure universal and equal access to safe and affordable drinking water for all", 6.3. "By 2030, improve water quality by significantly increasing recycling and safe reuse of wastewater worldwide," 6.a. "By 2030, expand international cooperation and support to strengthen the capacity of developing countries to implement water and sanitation activities and programs, including… the use of recycling and reuse technologies."

As we can see in the tasks of the SDG raises the issue of rationalization of fresh water use, its reuse of water, which on a large scale in the implementation of this area will save a significant amount of fresh water through recirculation.

The search for new ways of reducing the use of fresh water, technical solutions for rationalization in the field of water supply are formed in the context of increasing the use of fresh water for various industrial needs. For example, it is emphasised that one inhabitant of the planet uses an average of 13-14 thousand m^3 of fresh water per year, the most of the valuable resource is used for agriculture and industry (Fig. 2).

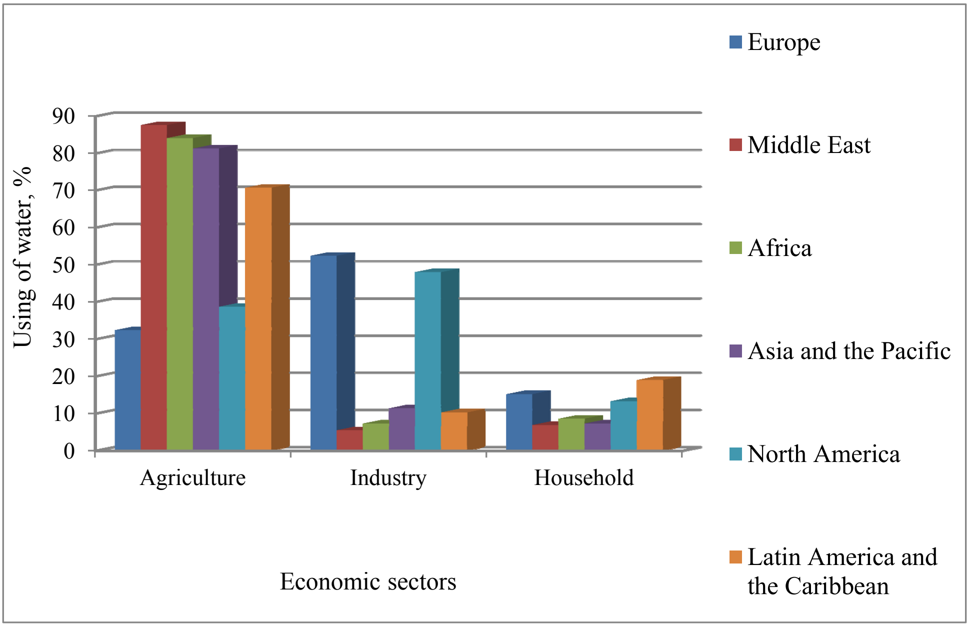

Fig. 2. Use of fresh water in the economic sectors of the world [18]

The greatest threat of water crisis is observed in low-water and arid regions of the world, which is caused by the natural climatic conditions of the territories. The results of the study of fresh water supply are shown in table 1.

Table1

The countries with the largest reserves of fresh water [17]

Country	**km^3**	**%**
Brazil	6950	14,8
Russia	4500	9,6
Canada	2900	6,2
China	2800	6,0
Indonesia	2530	5,4
USA	2480	5,3
Bangladesh	2360	5,0
India	2085	4,4
Venezuela	1320	2,8
Myanmar	1100	2,3
Total in the world	47000	100,0

The leaders in the number of the largest reserves of fresh water are countries such as Brazil and Russia. At the same time, the level of fresh water use from the total resources in different countries of the world shows that Russia is not among the leaders (Fig. 3).

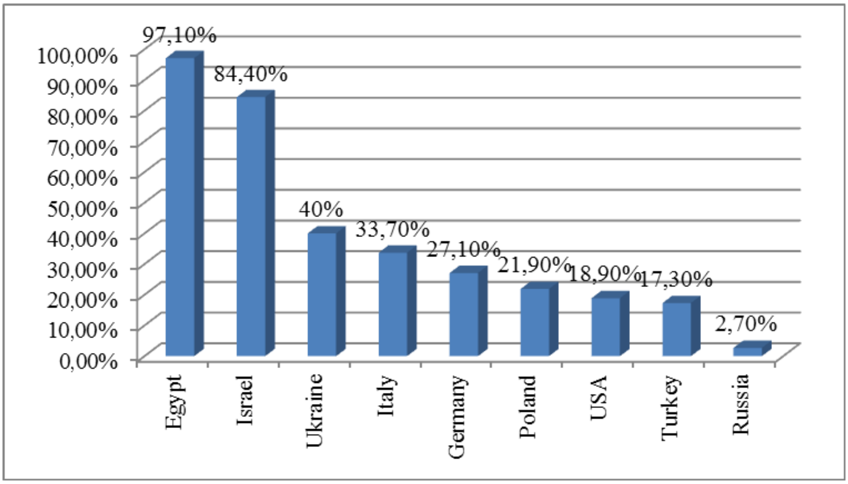

Fig. 3. The level of fresh water use from the total resources [179]

In the process of studying the structure of drinking water use in households around the world, it was found that most of it is used for domestic and technical purposes. Data on the structure of water consumption, water use in America, Australia and various countries in Europe, Asia and the amount of water consumed per person in households in different countries are presented in Figures 4 and 5 [1,2,5,6,7,10,15].

It is established that the share of water consumption from the water supply network to meet drinking needs is on average only 15%.

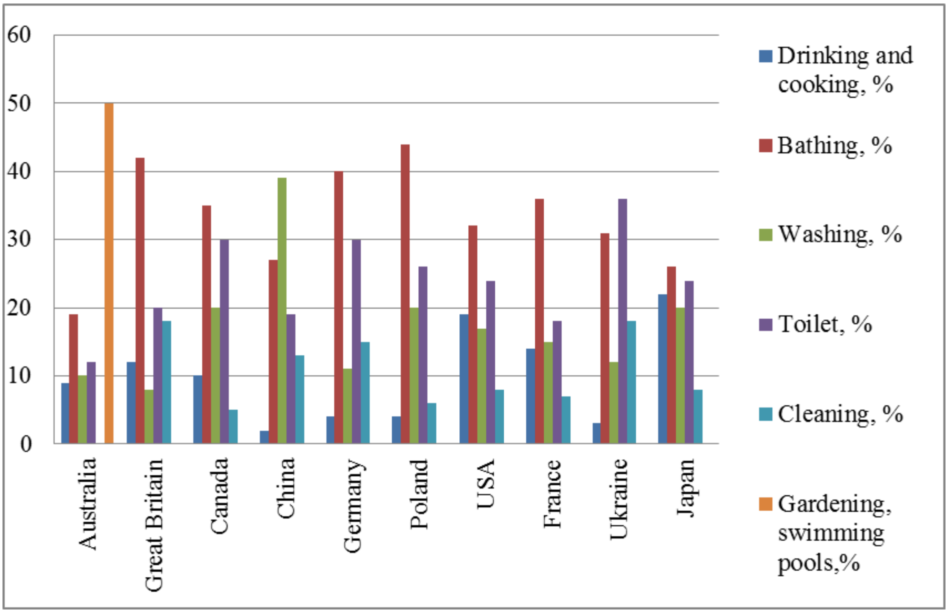

Fig. 4. Comparative analysis of the structure of water use in households in different countries

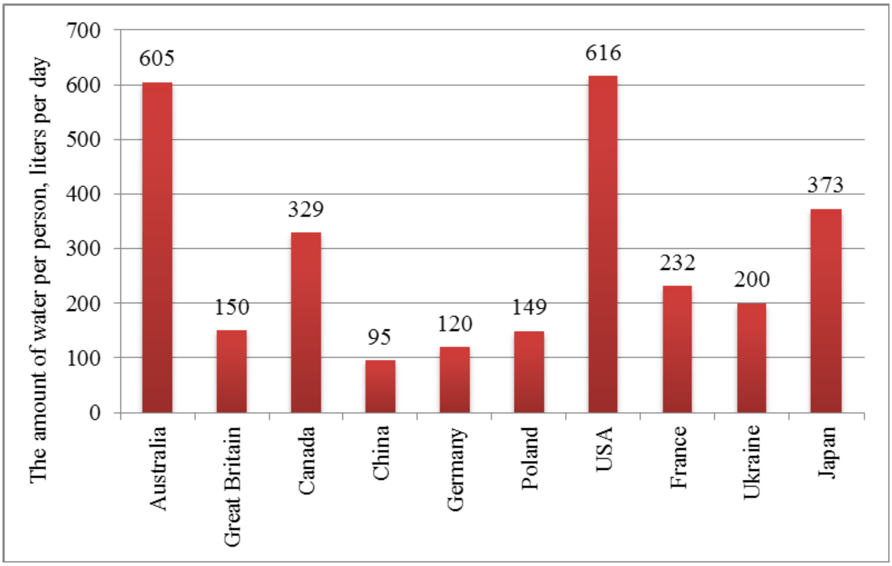

Fig. 5. The amount of water consumed per person in households in different countries

The leader in the use of fresh water is North America, namely the United States. In New York City, more than 600 liters per capita is used daily, which is the highest in the world, with a metropolitan population of more than 8 million [8].

Given the growing use of fresh water for domestic use and drinking tap water for domestic, technical purposes in households, it is advisable to study in detail the issue of water reuse, so-called recycling and suggest possible alternatives to existing water supply systems.

The ecological efficiency of the use of dual double water supply systems has been proven by their practical use in households in Germany, the USA, China, Malaysia, India, etc. However, in most cases, the dual system refers to the water supply system of the house, which includes in addition to the main water supply network, the second one, through which there is a reuse of the so-called "gray" water, or rainwater for technical needs.

Figures 6 and 7 show simplified diagrams of traditional and dual approach to the organization of water supply.

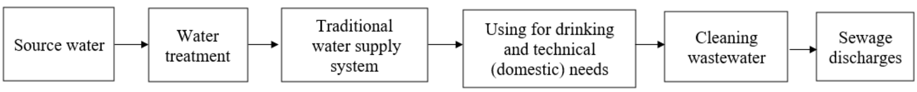

Fig. 6. Simplified diagram of the traditional approach to the organization of water supply

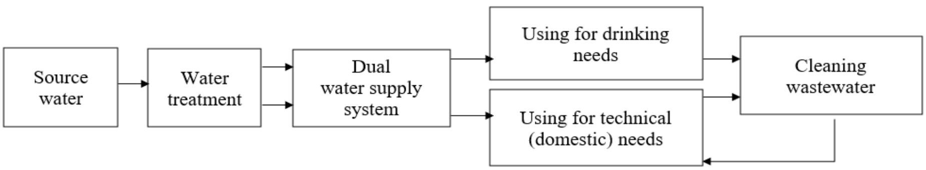

Fig. 7. Simplified diagram of the dual approach to the organization of water supply

METHODS AND EXPERIMENTAL PROCEDURES

In order to study the prospects of using dual (double) systems and their role in rationalizing the use of fresh water, the authors used theoretical methods, such as methods of analysis and synthesis to summarize information sources. Methods of systematic and comparative analysis were used in the process of studying the structure of water use and conducting a comparative analysis of consumption in households in different countries.

THE RESEARCH RESULTS AND DISCUSSIONS

Examples of the introduction of a double dual water supply system, where two separate water supply networks were created at the construction stage – for drinking and service water, are found in the study [18]. The authors analyze the prospect of creating a dual system with a double network of water pipelines in Shanghai. It is noted that the cost of double water distribution systems varies significantly due to the fact that the process of water purification, treatment power, materials may differ, depending on the initial quality of water, as well as the condition of the water supply network. About 3 million RMB is needed to build a double water distribution system for a residential area with a population of 3,000 families, which is about 2,000 RMB per family.

In China, it is widespread to use two methods of supplying drinking water to consumers. The first method is in barrels, the so-called bottled water, the second one is pipeline, using a double water distribution system.

In China, the first double water distribution system was established in Jinhua, in a residential area of Shanghai's Pudong district back in 1997. Since then, the technologies related to the development of double water supply systems have begun to develop rapidly. In the process of the Chinese experience in the implementation of the idea of double dual water supply systems, many technological problems arose, including the need to expand treatment processes, operational regulation of chemical indicators, sterilization and selection of pipes, etc., however, despite all the nuances, the profitability of this approach was confirmed.

In recent decades, many projects for double water distribution systems for residential areas have been implemented in China. Nowadays many engineering companies provide services for the design and construction of double water distribution systems. It has been proven that the double distribution systems are cost-effective and have high environmental importance for freshwater conservation in China.

Significant experience in the implementation of dual double water supply systems has been introduced in the USA. This can be confirmed by the study [3]. The location of such systems is shown in Figure 8.

There is a well-known experience of the American Virgin Islands and the Caribbean Islands [11], where the water supply in the utility network is carried out by two networks – for drinking and service needs. These are double distribution systems that involve the use of water for water supply from two different sources in two separate distribution networks. The two systems operate independently of each other within the same service area. These double distribution systems are used to supply drinking water through one distribution network and non-drinking service water through another. Service water is used for such purposes as firefighting, sanitary needs (toilets, laundry, washing), street cleaning, irrigation of decorative gardens or lawns. As the experience of these small areas and communities shows, double water distribution systems are economically and environmentally justified. The double systems are designed as two separate pipeline networks: a drinking water distribution system and a service water distribution system (purified or natural seawater).

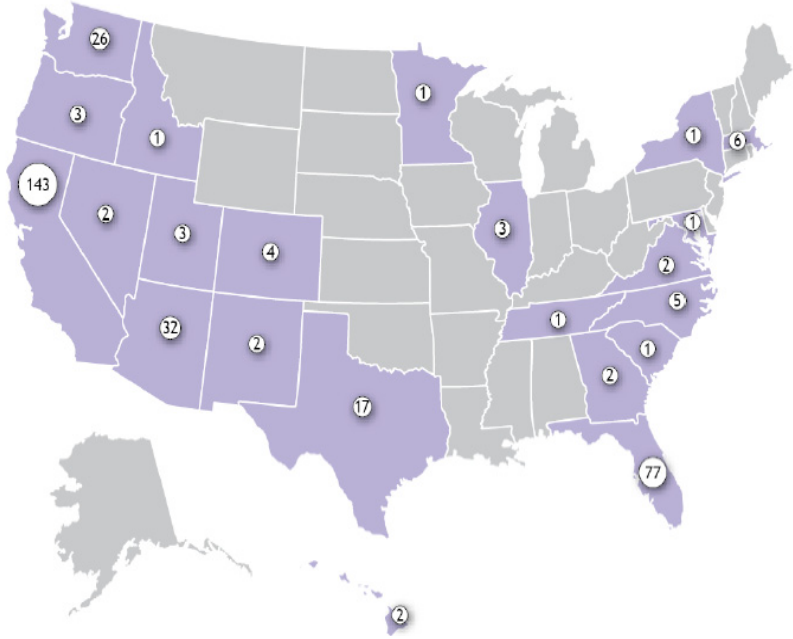

Fig. 8. Location of double dual water supply systems in the USA [3]

An important aspect of rational water use is the reuse of treated wastewater as service one for sanitary needs.

The problem of reusing wastewater after its treatment is being dealt with at the state level in the United States of America. In the arid states of Florida and California, a water reuse system has been introduced for industrial, agricultural, and landscape irrigation needs [4].

One of the oldest double water distribution systems in the USA is located in the Grand Canyon Village, Arizona, where since 1926 treated domestic wastewater has not been discharged into open water, but stored in special tanks for firefighting [14].

In the 70s of the twentieth century in the state of Florida in the city of St. Petersburg, the construction of a large-scale system of continuous water reuse began, where now about 40% of total water consumption of the city is secondary, which is used for domestic and sanitary needs in schools, hospitals, as well as for watering lawns, golf courses and filling fire hydrants [14].

There are examples of reusing domestic wastewater to meet drinking needs. In the Los Angeles area, restored water with a high level of purification has been used to combat South Carolina's drinking water shortage since 1962 [14].

Figure 9 shows the location of double water supply systems on the world map [3].

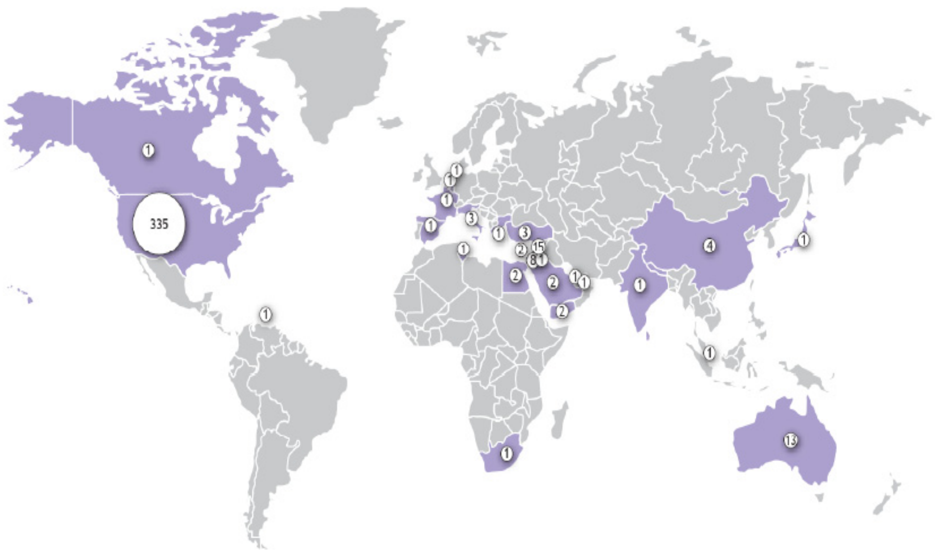

Fig. 9. Geographical location of double dual water supply systems in the world [3]

Table 2. List of dual double water supply systems in the world (excluding the USA) [3]

The name of the dual system	City or location	Country
Adelaide	Adelaide	Australia
Bolivar	Suburb of Adelaide	Australia
Brisbane	Brisbane	Australia
Caboolture	Caboolture	Australia
Goulburn Valley	Goulburn Valley	Australia
Gibson Island and Luggage Point WWTP	Suburb of Brisbane	Australia
Mawson Lakes	Suburb of Adelaide	Australia
Melbourne Water	Melbourne	Australia
New Haven	New Haven	Australia
Shoalhaven Heads	Shoalhaven Heads	Australia
Sydney Water/ Rouse Hill	Sydney	Australia
Virginia	Virginia	Australia
Wagga Wagga	Wagga Wagga	Australia
Bahrain	Bahrain	Bahrain
Flanders	Flanders	Belgium
Toronto	Toronto	Canada
Beijing	Beijing	China
Hong Kong	Hong Kong	China
Jinghua Residential Quarter of Pudong District Shanghai	Shanghai	China
Tianjin	Tianjin	China
Larnaca	Larnaca	Cyprus
Limassol	Limassol	Cyprus
Alexandria	Alexandria	Egypt
Cairo	Cairo	Egypt
Paris	Paris	France

Corfu	Corfu	Greece
Amsterdam	Amsterdam	Holland
Bangalore Water Supply and Sewerage Board	Bangalore	India
Afula	Afula	Israel
Beer-Sheva	Beer-Sheva	Israel
Eliat Eliat Israel	Eliat Eliat Israel	Israel
Kibbutz	Kibbutz	Israel
Netania	Netania	Israel
Tel-Aviv	Tel-Aviv	Israel
Haifa	Haifa	Israel
Sicily	Sicily	Italy
Sardinia	Sardinia	Italy
Turin	Turin	Italy
Tokyo Metropolitan Government	Tokyo	Japan
Jeddah	Jeddah	Saudi Arabia
Riyadh	Riyadh	Saudi Arabia
Singapore	Singapore	Singapore
Durban	Durban	South Africa
Consorci de la Costa Brava	Girona	Spain
Adra	Adra	Syria
Aleppo	Aleppo	Syria
Damascus	Damascus	Syria
Dera'a	Dera'a	Syria
Hama	Hama	Syria
Hassakeh	Hassakeh	Syria
Homs	Homs	Syria
Huran al-Awamid	Huran al-Awamid	Syria
Idleb	Idleb	Syria
Lattakia	Lattakia	Syria
Quneitra	Quneitra	Syria
Raqqa	Raqqa	Syria
Ras al-Ain	Ras al-Ain	Syria
Salamiya Syria	Salamiya Syria	Syria
Sweida	Sweida	Syria
La Soukra	La Soukra	Tunisia
Nigde-Bor	Nigde-Bor	Turkey
Konya-Kadinhani	Konya-Kadinhani	Turkey
Merkez	Merkez	Turkey
Sharjah	Sharjah	U.A. Emirates
Aden	Aden	Yemen
Hodiedah	Hodiedah	Yemen

Among the countries shown in Figure 9 and listed in Table 2, we see a clear trend towards the fact that most double dual water supply systems are located in countries where there is already a shortage of fresh water (Australia, Egypt, Syria, Israel, Saudi Arabia, etc.), therefore, since the end of the twentieth century, states have begun to take active measures to solve the problem of supplying drinking water and maintaining its quantity.

CONCLUSIONS

Taking into account the above examples of the implementation of double water supply systems, we claim that the issue of changing the structure of fresh water use is one of the main issues of the 21st century. It is urgent to plan and implement changes at the state and regional levels to re-equip existing water supply systems into two distribution networks: for drinking water and separately for service water. It is such changes today that will allow to preserve fresh water in the future and increase the ecological safety of drinking water supply systems.

The ingof dual water supply systems will be one way to solve the problem of rational use of fresh water in the future.

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MONITORING PARAMETERS OF THE ATMOSPHERE AND HYDROSPHERE AS A TOOL OF INTEGRATING ENVIRONMENTAL ASPECTS IN ENGINEERING EDUCATION

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ABSTRACT

The article describes ten years of experience in integrating the environmental component into the educational process of the engineering specialty and the parallel strengthening of the engineering component in the curriculum of the natural science (non-technical) specialty 101 Ecology. This is ensured through scientific cooperation of the departments of automation, industrial safety and ecology, in the process of which undergraduate, graduate and postgraduate students (PHD) are involved. It is shown that work on the development and maintenance of devices for monitoring the hydrosphere and atmosphere, installations of alternative energy, work with environmental databases mix organically in the curriculum of engineering specialties and at the same time allow students to form environmental consciousness. Studying climate change at the local level helps engineering students to better understand the connections in the hydrosphere and the atmosphere, and in parallel to understand the consequences of climate change on the state of local freshwater sources. As for the students of the Department of Ecology, such training helps to increase their motivation and assimilation of the educational material in the study of physical and technical modules of professional disciplines.

Keywords: environmental education, integrated engineering, monitoring.

INTRODUCTION

In the classical education system, there was initially a division of disciplines into humanities, natural and exact sciences, which diminished the importance and integrity of education. It enhances differentiation of courses, which initially require a synthetic approach, especially in the conditions of modern so-called information society.

For the professions of the future, the most important competencies are those common to all industries. As the researchers note, mastering these competencies will help the employee to increase the efficiency of his own professional activity, and will give the opportunity to move between jobs, even industries, while maintaining his relevance [1].

To increase the effectiveness of education, it is advisable to introduce integrated courses. To achieve this goal, it is advisable to introduce the following basic cross-cutting ideas:

- the meanings of the interaction of nature, man and society;

- the variety of forms of human knowledge [2].

Education, based on the integration of various methods and various sciences, contributes to a holistic awareness of the world and an increase in the creative potential of an individual: the co-evolution of nature and society determines the moral principles of harmonizing their existence. A synergistic approach to education involves the development of variable models of the educational process and course content, the fundamental principles of which will be integration and creative development of the individual.

It is well known that traditional engineering majors are more attractive to male students, but in interdisciplinary fields the situation is better. Today, when the total number of young people under the age of 18 is declining, no university majors can afford to recruit students from just one half of the population. In addition to the large number of girls, also a small proportion of young men believe that interdisciplinary specialties are easier and so they prefer them. This means that in terms of recruitment, the benefits are clear, but the recruitment of interdisciplinary graduates by companies raises questions. Studies of this problem have been carried out in Hungary. It is shown that it is more difficult for graduates of experimental interdisciplinary specialties to find a job, since employers don't trust anything new. In our opinion, one thing should not raise doubts: the introduction of interdisciplinary technologies in teaching classical professions can make understand complex disciplines easier for students [3].

METHODS AND EXPERIMENTAL PROCEDURES

In modern research on intersubject interaction, the following areas can be distinguished:

• creation of integrated courses based on two related disciplines;

• coordination of the content of the curriculum of various disciplines on the basis of a common conceptual apparatus;

• solving interdisciplinary problems by methods of various disciplines;

• project-based training with an emphasis on the interdisciplinary nature of the projects being created;

• organization of conferences, research schools on interdisciplinary topics;

• innovative methods: joint lectures by teachers of various disciplines, propaedeutic teaching, problem learning, etc.

The listed forms and methods receive methodological substantiation and are effectively implemented mainly on the basis of related disciplines or disciplines of the same cycle (humanitarian, professional, natural science, special). At the same time, the issues of organizing interaction between the subjects of the humanitarian and natural science, humanitarian and professional cycles remain insufficiently developed. Meanwhile, the humanitarian component should be organically integrated into the professional activity of an engineer, since it provides the professional with general scientific methods of cognition, forms his worldview.

In this study, interdisciplinarity is understood as a synthesis of fundamental highly specialized knowledge, as well as the experience of cognitive, humanistic, sociocultural and professional activities, reflecting systemic connections and relations of social and professional reality.

Among the goals, we chose those developed by [4]:

• awareness of the place and role of the profession as part of larger systems and society as a whole;

• the formation of a flexible value orientation, the development of over-professional ethical principles, reflection on professional activity from the standpoint of its harmonization with universal values.

An interdisciplinary approach implies the graduate's readiness for complex engineering activities, taking into account its social and environmental consequences, for working in interdisciplinary teams. Unfortunately, in practice, the implementation of this approach is not provided. In this regard, the tasks are, first of all creating a methodological system for improving the qualifications of teachers, developing mechanisms for designing and implementing engineering educational programs and curricula, taking into account an interdisciplinary approach. Further development of the system of retraining and advanced training of teachers presupposes a new methodology for determining the goals of educational, research and production activities; creation of optimal conditions for obtaining a new level of education in accordance with the public interest, as well as with the inclinations and abilities of the individual [5].

From the integration project and from the first years of running the integrated programme it is clear that environmental knowledge can be included in mechanical engineering education without compromising the engineering quality of the education. This is feasible:

- by using knowledge already included in the programme, such as laws of natural science, to obtain a systems perspective and overall framework by which the reasons for environmental and resource problems become clear at a principal level.

- by using this as a means by which specialised knowledge can be structured and given an overall meaning, and through which the connection between different subjects/courses becomes clearer.

- by giving examples in partly new ways, for example, by showing alternative applications and how engineering knowledge can be used to solve many of the existing environmental problems and prevent the generation of new ones.

Students experience the integration of environmental aspects in their education as positive and important. They also express a belief that it increases their attractiveness on the labour market [6].

THE RESEARCH RESULTS AND DISCUSSIONS

Below is given a brief description of the main research conducted with the participation of students and proved to be successful for the integration of ecological component into engineering education to show practical features of their implementation that could be useful for other universities.

Experiment of meteorological parameters measurement in the digital system. In different regions considerable variability of meteorological parameters can be observed. That's why it is important to study these parameters in a particular geographic location. Such studies have been organized in the Black Sea National University. They include an experimental set of tools for automatic digital control of environmental parameters for this purpose in the university. It consists of temperature sensors and photovoltaic solar cells, connected with Ethernet.

Since mid- summer of 2013 the complex was retrofitted with homemade anemometer. This anemometer has two functions: it measures wind speed and prevents further contamination of the surface of solar panels by birds. The anemometer of cup type allows only to measure wind speed, excluding its direction. The anemometer is made of stainless steel.

An analysis of the average daily wind speed showed that wind energy is proportional to the cube of its speed. The anemometer was calibrated with several independent methods. They include comparison with the standart anemometer and comparisons with data on wind speed of Mykolaiv meteorological stations: the variations of average daily and maximum values (given by different sources) in August 2013 - April 2014 were compared.

In the process of monitoring the influence of natural factors on the operation of solar panels, it was found that the influence of cloudiness is one of the main ones (Fig.1).

Thus, research on solar cells helped engineering students discover the relationship between atmospheric and hydrospheric phenomena, the impact of water on the strategic development of energy in the region. The formation of ecological thinking was continued with the study of climate change.

The study of local atmospheric parameters in terms of implementation alternative sources of energy. The design of the set of two polycrystalline silicon solar panels (each has capacity of 25W), installed on the roof of the university to monitor solar radiation, allows to explore the impact of batteries' orientation and to perform research on atmospheric transparency. To monitor wind speed there is an anemometer located beside batteries. This anemometer was calibrated using standard tools [7]. Solar panels are connected to the battery, and through an electronic switch to a microprocessor, which at the time of photocurrent measurement switches the battery on the reference load. The duration of a measurement is less than 0.1 seconds, and the interval of surveys is 1 minute, thus measurements do not affect the process of charging the battery. The results of photocurrent and wind speed measurements are processed by a microprocessor and passed on for archiving on a PC.

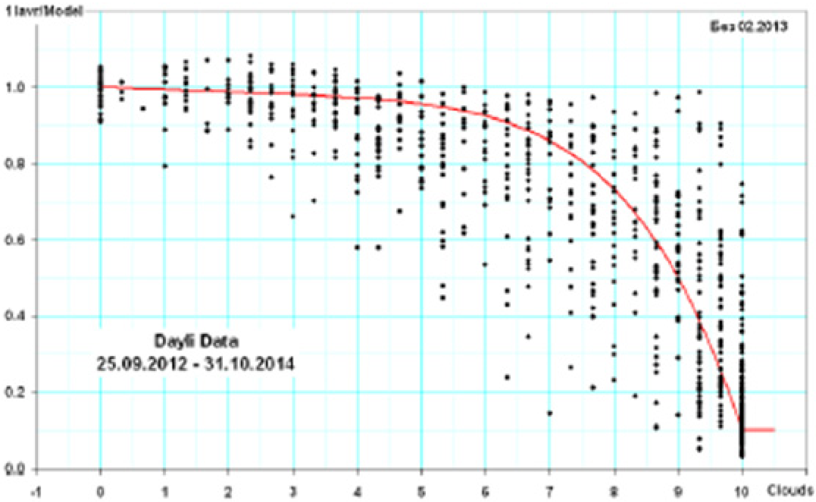

Fig.1. Empirical dependence of the cloudiness caused attenuation coefficient for daily values of solar cells current

Figure 2 shows examples of hours-long daily average wind speed variations and photocurrent of solar photovoltaic panels. Rate of 1000rpm according to anemometer corresponds wind speed of about 4.7m/s, maximum current of 1.7A at conditions 1.5AM - maximum light in summer days. Simultaneous measurements of wind and insolation were performed within 461 days of August 2013 to October 2014.

As expected, the largest wind was in winter, and the biggest insolation in summer. Daily average values of wind speed on the roof of the university changed from 0.5 to 5m/s, with the average value of approximately 1.85m/s. Mean values of the photocurrent in cloudless days changed from 0.43A in summer to 0.26A in winter. Given cloudy conditions (especially in winter) photocurrent decreases several tens of times, so the average of the photocurrent in multiday-interval reaches only 0.25A, which is about 7 times less than maximum photocurrent of the battery pursuant to the passport.

Photocurrent variations in multi-interval describes the empirical model [8], taking into account seasonal and diurnal variations of illumination for the cloudless sky, and the impact of the cloudness ball by meteorological observations.

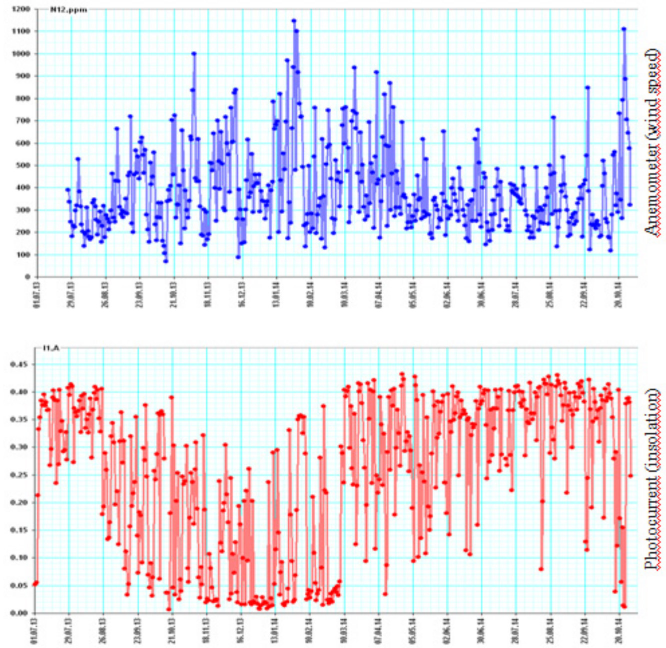

Fig.2. Variations of daily average wind speed and insolation

For convenience of further calculations photocurrent and wind speed values were normalized to the corresponding averages. Figure 3 shows a two-dimensional histogram of normalized daily average wind speed and insolation. Next to the axis are given simple, one-dimensional histogram probability of certain values of wind or insolation. The average value of wind and insolation corresponds to a point with coordinates (1, 1) on the two-dimensional histogram.

Histogram of insolation has two modes, with peaks near 1.6 at cloudless conditions in summer and 0.2 – at increased cloud cover in winter. Histogram of wind has a maximum value near 0.8. On the two-dimensional histogram summer mode has coordinates 1.0 for wind and 1.6 for insolation, winter mode - 1.2 and 0.2 for wind and insolation. That is really, wind turbines can complement solar panels a little in winter. But overall conditions prevail when there is sun and wind, or vice versa - there is nor wind neither sun. That is, low insolation - big rain, rain and fog in Mykolaiv stay until they are blown away by the wind. Cases where the wind "helps" the sun, or vice versa happen not often.

To ensure reliable power supply under conditions of low incoming solar energy or wind power, one should be able to accumulate, storage energy. Naturally, the battery capacity must be the greater, the longer are the "failures" in energy intake. In fact, battery performs averaging ripple of energy at a certain time interval. To determine the impact of energy storage calculations of moving average were done for the normalized average daily energy values on averaging intervals of 1 - 7 days. Relevant results are shown in Figure 3 as a probability histogram for 4 averaging intervals: 1, 3, 5, 7 days. The results for wind and insolation are given separately (upper charts), and simultaneous use of wind energy and insolation - in a ratio of 1:1 (chart below). These graphs should be interpreted as follows. We consider three options for energy complex at the same average annual capacity (roughly 1): wind turbine, solar installation, composition of wind turbines and solar installations with average annual capacity of 0.5 each. Each version of the complex has the ability to accumulate energy for 1 - 7 days.

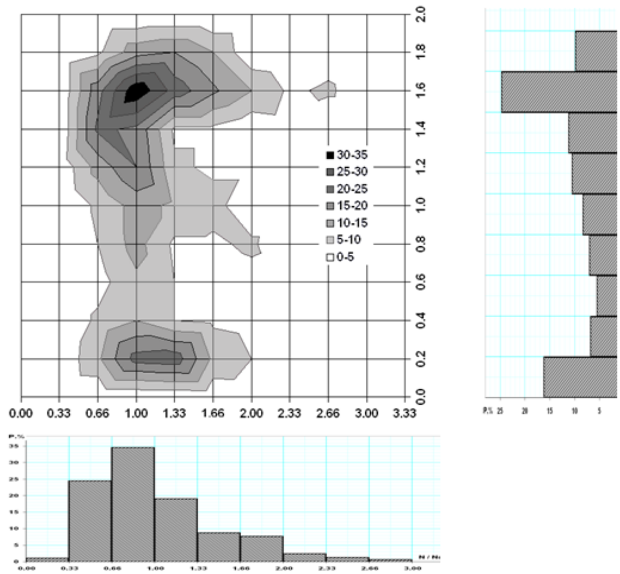

Fig.3. Mutual statistics of wind speed (horizontal axis) and insolation (vertical axis)

Using graphs, you can determine how often the flow of energy to the consumer will fit the range of capacities regarding the average annual values.

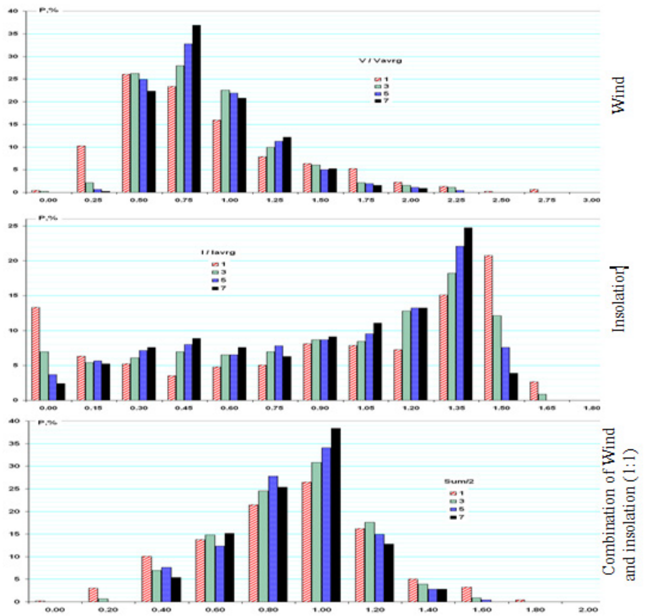

Fig. 4. Probable average values of wind, insolation and their combination for different averaging/accumulation intervals (1–7 days)

Figure 4 shows that with the increase of averaging interval all histograms become compressed closer to the average annual values - pulsation reduces. In addition, the histogram shows that cases of low values for wind energy supply occur much less frequently than for the sun energy. That is the cases of prolonged absence of the sun for a few days (weeks) occur much more frequently than such cases for wind. Windy weather is typical for Mykolaiv region.

Pretty optimistic view have the results for combination of wind and solar energy. Having a battery with 2 days capacity is enough to ensure that power does not fall below the threshold 0.3 of annual average. Given the cost of wind and solar power plants and accumulation systems, one could find the economic optimum of profitability ratio to make decisions on needed capacity.

The study of climate change. Climate change modeling is based on available temperature data. In order to achieve the greatest accuracy of models, all available data sources must be used, including insolation. In our time, if it is obvious that the density of terrestrial meteorological stations is not high enough, actinometric data must be supplemented by satellite data [9], for which various measuring systems are being developed, such as Photovoltaic Geographical Information System (PVGIS) [10].

PVGIS has been developed for more at the European Commission Joint Research Centre, at the JRC site in Ispra, Italy. The focus of PVGIS is research in solar resource assessment, and the dissemination of knowledge and data about solar radiation and PV performance. The best known part of their work is the online PVGIS web application. The largest uncertainty in estimating solar energy system output comes from the solar radiation data. Improving solar radiation data helps to make decisions based on the climate factor by reducing their uncertainty. The PV-GIS technique is an extrapolation of the results of actinometric measurements based on the results of satellite photographs of real cloud cover.

As a result of comparisons with our local data, we were convinced of the high reliability of the PV-GIS technique for estimating illumination at a specific geographical point (Mykolaiv), which has no special means for actinometric measurements (the nearest point in Odessa is about 110 km). Assuming that the reliability of the estimates for other geographical points on this model will not be worse than for Mykolaiv, we calculated the correlation dependences for the power of solar cells for points with different distances from Mykolaiv and direction approximately to the west via Odessa. From the database of the hourly values of PV-GIS, the values of solar cell power and temperature were selected for a 10-year interval. Average daily values were calculated from these data. The calculated average daily values were compared for different points, depending on their mutual remoteness. Similarly, the coefficients of determination for temperature were calculated.

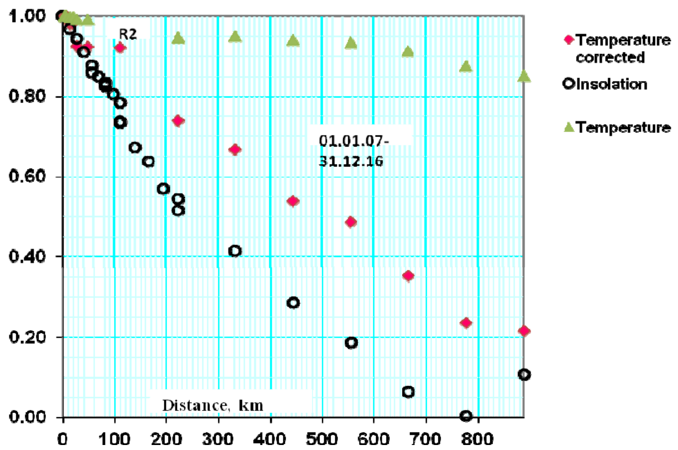

Fig. 5. Distribution of R^2 according to distance

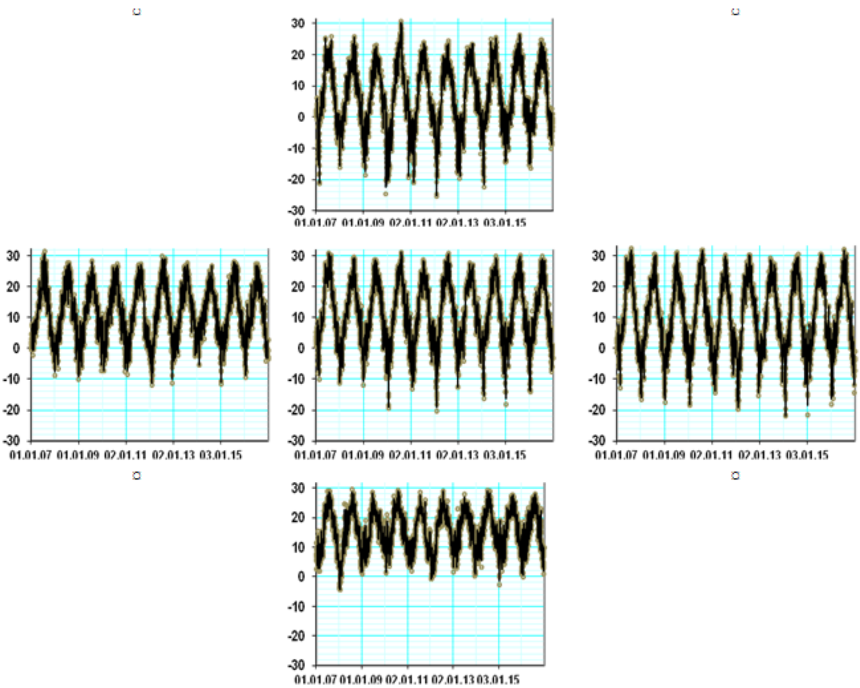

Fig. 6. Seasonal variations of temperature in the time interval 1.01.2007-31.12.2016 according to PV GIS (in the center is the data for Mykolaiv, around - according to the wind rose (east is to the right) in the points with a radius of about 800km)

In Figs. 5 and 6 we see that seasonal variations in the area of the South of Ukraine and within a radius of 800 km from Mykolaiv have a very high correlation, and the correlation corrected to exclude the seasonal component is close to the correlation of the illumination values. It is somewhat higher than the correlation of illumination, since the heating of the surface layer of the atmosphere depends less on short-term changes in cloud cover.

For better visual perception we have calculated squared moving average of temperature seasonal variations in Mykolaiv in the time interval 1.01.2007-31.12.2016 (Fig.7.). In Figs 8-10 are shown squared moving average, fluctuations of temperature and root-mean-square deviation from the moving average of the square of the temperature fluctuations according to PV GIS.

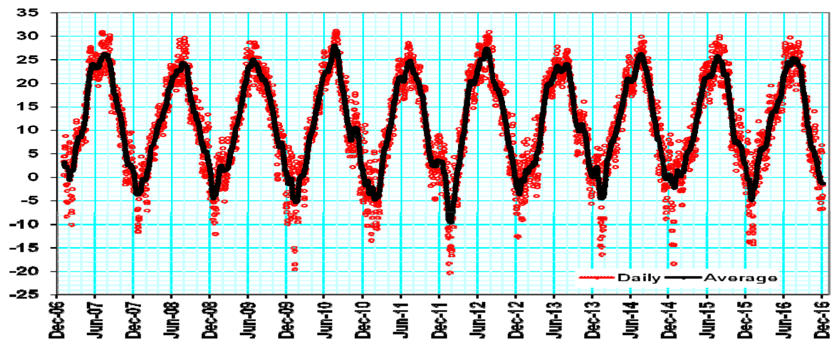

Fig. 7. Seasonal variations (with squared moving average) of temperature in Mykolaiv in the time interval 1.01.2007-31.12.2016 according to PV GIS

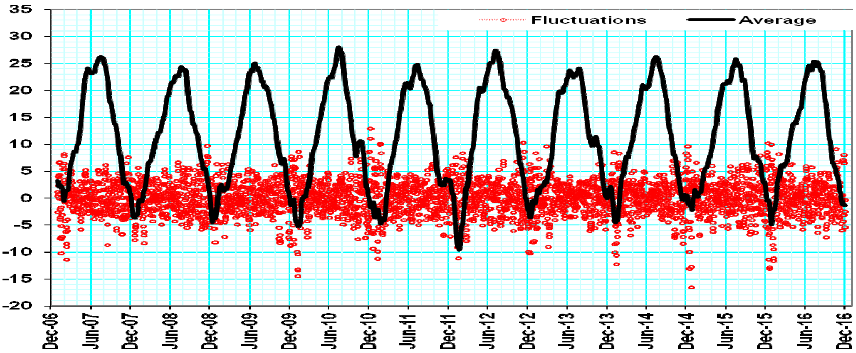

Fig. 8. Squared moving average and fluctuations of temperature in Mykolaiv in the time interval 1.01.2007-31.12.2016 according to PV GIS

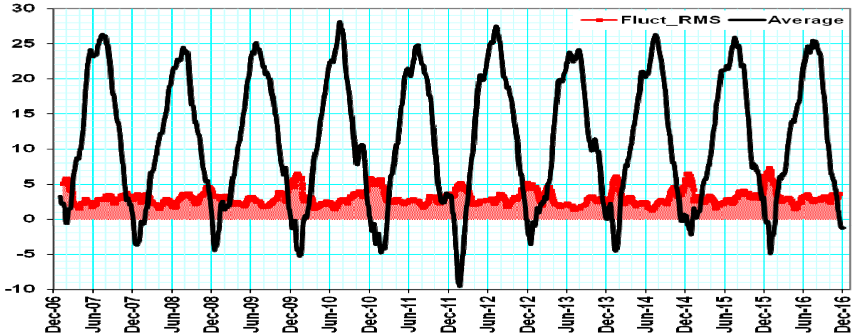

Fig. 9. Root-mean-square deviation from the moving average of the square of the temperature fluctuations in Mykolaiv in the time interval 1.01.2007-31.12.2016 according to PV GIS

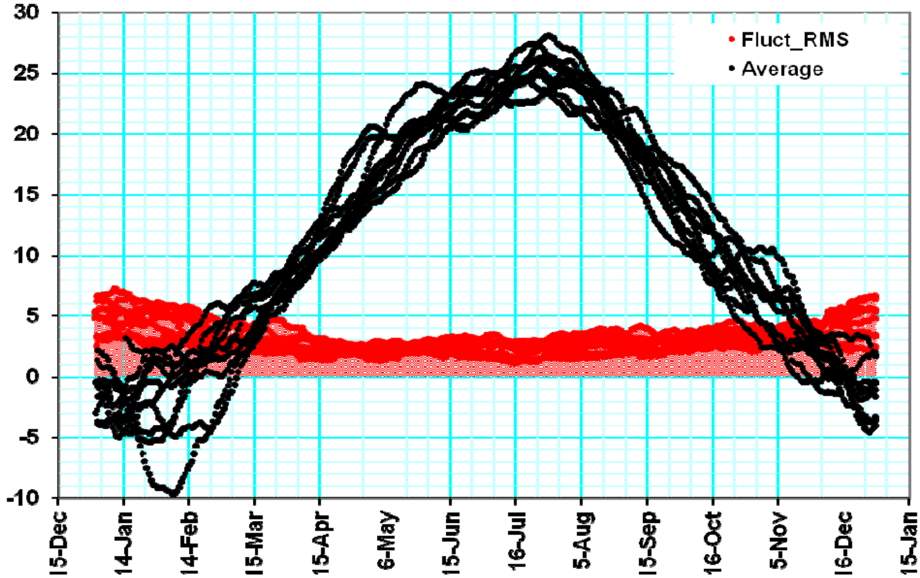

Fig. 10. Root-mean-square deviation from the moving average of the square of the temperature fluctuations in Mykolaiv in the time interval 1.01.2007-31.12.2016 (seasonal move) according to PV GIS

In Figs 9-10 we see, that root-mean-square deviation from the moving average of the square of the temperature in the winter periods of recent years has slightly increased. This coincides in the data of other sources on the increase in the uncertainty of winter temperatures.

Thus we see that PV GIS and other global measurement systems help to create a more accurate temperature field, which is necessary to determine the climate characteristics at points where actinometric observations are not carried out. In the future, this will allow the creation of more accurate models for predicting climate change and facilitate monitoring outside airports and large population concentrations (where meteorological stations are usually located). Based on these calculations, the Department of Ecology continues to study climate change and ways to adapt to it within the framework of the principles of sustainable development [11].

CONCLUSION

1. Since roughly 2012 Petro Mohyla Black Sea National University, Mykolaiv has been conducting an experiment to integrate the environmental component into engineering education, namely, into education in the specialty 151 «Automation and computer-integrated technologies». This specialty «Automation and computer-integrated technologies» was previously specialized in medical devices, but after reforming the classifier of professions, it expanded to a wider range of engineering knowledge. The experiment is ensured through scientific cooperation of the departments of automation, industrial safety and ecology, in the process of which undergraduate, graduate and postgraduate students (PHD) are involved. The most active students participate in performing problematic tasks, the writing of theses, patents and articles. For the rest of the students, the results of scientific research are being introduced into the educational process, which covers most professional disciplines to one degree or another. In parallel, according to the same scheme, the results of joint scientific research are being introduced into the educational process of specialty 101 Ecology.

2. As a result of this experiment, it was found that the involvement of students in the environmental monitoring automation in combination with the study of medical devices that show the influence of meteorological and environmental factors on human health, allows students to form a holistic view of the world around them, and deepens their understanding of natural sciences. This is expected to make them more effective and objective in dealing with practical professional problems.

3. Experience shows that research into the effectiveness of alternative energy installations helps computer science and engineering students to better feel the relevance of their profession in a post-industrial society and further helps them in finding employment. A detailed study and experience of working with sensor systems for monitoring environmental parameters is actively used by graduates who serve microclimate systems at enterprises. Practical environmental solutions help engineering students learn the fundamentals of sustainable development and environmental ethics.

4. For students in the 101 Ecology specialty, such training helps to interest them, increase motivation and facilitate the study of technical modules of professional disciplines. Further integration of environmental and engineering education is expected to help attract more girls to engineering and increase the interest of female students in the 101 Ecology major in tech parts of their education and career.

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PRACTICAL SOLUTIONS FOR THE RECONSTRUCTION OF WATER TREATMENT FACILITIES IN SMALL SETTLEMENTS

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ABSTRACT

The state of water resources and water supply of the population of Ukraine remains one of the major pressing threats to Ukraine's national security in the environmental field and the issue of adaptation of water resources management in the face of climate change and the uneven distribution of moisture in the greater territory of our country.

The presence of iron in water makes it unusable for drinking and domestic and industrial use. This problem is particularly acute for rural residents, suburban home owners, sanatoriums, and holiday homes, since it is the groundwater they use that contains a large amount of dissolved iron.

In the context of increasing anthropogenic pressures on the natural environment, the development of social production and the growth of material needs, there is a need to develop and comply with special rules for the use of water resources, their rational usage and environmentally friendly protection [1].

The indicators of artesian water quality from wells that provide drinking water supply to the residents of Goshcha urban village of Rivne region have been analyzed; recommendations on the design of the deironing station of the underground iron-containing waters have been substantiated. The basics of calculations for the conditions of filtering and flushing of station filters are given.

The main purpose of the article is to reveal the principal aspects of designing of a water treatment station on the example of a deironing station in Goshcha urban village.

The main tasks, which are covered in the article, include: assessment of the method of preparation of water to the requirements of "Drinking water"; indicators of artesian water quality from wells located on the territory of Goshcha urban village have been analyzed; the estimated parameters for design are given.

Keywords: water quality, iron content, iron removal stations, filter backfill.

INTRODUCTION

The problem of water purification and its supply to consumers is becoming increasingly important today. Water supply of settlements and industrial enterprises is carried out, mostly, from surface and underground sources. In the south and east of Ukraine, water consumers and water users use mainly surface water, and in the west and north – mostly groundwater.

Regarding water quality, surface water sources can have color values from 150 to 300 degrees of platinum-cobalt scale, turbidity up to 1500 mg/m^3, odor and taste [2].

Groundwater from protected underground horizons has a slight turbidity, color and odor at minimal values. But groundwater often contains significant amounts of iron, manganese, carbon dioxide and dissolved gases. The use of drinking water with a high concentration of iron contributes to allergic reactions, blood and liver diseases. Iron in groundwater can be in the form of ferrous ions, colloidal organic and inorganic compounds of ferrous and ferric iron. The concentration of iron varies between 1-10 mg/dm^3, but can sometimes be more than 25 mg/dm^3. Although most often the iron content is up to 5 mg/dm^3 [3].

Deironing of water on centralized water pipelines has been used since the end of the last century. The first deironing stations were built in Germany in Gaul (1863) and Charlottenburg (1874), [5] and by 1910 there were more than a hundred water deironing installations in Holland, Germany, and the United States. Water deironing installations, in which water was previously aerated on a special aerator, defended and fed to a filter with granular backfill, became the most widespread.

METHODS AND EXPERIMENTAL PROCEDURES

For more than a hundred years of water deironing technologies, a large number of methods have been proposed and implemented, but they can be grouped as follows:

- reagent-free;
- reagent;
- cation exchange;
- biochemical.

The first two methods relate to physicochemical methods and essentially involve the introduction of iron oxidants, but in the first method, this oxidant is oxygen. The task of the methods is to convert soluble forms of iron into slightly soluble forms of $Fe(OH)_3$, which is achieved by oxidation followed by its sedimentation or retention in the thickness of the filter backfill. You can remove divalent iron ions as follows:

a) oxygen:

$$4Fe^{2+}+O_2+10H_2O=4Fe(OH)_3+ 8H^+, \quad \text{or} \qquad (1)$$

$$4Fe^{2+}+8HCO_3+O_2+2H_2O=4Fe(OH)_3+8CO_2, \qquad (2)$$

Oxidation of 1 mg of iron bicarbonate produces 1.6 mg of free carbonic acid, the total alkalinity of water is reduced by 0.043 mg-eq/dm^3, the pH may decrease, the oxidation and hydrolysis of iron is slowed down;

b) chlorine:

$$2Fe(HCO_3)_2 + C1_2 + Ca(HCO_3)_2= 2Fe(HCO)_3 + CaC1_2 + 6CO_2, \qquad (3)$$

$$\text{or } 2FeSO_4+C1_2+3Ca(HCO_3)_2 = 2Fe(OH)_3 +2CaSO_4 +CaCl_2 +6CO_2\,, \qquad (4)$$

Oxidation of 1 mg of ferrous iron consumes 0.64 mg of Cl_2, and the alkalinity is reduced by 0.018 mg-eq/dm^3 for every 1 mg/dm^3 of removed iron. Oxidation occurs intensively at pH> 5.

c) potassium permanganate:

$$3Fe\,(HCO_3)_2\; + KMnO_4 + 2H_2O = KHCO_3 + 3Fe\,(OH)_3 + MnO_4 + 5CO_2; \qquad (5)$$

d) lime or soda in the presence of oxygen

$$4Fe(HCO_3)_2\; + 8Ca(OH)_2\; + O_2\; = 8CaCO_3 + 4Fe\,(OH)_3 + 6H_2O, \qquad (6)$$

$$4Fe(HCO_3)_2 + 8Na_2CO_3 + 10H_2O + O_2 = 16NaHCO_3 + 4Fe(OH)_3, \qquad (7)$$

In these methods, iron is converted into iron hydroxide, and a large amount of carbon dioxide can be released. The formed ferric flakes are retained in the clarifying filter, and in case of a significant iron content or a slow process of flake formation, a contact filter or settling tank is installed in front of this filter. The filters retain the formed iron hydroxide flakes according to the same laws as the fast filters during water clarification, but the sorption of unreacted ions of ferrous iron and oxygen is added. A film appears on the backfill grains, which has much greater sorption properties than the grains of pure backfill. Iron hydroxide enters the filter backfill in the form of sufficiently formed and large flakes, if after oxidation there is an intermediate tank, a reservoir, a settling tank. When water enters the backfill after oxidation, the process of iron retention takes place directly in the backfill simultaneously with the oxidation. At the initial moment, the backfill is first charged and becomes a catalyst. Therefore, at the initial moment, the cleaning effect may be insufficient.

In the practice of water supply, many types of heavy backfill are used. However, in recent years, much attention has been paid to filters with floating foam polystyrene backfill.

The method of cation exchange is used simultaneously with the softening of water. It consists in the exchange of cations of iron, calcium and magnesium for cations of sodium and hydrogen due to special filter backfills. This method is practically not used for preparation of drinking water.

The biochemical method provides for the colonization of special iron bacteria on an suitable carrier, followed by filtration on filters. Recently, much attention has been paid to this method as a fairly highly effective one. In the Netherlands and Germany, biological purification of water from iron is widely used, especially with the simultaneous removal of iron, manganese and ammonia. Dry filters are most often used for biological purification, but two-stage filtration facilities are also used, where the processes are as follows: adding a small amount of air to raw water, removing of iron in the first stage, intensive aeration, removing of manganese in the second stage, since microorganisms that oxidize manganese develop at a very low iron content in the water. Studies conducted on existing water deironing filters in Khabarovsk have shown that the existing facilities have a large microflora, represented mainly by iron bacteria Lertothrich and Gallionella. Undoubtedly, their impact on the purification process is positive, but it is impossible to calculate the growth of iron bacteria and buildings designed on this principle are sometimes difficult to control.

Most often, a reagent-free method is used for iron removal, since it is simpler and cheaper. The method consists in the fact that in the aeration device the water is saturated with oxygen, while carbonic acid is partially removed and iron is partially oxidized. Then the water is settled in tanks and filtered on filters, where the formed flakes of iron hydroxide are removed.

Aeration can be performed in special devices or use a simplified one. Simplified aeration is used if the iron content is up to 10 mg/dm^3, including not less than 70% of divalent iron, pH not less than 6.8, alkalinity above (1+ Fe^{2+}/28) mg/dm^3. If the capacity of the station is up to 3200 m^3/day and the iron content is up to 5 mg/dm^3, then the installations with a pressure deironing scheme are used.

If the source water contains more than 40 mg/dm^3 of free carbon dioxide and more than 0.5 mg/dm^3 of hydrogen sulfide, an intermediate tank with a free flow of water into it is provided in front of the pressure filter, and the supply of air into the pipeline is not expected. Pressure filters with a diameter of 1; 2; 3, 4 m loaded with quartz sand are used.

At stations of greater capacity conventional fast filters are used. The peculiarity of these filters is that the source water is poured in a continuous stream into the side pocket from a height of at least 0.5 ... 0.6 m. To improve aeration, pouring out of a gutter or perforated pipe is proposed.

For deironing of waters with iron content of 5 ... 15 mg/dm^3 sequential two-stage filtration is used - first through contact and then through clarifying filters. The filtration rate on the contact filter is 50 ... 60% higher than on the clarifying one.

If the process of deironing by the reagent-free method is going poorly, then they resort to the reagent method. In this case, oxidants are introduced into the source water: chlorine, potassium permanganate, lime, soda. Estimated doses of oxidizing agents are prescribed as follows.

Chlorine, mg/dm^3 – $D_{Chl}=0,7(Fe^{2+})$.

Potassium permanganate, mg/dm^3- $D_n= (Fe^{2+})$.

Dose of lime, mg/dm^3- $D_l=0,65[(CO) + (Fe^{2+})]$.

At high concentrations of iron to accelerate its sedimentation, lime and coagulant were added to the water.

At the National University of Water and Environmental Engineering schemes for water deironing with foam polystyrene filters were proposed. Such schemes are the simplest, most compact and economically feasible.

The method of deironing is chosen depending on the chemical composition of water, the degree of deironing, the productivity of the station, technological tests based on:
1) recommendations of normative literature;
2) positive experience of the operation of facilities in the deironing of water of the same or a similar aquifer;
3) trial deironing;
4) technological tests on experimental installations.

THE RESEARCH RESULTS AND DISCUSSIONS

At the moment, the water is deironed on a polystyrene filter with a diameter of 2500 mm with supporting layers of gravel. The flushing is water-air.

This scheme of deironing involves the supply of water from wells by pumps to a foam polystyrene filter with a diameter of 2500 mm. Filtering is performed by a downward flow from top to bottom.

A cap system is used to evenly distribute water over the filter area. The filter is washed with a mixture of water and air supplied by the compressor.

The flushing water is collected and discharged through the sewage collector to the settling tank, and then into the sewerage. The filtrate is collected and discharged to a clean water tank with a volume of 40 m^3, which is located directly in the station building. Water is disinfected with sodium hypochlorite.

Water quality after purification: there is a smell of hydrogen sulfide, more than 2 points, the iron content in the filtrate is more than 0.2 mg/l, according to other organoleptic and bacteriological indicators, the water quality after the filter meets the requirements of GOST 2874-82 "Drinking water". The protocol and conclusion of the study of drinking water quality at the deironing station of Goshcha urban village are given in table 1.

The population growth and the rise of degree of building improvement, increase in production volumes, as well as satisfactory quality of filtrate (color, taste) and unsatisfactory operation of the station (non-compliance with design parameters of work, removal of foam polystyrene from the filter into the sewerage, as well as a number of other reasons) force to undertake the reconstruction of the operating deironing station.

Table 1. Comparative table of water quality at different modes of filter operation

Indexes	Units measurement	The results of the analysis						Standard GOST 2874-82
		Regime №1		Regime №2		Regime №3		
		Water from a well	Water after the filter	Water from a well	Water after the filter	Water from a well	Filtrate	
1. Microbiological indicators								not more
- The number of microorganisms in 1 cm3 of water			<100		<100		<100	100
- The number of Escherichia coli bacteria in 1 dm3			<3		<3		<3	3
2. Organoleptic indicators								not more
- odor at 20^0 C	mark	4 (H_2S)	**4 (H_2S)**	3 (H_2S)	**2 (H_2S)**	5 (H_2S)	**3 (H_2S)**	2
- aftertaste at 20^0 C	mark							2
- turbidity at 20^0 C	mg / dm^3	2,25	0,75	1,8	0,36	1,65	**3,4**	1,5
- chromaticity at 20^0 C	degr.	42	4	59	5	25	**27**	20
3. Chemical parameters								not more
- pH		7,1	7,1	7,1	7,5	6,96	7,33	6,0 – 9,0
- total iron:	mg / dm^3	3,55	0,16	2,32	0,08	1,66	**1,41**	0,3
divalent	mg / dm^3	0,12	0,1	0,12	0,05	0,06	0,58	
trivalent	mg / dm^3	3,43	0,06	2,2	0,03	1,6	0,83	
- general rigidity	mol / m^3	6,9	6,9	6,9	6,9	6,9	6,9	7,0
- calcium	mol / m^3	5,2	5,1	5,2	5,2	5,2	5,2	
- magnesium	mol / m^3	1,7	1,8	1,7	1,7	1,7	1,7	
- sulfates	mg / dm^3	10,2	11,9	9,4	7,6	16,4	16,4	500
- chlorides	mg / dm^3	10	10	10,0	10,0	7,0	7,0	350
- ammonia	mg / dm^3	0,37	0,09	0,73	0,23	0,96	0,6	
- nitrites	mg / dm^3	<0,003	<0,003	<0,003	<0,003	<0,003	<0,003	
- nitrates	mg / dm^3	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	45
- oxidation	mg O_2/ dm^3							2
- fluorine	mg / dm^3							0,7 – 1,5
- manganese	mg / dm^3	0,16	0,03	0,16	0,01	0,15	**0,12**	0,1
- copper	mg / dm^3							1
- dry residue	mg / dm^3							1000
- total residual chlorine	mg / dm^3		**1,4**		**1,12**		0,28	0,3 - 0,5
- free carbon dioxide	mg / dm^3	59,8	26,2	52,4	26,2	76,7	47,5	
- hydrogen sulfide	mg / dm^3							
- alkalinity	mol / m^3	6,9	6,9	6,9	6,9	6,9	6,9	
- potassium + sodium	mg / dm^3	12,25	13,25	12,0	11,0	13,5	13,5	
- mineralization	mg / dm^3	367,8	369,8	366,8	364,8	372,3	372,3	

Station parameters after reconstruction:

• The capacity of the treatment station is 1740 m^3/day;

• 4 foam polystyrene filters: with a diameter of 1400 mm - 3 pieces, 1200 mm - 1 piece;

• 2 CWT: 1 with a capacity of 40 m^3, 1 with a capacity of 170 m^3;

• It is planned to replace pump units with more powerful ones.

The operation of the converted station is based on the method of simplified aeration, since organoleptic indicators of water quality fully allow the use of this method. It is envisaged to install an additional 3 filters with a diameter of 1400 mm and 1 with a diameter of 1200 mm. For the oxidation of iron it is necessary to install two air separators with a diameter of 630 mm each. Due to the uneven water intake (on weekends, pre-holidays and from 5 p.m. to 10 p.m. there is a shortage of water and there is not enough pressure on the upper floors of buildings) it is necessary to install an additional tank of clean water with a volume of 170 m^3.

Pressure losses for each specific section were determined by the expression:

$$h = 1{,}1 \cdot \frac{1000i}{1000} \cdot l, \tag{8}$$

where 1,1 is a factor that takes into account local pressure losses along the pipeline;

1000i - hydraulic slope of the site, increased 1000 times;

l section length, m.
Consider the features of the design of the station on the example of the operating deironing station in Goshcha urban village.

The capacity of the operating treatment station was 1200 m^3/day. Filtration was provided by a single foam polystyrene filter with a diameter of 2500 mm. Artesian water was fed to the upper part of the filter and aerated by freely pouring water from a height of 0.5 m onto the baffle plate. Then it got into the above filter space, passed the backfill layer and was discharged to the filtrate collection manifold. Filtration can be carried out in three modes: 1) downward filtration with water collection through the lower distribution system; 2) downward filtration with water collection through the cap drainage system; 3) two-stream filtration with water collection through the cap drainage system.

Additional 3 filters with a diameter of 1400 mm and 1 with a diameter of 1200 mm are designed. For oxidation of iron it is necessary to install two air separators with a diameter of 630 mm. Due to the uneven water intake (there is a shortage of water on weekends and pre-holidays), it is necessary to install an additional tank of clean water with a volume of 170 m^3.

According to [4], water quality does not meet current regulatory requirements [5, 6]. It is necessary to design the deironing station for productivity: daily 1700 m^3/day, hourly 72.5 m^3/hour, per second 20.14 l/s. The source water has an iron concentration of up to 5 mg/l.

Deironing of water according to the proposed technological scheme is as follows. Underground water through pipeline 1 enters the aerator 2, where the water is saturated with atmospheric oxygen to oxidize ferrous iron into ferric iron, free carbon dioxide and hydrogen sulfide are removed (fig.1).

The filtration speed regulator 3 is designed to remove air bubbles from the water and ensure a constant filtration rate throughout the filter cycle. From the bottom part of the filtration speed regulator, water enters the lower part of the filter and passes from the bottom up through the floating backfill. Retention of iron hydroxide occurs in the thickness of the floating foam polystyrene backfill, deironed water is collected in the above-filter space and is discharged through the pipeline 9 to the consumer.

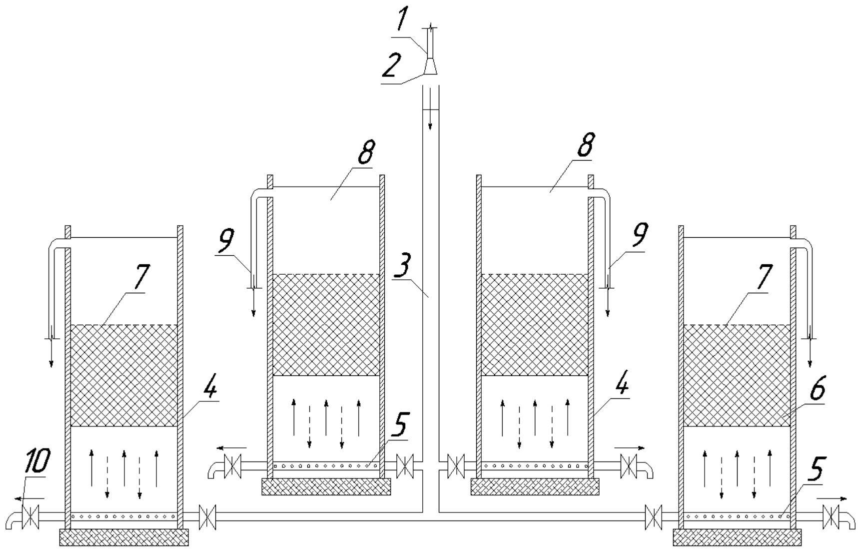

Fig. 1. Scheme of groundwater deironing by aeration and filtration on expanded polystyrene filters: 1 – source water supply pipeline; 2 - aerator; 3 - filter speed regulator; 4 - filter housing; 5 - distribution drainage system; 6 - floating expanded polystyrene backfill; 7 - holding lattice; 8 - superfilter space; 9 - pipeline for deironing water to the consumer; 10 - flushing pipeline.

As contaminants accumulate in the filter bed, the water level in the filter speed regulator increases, and when the maximum pressure loss is reached, the filter is flushed by opening the flush valve on pipeline 10. Clean water from the above-filter space passes through the backfill, expands and washes it and flush water is discharged into the sewerage through the pipeline 10. In this case, only one filter is washed, and the rest continue to work in the filtration mode, supplying additional flows of pure water through the passage windows 11 into the above-filter space of the washable filter. As the flushing goes, the water level in the above-filter space decreases, and when it reaches a certain level (set during adjustment works), the flushing is stopped by closing the valve on pipeline 10. The filter starts working again in filtration mode.

Disinfection of water is provided by sodium hypochlorite, which is taken by the dosing pump and fed into the collecting funnel (collects water from all pipelines 9 of filtered water).

The scheme of arrangement of filters is given in Fig.2.

The designed scheme of water deironing works as follows: water from wells is pumped to the deironing station by pipeline 5, where it is divided into two streams and enters the air separators 4, is freely poured out, being oxidized by atmospheric oxygen, from a height of 0.3 m onto the disk-shaped element and is fed to the bottom part of each filter through pipeline 6.

Filtration is carried out by upward flow from bottom to top through foam polystyrene backfill with a filtration rate of up to 7 m/h and a backfill height of 100 cm. As the filtration goes, the filtrate is collected in the above-filter space and is discharged through the pipeline 7 to the filtrate collection manifold 8, which supplies water to two clean water tanks with a volume of 40 and 170 m^3, where the water contacts with chlorine, is taken by pumps and supplied to the network to consumers.

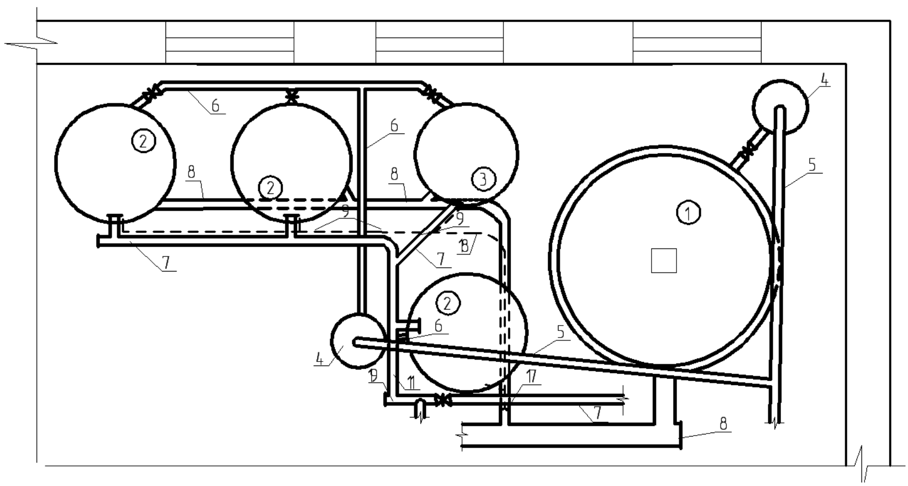

Fig. 2. Scheme of arrangement of filters:

1– foam polystyrene filter with a diameter of 2500 mm; 2 – foam polystyrene filter with a diameter of 1400 mm; 3 – foam polystyrene filter with a diameter of 1200 mm; 4 – air separator with a diameter of 630 mm; 5 – pipeline supplying water from the well; 6 – pipeline supplying aerated water from the air separator to the foam polystyrene filters; 7 – pipeline collecting filtrate from filters and supplying to the CWT; 8 – pipeline removing washing waters from filters; 9 – pipeline from the filter to the siphon; 10 – siphon to break the vacuum.

The water treatment station is designed to work evenly throughout the day [5].

$$Q_{tf} = 1740\ m^3 / day$$

The total area of filters is determined from the following expression:

$$F_f = \frac{Q}{TV_f^n - 3,6 n_{fl} \omega\, t_1 - n_{fl} t_2 V_{fl}^n},\ m^2 \quad (9)$$

Q - useful productivity of the station, m/day;

T - duration of the station’s operation during the day, 24 hours;

V^n_f - estimated filtration speed in normal mode, 7 m/h;

n_{fl} = 1 - the number of flushes of one filter per day during normal operation;

ω - flushing intensity, 18 l/(s·m^2);

t_1 - the duration of flushing, 3 min or 0.05 h;

t_2 - the duration of filter downtime due to flushing (0.17 h).

$$F_\phi = \frac{1740}{24 \cdot 7 - 3,6 \cdot 1 \cdot 18 \cdot 0,05 - 1 \cdot 0,17 \cdot 7} = 10,65\ m^2$$

Currently, the water treatment plant has one filter with a diameter of 2500 mm, it is necessary to install more filters so that the total filtration area of the filters was 10.65 m^2, so we take the number of filters equal to $n_f = 5\ pcs$, of which 1 – 2500 mm, 3 – 1400 mm, 1– 1200 mm.

The required area of one filter is according to the formula:

$$F_\phi = \frac{\pi d^2}{4},\ m^2 \tag{10}$$

d – filter diameter.

Substituting the values for the diameters of the filters we obtain:

for 1400: $F'_{f1} = \frac{3.14 \cdot 1.4^2}{4} = 1{,}54\ m^2$ $(F'_{f1} = 4{,}62\ m^2)$

for 1200: $F'_{f1} = \frac{3.14 \cdot 1.2^2}{4} = 1{,}13\ m^2$

for 2500: $F'_{f1} = \frac{3.14 \cdot 2.5^2}{4} = 4{,}9\ m^2$

The total area of all filters is $F'_{f1} = 10{,}65\ m^2$

Flushing water consumption:

$$q_{пр} = F_{ф1} \cdot \omega,\ л/с \tag{11}$$

for 1400:

$$q_w = 1{,}54 \cdot 18 = 27{,}72\ l/s$$

for 1200:

$$q_w = 1{,}13 \cdot 18 = 20{,}34\ l/s$$

for 2500:

$$q_w = 4{,}9 \cdot 18 = 88{,}2\ l/s$$

The diameters of pipelines are determined from the conditions of water velocities in them, which are taken in accordance with the norms [5].

CONCLUSION

The mode of operation of the filter is chosen taking into account local conditions on the basis of technical and economic indicators, costs, quality of source and purified water, duration of the filter cycle, water consumption for flushing, its frequency, the need to use reagents before filter facilities. The operating parameters of water treatment facilities are set observing the following recommendations:

1. The operating filtration rate is set in such a way that during the year the number of flushes does not exceed three per day.

2. Abrupt changes in filtration rate are not allowed.

3. The number of flushes must be coordinated with the work schedule of the treatment facilities and the number of filters currently in operation.

The end of the operating cycle and the need to flush the load is determined by the expiration of the protective action of the load (water quality deteriorates), or the achievement of the maximum possible pressure loss in the load (the filtration rate decreases below the set minimum level).

The duration of the filter cycle must be maintained at one…. two days. The filtration speed is set to 7 m/h it can be different for each filter.

It is recommended to flush the filters alternately, with an interval of at least three hours. Before flushing, the tank and the filter to be flushed, should be switched off. The duration of flushing should be 3… 4 minutes, the intensity of washing 12… 18 l/s m^2. After flushing, gradually, within 30 minutes, open the filter supply, and open the water supply valve to the tank immediately after flushing.

Loading of filter facilities to which non-chlorinated water is supplied must be disinfected once every 3 months with chlorinated water with an active chlorine content of 100 ... 200 mg/l with a contact duration of 8 ... 10 hours.

The upload should be reviewed monthly. At the same time, the general condition of the filter material surface, the distribution of contaminants (before and after flushing), the presence of pits, cracks, separation of the filter material from the walls, emissions of supporting layers to the surface, etc. are determined. Defects found during inspection should be eliminated immediately.

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PRACTICAL ASPECTS OF GROUNDWATER DEIRONING FOR DRINKING WATER SUPPLY OF SMALL SETTLEMENTS

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ABSTRACT

In Ukraine, the most common scheme of centralized water supply to the population is using both surface and groundwater from aquifers that lie deep from the ground surface.

The quality of piped drinking water depends on various factors, the main of which are the condition and quality of potable water source, the efficiency of water treatment facilities and water preparation technology, sanitary condition of water networks [1-2]. In modern conditions, almost all of these factors do not meet regulatory requirements, resulting in unfavorable conditions for obtaining drinking water of the required quality [3].

Groundwater often contains elevated levels of iron (for drinking water, the standard content is 0.2 mg/dm^3 [3]). Excessive amounts of iron in drinking water from groundwater sources negatively affect human health, cause odors, turbidity, water coloring, lead to overgrowth of water pipes, cause deterioration of operating water supply systems, poor functioning of textile, food, paper, chemical and other industries. Therefore, the problem of removing high iron content from water using modern physical and chemical methods and equipment is quite relevant.

Different forms and concentrations of iron in natural waters have necessitated the development of a number of methods, technological schemes and installations for water deironing [4-8].

The paper considers the main types of pollution of water supply sources. The existing types of filters, their technical characteristics and conditions of application have been analyzed. The method of flushing filters after the iron removal process and the mathematical apparatus for processing the research results have been considered. The peculiarities of the process of regeneration of granular backfill have been investigated and the regularities of change of its parameters have been established.

Currently, there is no universal economically justified option among the methods of water deironing. Each of the existing methods is used only within certain limits and has both a number of advantages and significant disadvantages [7, 8].

Keywords: deironing, plant of water, treatment water, polystyrene.

INTRODUCTION

In rural areas of Ukraine, about 98% of water supply systems have underground water intakes and only 2% take water from open reservoirs. The number of water pipelines that do not meet regulatory requirements, the lack of water protection zones was most typical for rural (over 75%), departmental (up to 60%) and municipal (about 50%) water pipelines. Municipal (35.6-38.1%) and departmental (25.7-28.2%) water pipelines did not have the necessary complex of treatment facilities in different years. 90% of rural water pipelines do not have treatment facilities at all, and 10% do not have the necessary water treatment complex. There were no disinfection systems in 22.3-36.2% of artesian water pipelines, depending on their departmental subordination. These shortcomings are reflected in the water quality of centralized potable water supply systems, which comes directly to the consumer. The state of the centralized water supply to the rural population is of particular concern from the sanitary and hygienic plan [4].

Groundwater is transparent, does not contain suspended particles. It is usually colorless, but often has a significant iron content, may have increased hardness and dissolved gases, is sometimes highly mineralized. Most groundwater is reliably protected from contaminated surface runoff. Its quantity and quality, to a lesser extent than surface water, depends on precipitation. Groundwater can occupy large areas, have mainly constant temperature (7…13°C), can be used for domestic and drinking needs without treatment or fairly simple treatment, often from iron and dissolved gases [11, 12, 13] .

Groundwater is characterized by close contact with a variety of rocks, difficult annual exchange between aquifers, lack of connection with the atmosphere and limited interaction with surface waters. Groundwater includes a difficult complex of gases, ions, particles of mineral and organic origin. The presence and interaction of these components determine the properties and features of water, the difference between groundwater in terms of both total mineralization and ionic and gas composition [12, 14].

Bringing the quality of drinking water in all settlements of the country to regulatory requirements demands a significant amount of investment for the reconstruction of existing (this applies to filtration facilities, reagent dosing units, introduction of technologies and facilities for pre-treatment of water before it enters treatment facilities) or construction of new water treatment plants. The solution to this problem is provided by implementing the measures of the National Target Program "Drinking Water of Ukraine" for 2011-2020 [5].

Flushing or regenerating of the filter backfill is the most important operation in their work. Improving the backfill washing is achieved in the following ways:

– additional surface flushing from the backfill;

– submerged jets;

– water-air and water-air flushing without expansion of backfill;

– pulsating flushing.

METHODS AND EXPERIMENTAL PROCEDURES

Flushing of filters with floating backfill is carried out by a descending stream of washing water from the above-filter space of the filter. The change in hydrodynamic pressure is caused by the phenomenon of self-oscillations that occur in the boundary layer due to the separation of liquid masses from the surface of the granules and their regrouping along the living cross section. These phenomena help to intensify the mixing of the backfill granules, the friction of its grains with each other and the separation of adhering contaminants and their removal by the flushing flow outside the filter.

At the end of the washing process, the filter layer becomes dense. At the same time, hydraulic sorting of granules is observed: larger, lighter polystyrene granules are located in the upper layers, and heavier, smaller ones are located in the lower layers. After washing and compaction of the backfill, the filter is switched to filtration mode.

To study and characterize the expansion of granular materials in the process of filter washing the following dependence is used:

$$\mathrm{Re} = \frac{Ar \cdot m^{4.75}}{18 + 0.61 \cdot \sqrt{Ar \cdot m^{4.75}}} \tag{1}$$

Where, m – porosity of the granular layer;

Re – Reynolds criterion – $Re = v \cdot d / \upsilon$;

v – speed of washing water, m/h;

Ar - Archimedes' criterion

$$Ar = \frac{d^3 \cdot (\rho_\beta - \rho_n) \cdot g}{\upsilon^2 \cdot \rho_\beta}, \tag{2}$$

υ – kinematic coefficient of washing water viscosity, m^2/s;

ρ_β, ρ_n – density of water and specific density of foam polystyrene, kg/m^3;

$g = 9.81$ m/s^2 – acceleration of gravity;

d – diameter of the foamed polystyrene granules, m.

For groundwater, the year-round water temperature is stable and is in the range of 8 ... 13ºC and the water density ρ_β= 1000 ... 998.98 kg/m^3, and the diameter of the granules d = 0.6 ... 5 mm.

Given the above, formula (2) is transformed into

$$Ar = 5{,}8 \cdot 10^9 \cdot d^3 \cdot (1000 - \rho_n). \tag{3}$$

We write an expression to determine the Reynolds number, replacing the speed with the washing intensity and substituting the accepted value of the kinematic viscosity coefficient of the washing water υ = 0.0000013 m^2/s for a temperature of 10˚C.

So,

$$\mathrm{Re} = \frac{I \cdot d}{0{,}0013}. \tag{4}$$

After transformations and solving equation (1), the researchers give the following dependence to determine the parameter of variable porosity m, which describes the process of washing granular filter backfill, where the direction of filtration flow is descending:

$$m = \left[\left(0.186 \cdot \mathrm{Re}^2 + 0.61 \cdot \mathrm{Re}\sqrt{0.093 \cdot \mathrm{Re}^2 + 18 \cdot \mathrm{Re}} + 18 \cdot \mathrm{Re}\right) / Ar\right]^{0.21} \tag{5}$$

The above dependence allows us to determine the porosity of the granular medium in a wide range of changes in its state - from the beginning of expansion to the moment of its transition to a suspended state.

For each grain size there is an optimal washing intensity and relative expansion of the backfill, which will be the best degree of washing of the grains of the filter layer.

The peculiarity of filters with foamed polystyrene backfill is that the speed of the wash water is sufficient to determine only by the value of the relative expansion. Washed from the partially expanded layer of contaminants will settle under the action of gravitational force even at the minimum value of the speed of the wash water. Under this condition, the problem of transporting the contaminants washed from the backfill, is greatly simplified.

Studies to determine the relative expansion and other hydraulic characteristics of the floating filter backfill were carried out on an installation consisting of a filter pump with the floating backfill in the submerged state inside.

Foam polystyrene frothed by steam in industrial conditions with an equivalent diameter of de = 1.246 mm and bulk density ρ_n = 70 kg/m^3 was used as a filter backfill. The experiments were performed in two modes: constant (when the water for rinsing was fed from the mixing tank at constant pressure) and variable (water was fed directly into the pump and at the time of rinsing its supply stopped) water pressure over the retaining grate of foam polystyrene filter.

In addition, in tower-type installations, the backfill regeneration process runs with a change in the water level above the retaining grate, as water is supplied from the tower tank and not by flushing pumps.

To achieve this goal, we will correct the formula (5), using the selection method we will determine such an exponent of the general expression, at which the results obtained in the calculations will be as close as possible to the real ones obtained in experiments on a laboratory installation.

Substituting the obtained formulas in the expression for determining the relative expansion, then for the case of washing the filter with constant pressure the value of the relative expansion of the floating foam polystyrene backfill is obtained

$$e = \frac{1 - m_0}{1 - \left[\frac{I \cdot (21.3 \cdot I \cdot d + 1{,}38)}{5{,}8 \cdot 10^5 \cdot d^2 \cdot (1000 - \rho_n)} \right]^{0{,}185}} - 1, \quad (6)$$

If the washing of the floating backfill filter is performed with a variable pressure above the retaining grate, as in the case of a tower installation for deironing, the correct expression will be:

$$e = \frac{1 - m_0}{1 - \left[\frac{I \cdot (21.3 \cdot I \cdot d + 1{,}4)}{5{,}8 \cdot 10^5 \cdot d^2 \cdot (1000 - \rho_n)} \right]^{0{,}195}} - 1, \quad (7)$$

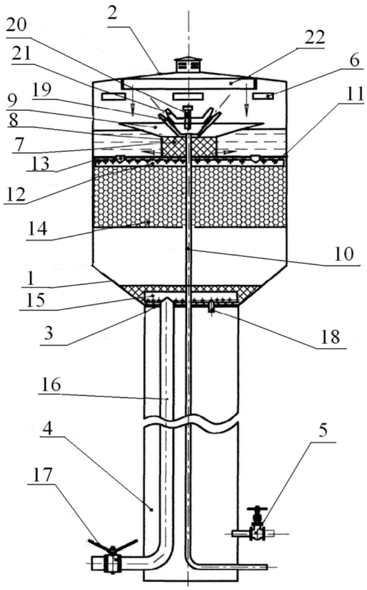
In the obtained dependences $e = f(I, d, \rho_n, m_0)$, that is, the relative expansion of the foam polystyrene backfill depends only on the washing intensity, diameter, specific density of the filter backfill granules and the initial porosity. This makes it possible to use expressions (6) and (7) in engineering calculations of the process of regeneration of floating backfill with any granulometric composition.

THE RESEARCH RESULTS AND DISCUSSIONS

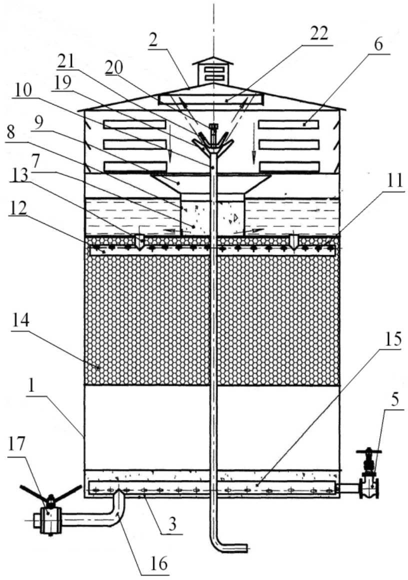
In small rural settlements it is not economically feasible to build separate blocks of treatment facilities, therefore, installations that allow combining several different functions are becoming relevant.

One of the technical and economic solutions for the modernization of existing water treatment complexes (installations) in rural areas are tower-type installations for deironing, that is, those where a filter for water purification is built directly inside the metal water tower, they act as a regulating and water treatment plant at the same time. Moreover, such a treatment plant is compact, quite cheap and easy to operate.

The State Committee of Ukraine for Water Management has decided to build a pilot plant for the deironing of drinking water tower type in the village of Vygoda, Zhytomyr region. The technical essence of the invention is illustrated by the drawing (Figure 1) which shows a General view of the pressure and non-pressure device of the tower type.



a) Tower type installation



b) Column tower

Fig.1. Scheme of installations for water deironing:

1 – tank tower; 2 – roof; 3 – bottom; 4 – trunk; 5 – crane; 6 – openings for air passage; 7 – contact loading; 8 – reception custom; 9 – funnel; 10 – source water supply pipeline; 11 – solid partition; 12 – aerated water supply collector; 13 – branch pipes; 14 – floating filter load; 15 – collector; 16 – flushing water pipe; 17 – crane; 18 – a branch pipe of pure water; 19 – aerator; 20 – bolt; 21 – the second glass; 22 – custom

The use of the aerator of the proposed design provides vacuum, with elements of cavitation and dispersion of water, the extraction of dissolved gases, which leads to an intensification of saturation of degassed water with oxygen, and thus to improve its cleaning quality. Keeping the floating filter load in a solid state continuously increases the reliability of the loading of the device partition. The simplicity of the proposed design allows the completion of existing water towers for drinking water treatment plant without the need to manufacture metal-containing filter housings and the need for construction work.

Scientists of the National University of Water and Environmental Engineering (Rivne) have developed a tower installation that allows not only high-quality water treatment, but also creates a regulatory volume and the required pressure in the water supply network.

Figure 2 shows the technological scheme of the tower column with a device for water deironing. This installation can be used when the content of total iron in the inlet water is up to 5 mg/dm^3. While the ferrous iron must be at least 70%; pH greater than 6.5; alkalinity not less than (1 + Fe^{2+} / 28) mmol/dm^3; free carbon dioxide in terms of CO_2 less than 80 mg/dm^3 [8].

The implementation of this object was carried out on the reconstructed towers with foam polystyrene filter located in the settlements of Rivne and Vinnytsia regions.

The tower installation includes (figure 2): a tower tank with ventilation holes, a tower trunk inside which there is the source water supply pipeline, on which there is a latch, an aerator is placed at the end of the pipeline, from where water enters the air separator - filtration speed regulator connected to the bottom part of the tower, where there is a foam polystyrene filling. To keep the foam polystyrene in the submerged state, a retaining grate made in the form of a cell structure is installed on top of the filter. The cells are closed by frames, which are tightened with stainless steel mesh.

In the trunk of the tower there is a pipeline of intake of filtered water with a latch, in the lower part of the trunk of the tower there is a pipeline of drainage water with a latch. The tank of the water tower on the outside and inside will be equipped with stairs, hatch, level sensors and drain pipe, which eliminates overfilling of the tank with water.

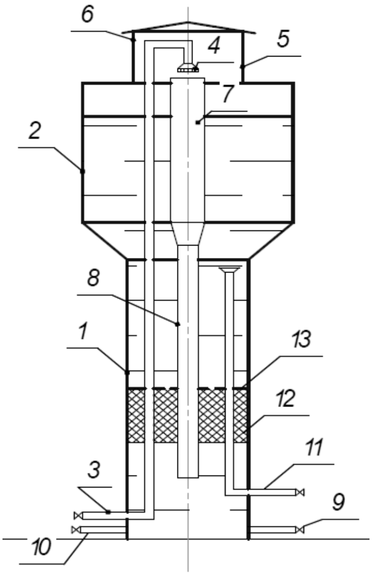


Fig.2. Structural scheme of the tower-column with a polystyrene filter:

1 - the trunk of the tower; 2 - tank towers; 3 - inlet water supply pipeline; 4 - aerator; 5 - metal casing; 6 - ventilation openings; 7 - air separator; 8 - aerated water bypass pipeline; 9 - flushing water drainage pipeline; 10 - drain pipeline; 11 - filtered water intake pipeline; 12 - expanded polystyrene backfill; 13 - holding lattice.

The main control parameter in such an installation is the water level in the tower tank, controlled by electrode level sensors or the water pressure in the pressure pipeline, which is controlled by an electrical contact manometer. Therefore, the operation of the filter is directly related to the operation of the pump and is equal to the water supply by the pump unit, that is, the filter operates in intermittent mode.

At the first filtering at first latches the valves on the flushing water drain pipe and the latch on the source water supply pipe are open, and the latch on the filtered water intake pipe is closed. That is, the first portions of water are discharged. This continues until a catalytic film (approximately 1.5 hours) appears on the grains of the filtration backfill, which helps to provide the desired deironing effect. After that, the latch latch on the pipeline of the filtered water intake is opened, and and the latch on the pipeline of the washing water is closed and then the normal filter cycle continues. After washing, the catalytic film on the grains does not disappear, ie such an operation is performed only when the first use of the filter backfill.

According to research by Kulskyi L.A. found that the bulk of contaminants are retained in the first in the course of water movement layers of backfill thickness of 15-20 cm and on its surface.

Therefore, in this dissertation, as a filter material for water deironing plants, it is proposed to use a combined expanded polystyrene backfill, which consists of approximately 20% of granules foamed with boiling water. When foaming with boiling water, it is possible to obtain granules of small equivalent diameter and significant specific density with a more developed specific surface of the granules, which easily changes during their foaming. However, as mentioned above, the cost of backfilling obtained by hand with boiling water is quite high, and the work performed is very time consuming. Therefore, to reduce the cost and simplify the preparation of the backfill, it was proposed to use steam-expanded polystyrene in production conditions, the volume of which can be about 80% of the total.

During the operation of the installation, field studies of the parameters of the expanded foam polystyrene filter in the mode of filtration and washing were carried out. The research results are shown in table 1.

Table 1

The results of chemical analysis of water samples before and after deironing, taken directly from the sampler after the tower for the entire period of the filter cycle

Indexes	Unit of measurement	Groundwater (artesian water)	Purified water (filtrate)		
			2 hour	48 hour	96 hour
pH	pH units	7,35	-	-	7,3
Alkalinity	mmol / dm^3	8,1	-	-	7,8
Rigidity	mmol / dm^3	6,8	-	-	6,7
Total iron	mg / dm^3	2,17	0,12	0,09	0,05
Iron hydroxide is trivalent	mg / dm^3	0,85	0,1	0,08	0,05
Divalent iron oxide	mg / dm^3	1,32	0,02	0,01	-
Nitrates	mg / dm^3	1,93	-	-	1,72
Oxidation is permanganate	mgO_2 / dm^3	0,74	-	-	0,88
Dry residue	mg / dm^3	510	-	-	505

Figure 3 shows the results of the process of deironing in the tower column (duration of the filter cycle was 96 hours). Since the installation operates in intermittent mode, it can be observed that after long stops (at night time) there is a slight deterioration in the quality of the filtrate.

The regulating volume of the installation is quite large, which provides intensive mixing of water in the tank of the tower and helps to reduce the concentration of iron hydroxide that enters the water supply network of the settlement with purified water.

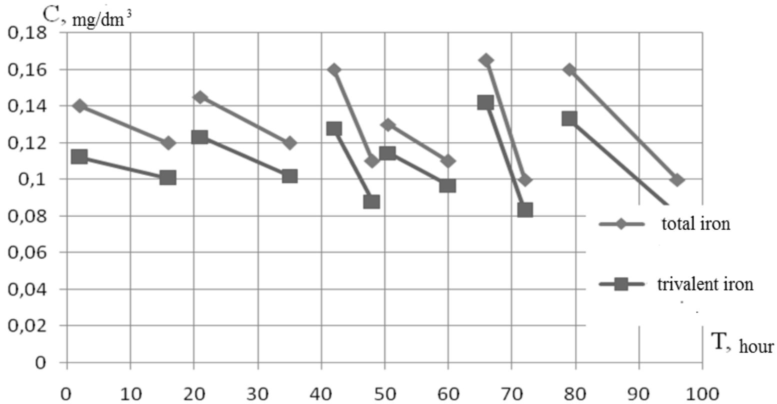


Fig.3. Graphs of total and trivalent iron content in purified water during the filtercycle

According to research, during the entire period of operation of the implemented tower installation, the concentration of iron in the filtrate did not exceed the permissible norm of 0.2 mg/l, where the concentration of iron in the source water ranged from 1.25 to 3.04 mg/l, and the effect of iron removal was 96 … 98% [9, 10].

The daily distribution of water consumption is presented on Figure 4.

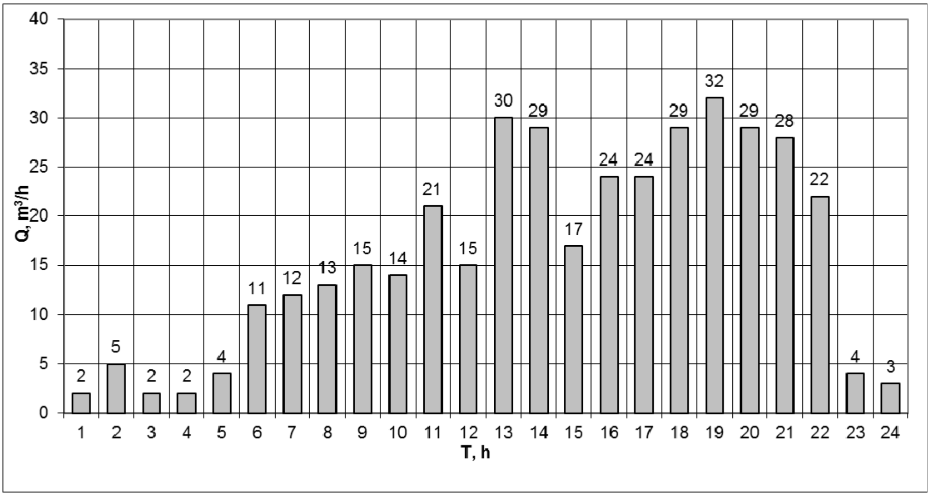


Fig. 4. The graph of the dependence of iron concentration on the duration of washing after a filter cycle lasting 3 days.

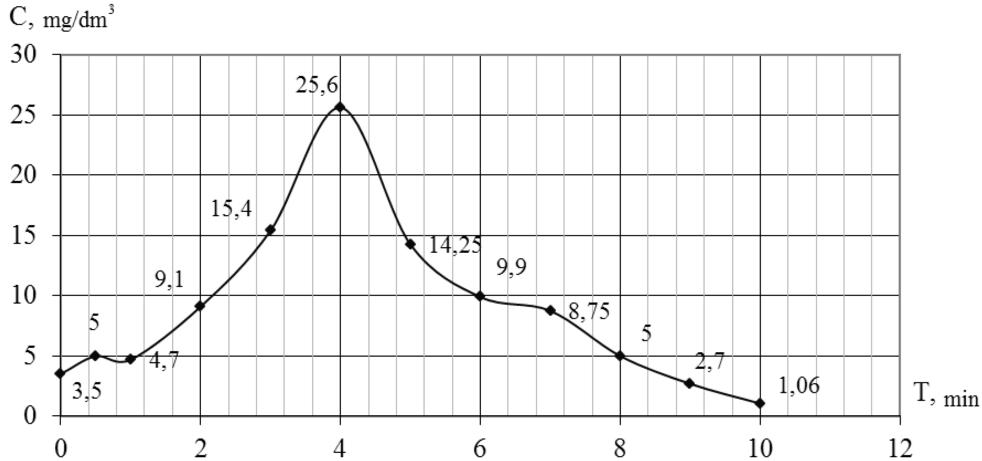


Fig.5. The graph of the dependence of the concentration of iron in the wash water on the duration of the wash

During the observation period, the water quality after filtration at this installation fully met the standards of State sanitary rules and regulations "Hygienic requirements for drinking water intended for human consumption" (the concentration of iron in the filtrate did not exceed the permissible level of 0.2 mg/l, with iron concentration in source water ranged from 1.25 to 3.04 mg/l, and the effect of deironing was 96… 98%), which illustrates the effectiveness of the proposed technology for the preparation of iron-containing groundwater in rural areas of Ukraine.

CONCLUSION

During the initial start-up of the installation, the cleaning efficiency is insufficient. This continues until a catalytic film consisting mainly of iron compounds appears on the grains of the filtration backfill. After washing, the catalytic film is not washed from the surface, that is charging of backfill is carried out once.

With a 4-day filter cycle, the purified water meets the standards in quality and the iron content is 0.05 mg/l. However, the use of such long filter cycles can lead to cementation of the backfill, if the washing is performed poorly. As the filtration proceeds, the content of flakes of ferrous compounds between the granules of the backfill increases, which indicates an increase in pressure loss and a decrease in the capacity of the water treatment plant. Therefore, such devices should be switched to flushing mode [10].

After long stops (at night time) there is a slight deterioration in the quality of the filtrate. However, the regulating volume of the installation is quite large, which provides intensive mixing of water in the tank of the tower and helps to reduce the concentration of iron hydroxide that enters the water supply network of the settlement with purified water.

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MATERIALS DESIGN FOR WATER PURIFICATION: RECENT TRENDS

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ABSTRACT

One of the most important global tasks, if not the most important, is to provide the inhabitants of our planet with high-quality drinking water. Here we reviewed the recent advances in the application of nanoporous materials for wastewater treatment, considering a very special case of heavy metal ions adsorption. We considered nanoporous activated carbon sorbents to be used as an inexpensive analog of zeolites and polymeric materials for the preparation of filtration membranes and to be approaches to nanofiltration, adsorptive separation of heavy metal ions and discussed considering the possible fundamentals and mechanisms of adsorption. In addition, the preparation and properties of noble metal nanoparticles were considered as promising components of nanomembranes with antibacterial potential.

Keywords: heavy metals, noble metal nanoparticles, nanofiltration, nanoporous activated carbon sorbents, water treatment

INTRODUCTION

Clean drinking water is a basic human need [1]. However, according to the World Health Organization, 663 million people in the world — that is, one in ten — do not have access to clean water. In many developing countries, the high cost of treatment systems prevents all the segments of the population from obtaining clean drinking water [2]. By 2025, half of the world's population will be living in water-stressed areas. Re-use of wastewater is becoming an important strategy for many needs [3]; the problem of drinking water is of the highest priority today for most countries, especially in densely populated and developing countries. The main reasons for this situation are population growth, intensive drought, mining, oil pumping, the widespread use of chemicals on farms, etc. Wastewater can be divided into two categories, namely, urban wastewater, including fluids discharged through households and industrial wastewater. When treating wastewater, first of all, components identified with waterborne diseases should be considered, and it must be ensured that the treated water does not contain any pollutants that could antagonistically affect the strength of people and nature. With conventional treatment methods, wastewater is treated in stages. In the first stage, suspended solids are removed by physical forces; the secondary stage mainly eliminates biodegradable compounds, and the third stage mainly involves filtration and disinfection to remove biological pathogenic compounds.

Human activity is currently the critical "pressure" on nature and prevents it from fully purifying water resources [4]. However, by minimizing the negative impact on nature and improving water treatment technology, people can address this global issue [5]. Known physical, chemical, and combined physicochemical methods cannot provide the new levels of purity required by the regulations. We cannot reach this aim without using additional expensive chemicals for coagulation, sedimentation, etc. Typically, this increases operating costs although the concentrating can produce more hazardous solid wastes.

Typical water treatment is the purification of water coming from natural sources into the water supply network [6, 7]. The surface waters of natural springs are clarified before feeding into the water supply system, removing suspended and colloidal particles by coagulation, settling, and filtration, decolorizing and disinfecting with liquid chlorine, chlorinated lime, ozone, and ultraviolet rays [8]. Water is softened, and an excess of calcium and magnesium salts are removed by treating waters with lime, soda, or passing them through ion-exchange filters. The amount of iron salts in the water is reduced by aeration, followed by filtration. To remove dissolved gases such as carbon dioxide, hydrogen sulfide, and methane, as well as an excess of fluorides and radioactive substances from the water [9, 10], the water is resorted to aeration, filtration through activated alumina, decontamination. Water deodorization is carried out with activated carbon, ozone, chlorine dioxide, or potassium permanganate. Reagent and disinfection systems, mixers, settling tanks, clarifiers, contact cooling towers, and other industrial equipment are used for water treatment. Besides, membrane methods are increasingly used for water purification. A new generation of membranes for filtration, disinfection, and desalination of water are membranes based on graphene and carbon nanotubes, characterized by a high water transmission rate, exceptional selectivity, resistance to bio-fouling, and strong antimicrobial properties. So far, only a small part of such membranes and filters are at the pilot testing stage in the world, but their commercialization is quite real due to the rapid growth of graphene production. In Ukraine, the production of graphene, carbon nanotubes, and new carbon materials based on them is very small, and it is too early to talk about the introduction of the latest generation of membranes. One of the most important global tasks, if not the most important, is to provide the inhabitants of our planet with high-quality drinking water. Membrane methods are widely used to solve this problem. The membrane technology and membranes of various types are described in detail in [11]. The main directions of development of membrane technology and related technological processes, according to [12–21], are i) Membrane wastewater treatment processes with the release of valuable components in mechanical engineering, pulp and paper, textile and food industries, utilities, and other industries; ii) Processing of secondary raw materials with the release of valuable components (including baby food and dietary food) from milk, cheese, and curd whey, corn and potato starch, rapeseed, soybeans, and other food products; iii) Cation-conducting polymer membranes for electrochemical generators; iv) Membrane sensors and biosensors for compact high-sensitivity control systems and devices; v) Membrane dispensers and prolongers of drugs with controlled dosage rate into tissues and organs, coverings on wounds and burns, artificial pancreas; vi) Membrane processes for bacteriological control of water, blood serum analysis, devices for plasmapheresis and blood oxygenation; vii) Selective mass transfer processes for the extraction and concentration of chemical products from various media (membrane extraction); viii) Scientific foundations for the formation of membrane catalysts and membrane catalytic reactors, membrane systems for the separation and concentration of components and membrane reactors for waste-free processes of product formation with minimal energy consumption without wastewater discharge; ix) Scientific bases for obtaining new classes of thermally and chemically resistant membrane-forming polymers with functional groups of different nature, including aromatic polyamides, polyimides, polyamidoimides, polyheteroarylenes, etc.; x) Principles of directional design of poly-siloxanes/silica composites [22-33], which are temperature resistant, chemically resistant, and highly selective membranes for microfiltration, ultrasonic filtration, and nanofiltration.

The main tasks are to develop membranes of new generations with a purposefully formed structure. This approach will allow, when choosing certain separation modes, to increase the permeability and selectivity of membranes for target components. The latter could lead to the achievement of stability of the functional characteristics of the membrane filtration. At the same time, it is actually to develop new membrane processes to solve applied problems. The same is true for the optimization of technological schemes of available processes. To date, the existing membrane equipment allows wastewater treatment, including the regeneration of waste detergent solutions, separation of oil-water emulsions, oil-and-oil plant effluents, ship bilge water, tanker ballast water, oily water from cleaning the waters of ports and platforms for offshore oil production, etc. The capacity of these plants is in the range of 150–6,000 liters per hour. The created stations for complex wastewater treatment from dyes and surfactants provide a 95% degree of recycling water use with a productivity range from 5 to 50 cubic meters per hour. Plants for wastewater treatment of electroplating industries provide 98% purification from salts of heavy metals with a performance range from one to twenty-five cubic meters per hour.

The conceptual basis is the emergence of highly non-equilibrium modes of mass and electric mass transfer through selective membrane layers with an increase in the role of external control factors (pressure and temperature gradients, electric potential; controlled change in the composition of the medium; non-stationary actions) in the separation processes. Under these conditions, the separation efficiency is highly dependent on the structural features of membranes at various spatial scales, as is the case in the most efficient biomembranes. This approach to the problems of membrane separation, in contrast to today's traditional quasi-equilibrium approaches, opens up fundamentally new possibilities for increasing the permeability and selectivity of target components during their transfer through the membrane. This requires, first of all, the development of new approaches to the synthesis of membrane materials, to the formation of membrane layers, to their modifications. In fact, the main direction will be the design of membranes at the molecular level, when the purposeful formation of "transfer paths" of target components, e.g., ions, molecules, colloidal particles of nanometre size, is directed taking into account the entire set of factors determining their movement, including the effect of ligand environment, solvation shells, and acting forces. At present, these ideas have already been partially implemented in the development of a number of ion-exchange membranes based on rigid-chain polymers. Research is underway on the design of reverse osmosis [34], some types of ultrafiltration membranes, for example, membranes with a charged surface.

A century of new technologies and materials have completely transformed the entire sphere of human activity (the state of the industry, agriculture, everyday life, medicine, health care, etc.). At the same time, the XXI century can be called the century of waste accumulation and prevention of environmental pollution. This requires huge funds, which disrupts the normal development of world civilization. The processes of sustainable development of society and the state are directly related to solving the main global problems of mankind—living safety, providing the population with ecologically clean food and drinking water, creating an appropriate balance between solving socio-economic problems, and preserving the environment. They are recorded in the decisions of the Special Session of the UN General Assembly on Ecology and Sustainable Development in June 1997. Recently implemented modern technological processes for the production of various substances and materials, as well as the treatment of waste and wastewater, strange as it may seem, increase the total volume of waste. The existing world statistics indicate that at present up to 12% of the feedstock is converted into the final product, and approximately 90% at different stages of production and consumption pass into waste, which at the same time can be a valuable raw material representing is a semi-finished product, the processing of which can be several times more profitable than standard raw materials, of course, provided that environmentally friendly technologies are implemented and high-quality competitive products are obtained. In this regard, it is already possible to make an assumption today that the 21st century will be largely devoted to the creation of environmentally friendly and, most importantly, low-cost economically and technologically sound processes for processing materials, waste, and obtaining useful and necessary products for society on their basis. One of the first, if not the very first, among such technological processes is a membrane process, other non-traditional and combined processes for processing substances and materials. Membrane methods for the separation of liquid and gaseous media have already taken a strong place in the arsenal of industrial-technological processes, although the full formation and return of membrane science and technology is expected in the 21st century. There are areas where membrane technology has no competitors at all. Here we should mention the apparatus "artificial kidney", the creation of ultrapure substances and zones in microelectronics, the release of thermo-labile biologically active substances, etc. The importance of membrane technology in recent years has increased dramatically, primarily as a technology that can bridge the gap between industry and the environment. Membrane technology has received the status of critical technology, as well as catalysis, molecular design, new materials, genetic engineering, and other world priorities. To this it is necessary to add the interconnection of these technologies and, unlike a number of others, membrane technology serves the directions of development of science and technology and, first of all, such as ecology and rational nature management, fuels and energy, information technology and electronics. Indeed, the development of membrane technology is one of the largest cross-sectorial tasks, accounting for the fact that its use has no negative impact.

Therefore, the first successes for the use of nanomaterials show a high potential of nanotechnologies in water purification, clearly, the most intensive research is carried out in the wide areas of adsorption/separation with nanoporous sorbents and photocatalysis with nanoporous catalysts and sorbents.

Membrane systems are increasingly used for water purification and a new generation of membranes for filtration, disinfection, and desalination of water are produced. These new membranes based on graphene and carbon nanotubes are characterized by a high water transmission rate, exceptional selectivity, high resistance to bio-fouling, and strong antimicrobial properties. So far, only a small part of such membranes and filters are at the pilot testing stage in the world, but their commercialization is quite real due to the rapid growth of graphene production. In Ukraine, the production of graphene, single-wall and multi-walled carbon nanotubes, and new materials based on them is very small, and so there is no base for their future introduction in the construction of the latest generation of membranes.

Classifying the existed membranes, one can found different nanoporous materials used in water purification processes. In modern ultrafiltration and nanofiltration, the current development level allows operating with polymeric nanofibres of different chemical nature to be used as membranes [35]. Nanoporous polyacrylonitrile and polyvinylpyrrolidone polymers, e.g., in the form of cloth, can be used for the removal of bacteria and other microorganisms in order to prevent the contamination of waters [36]. Double-stage integrated microfiltration and nanofiltration plus forward osmosis for treating dairy wastewater could be carried out with the integration of polymeric membranes with hollow fibers [37]. Recently, for nanofiltration of dairy wastewater, it was applied many commercial nanofiltration membranes [38-40] those are based on cellulose, polyamide, poly(piperazine-amide), poly(m-phenylene isophthalamide), and the poly(piperazine-amide) as well as its layer on the thin-film composites. Commercial ultra-filtration and nanofiltration polymeric membranes allow us to improve water quality with textile ultrafiltration membrane modules [41]. A pilot-scale membrane bioreactor was constructed in order to run two membrane modules in parallel for the treatment of model textile wastewater; however, the de-coloration of anionic and cationic dyes is low. This observation can be attributed to the low biodegradability of dyes that required membrane bioreactors with novel effective membranes, including nanostructured ones. New nanofiltration membranes contribute to sustainable development in the textile industry by improving the water quality of treated textile wastewater what helps to reduce freshwater consumption and pollutant discharge [41]. In this direction, the production engineers have frequently used the modified nanopore membranes for the ultrafiltration of wastewater [42]. A shown earlier [43], dendrimer polymers can be successfully used in the desalination and recovery of metal ions from aqueous solutions. Well-organized multilayer structures of membranes can be applied for water purification, with applications in wastewater treatment, biomedicine, chemical, and food industries [44].

Besides, one should consider ceramic ultrafiltration and nanofiltration membranes; they are frequently in use for the separation of oils, emulsions, and silts, which should considerable potential in a course of pressure-driven membrane processes [45].

A separated class of them is microporous and nanoporous termed ceramic water filters most frequently take a part in water filtration: to remove bacteria and chemical contaminants [46]. In industry ceramic membranes are utilized for separates dyes and salts from used waters [47]. Oxide nanomaterials are of special interest for the purification process, nanomembranes with alumina and titania nanocrystalline materials are considered to be valuable filters to remove partially the ions and could successfully separate all the microorganisms from drinking waters [48]. The alternative direction in these studies is polyurethane nanofibrous filters modified by nanoparticles of copper oxide, as they can be used for water filtration combining with antibacterial treatment [49]. Modern technologies allow inkjet printing of graphene oxide membranes on polymeric supports. These inkjet-printed materials showed highly effective water purification by nanofiltration [50]. Industrial microfilter and nanofilter pumps are elaborated for water treatment in pressure-driven membrane processes to be used within membrane modules [51]. Adsorption and separation with nanoporous zeolite membranes are frequently applied for dehydration of water/ethanol mixtures [52]. Ceramic/polymeric fibers are in use for oil/water emulsions separation [53]. Bifunctional mesoporous silica nanoparticles could be used for various dyes (cationic and anionic) removal from water with easy regeneration [54]. Zeolites and silica hybrids porous materials are prominent sorbents for effective adsorption of heavy metal ions [55, 56]. Phosphoryl functionalized mesoporous silica should high selectivity to uranium (VI) adsorption in a wide range of pH values [57]. Novel tridimensional porous graphene hydrogels can be a valuable component of advanced filters for adsorbing and removing different pollutants, e.g. antibiotics, dyes, and heavy ions [58]. Besides, magnetic nanoparticles as high capacity/selectivity sorbents can remove toxic metal ions, radionuclides, organic and inorganic solutes/anions [59].

Photocatalytic degradation of organic components of wastewaters can be carried out with nano-titania deposited by electrophoresis. These nanomaterials are used in the modern purification systems for wastewater purification in the light industries before discharge into the ecosystem [60] Flexible ceramics with nanoscale zinc oxide tetrapods and hybrid metal oxides are also in use for photocatalytic degradation of organic substances, manly methylene blue [61], the same is true for iron-doped zinc oxide nanowires which are frequently composed the water purification system that decolorized and oxidized organic dyes by photocatalysis [62].

Fundamentally new possibilities of membrane separation can be achieved by forming defect-free membrane layers of submicron thickness. In this case, as follows from the theoretical results, unusually high values of the transfer selectivity for the target components can be achieved with an overall high level of porousness. In fact, we are talking about a nanoscale technique for membrane separation, similar to nanoelectronics.

Such, for example, can be working on the use of the above external control actions on the transfer of target components, up to the implementation of their active transfer. Usually, such a situation is realized in ion transport (in the concentration of ions under the conditions of electrodialysis). In this program, the problem is broader. As shown by our researchers, active transfer of neutral, in particular, vapor components can be realized in membrane systems (the process of "electro-evaporation"). Fundamental and prospecting work in this direction can also lead to new fundamental results, to the discovery of new membrane processes.

Microfiltration membranes with pore sizes from 0.5 to 10 microns trap suspensions, colloidal impurities, algae, and large bacteria. Ultrafiltration membranes with pores sizes from 10 nm to 500 nm can purify water from viruses, bacteria, and large macromolecules. Typically, reverse osmosis membranes have the smallest pores of microporous and mesoporous range of 1–10 nm. According to another classification, the reverse osmosis membranes have pores that are less than 1 nm in size. These nanopores, ultra-small micropores, allow us to remove various molecules and ions from solutions, including monovalent ones. The terms nanofiltration and nanomembranes appeared in the late 1980s. Today, they are in wide use because of the rapid development of nanotechnology. It is usually believed that the pore size of effective nanofiltration membranes is several nanometers. However, in some cases, this range is extended to 100 nm. This is a generally accepted concept that nanoscale objects have dimensions less than 100 nm in at least one dimension. In terms of the degree of purification, these membranes occupy an intermediate position between those used for ultrafiltration and reverse osmosis. Nanomembranes do not allow most organic molecules, almost all viruses, di- (or more) valent ions to pass through. All three types of membranes operate in the nanoscale range. Thus, we can say that nanotechnology began to be used in water treatment and water purification long before the appearance of this term. Now their application is expanding both in the EU and in other countries. For example, in Switzerland, ultrafiltration, nanofiltration and reverse osmosis installations provide residents with high-quality drinking water from lakes and karst underground sources [63].

Where necessary, new sewage treatment plants can be put into operation, and membrane technology could be applied for the treatment of municipal wastewater. Membrane units can be used for the post-treatment of wastewaters, for example, this can be done with HUBER VRM flat ultrafiltration polyethersulfone membranes with a pore size of 38 nm [64]. In Europe, the production of membrane cloth and membrane filter modules based on it for ultrafiltration, nanofiltration, and reverse osmosis is showed a significant rise. The volume of production will be millions of m^2 of cloth and a hundred thousand filter modules per year. Assessing the potential of nanotechnology to improve the efficiency of water purification and water treatment, the experts named membrane technologies one of the most promising areas of development and identified priority projects related to improving energy efficiency. Among the first five are solutions based on membrane technologies, namely, the design of nanostructured polymer membranes for successful water purification and water treatment.

Generally, nanotechnology is defined as a set of methods and techniques that provide the ability to controllably create objects that include components with dimensions less than 100 nm, at least in one dimension, and, as a result, acquire fundamentally new qualities. Modern studies that carried out in many laboratories around the world show that such properties of synthesized nanomaterials as large specific surface area and volumetric porosity, high permeability and sorptive capacity, high resistance to biofouling, and the possibility of chemical functionalization allow them to be effectively used to obtain pure water [65, 66]. Nanomaterials and nanocomposites based on carbon nanomaterials are proposed for the adsorptive removal of cations and anions from waters [67, 68]. They can be also in use for water cleaning from petroleum products [69, 70]. Last decade, for teams of researchers, the main goal is to create the perfect water filter. Many teams are working to develop a prototype membrane that can filter water more efficiently with less energy. This device is made up of layers of graphene, a material a hundred thousand times thinner than human hair [71-74]. They get it from graphite through an oxidation process, and the process is very scalable. This, in turn, means that the membranes can be adapted for use both for filtering tap water and in large tank systems. Typical membranes create a labyrinth for water and dissolved molecules. The water flows through a series of layers, separated by spaces specially designed to trap various particles, toxic organic molecules, and bacteria [75-78]. There are many different types of molecules that need to be removed; the most obvious way to solve this problem is that we need to control the interlayer space in the membrane or porosity in nanoporous sorbents [79-83]. Researchers have a lot of work to do, but they hope that their developments will bring closer solutions to the problem of water treatment around the World. In fact, this will make drinking water available to everyone.

In addition, International Standards require more efficient separation systems than those used nowadays. Nanotechnology can significantly affect the field of wastewater treatment in the near future. Nanotechnology is aimed at improving existing methods by increasing the efficiency of processes and increasing the reusability of nanomaterials. Nanomaterials are endowed with unique properties, such as a high ratio of surface to volume, high reactivity, and sensitivity, the property of self-assembly on substrates for film formation, high adsorption, etc. Due to these properties of nanomaterials are effective against various organic and inorganic pollutants, heavy metals, as well as against various harmful microorganisms that are present in contaminated water. Fresh drinking water is one of the most important nowadays for most terrain areas, especially for developing countries having densely populated regions.

For example, in India, 80% of diseases are caused by bacterial contamination of drinking water [84]. Improving the technology of water purification to minimizing the negative impact on nature is the main direction of current research. Instead of chlorine, which easily reacts with organics in many wastewaters, today's scientists and engineers propose irradiation with ultraviolet light in the presence of photocatalysts. This approach prevents the formation of toxic halogenated compounds. However, the ultraviolet light disinfection has an arbitrary effect only with ozonization that cannot be realized in some cases [85]. The high potential of nanotechnology in water purification has nanomaterials that showed the first successes in the last decade in the range of approaches as nanofiltration, adsorptive separation, and nanocatalysis [86-89].

Activated carbons refer to a wide range of carbonized materials of a high degree of porosity and high surface area. Typically, activated carbons have many applications in the environment and industry for the removal, retrieval, and separation in liquid and gas phases and also for the removal of toxic metal ions [90-93]. Here in Ref. [94], chemical activators used to produce activated carbon were reviewed. The preparation stage, especially the selection of the chemical activator agent is a major point that controls the performance and applicability of porous materials [95-98], the same is true for the selective surface modification with chemical methods.

The chapter considers our latest achievements in the preparation and studies of various carbon nanomaterials for wastewater treatment. We directed much attention to the adsorptive properties and nanoporosity of activated carbon-related materials concerning the removal of inorganic pollutants, and including theoretical adsorption foundations, those will be discussed.

We consider copper ions as typical heavy metal ions since copper has many applications as an essential trace element supporting the growth of plants and animals. But, the accumulated copper ions can cause serious health harm. At the modern level of consumption, engineers can purify the copper contaminated wastewater by means of carbon adsorbents. Copper concentrations in drinking water vary widely depending on water characteristics, such as pH, hardness, and copper availability in the distribution system. The copper levels in drinking water can range from ≤0.005 to >30 mg per liter, with the primary source most often being the corrosion of interior copper plumbing. Levels of copper in running or fully flushed water tend to be low, whereas those of standing or partially flushed water samples are more variable and can be substantially higher. This adsorptive remediation satisfies the diverse demands on sustainability and environmental friendliness. To achieve high efficiency of ions uptake, it seems to be the most reasonable technique. The results of these studies could be used in the design of membranes for the elaboration of new nanoporous materials and effective nanofiltration, adsorption, and separation of inorganic ions.

Without doubts, water is an essential resource; however, population growth and overexploitation of groundwater and surface water have resulted in water scarcity. As a result, the demand for freshwater is sharply increasing, in addition, water is intensively consumed for agricultural irrigation, which is associated with global climate change. According to the United Nations Children's Fund in 2015, 844 million people still lacked basic water services, and among them, almost 159 million people continued to use drinking water directly from rivers, lakes, and other surface water sources. Commercial and agricultural activities play a major role in the organic and inorganic pollution of waters. The real problem with water consumption and with sanitation in the developing world is that too many people lack access to safe and cheap water supply technologies and sanitation components. The spread of a wide range of impurities in flood and groundwater has become a serious problem worldwide due to population growth, rapid industrialization, and prolonged droughts. The presence of pollutants in the form of heavy metals, inorganic compounds, as well as pathogenic biological compounds is a series of threats to the improvement of human living conditions and proper sanitary living conditions, as well as to the environment. Thus, limiting the removal of such contaminants has become a priority for researchers. By default, wastewater is any water that has been adversely contaminated by natural contamination and microorganisms that have degraded the original water quality. To develop a cost-effective wastewater treatment technology at a low cost, nanotechnology offers unique options because it allows the use of nanoscale materials efficiently. Nanomaterials usually have excessive reactivity, a large unique surface area, and special properties arising from the influence of the size factor. Metallic nanomaterials possess interesting magnetic, electrical, photothermal, and other excellent physicochemical properties, which make them promising for many different applications in various fields: in biomedicine (in cancer therapy and cell imaging as drug carriers), in healthcare (ultraviolet disinfection and local medicines), and in ecological post-treatment devices (in adsorbents and filters, as well as for deep cleaning and disinfection of water). When treating water, metallic nanomaterials can be used as highly efficient nanocatalysts for the decomposition of toxic compounds, for water purification, and as highly sensitive sensors for detecting trace amounts of toxic contaminants, as well as antimicrobial agents. Metallic nanomaterials, with their exceptional antibacterial properties and high specific surface area, are widely regarded as the most promising antimicrobial agents. In addition, the complex antibacterial mechanism of nanomaterials' action limits the development of bacterial resistance. The antibacterial properties of metallic nanomaterials strongly depend on the composition, size, and shape of their nanostructures. In this chapter, we will also present some of our advances in the synthesis and application of metal nanoparticles prepared using plant extracts for further implementation in water purification technologies.

METHODS AND EXPERIMENTAL PROCEDURES

Preparation and characterization of nanoporous sorbents

We showed the modification preparation methods used in the preparation of porous materials. Considering in the terms of surface area and efficiency, activation with alkaline metal hydroxides shows better results for the preparation of nanoporous activated carbons for various applications. Also, the comparison of the physical mixing method and the impregnation method in the activation with alkali metals indicates that the activated carbon obtained through physical mixing had a higher porosity than the activated carbon produced by the impregnation method. In our work, the nanoporous activated carbons were derived from a natural source, e.g., fruit stones of *Prunus Armeniaca*. Such granular nanoporous activated carbons are relatively cheap; they are thermal and mechanical stable carbon solids. Typically, the particle size of nanoporous activated carbons ranges from 0.5 to 1 mm. The nanoporous activated carbons prepared by alkaline impregnation, carbonization, and physical activation with steam have large specific surface areas of 785–1300 m^2/g range, they also have significant pore volumes of 0.41–0.60 cm^3/g that are found by adsorption-desorption studies with water vapor as a probe molecule. Nanoporosity is a relatively new term and combines the effects from the presence of micropores ranged from 0.5 to 2 nm and mesopores ranged from 2 to 30 nm in the porous solids. Under this consideration and taking into account the microstructure level, we will draw attention to transport macroscopic channels. They are not in the nanoscale level and typically have micrometer sizes. However, they are presented in the natural sourced nanoporous activated carbons, prepared from porous lignin and cellulosic raw materials, where maintain a system of microscopic feeding channels from respective plants. Typically, these channels are the rests of the system of mass transfer capillaries. This system has developed porous and capillary structures. Usually, when the pore walls are carbonized, the residual architecture contributes to good kinetic parameters of adsorption from wastewaters.

Oxidation modification is the most prominent approach to be used for ion-selective adsorption. Before use, granular nanoporous activated carbons were washed with 3 mass% HCl to remove inorganic salts from the nanoporous carbon bulk volume. Washing procedures are repeated with deionized water (DW) to reach the wash water's pH of 6.0. Typically, the deashed and washed samples were subjected to oxidation, which was carried out under standard oxidation protocol. Some typical example of this protocol is earlier reported (see, for example, the protocol recommended by Jaramillo and coauthors in earlier 2010 [98]).

The intensity of the oxidative treatment is regulated by the amount of HNO_3 or H_2O_2 oxidants concerning the mass of the initial sample. The temperature of the oxidation process and the processing time are also crucial parameters that have much effect on the intensity of the oxidant. The processing time has a considerable impact in the case of non-intensive oxidation with H_2O_2 solutions. These solutions are weaker oxidants than concentrated HNO_3 solutions. That is why in the case of oxidation with hydrogen peroxide, the processing time is much longer. In general, the aforementioned conditions regulate the formation of surface oxygen-containing functional groups and have a negative impact on the nanoporous structure.

For oxidation, a solid nanoporous activated carbon mass of 2 g was refluxed with from 5 to 30 mass% HNO_3 solutions (60 ml) at 80℃ for 2 hours. The prepared NAC-HNO_3-% samples were dipped in with DW, washed, and decanted with a Schott filter. The acid rests were washed with a rinsed DW to neutral pH range. After the oxidation, the oxidation products were air-dried in a dryer at 120 ℃ for 27 hours. The same oxidation was carried out with 10 and 30 mass% H_2O_2 solutions. The carbon mass of about 2 g was immersed in 50–100 ml of 10 and 30 mass% H_2O_2 solutions and held in the oxidant for the processing time of 4 hours. The filtered NAC-H_2O_2-% samples were treated as reported above, namely, washed under pH-metric control and air-dried.

The bulk density (γ) was measured by the weight measuring in a given volume while the water vapor sorption volume (V_S) was found using the static desiccator method at room temperature. Nitrogen adsorption-desorption isotherms for studied sorbents were recorded at liquid nitrogen temperature (-196 ℃) with TriStar C10900A, Micromeritics ASAP 2020 (Micromeritics, U.S.A.), and Kelvin 1042 automated gas adsorption analyzers. Before physisorption measurements, all samples were outgassed at the temperature range of 120–180 ℃ for 4 h under flowing pure nitrogen gas (99.995%) or at lower temperatures of 100–120 ℃ in a vacuum oven. From the adsorption data, the specific surface areas of Brunauer–Emmett–Teller (S_{BET}) and micropore areas (S_{micro}) were determined. To elucidate the pore structure and for further analysis, we processed the isotherms with different adsorption models, which are derived within the two-dimensional nonlocal density functional theory in the framework of approaches proposed by Jagiello and Olivier [99]. The model of Jagiello and Olivier which is most suitable for such and related carbon nanoporous materials consider carbon pores, such as slit-shaped ones. These pores according to the authors have the surface with energetic heterogeneity of adsorption sites and geometrical corrugation. According to the model, the pore size distribution can be found was from the isotherms with the Micromeritics SAIEUS program. The choices of models were performed given the best-fit carbon–N_2 model for porous carbons with heterogeneous surfaces to be used in the calculation. The proposed model in the framework of two-dimensional nonlocal density functional theory can be used in pair with the models available within quenched solid density functional theory ones. According to Puziy and coauthors [100], for microporous (nanoporous) activated carbons, the application of both models could lead to similar results.

Morphologic features were also examined with a Jeol JSM 6060LA scanning electron microscope that was employed to imagine the surface defects. High-resolution transmission electron microscopy images were recorded on a JEM-2100F transmission electron microscope operated at the accelerated voltage of 200 kV. The total concentration of surface oxygen-containing functional groups was found from the data of thermal analysis. The Boehm titration was used to quantify certain types of existed oxygen-containing groups (C_{fg}). The temperature-programmed desorption as control and additional analysis method. The temperature-programmed desorption experiments for dry samples were performed as reported in Diyuk and coauthors [101-103] using a thermogravimetric analyzer, which outlet was attached to a gas cell of a two-beam infrared spectrometer. The thermogravimetric analyzer is operated in argon gas medium and using spring balances. From the area of the resolved temperature-programmed desorption peaks, Oxygen-containing surface groups' quantification was done. Also, the oxygen content was determined with Cameca Camebax and Cameca SX100 electron microprobes. The CHNO analysis was performed on a Perkin Elmer Series II 2400 elemental micro analyzer; the estimated error at the CHNO analysis was 0.5 wt%. Before analysis, the intensive vacuum drying at 127 °C was done to remove physisorbed water; the drying duration was prolonged up to 5 hours.

The surface chemistry changes after the surface oxidation were investigated employing Fourier Transform Infrared (FTIR) spectroscopy that performed in attenuated total reflection (ATR) mode. For FTIR ATR studies, an IRPrestige 21 Shimadzu spectrophotometer was equipped with a MIRacle module designed by the Pike Technology with ZnSe crystal, the ZnSe crystal spectra were recorded as a background at the spectra recording. The ATR spectral range, where the spectra were collected, was from 4000 to 520 cm^{-1}. All spectra were recorded at a spectral resolution of 2 cm^{-1}. Each spectrum is the average of 1000 continuous scans.

Adsorption properties and capacity of nanoporous activated carbons were investigated using batch equilibrium experiments, the adsorption capacities towards Cu^{2+} ions were determined through a series of experiments and the concentration changes were controlled with ultraviolet-visible (UV-VIS) spectrophotometry. A batch adsorption experiment from the water solutions, also known as immersion experiment, is the most common test used to measure adsorption equilibrium and adsorption kinetics. It consists of the addition of a known mass of sample to a fixed volume of water solution of Cu^{2+} at an initial concentration [104]. To increase the sensitivity of the spectrophotometric method, we used bis(cyclohexanone)oxaldihydrazone as a colorimetric agent [105]. For adsorption measurements towards Cu^{2+} ions, the wide range concentrations were examined in the range up to 1×10^{-4} M of Cu^{2+} in solutions, the measurements were done with a step of 0.5×10^{-4} M. To prepare the solution series, stock solutions of Cu^{2+} ions were diluted with DW. For example, standard Sigma-Aldrich Cu(II) nitrate hemi(pentahydrate) was dissolved in DW to prepare the stock water solution of 6×10^{-4} M of Cu^{2+}. In the same way, the most diluted solution of 7×10^{-5} M of Cu^{2+} can be prepared.

In a typical adsorption experiment, about 50 mg of preliminary dried sample was immersed into a 20 ml water solution of copper ions. The resulted sorbent suspensions containing a known concentration of Cu^{2+} were thermostated at 25 °C and shaken at 150 revolutions per minute for a day. For this type of sorbent, the adsorption equilibrium is established rather quickly, within 15 hours, typically, for the convenience of measurements, within 24 hours was chosen. Adsorption measurements were carried out at a fixed pH value of 5.5 under a pH-metric control with the Mettler Toledo instrument. After adsorption, the resulting solutions were filtered through a Whatman 41 filter paper in fresh flasks. They were sampled for the spectrophotometric analysis that was carried out on a UV-1900 Shimadzu UV-VIS spectrophotometer with 1 cm quartz cells. The analyses of the water Cu^{2+} solutions were conducted as reported in [106]. The pipetted aliquots of 5 ml and 2 ml of ammonium acetate buffer were placed in 25 ml conical flasks to be diluted with DW. The prepared solutions by default contain no more than 70 mg of Cu. A 3 ml of bis(cyclohexanone)oxaldihydrazone was added to the water solutions at a pH of 8–9. A highly chromogenic complex with copper ions was adsorbed at ~600 nm, at the extinction coefficient of 16,000. All the intensity measurements were performed considering the optimal measurement delay time of 10 min. As the result of analysis, the equilibrium capacity of Cu^{2+} (*a*, mol/g) was found by the equation:

$$a = (C_0 - C_e) \times V/m, \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cu^{2+} (mol/l), respectively, V is the fixed volume of water solution of Cu^{2+} solution (L), and m is the known mass of sorbent sample (g). The removal percentage (R) was found from the following equation:

$$R = (C_0 - C_e) \times 100/C_0, \quad (2)$$

To control the results of spectrophotometric measurements, which are usually limited due to errors when the measurements carried out at very low concentrations of the copper ions in water solutions, all samples were also analyzed by flame atomic absorption spectrometry (FAAS) at the mainline of Cu at 324.754 nm. Because of the instrumental limitations of the technique, spiked samples were diluted to adjust the analyte absorbance within the linear working range [106]. All measurements were carried out in triplicate on a Carl Zeiss Jena FAAS N1 spectrometer with an air–acetylene flame.

Synthesis of nanoparticles

Syntheses of silver and gold nanoparticles were carried out using direct interaction of aqueous plant extracts of elderberry (*Sambucus nigra*) [107] and blackcurrant (*Ribes nigrum* L.) [108], and the solutions of metal salt, as precursors, e.g., silver nitrate ($AgNO_3$), and tetrachlorauric acid ($HAuCl_4$), respectively. Noble metal nanocolloids were prepared at various reaction parameters, namely, varying volume ratios and concentrations of the reagents, pH of the reaction mixture, temperature, from room temperature to 65 °C, and time (up to 24 hours). Since the formation of metallic nanoparticles is followed by the release of nitric and hydrochloric acids, sodium hydroxide solution was used for pH control. The importance of pH adjustment was observed as a key factor for the production of stable metal nanoparticles.

In a typical synthesis, certain volumes, which milliliter quantities are based on the previous optimization experiments, of plant extract, 10 mM aqueous solutions of sodium hydroxide solution and $AgNO_3/HAuCl_4$ (1 mM or 10 mM) were added to the Erlenmeyer flask and kept under continuous stirring and heating at a defined temperature in dark. Aqueous and aqueous-ethanol extracts of juniper (*Juniperus communis*) [109], goldenrod (*Solidago canadensis*) [110], clove (*Syzygium aromaticum* L.) [111], and peppermint (*Mentha piperita*) [112] were used for the synthesis of gold nanoparticles. Syntheses were performed at an ambient laboratory temperature of 23 °C, by the direct interaction of the plant extracts with 1 mM $HAuCl_4$ aqueous solution under continuous stirring. Amounts of extracts were normalized to dry matter content, estimating 0.25–1.5 mg/ml of the dry matter in the final solution. In a typical synthesis, the estimated volume of plant extract was diluted by double distilled water followed by the addition of 1 mM $HAuCl_4$ solution. All syntheses were monitored by UV-Vis spectroscopy.

Characterization of nanoparticles

An initial characterization of the synthesized nanoparticles was monitored using a UV-Vis spectrophotometer (UV-1800 Shimadzu, Japan). The spectra were recorded at laboratory temperature, against double distilled water in the wavelength range of 300–1100 nm at a resolution of 1 nm. The samples with high intensity were diluted with double distilled water to obtain spectra with absorbance lower than 1 abs. unit. The images of nanoparticles were obtained by use of the TEM JEM 2000FX (JEOL, Japan) at an accelerating voltage of 160 kV. A drop of nanoparticles' solution was positioned on Cu-grid with holey carbon film. After drying on air, the sample was examined with TEM. A large angle JEOL JED-2300 T CEN-TURIO SDD (silicon drift) detector was used for an energy-dispersive X-ray spectroscopy analysis. The particle size intensity distribution was determined by the dynamic light scattering method on a Zetasizer Nano ZS (Malvern Instrument).

Antibacterial activity of nanoparticles

The antibacterial activity of the silver and gold nanoparticles prepared using extract of elderberry (*Sambucus nigra*) was examined by a generally accepted antibacterial test using different groups of experimental bacterial strains. Two gram-negative bacterial strains (*E. coli* ATCC 25922 and wild clinical strain) and two gram-positive (*S. aureus* ATCC 25923 and wild clinical strain) were studied. The wild clinical strain of *S. aureus* was isolated from the cat's throat and the wild clinical strain of *E. coli* was isolated from fecal matter. All strains were received from the Collection of Microorganisms of the Department of Microbiology, the University of Agriculture in Krakow, Poland. The stock cultures were grown separately in a nutrient Tryptic Soya Agar (TSA, EMAPOL, Poland) with 5% of blood agar medium. Bacteria strains were cultivated on Petri dishes at 35 °C for 48 hours. Afterward, the strains were added into the flask with liquid Tryptic Soy Agar medium and cultivated for 24 hours. Flasks were kept on incubator cum shaker at the speed of 150 rpm. After 24 hours of incubation, the samples of 1 mL of a fluid with bacteria were taken from cultivation; the optical density was adjusted to 0.1 McFarland, corresponding to 108 CFU/mL at 600 nm. 1 milliliter of bacterial liquid culture was introduced to a test tube with 9 mL of nanoparticles solution with four varying solution strengths of silver nanoparticles (3.125, 6.25, 12.5, and 25 mg/L). Then 1 milliliter of the suspension was taken from the test tube and introduced to the Petri dish and poured with TSA medium, and incubated for 15, 180, and 300 minutes at 35 °C. The CFU of bacteria was calculated after 24 hours of incubation by the plate-count method of viable cells. The experiment was performed in a triplicate.

THE RESEARCH RESULTS AND DISCUSSIONS

Nanoporous sorbents for the removal and recovery and general consideration of porosity: anyone who studies adsorption properties is faced with porosity-related issues. The porosity is important in water purification via adsorption processes to assess the effect of internal diffusion on their rate, as well as for the preparation of optimal structures in the production of fillers. There are many types of porous systems, and even in one sorbent, the pores can vary significantly both in shape and size.

The pore classification adopted by the International Union of Pure and Applied Chemistry is based on the following principle: each pore size range corresponds to characteristic adsorption properties, which are expressed in adsorption isotherms. The boundary between the different classes is not rigidly defined, since it depends both on the shape of the pores and on the nature of the adsorbate molecules. When studying advanced and developed porosity, the following parameters are used: pore volume, pore size distribution, and average pore radius. The average pore size is determined from the ratio of pore volume and surface area. The size distribution of mesopores is determined by the method of capillary condensation while the size distribution of wide mesopores and macropores can be found with mercury porosimetry. The distribution of micropores is found from adsorption isotherms in the area of volumetric filling of micropores, prior to the onset of capillary condensation in the mesopores.

If compare the International Union of Pure and Applied Chemistry classification with that of Mays [113], it will be clear that three categories of pore dimensions have existed. As stated by Thommes et al. [114], they are differentiated by diameter D: micropores ($D < 2$ nm), mesopores (D ranges between 2 and 50 nm), and macropores ($D > 50$ nm). According to Mays' scheme [113], there are differentiated nanopores ($0.1 \leq D \leq 100$ nm), micropores ($0.1 \leq D \leq 100$ um), and millipores (0.1 ≤ D ≤ 100 mm) in the sorbents. Both classifications have cons and pros. Mays referred to the term "nanopores" as any pore with size below 10 nm cross-sect size ranges recommended by the International Union of Pure and Applied Chemistry to distinguished micropores and mesopores. Functionalization of nanoporous carbon sorbents will take place in the pores ranged from ultra-small to small nanopores, 0.5 ≤ D ≤ 2.0, the specific surface area has a better positive correlation with the maximum adsorption capacity, and according to Kaludjerović, Noroozi and Mehdipour, and Roque-Malherbe [115–117], showing a leading role of nanopores. These nanopores are about 97–96% of available pores in nanoporous carbons.

Adsorption is required for the concentration of inorganic and organic substances on the surface or in the porous volume of solids. At least two components are involved in the adsorption process. A solid substance, on the surface or in the pore volume of which the absorbed substance is concentrated, is called adsorbate. The absorbed substance, which is in the gas or liquid phase, is called an adsorptive, and after it has passed into an adsorbed state, it is called an adsorbate. Any solid substance has a surface and, therefore, is potentially an adsorbent. However, the technique uses solid adsorbents with a highly developed inner surface. The development of the inner surface in a solid is achieved by creating special conditions in the process of its synthesis or as a result of additional processing.

Despite the diversity of the nature of adsorption forces, all adsorption phenomena can be divided into two main types: physical adsorption and sorption based on the forces of chemical interaction. Physical adsorption is caused by molecular forces. In most cases, dispersion forces make the main contribution to the interaction energy. Molecules of any adsorptive possess fluctuating dipoles and quadrupoles, which cause instantaneous deviations of the electron density distribution from the average distribution. When the adsorptive interact with atoms or molecules of the adsorbent, the motion of fluctuating dipoles (quadrupoles) acquires a systematic and strictly ordered character, which causes the appearance of attraction between adsorbent and adsorptive.

These so-called dispersion forces got their name due to the fact that the phenomenon of dispersion of light is caused by a similar cause. Dispersion forces do not depend on the nature of the distribution of the electron density of adsorptive molecules, their value is approximately constant for adsorbents of any chemical nature, and therefore the interaction caused by them is nonspecific. In some cases, dispersive forces are enhanced by electrostatic forces caused by orientation and induction effects. Orientation forces arise when polar molecules interact with a surface containing electrostatically charged particles, e.g. ions or dipoles, induction forces are caused by a change in the electronic structure of adsorptive and adsorptive molecules under the action of each other. The appearance of dipole moments in the adsorptive molecules induced by charges and adsorbent and the appearance of dipole moments in the adsorbent surface groups under the action of the charges of the adsorptive molecules.

Having a specific character, the interaction caused by electrostatic forces depends on the chemical nature of the adsorptive. The contribution of specific interactions to the total interaction energy upon the adsorption of any molecules on electrically neutral carbon adsorbents is practically about zero, and upon the adsorption of polar molecules on zeolites with a heteronomous character, it is commensurate with the contribution of the nonspecific component. In some cases, a specific interaction can be enhanced by the formation of a hydrogen bond between the adsorbed molecule and the adsorbent molecules.

A typical example of adsorption with the formation of a hydrogen bond is the absorption of water and alcohols on silica gel, the surface of which is covered with hydroxyl groups.

Nanoporous activated carbons

The pristine samples of nanoporous activated carbons have a certain amount of mineral admixtures. The content of inorganic admixtures is below 0.5 wt%, according to the thermogravimetric data. Chemical analysis showed mostly Na, Ca, Fe, and Si in the ash composition. The role of inorganic salts in the composition of nanoporous carbon will have no effect on the adsorption of Cu^{2+} ions.

In fact, chemical analysis data are summarized in Table 1; the oxidative treatment with acids and oxidant solutions additionally reduces the ash content, which is found to be below 0.3 wt%.

Table 1. Elemental CHNO analysis of nanoporous activated carbons (NACs).

Sorbent	Element content (wt%)			
	C	H	N	O
NAC	95.2	1.0	Trace	3.8
NAC-H_2O_2-10	95.4	1.2	Trace	3.4
NAC-H_2O_2-30	91.0	1.2	Trace	7.8
NAC-HNO_3-5	90.5	1.5	0.5	7.5
NAC-HNO_3-30	78.8	1.5	0.7	19.0

Table 1 shows the composition changes and the oxygen content increases remarkably. The ATR spectra (Figure 1a) showed the most intensive bands, as can be seen from this figure (see Figure 1b) oxidation is a reason for the morphologic changes in the nanoporous structure. The oxidized samples of nanoporous activated carbons have strong bands in their ATR spectra in the range of 1739–1712 cm^{-1}. These strong bands can be attributed to carboxyl, anhydride, and lactone surface functional groups, which are characterized by prominent ν(C=O) stretching bands. For the nanoporous activated carbons, these bands are of low intensity, as can be seen from the ATR spectrum (Fig. 1a), this means in particular that the concentration of carboxyl groups on the surface of the pristine nanoporous activated carbons is negligible.

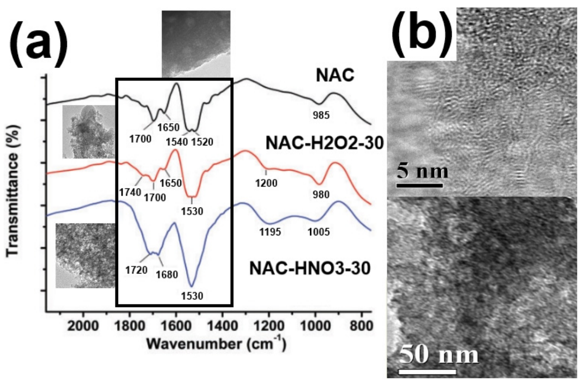

Fig. 1. (a) Typical ATR spectra and (b) TEM micro photos of NAC: nanoporous activated carbons before and after oxidation. The left panel represents typical layer nanostructures and nanopores.

Really, the carboxyl, anhydride, and lactone groups are formed because of oxidation treatment. Before oxidation, the ATR spectra of the nanoporous activated carbons and NAC-H_2O_2-30, show the band component assigned to the vibration ν(C=O) mode of quinolic groups, which are observed in the ATR spectra at 1700 cm^{-1}. Surprisingly, the band that can be ascribed to this vibration mode is registered at 1680 cm^{-1} in the ATR spectrum of the NAC-HNO_3-30 sorbent. As suggested, the aforementioned groups modify the surface walls of nanopores (Figure 1b).

Figure 1a presents spectral bands associated with skeletal vibrations of the C=C bonds, namely, the conjugated C=C bonds in the graphenic fragments. They are characterized by the strong absorption in the spectral range of 1650–1700 cm^{-1}, the wavenumber range that is frequently attributed to such kinds of vibrations. At smaller wavenumbers, the vibration bands that corresponding to frequencies of aromatic C=C bonds are appeared, in the wavenumber range of 1510–1550 cm^{-1}. Surprisingly, the respective spectral feature of C=C bonds can be found for all oxidized registered for all nanoporous activated carbons that are studied. For the oxidized nanoporous activated carbons, the intensive absorption bands are peaked at about 1200 cm^{-1}. Presumably, they are attributed to the strong vibration of phenolic groups, mainly to ν(C–OH) group vibrations. These phenolic groups can be formed because of oxidation. Ether groups can be also formed at the oxidation of nanoporous structures and the respective absorption bands could be seen in the wavenumber range 981–1000 cm^{-1} assigned to ν_s(=C–O–C) vibrations addressed as recommended by [118]. As can be seen from the analysis of ATR spectra, it imagines the formation of additional carboxyl and phenol groups as a result and because of the oxidative treatment.

Table 2. Surface oxygen-containing groups in nanoporous activated carbons (NACs)

Sorbent	Boehm titration against thermal analysis data (mmol/g)		
	Carboxyl groups	Anhydride and lactone groups	Phenolic groups
NAC	0.08/0.1	0.0/0.0	0.2/0.5
NAC-H_2O_2-10	0.15/0.2	0.15/0.20	0.3/0.8
NAC-H_2O_2-30	0.25/0.20	0.5/0.45	0.9/2.0
NAC-HNO_3-5	0.8/0.6	0.8/1.2	0.4/0.9
NAC-HNO_3-30	1.9/1.5	2.0/4.1	1.5/3.0

Table 2 sums up the concentration of the surface groups determined by the temperature-programmed desorption experiments and from the results of the Boehm titration. The surface acidity can be dramatically increased by oxidation treatment as revealed by the thermal analysis and titration data. De facto, carboxyl, anhydride, lactone, and phenolic groups can attribute to high acidity. The sum of the concentration of carboxyl, anhydride, and lactone groups was recalculated per unit surface area of micropores or per gram of sorbent and future can be assigned as C_A. This magnitude can help to correlate the adsorptive capacity of the nanoporous solids with the aforementioned acidic groups. Thermal analysis showed that the application of hydrogen peroxide as an oxidant is caused the significant increase of the content of phenolic, anhydride, and lactone groups while the increment of carboxyl groups is low. The amount of carboxyl groups in the prepared nanoporous activated carbons is below 2 mmol g^{-1}.

Considering the adsorption of copper ions, in the case of, it should be mentioned that phenolic groups do not dissociate under pH = 5.5, and they have no possibilities to react with Cu^{2+} through ionic exchange mechanism and by the complexing mechanism of the copper cations with surface functional groups. Suggesting formation of the adsorption complexes of copper occurs only with a certain type of the oxygen-containing groups.

By the fact, the field of solid-state nanopores and nanochannels has grown exponentially and recent advances have greatly expanded applications in sensing and separation science and improved our understanding of the mechanisms that govern ion transport in nanometer-sized channels and pores. A stochastic nanopore sensing method for the detection of Cu^{2+} ions is reported earlier by employing a chelating agent, and trace amounts of copper ions could be detected with a detection limit of 40 nM [119]. Importantly, although bi-charged ions can form chelates since the event residence times and/or blockage amplitudes for these metal chelates are significantly different from those of copper chelates, these metal ions do not interfere with Cu^{2+} detection. This chelating reaction approach should find a useful application in the development of nanopore sensors. Surprisingly, in Ref. [120], the authors reported that Cu^{2+} ion adsorption is an entropy-driven endothermic process, possibly involving both outer-sphere and inner-sphere complexes. This makes possible filtering ions by size and charge and invests great effort in the development of new selective separation technologies to remove and concentrate target ions from solution. Nanoporous activated carbon materials are among promising candidates to achieve these goals and the ion-selective channels are prototypes to be used for the efficient separation of ions [121]. Such technologies hold the promise of economically efficient and environmentally friendly water desalination methods and to revolutionize the removal of toxic and heavy metal ions to obtain fresh water. All types of surface oxygen-containing groups are intensively formed when the nanoporous activated carbons are oxidizing with nitric acid, and their total concentration is very significant as compared with that form due to the oxidation reaction with H_2O_2. From the results of titration, the carboxyl groups in the nanoporous activated carbons prepared by oxidation with HNO_3 have a content percentage of 50–60%; the total content of acidic carboxyl groups and anhydride and lactone groups reaches 70% and the rest 30% are phenolic groups. The related concentration of oxygen-containing groups obtained by two methods is listed in Table 2. The data distinction is probably because the thermal analysis method has systematic errors since reacting carboxyl groups and phenyl groups can form anhydride and lactone groups, and other similar groups. That is why the titration results are directly characterized the oxygen-containing groups as adsorption centers available for charged heavy metal ions in an aqueous solution. The oxygenolysis impacts the porosity since an increase in the oxygen content is accompanied by the destruction of the wall microstructure.

In fact, the nanoporosity reduction, up to three times, depends on the strength of the oxidant and its concentration in water solutions. After the most aggressive treatment with the concentrated solution of nitric acid, the nanoporosity shows significant reduction, and the specific surface area and the specific volume related to the nanopores reach a minimum value as in [105]. Considering the total pore volume its decrease due to oxidation varied in the range from 5% to 20%. Typically for oxidized porous carbons that the packing density γ shows an increase with the oxidant concentration. Two types of nanopores are presented in the nanoporous activated carbons, where the smallest slit nanopores have sizes ranging from 1.0 to 1.4 nm and the larger nanopores with a size of 3.2–3.5 nm are also present. Oxidative treatment slightly increases the average size of the small nanopores to 1.2–1.5 nm. However, treatment with nitric acid diminishes the total number of small nanopores. The large nanopores (mesopores) with a width of about 3–4 nm are typically formed upon chemical destruction of nanopore walls. The application of strongly oxidants most often is caused by the transformation of nanopores, and widening of small nanopores is a reason for the formation of additional large nanopores that belonging according to the International Union of Pure and Applied Chemistry classification to micropore range. Oxidation with 30% HNO_3 can result in forming new 1.8-nm nanopores. From structural considerations, staked graphene-like layers as basic units of the architecture of nanoporous solids undergo oxygenolysis and degrade, so, without a doubt, the reason for this is the fracturing of the nanopore walls. In light of these observations and suggestions, we will state that oxygenolysis caused the pore wall destruction is the fast process taking place in the presence of strong oxidants. The graphene-like carbon matrix is transformed during oxidation, and, from a structural point of view, the oxygenolysis is one of the reasons for the nanopores expansion and the appearance of new large nanopores. On this background, the adsorption capacities of sorbents towards Cu^{2+} should differ significantly.

Typically, the adsorption data, which are taken from the equilibrium studies, showed that the highest efficiency can be found for the sorbents which surface and architecture were subjected to the action of strong oxidant. Typically, one of the most valuable sorption efficiency parameters, the percentage removal R reaches the value from 50% and above 80% at a low concentration of copper ions. This could be due to the high concentration of the oxygen-containing functional groups that decorated nanopore walls. Different isotherm models can fit the experimental equilibrium data. To find the best-fitting curve and to choose an appropriate model, the linear and nonlinear least-squares methods can be used to reach a minimal sum of the squared deviations of the theoretical values from the experimental points. The principle is to select the model parameters in such a way as to take a minimal residual factor (R_f) factor, which is a measure of the agreement between the data determined by theoretical models and the equilibrium adsorption ones. At the first, the Langmuir isotherm can describe the experimental data in a simple way. The Langmuir isotherm model can represent the experimental equilibrium data in the case of a homogeneous surface. When using the Langmuir isotherm model and considering energetic issues, the adsorption energy will be constant over all adsorption sites. Two-parameter Langmuir equation that can be used to fit the adsorption data, in the form of the following equation

$$C/a = 1/(K_L a_m) + C/a_m, \quad (3)$$

where a_m is the maximum adsorption capacity of the adsorbent corresponding to complete monolayer coverage on the surface (mg/g), and K_L is the Langmuir adsorption constant (L/mg), C is the equilibrium concentration of Cu^{2+} ions in solution (mg/L), a is the equilibrium adsorption capacity of Cu^{2+} on the adsorbent (mg/g) to be used to fit the experimental data.

Alternatively, the Freundlich isotherm can be used to describe the adsorption that passed on the heterogeneous surface with varied affinity. This Freundlich model is empirical and, in the first approximation, the Freundlich adsorption equation can be rearranged as

$$\ln a = \ln K_F + 1/n_F \ln C, \quad (4)$$

where K_F is the Freundlich adsorption constant and nF is the empirical parameter related to the surface heterogeneity. To the best of our knowledge, the Langmuir model cannot fit exactly the experimental adsorption data. This is because of the high heterogeneity of carbon surface. That is why the Freundlich model accounted for high heterogeneity showed a good fit. Table 3 sums the model parameters describing the fits within the models and the best model-to-data fit with the Freundlich isotherm with a high R-factor of >0.99 that confirms an energetically heterogeneous surface. The Freundlich isotherm constant K_F depends on the oxygen heteroatom amount.

Table 3. Selected Freundlich and Dubinin–Radushkevich model constants describing Cu^{2+} adsorption onto nanoporous activated carbons (NACs)

Sorbent	Freundlich model constants		Dubinin–Radushkevich model constants		R
	$K_F \times 10^4$	n_F	$K_{DR} \times 10^2$	a_m (mkmol/g)	0.999/0.999
NAC	2.0	3.6	9.0	220	0.999/0.997
NAC-H_2O_2-10	2.5	3.6	9.0	265	0.999/0.999
NAC-H_2O_2-30	5.7	3.1	10.5	610	0.997/0.998
NAC-HNO_3-5	8.3	3.3	9.1	840	0.999/0.997
NAC-HNO_3-30	10.1	3.5	10.2	1180	0.998/0.999

From the tabulated data, it is clear that surface oxidation increases the total number of adsorption centers, some of them have a higher affinity towards the copper ions. When the “nF” term, which is in the range of 1.5–1.8, there is a complex dependence against the oxygen heteroatom amount and the content of oxygen-containing acidic groups.

Adsorption that takes place onto heterogeneous surface one can describe with a hybrid isotherm, for example with the Redlich–Peterson isotherm model that combines features of the Langmuir and the Freundlich isotherm models. But, according to [105], the Redlich–Peterson constants show unreasonable changes and differ up to 20 times for a series of oxidized activated carbons, so, the assumptions of the model are beyond the objects under investigation. The adsorption data were also fitted with the two-parameter Dubinin–Radushkevich isotherm model:

$$\ln q_e = \ln Q_{DR} - K_{DR}\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2, \quad (5)$$

where q_e (mmol g^{-1}) is the amount of metal ions adsorbed, Q_{DR} (mmol g^{-1}) is the maximum adsorption capacity of metal ions, Q_{DR} (mol^2 kJ^{-2}) is the Dubinin-Radushkevich isotherm constant, C_e (mol dm^{-3}) is the equilibrium concentration of metal ions, R is the gas constant (8.314 J/mol K), and T (K) is the absolute temperature in Kelvin. This well-known model can fit the data and describe the adsorption in microporous/nanoporous solids. A reasonable mathematical description could be obtained in the paradigm of the two-parameter Dubinin–Radushkevich isotherm model if one considers the isotherm models beyond the Freundlich isotherm. From modeling the Freundlich equation, the substantial heterogeneity of the surface, as found, could be related to the nanopores (micropores) that accounted in the framework of the Dubinin–Radushkevich model of adsorption isotherm. Heterogeneity of nanoporous walls means that the Freundlich model of adsorption isotherm should describe the experimental adsorption data in the best way that works, but, this description is empirical by definition and has no physical meaning. The correct modeling can be carried out only within the Dubinin–Radushkevich model of adsorption. The surface heterogeneity should be considered and understood due to different types of adsorption sites presented on the nanoporous carbon surface. Oxidation has a positive effect on the adsorption capacity and adsorption kinetics, consequently, the maximum adsorption capacity am can increase up to five times and increase with the surface concentration of accessible oxygen-containing acidic groups reaching a plateau. Consequently, it is not surprising that the best adsorption takes place in the presence of the most acidic carboxyl groups and anhydride and lactone groups. Structurally these groups are functionalized on the outer surface of the available nanopores involved in the adsorption of Cu^{2+} ions. Considering the nonlinearity effect, the main reason for the existed correlations is the fact that the intensive oxidation with concentrated solutions of oxidant can decompose the oxygen-containing groups, and so, can limit the amount of newly formed oxygen-containing groups. This limitation cannot be overcome in the solutions. As one can see from Table 3, one can suggest the same type of correlations for the Freundlich and the Dubinin–Radushkevich models. Absorption energy E_{DR} estimated in the framework of the nanopore model of the Dubinin–Radushkevich is about 25 kJ per mole. This value is partially constant that only slightly depends on the oxidation degree of the carbon surface. This situation has the right to be when similar oxygen-containing groups are adsorption sites.

Today, intensive adsorption studies were performed and the most common idea that the oxygen-containing groups favor the metal ions adsorption according to Alvarez-Merino and coauthors [122] and Dastgheib and Rockstraw [123]. The most possible mechanism of adsorption could be the complexing with the formation of metal surface complexes, according to Chen and Lin and Chen and coauthors [124, 125], or ion exchange that takes place with the participation of strong acidic surface groups, according to De Mesquita and coauthors [126]. On the other hand, Puziy and coauthors [127] reported that the presence of the strong acidic groups does not be a guarantee for good adsorption of Cu^{2+} ions. That is why the role of the surface groups in nanoporous solids should be considered balanced. According to the findings of Terzyk and coauthors [128-131], the reason for easy adsorption should be an optimum balance between the strength of intermolecular forces and the molecular properties of the adsorbate. According to Terzyk [129, 130], from studies of microporous and nanoporous adsorbates, it is clear that the interactions between solute and surface groups can lead to the blockage of small micropores and observed experimentally when the primary micropores are filled [131]. From simulation will be clear that large nanopores and micropores can almost vanish at acidic pH. On other hand, the protonation of surface oxygen-containing groups supports the adsorption by increasing heterogeneity of carbon surface [128]. From this consideration, the nanoporous architecture and the nanopores size distribution are not the factors that determine the adsorption capacity. Nevertheless, for efficient adsorption, the nanopore should be of optimal size and the coverage with certain oxygen-containing groups should also be at some optimal level [130, 131]. For developed nanoporous architecture very narrow slit-like nanopores inside the bulk volume could often be blocked when water molecules filling pores or Cu^{2+} ions adsorbed at the entrance to the pore. But, the volumetric parameters of nanopores and the total pore structure will change in the course of oxidation and widening that reducing for some extent steric hindrances those restricting the diffusion of ions. We postulated that nanoporous activated carbons oxidized with nitric acid showed the highest adsorption capacity towards Cu^{2+} ions. For the oxidized sorbents, the decrease of the specific surface area and specific surface volume is explained only by the reduction of nanoporosity. So, the carbon atoms from the nanopore walls actively participate in the oxidation reactions and the functional groups that necessary for selective uptake can form inside the nanopores. From the pore size distribution functions, the size of nanopores slightly increases after oxygenolysis and new nanopores (micropores/mesopores) are found in the nanoporous architecture. The decreasing number of nanopores well corresponds with the marked decrease in the total pore volume; the formation of many new open nanopores can compensate for that decrease. The results of adsorption cannot be explained considering the porous structure of sorbents only, however, the porosity reduction should affect the adsorption of Cu^{2+}. The surface groups of different acidity can be a factor regulating the adsorption equilibria. Notably, the concentration of the most acidic carboxyl groups and anhydride and lactone groups in the NAC-HNO_3-5 and NAC-HNO_3-30 as compared to that in other sorbents is significant, so, one can suggest that adsorption of Cu^{2+} ions is because of the reaction of Cu^{2+} with the most acidic carboxyl, anhydride, and lactone groups, and these findings is crucial. The fact is that the experimental isotherms for nanoporous activated carbons are in very good agreement with those predicted in the framework of the Dubinin–Radushkevich isotherm model meaning that the adsorption of copper ions is localized in the nanopores. Suggesting reason for the high recovery and effective adsorption is better coordination of the copper cation in the pore confinement. This better coordination could be resized with some neighboring functional groups in the open porous structure. In practice, the aforementioned coordination can be implemented only in the small nanopores. A decrease in the surface of nanopores is accompanied by an increase in the total concentration groups, up to 3 mmol per gram, and under this condition becomes possible interaction of one Cu^{2+} ion with two adjacent carboxyl groups. In dynamic adsorption, the potential mechanism of Cu^{2+} ions recovery is the formation of surface complexes in the nanopores. In this uptake, a pair of carboxyl groups and other groups can be involved through partial hydrolysis of anhydride and lactone groups and the proposed correlations showed a complex character of dependence. Besides, accompany with oxidized nanoporous activated carbons one can use noble metal nanoparticles to reach antibacterial effect to which will be dedicated in the following paragraphs.

Noble metal nanoparticles

Various methods used to synthesize nanoparticles: hydrothermal synthesis, co-precipitation, microemulsion, inert gas condensation, ion sputtering scattering, microwave, pulse laser ablation, sol-gel, spark discharge, sonochemical, and biological synthesis are available in the armory of a modern scientist [132-139]. The synthesis of metal nanocomposites can include spray pyrolysis, liquid infiltration, ball milling, chemical vapor deposition, physical vapor deposition, chemical sol-gel, and colloidal processes. Physical methods usually require the utilization of highly expensive equipment and lead to a quite expensive product. Therefore, traditional wet chemistry methods are recognized as more preferable. However, the synthesis chemistry of nanoparticles is the chemistry of highly diluted solutions. The necessary use of often toxic reducing and capping agents leads to the production of a large amount of toxic wastes. Consequently, the development of biological or so-called green synthesis methods is an object of extensive studies in the scientific world. Biological methods consist of the application of biological materials — plants, fungi, and bacteria. Such methods are cost- and time-effective and environmentally friendly.

The resulted metal nanoparticles in the typical synthesis using plant extract [140] gives metal nanomaterials in a variety of shapes such as rod, cluster, cube, sphere, cage, etc. Traditional wet-chemistry methods and some plant extracts produce almost spherical nanoparticles (Figures 2a and 2b). In other cases, some compositions of extracts that produce the irregularly shaped nanoparticles can be obtained (Figure 2c).

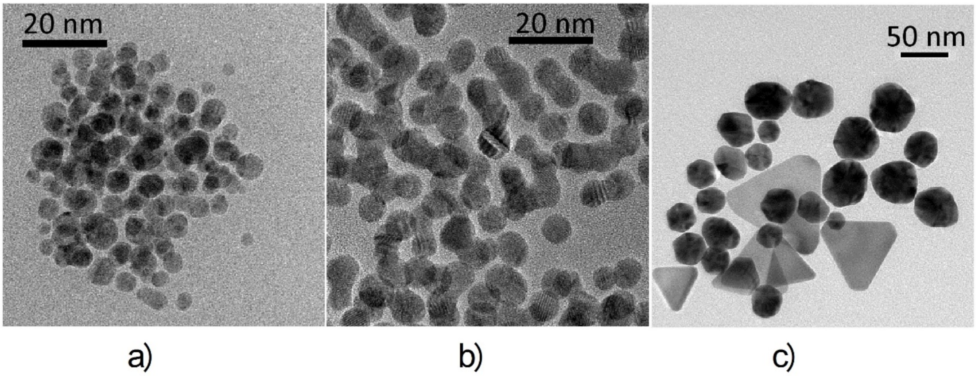

Fig. 2. Transmission electron images of phytosynthesized a) silver, b) spherical gold and c) non-spherical gold nanoparticles.

The shape of materials influences the optical properties what can benefit photocatalytic properties and make them prospective for sensor materials. For example, irregularly shaped nanoparticles with response in the near-infrared range (Figure 3) can be used in surface-enhanced Raman spectroscopy for the detection of ultra-low concentrations of organic pollutants in water [141].

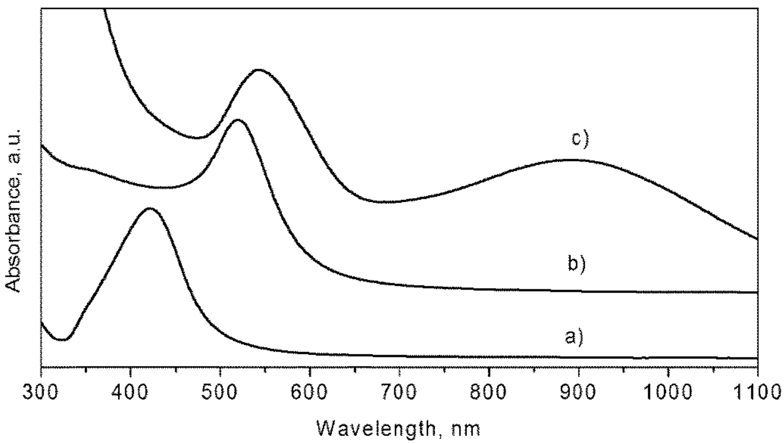

Fig. 3. UV-Vis spectra of a) silver, b) spherical gold and c) non-spherical gold nanoparticles prepared using plant extracts.

Silver nanoparticles in water disinfection

The use of silver nanomaterials in water treatment technologies with the aim of preventing the growth of harmful microorganisms is approved by the World Health Organization. Silver nanoparticles can be used for purification in water filtering apparatus due to their enhanced antimicrobial nature in contaminated water. General schema is presented in Figure 4.

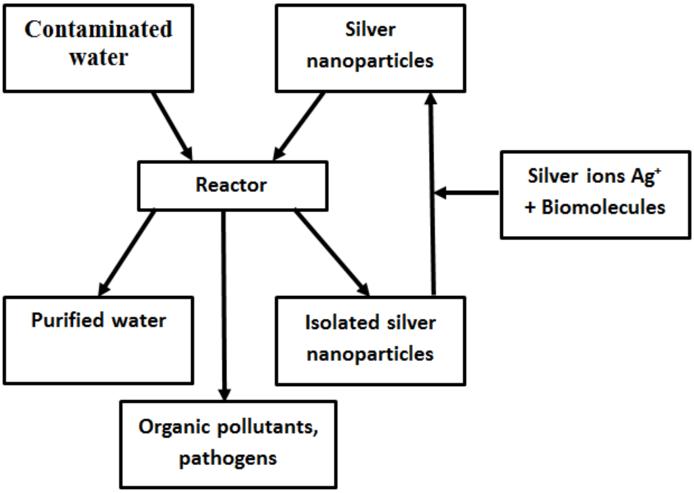

Fig. 4. Scheme of application of phytosynthesized silver nanoparticles in removing water contaminants.

Antimicrobial properties of silver

Silver nanoparticles have immense antimicrobial properties. Therefore, it has been used in applications like disinfection of medical devices and home appliances as well as for water treatment [142, 143]. It is suggested that silver ions interface with the thiol groups of proteins, which causes the inactivation of respiratory enzymes and generates the reactive oxygen species [144]. In other work reported that silver ions can prevent DNA replication [145]. The photoactivity of silver nanoparticles within sight of UV light with further an enhanced UV inactivation of viruses and bacteria is also reported [146]. Silver nanoparticles also produced a 76% reduction of *Bacillus subtilis* after its application in an aerosol form [147].

The potential in removing phenols, textile dyes, and microbial contaminants from the water was investigated for silver nanoparticles prepared using ethanol leaf extracts of *Ocimum sanctum* and *Artemesia annua*. Phytosynthesized silver nanoparticles were effective as a catalyst in the reduction of 4-nitrophenyl phosphate within 20 min in the presence of $NaBH_4$ [148] and as an adsorbent of toxic textile dyes (namely: Reactive Blue 4, Reactive Orange 4, and Reactive Red 120) from aqueous solutions. Furthermore, these biosynthesized nanoparticles demonstrated excellent antimicrobial properties in application to river water.

Silver nanocomposites with soil were prepared using silver nanoparticles synthesized using *Ocimum tenuiflorum* [149]. The adsorption efficiency in respect to removing reactive turquoise blue dye was about 96.8%.

The ability to absorb pyrene, anthracene and phenanthrene by silver nanoparticles prepared wet chemical and green method using extract of garlic (*Allium sativum*) was studied [150]. The efficiency of green synthesized silver nanoparticles was in 3 orders of magnitude higher than nanoparticles prepared by the wet-chemistry method. The excellent antibacterial activity on both gram-negative and gram-positive bacteria showed the spherical silver nanoparticles with a size of 12.4 nm ± 1 nm synthesized using fresh aqueous tuber extract of *Jatropha heynei* [151]. It is recognized as promising inhibitory activity against total *Coli* forms in the drinking water.

Silver nanoparticles prepared using *Abutilon indicum* leaf extract have shown powerful antibacterial activity on *Bacillus subtilis*, *Staphylococcus aureus*, *Salmonella typhi*, and *Escherichia coli* [152]. At the same time, while the impregnation of silver nanoparticles prepared with *Ipomea carnea* extract with a cellulose acetate membrane to form a designed antimycobacterial membrane exhibited a strong inhibition on *Mycobacterium smegmatis* [153]. In many cases, the exact mechanisms behind these activities cannot be assumed.

Hybrid bead-bound silver nanoparticles were formed successfully by a green procedure using *Ulva flexuosa* via a facile single-step green procedure onto the copolymer beads without causing any physical damage to the surface of beads [154]. The stable immobilized silver nanoparticles at a concentration of 300 mg demonstrated prominent antibacterial traits which resulted in 100% bacterial reduction within six hours of contact time for all the bacterial strains. Complete inhibition was achieved with an increase in the contact time as well as with the increase in the amount of the silver nanoparticles bound copolymer beads.

Francis *et al*. synthesized gold and silver nanoparticles from the leaf extract of *Mussaenda glabrata* and evaluated their capacity to inhibit pathogenic microorganisms. The nanoparticles showed outstanding antimicrobial activity against *P. aeruginosa*, *E. coli*, *A. niger*, and *Penicillium chrysogenum* [155].

Besides, their catalytic capacities make them suitable for dye degradation, such as reported by Veisi *et al*. in their research, where green synthesized silver nanoparticles from the leaf extract of *Thymbra spicata* decreased different dyes, such as nitrophenol, rhodamin, and methylene blue [156].

Inhibition of bacteria by application of highly monodisperse spherical silver nanoparticles with controlled size prepared with elderberry extract also was studied. The significant growth inhibition of *E. coli* ATCC 25922 was observed already after 15 min in 6.25 mg/L concentration of silver nanoparticles in experiments described in the Experimental part. No colonies of the bacteria were detected after 3 hours of incubation at 35 °C in 3.125 mg/L concentration. The same effect was noticed after 5 hours of incubation. A similar effect was observed for *E. coli*, wild clinical strain. Significant inhibition growth for *S. aureus* ATCC 25923 strain was recognized after 15 min in both 12.5 and 25 mg/L concentrations of the silver nanoparticles colloids, however, no colonies were detected after longer incubation (3 hours and longer). A lower concentration of silver nanoparticles had a similar effect and we can conclude that any of the applied concentrations was effective if the incubation took 3 hours and more. Better results were observed for the wild clinical strain of *S. aureus*. The bacteria growth was inhibited already after 15 min in 3.125 mg/L concentration and after 3 and 5 hours of incubation in 3.125 mg/L concentrations showed total growth stop. The antibacterial effect of silver nanoparticles showed the best effect on *E. coli* strains. These results are in contradiction with some other studies, in which better effect was observed for *S. aureus* strains than for *E. coli* strains [157]. However, the differences in the effect of silver nanoparticles are not so significant.

In addition, the wide variation of pH, ionic composition, ionic strength, and natural organic matter can induce the aggregation of silver nanoparticles in natural waters. This results in widely varying antimicrobial activities and toxicities [158]. For water treatment, noble metal nanoparticles can be used in different forms. Usually, they are synthesized separately and then deposited on other material – support. This support can be chemically inert. This means that support does not react with pollutants, but prevents the aggregation of nanoparticles, for example, the nanoparticles of silver, gold, or platinum, and other noble metals supported on alumina [159]. Metals nanoparticles may be deposited on active support, which participates in the overall mechanism [160]. For example, silver nanoparticles enhance the photocatalytic activity of zinc oxide.

Antimicrobial properties of gold

Gold is one of the most stable elements and more stable than silver [161]. However, gold ions are toxic for almost all organisms, due to their high oxidizing ability. Having a low activity against bacteria, gold nanoparticles showed fungicidal activity. Ahmad *et al.* reported that antifungal activity depended on the particle size of the gold nanoparticles [162]. As expected, activity increased with a decrease in the particle size, due to an increase in the specific surface area of gold nanoparticles, which enhanced the interaction between gold and the binding sites of the plasma membrane proteins, resulting in the inhibition of H^+-ATPase-mediated proton pumping [163]. Gold nanoparticles with a size of 50–100 nm prepared using *Acalypha indica* extract were active against *E .coli* alone with MIC at 160 µg, and it was observed to inhibit its swarming motility and to make the cell leak out proteins [164]. Gold nanoparticles prepared using *Punicagranatum* L. extract were utilized for the preparation of a new series of chitosan–gold hybrid nanoparticles (CS–AuNPs) [165]. The antibacterial activity of CS–PE–AuNPs displayed a synergetic effect against methicillin-resistant *S. aureus* with MIC and MBC values of 15.6 and 62.5 µg/mL, respectively. Another possible application of gold nanoparticles to wastewater problems is sensors for the determination of toxic organic compounds. Thus, silver core – gold shell (Ag–Au) nanostructures can be used in microelectrodes and assess their performance as surface-enhanced Raman scattering substrates to detect and quantify toxicants. The surface-enhanced Raman scattering enhancement factor for the Ag–Au nanostructures was estimated to have a maximal value of 6.51×10^5. Combining a data reduction technique with a linear classifier, both identification and quantification were demonstrated with 100% success. The toxicants thiram, thiabendazole, malachite green, and biphenyl-4-thiol were all detected and identified at 1 ppm [166].

Antimicrobial properties of other noble metals

The microbiological properties of platinum nanoparticles in an aqueous environment have been investigated [167]. It is thought that platinum nanoparticles can damage cell walls and cause the release of substances (cytosolic proteins) for both bacteria and fungi [168]. In addition, the platinum-based toxic effects based on the interaction with cellular components inside the cytoplasm and inside the nucleus have been reported [169]. Similar to gold nanoparticles, the bactericidal properties of platinum nanoparticles depend on the size (<3 nm), whereas large nanoparticles led to enhanced growth of bacteria.

However, platinum nanoparticles capped with bioactive compounds could be used as promising antibacterial and antifungal agents [170]. The bactericidal activity of the greenly synthesized platinum nanoparticles (extract of *Taraxacum laevigatum*) was evaluated against gram-positive bacteria (*Bacillus subtilis*) and gram-negative bacteria (*Pseudomonas aeruginosa*). The findings revealed that the platinum nanoparticles exhibited significant antibacterial activity against both strains, making them promising antibiotics that could overcome bacterial resistance [171].

Antimicrobial effects of other noble metals nanoparticles have been also reported, for example, for palladium and ruthenium. Palladium, which is widely used as a catalyst for many chemical reactions, has been also tested as an antimicrobial agent. Interestingly, palladium nanoparticles are more effective for gram-positive bacteria than gram-negative bacteria and exhibit size-dependent antimicrobial activity [172]. The proposed mechanisms of antimicrobial activity consist in the interaction of metal ions with thiol groups of bacterial enzymes with further denaturation, inhibition of bacterial respiratory mechanism, attack and destruction of bacterial DNA, direct disruption of the bacterial cell membrane, and the production of reactive oxygen species [173]. However, extensive accumulation of palladium nanoparticles in vacuoles of *Tetrahymena thermophila* [174] could cause biological concentration of palladium in the environment, and thus, unpredicted influence on other aquatic organisms. It has been reported that ruthenium nanoparticles are used as an oxide for antimicrobial agents [175]. Ruthenium oxide nanoparticles under near-infrared light exhibit good bactericidal activity with mechanisms similar to that of palladium nanoparticles.

CONCLUSION

Many factors influence the adsorption, including the presence of various oxygen-containing groups and the specific features of the porous structure. Among the major factors considered, one should account for the stock solutions' pH, ionic strength, and the content of heavy metal ions. The influence of certain factors on adsorption is not completely clear. Depending on concentrating conditions and the efficiency of complexing or ion-exchange reactions, adsorption capacity depends on many of the aforementioned factors directly or indirectly. The Freundlich and the Dubinin–Radushkevich isotherms are modeled reasonably well the adsorption data at the considered concentration range, but, the results of this Cu^{2+} adsorption modeling have a physical meaning if one considers the paradigm of Dubinin–Radushkevich equation, which is adequately considered the surface heterogeneity of the oxidized carbon surface and suggested cations adsorption inside the nanopores. Within the hypothesis of the mechanism of adsorption of the copper ions by complexing, the reason for efficient adsorption is the simultaneous action of adsorption centers. From this consideration, accounting for all pros and cons, a special nanoporous activated carbon type can be developed for use in ultrafiltration membranes for wastewater and drinking water treatments. The adsorption capacity of these membranes could be compared with a granular activated carbon and an activated carbon fiber. In this filtration, the oxidized carbon surface should significantly extend the membrane performance and can be a promising tool for the hybrid processes for wastewater and water treatment.

Nanoparticles, due to their high surface/volume ratio, exhibit totally different characteristics compared to the bulk forms of the same materials; this makes them much more active. The unique characteristics of these nanosized noble metals have great advantages for antibacterial and antifungal applications in different fields. Metallic nanoparticles of gold, silver, platinum, and palladium, in a pure form or alloyed with other nanoparticles, are prospective to be used in water additional purification. Nanoparticles of gold metal have been widely used in biomedical applications, disease diagnostics, separation, and pharmaceutical sciences. Silver metal nanoparticles are being used in antibacterial applications, and due to such advantageous properties, they have recently been integrated into commercial wound dressings and medical implant coatings, which are all available on the market. Additionally, platinum metal nanoparticles are in use today in biomedical applications. Moreover, palladium metal nanoparticles have been extensively used in antibacterial applications. One of the most promising applications of nanotechnology is water, wastewater treatment, and remediation. This includes different mechanisms such as adsorption of pollutants, heavy metals, removal and inactivation of pathogens, as well as diversion of toxic materials into less toxic compounds. Presently, various nanotechnologies with nanoparticles, nanopowders, and nanomembranes are being employed for the removal of chemical and biological substances such as heavy metals, phosphate, nitrate, nitrite, and ammonia nutrients, algae, including cyanobacterial toxins, viruses, bacteria, and parasites. That is why our contribution in green preparation of noble metallic nanoparticles and nanoporous sorbents will be valuable addenda to existed achievements in the field of creating composite filters for water purification and adsorptive separation from toxic and harmful ions and biota.

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WATER SECURITY COURSE AS AN EDUCATIONAL MODULE TO ACHIEVE THE GOALS OF SUSTAINABLE DEVELOPMENT

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ABSTRACT

One of the main problems of the modern education system is the formation of its content. Determination of the theoretical foundations of an integrated approach has scientific value (due to definition of its specifics) and social value (modernize of specialists' training) and applied value (ensuring of continuity of the objectives and content of students' education according to their studies profile). It is suggested to use the integrated approach in the students' preparation process.

Purpose research is creation of effective didactic system of interdisciplinary knowledge of natural-science courses of environmental education with special an emphasis on professional orientation.

Object is education content of the students' preparation process, namely, students' training of the environmental specialty.

Subject is the integrated approach to form education content in the students' preparation process.

Method. Methods of the analysis, synthesis of knowledge, educational experiment and mathematical statistics were used for fulfilment of the purpose.

Results. The educational experiment on the implementation of the integrated approach has shown effective results in improving the quality of students' knowledge. The research covered students of environmental directions of universities. The effective didactic system of interdisciplinary knowledge of natural-science courses was created. Levels, goals, meaningful lines of the integrated approach to students-environmentalists teaching are defined. As a result of research the concept of integration approach of environmental education is developed and a specific of the teaching is defined, efficiency of methodical system of ecologists' preparation is introduced and experimentally checked.

Conclusions, Recommendations and Future directions. The integrated approach to education is a special type of designing its content which opens the system of interdisciplinary communications, and it also coordinates, unites and systematizes knowledge about the main natural-science theories, basic categories, and principles of the modern natural-science picture of the world. The study is proved the didactic effectiveness of the integrated approach to form of content of natural science courses. The prospect of further research activities is to improve the theory and practice of integrated study of natural courses on the basis of the developed conceptual provisions of the education content integration, and also to improve the methodology of assessing the quality of students' knowledge during study of integrated courses.

Keywords: natural education, education content, an integrated approach, water security course.

INTRODUCTION

Improving the content of education as a strategic priority and a key direction of higher education reform was evidenced by the 2015 Yerevan Communiqué, the Paris Communiqué of 2018 (the core mission of the Bologna Process and the main objective of structural reforms have been to ensure and enhance the quality and relevance of learning and teaching) and recently reaffirmed by the Rome Communiqué of 2020, inter alia, through the adoption of "Recommendations to National Authorities to Improve Teaching and Learning in higher education in the EHEA "(Recommendations to National Authorities for the Enhancement of Higher Education Learning and Teaching in the EHEA) [13; 14; 26].

According to the priorities of the Rome Communiqué and the Recommendations on National / Government Support / Action to Improve Higher Education Teaching and Learning in EHEA Ukrainian higher education institutions should improve teaching and learning in in the context of student-centered and competence-based approaches, paying tribute to innovation and structured dialogue with stakeholders, taking into account data empirical research and scientific research [26]. The methodology of content formation is a complex problem [5-7]. The content of education is a system of scientific knowledge, practical skills and abilities, as well as ideological and moral-aesthetic ideas that need to be mastered during the learning process [17; 18].

Objective factors influencing the education content include:

- the level of science and technology development, accompanied by the development of new theoretical ideas and significant changes in the improvement of technology. For example, the content of natural education required changes in the development of molecular biology, genetic engineering, green chemistry, etc. ;
- the needs of modern society in the training of the younger generation (what it should be, what qualities they should have, etc.);
- the direction of state policy.

The development of the processes of differentiation and integration in the historical aspect shows that science itself has identified the means and methods to overcome the limitations of the disciplinary approach. The opposite approach is called integrated or interdisciplinary. The integration of scientific knowledge is carried out in various forms, ranging from the use of concepts, theories, and methods of one science in another and ending with the emergence of the XX century system method. Today, the latter acquires special significance because it allows us to consider objects and phenomena in their relationship and integrity.

So, one of the leading trends in the development of science is integration. Integration processes in science are manifested in the following forms: organization of research on the border of related scientific disciplines; development of scientific methods that are important for many sciences; search for general theories, principles, which could be reduced to an infinite variety of natural phenomena (for example, the hypothesis of "Great Union" of all types of fundamental interactions in physics, global evolutionary synthesis in biology, physics, chemistry, etc.); development of theories that perform general methodological functions in science (general systems theory, cybernetics, synergetics); changing the nature of the tasks solved by modern science − they become complex, require the participation of several disciplines (for example, environmental issues) [1–4; 8–11].

The process of Ukraine's accession to the single European space and the signing of the Bologna Convention provides for the modernization of the content of higher education, a change in its philosophy. The culture of the XXI century ceases to be sectorial because now its development is under the sign of integration when a new type of professional must be formed, focused on innovation and addressed to the interests and values of man and society. Philosophy of the educational process of the XXI century aims at systemic pluralism, the dialogue of different concepts, the complementarity, mutual enrichment of different positions, the infinite space of opportunities for teachers and students [12; 13; 15; 16; 27] Therefore, the higher school faces the task of training a new generation of professionals who must meet today's requirements. Natural education has great potential to directly address sustainable development issues and environmental issues. The content of natural education is focused on integrated courses, the search for new approaches to structuring knowledge as a means of holistic understanding and cognition of the world [19]. So, the research focus is a need to reorient curricula, to introduce issues developed based on an integrated approach [20–25]. As an example of how the content of natural education through the didactic system of an integrated approach solves the issues of understanding sustainable development, we have created an interdisciplinary training course.

The purpose of research is the creation of an effective didactic system through the integrated approach of a natural education for example of water security course with a special emphasis on professional orientation.

The object is the natural education content of the students' preparation process, namely, students' training of the environmental specialty.

The subject of the research is the content of the interdisciplinary course on water safety for students of environmental specialties of universities.

METHODS AND MATERIALS

Using partial scientific methods (component analysis of ecological knowledge, postoperative analysis of subject skills, etc.), general scientific methods (educational experiment, etc.), organizational, empirical, and methods of mathematical statistics determined the principles of selection of educational material, created the content of integrated training course, staging an educational experiment, summarized its results and analyzed the data.

To evaluate the completeness of students' knowledge and skills were defined by the ratio of the notions number of applied by students to the number of definitions that can be used. The tasks consisted of their reproductive level of educational material. The quantitative characteristic of the completeness of the knowledge factor was the acquisition coefficient of knowledge by students. The formula 1 used for this:

$$\overline{K} = \frac{\sum N_i}{n\sum N} \times 100\%, \text{ where} \qquad (1)$$

n – the total number of students who performed work;

$\sum N$ – the number of correct answers in the test;

$\sum N_i$ – the number of correct answers of students.

RESULTS AND DISCUSSIONS

This study is implemented by Programme EU Erasmus+ Jean Monnet Activities as part of the interdisciplinary European studies in Petro Mohyla Black Sea National University. The effective didactic system of interdisciplinary knowledge of natural-science courses, namely the water security course, was created.

Principles, meaningful lines of the integrated approach to students-environmentalists teaching are defined. The principles of selection and structuring of educational material for the preparation of students-environmentalists are defined and substantiated.

These are the principles:

- systematic (systemic factors are the goal of natural education in the context of the integrated approach, leading laws and theories, basic categorical concepts, principles of natural science, objects of study);
- interdisciplinary connections;
- fundamentalization;
- professional orientation of the education content; orientation of the content of training to the disclosure of environmental problems, such as climate change, sustainable development, environmental status of water resources (Bezsonov et. all 2017; Mitryasova & Pohrebennyk 2020).

The integrated approach to education is a special type of designing its content that opens the system of interdisciplinary communications, and it also coordinates, unites and systematizes knowledge about the main natural-science theories, basic categories, and principles of the modern natural-science picture of the world.

Levels of the integrated approach implementation are internal disciplinary and interdisciplinary of knowledge and the highest level – methodological synthesis (fig. 1). Internal and interdisciplinary integration is being implemented through selection into the content of education the facts, concepts, laws, methods, theories according to specialization and humanization. Dialectic categories are set off at the level of methodological synthesis, for example, unit, system, structure, element, cause, consequence, content, form, causality, randomness, pattern, etc.

The teaching course for Master's students in Environmental Science covers the main topics, such as water resources, water quality, climate change, integrated water management, water policy and law issues.

First of all, the training course presents European practices in the water security field. The content is constructed according to the leading aspects of the concept of sustainable development, namely the ideas of integration of knowledge to make optimal management decisions. The latter is based on the environmental imperative, ideas of co-evolutionary development of human, society and nature, urgent problems of climate change and issues of environmental pollution, ideas of responsibility for the quality of the environment, in particular water resources (Mitryasova & Pohrebennyk 2017). The course helps students to learn effectively on the evolution of intergraded water and environmental management of the European Union, thus to develop their awareness in the issues of European studies.

The course constructs on the interdisciplinary basis and covers key elements of the strategy for sustainable development and European experience in the field of the environmental water recourses policy (Mitryasova, Koszelnik et. all 2020; Mitryasova &Pohrebennyk 2020▪). The course includes such issues: water resources; climate change; water monitoring; water pollution control; water management; water quality; water purification and European practices of water policies. As an interdisciplinary course, the one focuses the integration of environmental policy requirements into other policy areas. Also, the course compresses the international dimension, with the role of the EU in international environmental motions (e.g. Kyoto Protocol, UNESCO Roadmap for Implementing the Global Action Programme on Education for Sustainable

Development, Sustainable Development Strategies), the International Water Security Network, and so on and the impact of European policy on other regions of the world (Table 1).

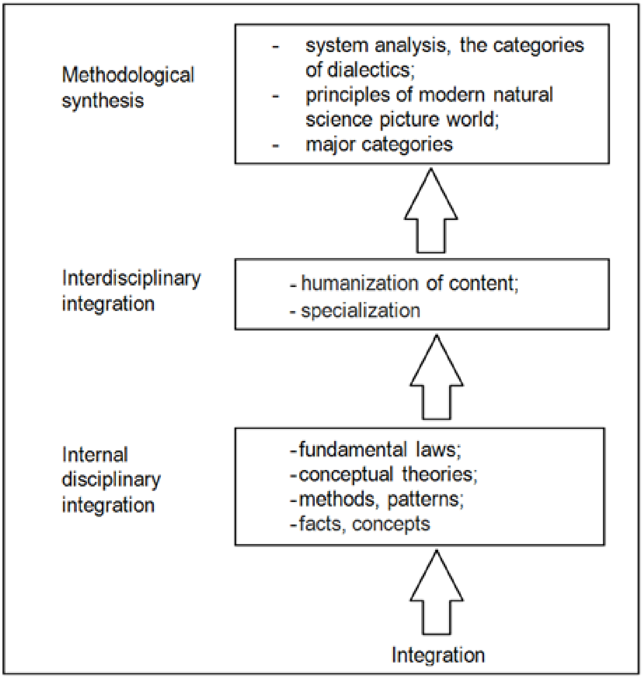

Fig. 1. Levels and directions of the integrated approach implementation

The most important aspects of integrated approach are component, functional and prognosis (fig. 2). Component aspect of integrated training responds to the question «what are integrated?». Functional component of integrated learning manifests itself as functioning of the intra- and interdisciplinary connections and responds to the question «how are integrated?». Prognosis aspect of integrated learning has two areas: genetic and prospective so demonstrates basic and promising concepts and ideas.

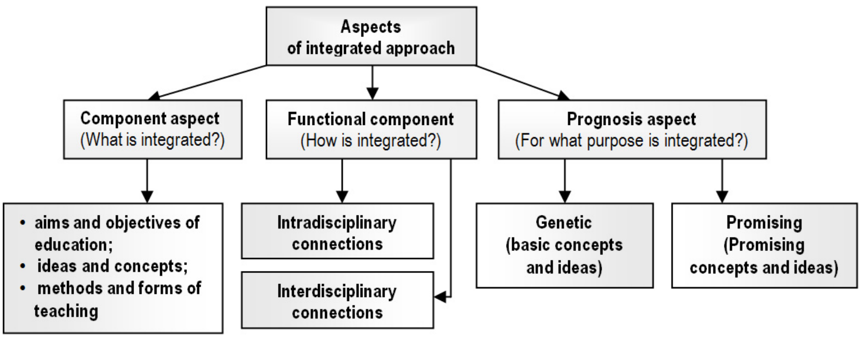

Fig. 2. The most important aspects of integrated approach

The course is interdisciplinary and connects the policy and tools of water monitoring and management, principally addressing EU and Ukraine practices of water quality, water resources, biodiversity, and, fisheries and their progressive integration.

Students' learning outcomes:

• understand the difference between policies and tools of EU and Ukraine for water monitoring and management;

• explain goals and system of water management at national, regional/EU and global levels;

• understand and articulate key ecological challenges to water management;

• articulate and understanding of the evolution of systems thinking, ecosystems thinking, the ecosystem approach and ecosystem services, and the implication of this for the continued evolution of integrated water and environmental management contexts;

• understand and use topical and correct terminology related to the environmental management in the field of water security;

• ability to conduct analysis, synthesis, creative reflection, evaluation, and systematization of various information sources in researching the field of water security;

• make use of information sources about global instruments and multilateral environmental agreements as well as EU environmental policy in the field of water security;

• knowledge of the basic principles, types, methods and means of environmental water monitoring and their ability to assess and predict the state of the objects of the environment;

• understand and explain the influential quality of water to health, research and development, water security and other cross-cutting issues;

• understand of the water management system and procedures for activities of enterprises to water security, its functions, tasks at the global and national levels;

• knowledge of the latest advanced technologies and innovations in the field of water security;

• discuss the evolving policy and tools of water monitoring and management, principally addressing EU and Ukraine practices of water quality, water resources, biodiversity and fisheries and their progressive integration.

Table 1. The main content of the course

№	Topic	Main issues of the topic
1.	The role of the EU in international environmental motions (e.g. Kyoto Protocol, UNESCO Roadmap for Implementing the Global Action Programme on Education for Sustainable Development, Sustainable Development Strategies).	History of the formation of the EU environmental foundation; the EU's place in international environmental law; EU institutions in the field of environmental protection; legal support for the concept of "sustainable development" in the EU.

2.	The strategies of EU environmental policy.	General characteristics of EU environmental policy; the United Nations Environment Programme; UN climate conferences and the EU position; United Nations Environment Programme (UNEP), UN Climate Change Conferences: Bali, Poznan, Copenhagen, Cancún Transatlantic relations and climate change / EU & US relations on environmental issues.
3.	Water and development in Europe: environmental sustainability as a precondition of European environmental policy and its best practices in water monitoring.	Water in numbers and facts; water Framework Directive as the main document for water monitoring; status of water resources; types of state water monitoring; a new order of water monitoring in Ukraine; comparative analysis of the monitoring format: as it was and how it will be; European experience in water monitoring.
4.	Implementation of sustainable development programs to post-soviet countries.	Characteristics of sustainable development content from the UN's views; the role of ecological security in the sustainable development; environmental security of aquatic ecosystems: priority factor in development; assessment of environmental component in the region's development; effectiveness of the implementation of sustainable development programs in the post-soviet countries.
5.	Water resources, water quality and climate change.	The water-resource potential of the hydrosphere; distribution of water resources; water resources of Ukraine; factors of formation of water composition; properties of natural waters; general requirements for drinking water quality in the world; requirements for water quality in Ukraine; drinking water and human health; adaptation to climate change.
6.	Integrated water management: challenges for the 21st century.	Water is the matrix of life; regional aspect of water supply: history question; characterization of water treatment stages; EU experience.
7.	Water policy and law: a comparative analysis of European and Ukrainian practices.	Water is the global agenda of the United Nations; integration is a key trend in water management; integrated flood risk management; integrated water resources management by basin principle.
8.	Urban water services: practices of developed European countries.	Water supply systems: circulating water supply; centralized drinking water supply; local or decentralized water supply; cold and hot water supply; Ukrainian experience of normalization of drinking water quality; where can we drink tap water? Experience of EU; drinking water quality standards in Ukraine and EU countries.

9.	Basics of freshwater ecology. The best practices in water purification in the EU member states.	Water policy on the definition of international waters; international water management experience; a sphere of EU influence on water policy formulation; principles of sustainable water management in Ukraine.
10.	Challenges for Ukraine in water security policy and practice due to association with the EU.	The water footprint of the country; the Urban Waste Water Directive; urban wastewater treatment plants; urban sewage treatment technology; the Marine Strategy Directive; the Drinking Water Directive; the Flood Directive; the Nitrate Directive.

Due to the peculiarities of the research tasks in the educational experiment, there were no control groups. This fact is explained by the fact that we investigated the completeness of the acquisition of knowledge of the new content of educational material according to the program created by us. It would be incorrect to create control groups where such content of educational material is not studied by students.

A test form of knowledge control was used to assess the completeness of mastering the content of educational material. The test tasks included questions of the reproductive level regarding the key concepts of the training course.

The coefficient of completeness of knowledge was determined by formula 1. The lower limit of availability is taken as a coefficient of 0.6, which corresponds to a satisfactory level of knowledge. Based on the obtained data, the quantitative processing of the results, which was carried out for each year (the experiment was conducted for three years), and then the average data were derived. It is proved that the selected educational material is quite fully assimilated by students, as evidenced by the average coefficient of 0.85.

To test the strength of knowledge and determine the degree of forgetfulness, a slice of knowledge was performed two weeks after studying the course. The coefficient of knowledge strength was defined as the ratio of the number of elements of knowledge that remained in the memory of students after some time to the sum of the elements of knowledge contained in the test. It is established that more than half of the knowledge remains in the memory of students. It is determined that the degree of forgetfulness is 3−5% of the previous ones.

Thus, in the process of forming students' knowledge, the tendency to increase their educational activity, interest in carrying out independent scientific research, in expressing original views on environmental issues discussed during classes was determined.

CONCLUSIONS

A didactic system of an integrated approach has been created, which has shown fairly high efficiency. This system covers the principles of selection of educational content, levels of implementation of the integrated approach. The study is proved the didactic effectiveness of the integrated approach to the form of content of the natural science course of water security. The course is interdisciplinary and connects the policy and tools of water monitoring and management, principally addressing EU and Ukraine practices of water quality, water resources, biodiversity, and fisheries, and their progressive integration. The coefficient of completeness of knowledge was determined. It is proved that the selected educational material is quite fully assimilated by students, as evidenced by the average coefficient of 0.85.

The integrated approach itself extrapolates all modern processes of the development of scientific knowledge and is relevant in the formation of the content of natural education in solving issues of students' understanding of sustainable development. The prospect of further research activities is to improve the theory and practice of the integrated study of natural courses based on the developed conceptual provisions of the education content integration, and also to improve the methodology of assessing the quality of students' knowledge during the study of integrated courses.

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ORGANIZATION OF MONITORING OF THE SOUTHERN BUG RIVER WITHIN THE BUGZKYI GARD NATIONAL NATURE PARK

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ABSTRACT

The article is devoted to the peculiarities of water monitoring in the territory of the Bugzkyi Gard National Nature Park. The organization of monitoring of the main river of the park should be based on hydrodynamic and hydrometric characteristics of the flow. In the work, the authors provide a detailed analysis of the riverbed and flow velocity. They offer a scheme of spatial location of control points and calculation of river water sampling time for monitoring.

Keywords: water monitoring, water flow, main river, river velocity, hydrometric indicators.

INTRODUCTION

The Bugzkyi Gard National Nature Park was created to preserve the unique biotic and landscape diversity of the Southern Bug River valley and its tributaries. The main river is the core of a holistic system of unique natural complexes. The park has favorable conditions for the preservation of a large number of relict and endemic representatives of flora and fauna.

The object is not a wide strip stretching along the riverbed. It is surrounded on all sides by lands with intensive economic load. The natural complexes formed within the park are very vulnerable. Today they exist in extreme conditions of aggressive anthropogenic impact. Any changes in this nucleus caused by natural or artificial factors can lead to degradation and death of the system as a whole. Therefore, the problem of the park's existence is relevant and requires an attention of scientists, public and authorities. It is possible to ensure its preservation under the conditions of systematic complex ecological monitoring of the condition of both individual components and the system as a whole. An important part of this monitoring is the observation of the system-forming element – the Southern Bug River.

Within the National Nature Park (NNP), the main river is a unique, complex natural object. It is possible to obtain reliable information about its current state under the conditions of detailed study and analysis of the main characteristics of the water flow, which are crucial in system of general monitoring. Therefore, the aim of our work was to develop a scheme for monitoring the river, based on its hydrodynamic characteristics.

To achieve this goal, the key objectives of the study were identified:

1) to study the features of the hydrography of the NNP and the factors of its formation;

2) to determine the hydrometric parameters of the main river;

3) to make recommendations for the spatio-temporal organization of the water monitoring system in the park.

The object of the study was the hydro network of Bugzkyi Gard National Nature Park.

The subject – hydrometric features of the riverbed.

To develop recommendations for water monitoring introduction we analyzed the nature of the movement of water in the river.

Depending on the hydraulic characteristics of the water flow, there are uniform, uneven and unless (variable) movement [5].

With a uniform motion of the flow rate, a transverse (alive) section, water consumption is constant along the length of the flow and do not change in time. Such a motion can be observed in artificially created beds with a constant inclined and cross-section.

At uneven motion, sliding, speed, live sections do not change in this generation in time, but vary by the length of the flow. This movement is observed on the rivers during bounds, as well as in the contender. Uneven movement can be slowed down and accelerated. With a slow motion, the curve of the free water surface takes the shape of the trailer. The sloping of the water surface becomes less inclined to the bottom, depths increasing. When accelerated, the curve of the free surface of the flow is called a slump curve. In this case, the depth along the flow decreases, but the speed and inclination of the aqueous surface are increasing.

At unstable movement all hydraulic stream elements (slope, speed, area of living cross section) in a certain area vary in time and in length. An unsteady movement is the characteristic of rivers while flooding and rainy floods [4, 5, 7].

METHODS AND EXPERIMENTAL PROCEDURES

For the investigated section of the Southern Bug River characteristic is the uneven movement of the water flow of the slow motion movement alternate with segments of accelerated motion.

The main characteristic of the movement of water is the speed of water flow. We need exactly this to define the time of sampling of water on each section of the river.

The speeds of rivers are measured by float, hydrometric turntables or other devices. The method of floats was used by us during the study. Surface floats are used to measure the surface velocity.

To define the speed, we pre-divided the river into separate segments with a monotonous character of the river course (Fig. 1).

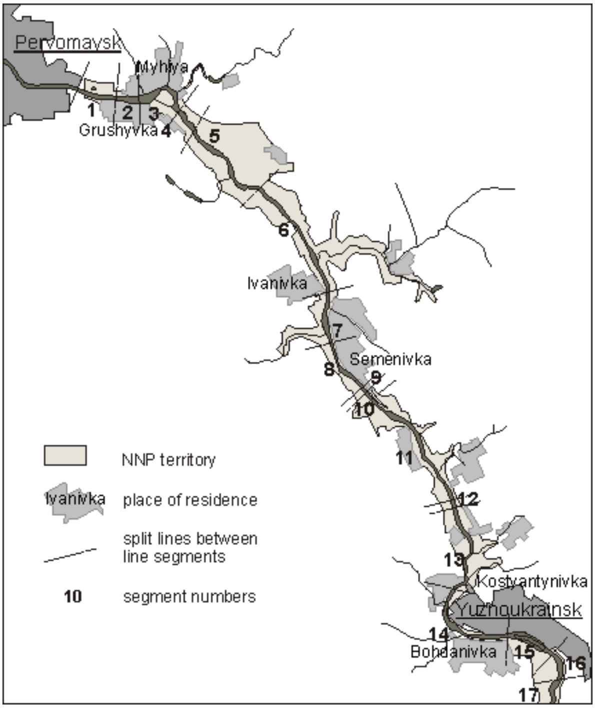

Fig. 1. Scheme of the hydro network of Bugzkyi Gard NPP

In each of the defined segments 4 range shores were recorded: launch, the reference, middle and the end of reference. The distance between the range shores was defined depending on the length of the segment. The length between the frame of the reference and the end of the reference was 100 m. For short segments it was 20 m. Two observers recorded the time of passing a float distance from the beginning to the final range shore. On the average, the flow of depths was carried out.

Thus, the surface speed in the middle of the water flow was defined. The breeze was not taken into account. The studies were carried out under the conditions of the pin. The research time was elected to the east or after sunset. As well as in the afternoon in the absence of wind.

The speed was calculated by the formula (1):

$$V = \frac{L}{t} \quad , \tag{1}$$

where *L* is the distance between the principles and final breeds, *t* – the time of passing by float distance.

The speed of water flow in the rivers are uneven at different points of the stream. They change in depth and in width of the stream. At the depth of the smallest speeds under the influence of roughness the channel is observed at the bottom. The speed increases from the bottom at first very quickly and at some depth reaches the magnitude close to the average flow rate. Further, the speed will grow more slowly to the flow surface. On the water surface the speed is the largest in the middle part of the flow and the circle of shores is the smallest.

The distribution of speeds in the watercourse is very influenced by the relief of the bottom, ice cover, speed and direction of the wind. In the presence of a rise, the flow rate is gradually growing from the bottom to the top of the increase, and then sharply increases. The speed of the tract of river is smaller than on the rifts. Therefore, to organize the river monitoring it is expedient to use medium speed. There are several methods for defining the average speed of the water flow. It can be calculated or measured.

The average speed is calculated in several ways.

1. To calculate the average speed on the vertical, it is necessary to divide the speed of the vertical depth [2].

2. In order to calculate the average speed in a living section, it is necessary to have water flow (Q) in m^3/s and the area of the living cross section (w) in m^2 [2, 4. 5, 7].

3. In the absence of direct measurements to calculate the average speed, the Shezi's formula can be used [1].

To measure medium speeds, we can use:
– six-point method (measurements at 0.2, 0.4, 0.6 and 0.8 depth below the surface and as far below the surface as possible and above the bottom);
– five-point method (measurements at 0.2, 0.6 and 0.8 depth below the surface and as low as possible below the surface and above the bottom);
– three-point method (measurements at 0.2, 0.6 and 0.8 depth below the surface);
– the one-point method (measurements at 0.6 depth from the surface). In the 0.6 depth method, the speed observation made at 0.6 depth below the water surface vertically is used as the average vertical speed. Actual observations and mathematical theory have shown that the 0.6 depth method gives reliable results [3, 4].

The speed of 0.6 depths was defined using deep floats. We used the same creations as to define the surface speed.

THE RESEARCH RESULTS AND DISCUSSIONS

Hydrographical network. Peculiarities of physical and geographical position of the region contribute to the formation and development of unique elements of its hydrological network. The location of the area in the contact zone of tectonic macrostructures (Ukrainian Crystal Shield and the Black Sea Basin) and natural zones (forest-steppe and steppe) is important. This affected the hydrometry, hydrodynamics and nature of the water regime of the main river and its tributaries.

The northern land border of the park is located 4 km downstream from the Pervomaisk waterfall (195.3 km from the mouth). South – 4 km above the water post Voznesenskaya HPS (in Olexandrivka village, 133.4 km from the mouth). The northern water boundary coincides with the land. The southern one is on the same level with the tail part of the Olexandrivsky Reservoir – 16.9 m.

Thus, the park includes a section of the river with a natural bed of about 43 km (Fig. 1). In addition to this, it includes lower parts of the tributaries of the first order: left – the rivers Dry Tashlyk, Mygiysky Tashlyk, Velyka Korabelna, Mertvovod (with right tributary of the river Arbuzynka), right – the river Bakshala. The large beams with constant watercourses should also be noted. On the left bank are Tsyganova, Didova, Popova, Mimrykova, Batratska, on the right – Dubova and Romanova.

The maximum mark of water in the Southern Bug on the border of the NNP with Pervomaisk is 56.8 m. The minimum is 16.9 m, on the border with the Olexandrivsky Reservoir in the vicinity of Yuzhnoukrainsk. The fall of the river is 39.9 m; the average slope is 0.93 m/km (Fig. 2).

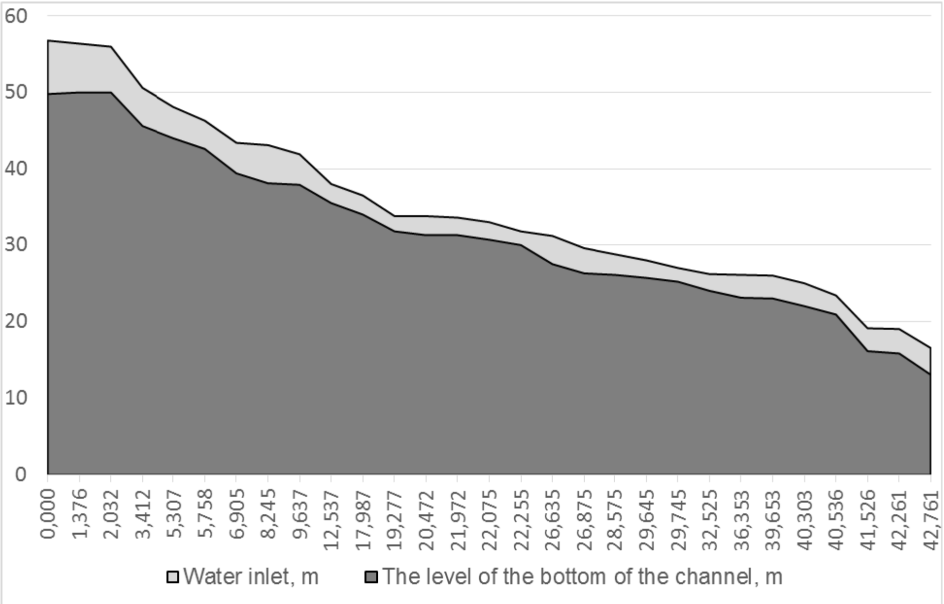

Fig. 2. Longitudinal profile of the riverbed of the Southern Bug within the Bugzkyi Gard NPP

The Southern Bug River is the main waterway of the region. It is a flat river that flows within the forest-steppe and steppe zones of the temperate zone. It originates on the Volyn-Podilska upland near the village. The font of the Khmelnytsky region flows into the Bug estuary of the Black Sea. The length of the Southern Bug River is 792 km, the area of the basin is 63,700 km^2, the depth varies from 1.5 to 8 m and the width of the channel is from 50 to 250 m. The velocity of the water flow is 0.1–0.4 m/s.

In the upper reaches of the Southern Bug River it forms its flow among the lowland banks, mainly in the swampy valley. In the area of Pervomaisk city, the river crashes into a crystalline massif of rocks and flows in a rocky porous channel to the city of Yuzhnoukrainsk city (within the NNP). Closer to the Olexandrivka village riverbed and lower part of the valley are flooded by the waters of the Olexandrivsky Reservoir. Below the dam, the river has a flatbed composed of less water-resistant rocks and alluvial deposits.

The river is fed by melting snow in the spring (partly in winter), rainfall at other times of the year, as well as by groundwater. In the formation of runoff of the Southern Bug, the contribution of meltwater to Vinnytsia city is, on average, 50 % of annual runoff, closer to the source – 80 %. The afforestation of the catchment is 4 %, wetlands – 1 %, lake – 0.3 % [6].

The water regime of the Southern Bug River is characterized by uneven runoff distribution throughout the year. In spring there is a well-defined peak of floods, the rest of the time – low runoff is limited to some increase in autumn and during winter thaws.

Maximum flow and water levels are observed, on average, in the second and third decades of March. The amplitude of fluctuations of flood and boundary water levels can reach 3–5 m in the upper reaches and 7–9 m in the area of Pervomaisk city–Olexandrivka village. The average duration of spring floods does not exceed two months at the average level of 460 sm.

Limit levels are set in mid-May–early June and last until December. Minimum levels are usually observed in August-September. Summer-autumn rises in water levels in the river are small and short-lived.

Freezing of the Southern Bug River begins in the second decade of December. Early freezing was observed in mid-November, late – in January. The river is cleared in the first – second decades of March. The maximum number of traffic jams can be 9–11 per year. Their duration varies from a few hours to 10–12 days. The most common rises in water levels during periods of congestion range from 0.5 m to 1.5–2.5 m (March 26–28, 2003, the rise in water levels near Pervomaisk city was 3.8 m, and in the same the period of 1980 recorded a rise in water of 6.7 m). Since 2003, the ice cover is not stable and no congestion with rising water is observed.

The process of modern hydrography formation within the NNP (Fig. 1), which continues under the influence of exogenous factors, began in the late Pliocene after the regression of the Pontic Sea. Just at this time the hydrogrid in the Archean-Proterozoic crystalline rocks is laid. During the Pleistocene and Holocene while the Quaternary glaciations, the area was in the extraglacial zone. This determined the peculiarities of the river valleys morphology.

The nature of geological and tectonic structure of the territory led to the alternation of genetically different types of river valleys. The heterogeneous nature of the geostructure led to the division of the studied section of the main river into sections. Segments of the canyon-like valley have steep rocky shores. They alternate with sections of the terraced valley, within which there are well-defined I–III floodplain terraces and a fairly wide floodplain. This valley is unique in terms of flat terrain.

Within each of these plots, the morphometric characteristics (width of the channel, depth, slope, fall) are homogeneous (Tables 1, 2).

Table 1. Morphometric characteristics of the Southern Bug riverbed

Point number	Distance from the park boundary, km	Water inlet, m	The level of the bottom of the channel, m	Width, m	Depth, m
1	0	56,8	49,8	200	7,0
2	1,376	56,4	50,0	180	6,4
3	2,032	56,0	50,0	290	6,0
4	3,412	50,6	45,6	230	5,0
5	5,307	48,1	44,0	237	4,1
6	5,758	46,3	42,6	190	3,7
7	6,905	43,4	39,4	160	4,0
8	8,245	43,1	38,1	290	5,0
9	9,637	41,9	37,9	120	4,0
10	12,537	38,0	35,5	150	2,5
11	17,987	36,5	34,0	194	2,5
12	19,277	33,8	31,8	140	2,0
13	20,472	33,8	31,3	111	2,5
14	21,972	33,6	31,3	120	2,3
15	22,075	33,0	30,7	120	2,3
16	22,255	31,8	30,0	110	1,8
17	26,635	31,2	27,5	110	3,7
18	26,875	29,6	26,3	100	3,3
19	28,575	28,8	26,1	115	2,7
20	29,645	28,0	25,7	150	2,3
21	29,745	27,0	25,2	140	1,8
22	32,525	26,2	24,0	110	2,2

Point number	Distance from the park boundary, km	Water inlet, m	The level of the bottom of the channel, m	Width, m	Depth, m
23	36,353	26,1	23,1	150	3,0
24	39,653	26,0	23,0	318	3,0
25	40,303	25,0	22,0	389	3,0
26	40,536	23,4	20,9	364	2,5
27	41,526	19,1	16,1	200	3,0
28	42,261	19,0	15,8	150	3,2
29	42,761	16,5	13,0	130	3,5

Table 2. Hydrodynamic characteristics of the Southern Bug River

Point number	Distance between points, m	Slope, m/km		Fall, m		The average speed of the river between points, m/s
		on the surface	at the bottom	on the surface	at the bottom	
1	0					0,2
2	1376	0,4	0,2	0,29	0,15	0,2
3	656	0,4	0,0	0,61	0,00	0,4
4	1380	5,4	4,4	3,91	3,19	0,3
5	1895	2,5	1,6	1,31	0,84	0,3
6	451	1,8	1,4	3,99	3,10	0,4
7	1147	2,9	3,2	2,53	2,79	0,3
8	1340	0,3	1,3	0,22	0,97	0,3
9	1392	1,2	0,2	0,86	0,14	0,3
10	2900	3,9	2,4	1,34	0,83	0,3
11	5450	1,5	1,5	0,28	0,28	0,2
12	1290	2,7	2,2	2,09	1,71	0,3
13	1195	0,0	0,5	0,00	0,42	0,2
14	1500	0,2	0,0	0,13	0,00	0,2
15	103	0,6	0,6	5,83	5,83	0,3
16	180	1,2	0,7	6,67	3,89	0,4
17	4380	0,6	2,5	0,14	0,57	0,3
18	240	1,6	1,2	6,67	5,00	0,4
19	1700	0,8	0,2	0,47	0,12	0,3
20	1070	0,8	0,4	0,75	0,37	0,3
21	100	1,0	0,5	10,00	5,00	0,3
22	2780	0,8	1,2	0,29	0,43	0,3
23	3828	0,1	0,9	0,03	0,24	0,2
24	3300	0,1	0,1	0,03	0,03	0,2
25	650	1,0	1,0	0,02	0,02	0,5
26	233	1,6	1,1	6,87	4,72	0,5
27	990	4,3	4,8	4,34	4,85	0,5
28	735	0,1	0,3	0,14	0,41	0,3
29	500	2,5	2,8	5,00	5,60	0,4

Plot 1. It starts from the border of the Bugzkyi Gard NPP. The channel is wide, straight, without islands, the relief of the bottom is homogeneous, underwater exits of native rocks can occur. The flow is uniform (0.2 m/s), slow because the slope drop on this section is only 0.29 m/km.

Plot 2. The boundary of the transition from the previous plot is clear. It is determined visually due to the presence of a large number of different sized thresholds. Monolithic protrusions of crystalline rocks in the form of islands break the continuous water flow into numerous brunches. Some of the islands are covered by water during floods. The relief of the channel is very difficult. The floodplain is poorly expressed, periodically occurs in the form of narrow (up to 10 m) strips. Exceptions are the mouth sections of the beams, where it can expand up to tens of meters. Within the plot, the slope of the water flow increases to 5.5 m/km, and accordingly its speed increases. It reaches 0.4 m/s. In terms of hydrodynamic parameters, the area is very similar to mountain rivers.

Plot 3. Has a short length. It is characterized by a straightened channel without islands, low current speed and a narrow floodplain with reed-covered shores. This significantly reduces the flow rate in the coastal strip.

Plot 4. The outcrops of crystalline rocks divide the channel into three arms. The extreme eastern sleeve is the main one. A powerful water flow made its way along a clearly defined fault, laid in the erosion-resistant rocks. That is why in this place the river has a steep rocky left bank. The flow velocity in the area is 0.4 m/s.

Plot 5. After a rapid current, the water flow slows down. Here, the Southern Bug reaches a flat area with single outcrops of crystalline rocks along the shore and in the channel. During this period there are single islands, as well as cascades of low-power low rapids. The flow velocity is 0.3 m/s.

Plot 6. This section is special because in its middle part the largest tributary flows into the main river, the mouth of which is located within the park. This is the Velyka Korabelna River. Near its mouth (several kilometers upstream and downstream) the flow velocity slows down to 0.2 m/s the relief of the bottom is simplified, the rapids are leveled. The nature of the current in this area resembles a calm plain river. The valley is terraced with well-defined in relief fragments of 1–3 floodplain terraces. The floodplain strip expands significantly and becomes continuous along the riverbed on both sides.

Plot 7. The speed and nature of the current is very similar to plot 5. Throughout the section, the channel is a continuous strip of low rapids.

Plot 8. The gradual slowing of the flow indicates the transition between sections. Here the flow velocity is 0.2 m/s. The plot is straight, oriented from north to south, the slope is insignificant. It gradually decreases from 0.41 m/km to almost 0 m/km. The valley is terraced with separate single rocky outcrops of native rocks.

Plot 9. A sharp change in the speed of the current and the turn of the channel to the southwest indicate the transition to the next plot. It is the shortest, but has a significant drop – about 5 m/km. This causes an increase in flow velocity to 0.3 m/s.

Plots 10, 11, 12, 13. These plots are very similar in morphological structure of the valley and riverbed. The relief of the bottom is complex with numerous outcrops of crystalline rocks, forming a continuous cascade of thresholds of medium power. The water flow encounters many obstacles in its movement. In addition to the complex terrain, the movement is also inhibited by numerous turns of the channel. The flow velocity ranges from 0.3 to 0.4 m/s. The slope of the water sometimes reaches 10 m/km, but the small depth (1.8 m) and considerable roughness of the channel do not allow to increase the speed of water movement too much. In plot 13 there are well-marked in relief remains of the old channel. During floods, part of the river flows into the old channel.

Plot 14. The boundary of the plot corresponds to the change of the channel relief and the slowing down of the flow velocity to 0.2 m/s. The segment is quite long, straight, oriented from west to east. The slope is only 0.03–0.24 m/km.

Plot 15. The transition from the previous section is clear. The channel is divided into separate arms by large indigenous islands. The small width of each of the arms, a sufficiently large depth

(3 m) and a significant slope of the river (over 6 m/km) on this segment, determine the formation of special hydrodynamic conditions. The water flow here has a maximum speed – 0.5 m/s. This is the largest figure in the studied segment of the Southern Bug within the park. Bogdanivska HPS is located on the right arm.

Plot 16. The end of the line of islands indicates the transition to the next section. Water is combined in one stream, slows down its flow to 0.3 m/s. The decrease in velocity can be explained by a small slope – 0.14–0.41 m/km, an increase in the cross-sectional area of the flow. However, it remains quite high because it has some margin of inertia from the previous plot. The length of this segment is not large – about 700 m, so the current does not have time to slow down.

Plot 17. The last plot with the natural regime in front of the Olexandrivsky Reservoir. Unfortunately, it is significantly reduced by raising the water level. In modern conditions it is only 500 m long. Within its boundaries is a porous channel with a large number of islands of different sizes. In some places the depth reaches 3.5 m. The very difficult relief of the bottom and the significant slope of the flow (5–5.6 m/km) determined the flow velocity of 0.4 m/s.

The conducted detailed analysis is the basis for the development of the scheme of spatio-temporal organization of monitoring of the main river of Bugzkyi Gard NNP. The proposed organization of monitoring studies is relevant for studying the quality of river water.

In the absence of continuous monitoring of water quality in natural reservoirs to study the behavior of chemicals that enter the river from the outside, we propose to determine the spatial and temporal dynamics of the polluted volume of water.

To get objective information about what happened to the contaminated water, where, at what stage, and how it changed, we need to know when exactly the contaminated volume of water will pass through the control point. And during the passage of the corresponding wave of catching up, a sample of water must be taken from the river (Table 3).

Table 3. Water sampling regulations for monitoring

Plot number	Length of the plot, m	The average flow rate at the site, m/s	Time	Time with increase
1	0	0,2	0	0
1	1376	0,2	1 hours 55 minutes	1 hours 55 minutes
2	656	0,4	0 hours 27 minutes	2 hours 22 minutes
3	1380	0,3	1 hours 17 minutes	3 hours 39 minutes
3	1895	0,3	1 hours 45 minutes	5 hours 24 minutes
4	451	0,4	0 hours 19 minutes	5 hours 43 minutes
5	1147	0,3	1 hours 03 minutes	6 hours 46 minutes
5	1340	0,3	1 hours 14 minutes	8 hours 00 minutes
5	1392	0,3	1 hours 17 minutes	9 hours 17 minutes
5	2900	0,3	2 hours 41 minutes	11 hours 58 minutes

Plot number	Length of the plot, m	The average flow rate at the site, m/s	Time	Time with increase
6	5450	0,2	7 hours 34 minutes	19 hours 32 minutes
7	1290	0,3	1 hours 12 minutes	20 hours 44 minutes
8	1195	0,2	1 hours 40 minutes	22 hours 24 minutes
8	1500	0,2	2 hours 05 minutes	24 hours 29 minutes
9	103	0,3	0 hours 06 minutes	24 hours 35 minutes
10	180	0,4	0 hours 08 minutes	24 hours 43 minutes
11	4380	0,3	4 hours 03 minutes	28 hours 46 minutes
12	240	0,4	0 hours 10 minutes	28 hours 56 minutes
13	1700	0,3	1 hours 34 minutes	30 hours 30 minutes
13	1070	0,3	0 hours 59 minutes	31 hours 29 minutes
13	100	0,3	0 hours 06 minutes	31 hours 35 minutes
13	2780	0,3	2 hours 34 minutes	34 hours 09 minutes
14	3828	0,2	5 hours 19 minutes	39 hours 28 minutes
14	3300	0,2	4 hours 35 minutes	44 hours 03 minutes
15	650	0,5	0 hours 22 minutes	44 hours 25 minutes
15	233	0,5	0 hours 08 minutes	44 hours 33 minutes
15	990	0,5	0 hours 33 minutes	45 hours 06 minutes
16	735	0,3	0 hours 41 minutes	45 hours 47 minutes
17	500	0,4	0 hours 21 minutes	46 hours 08 minutes

We have data on the redistribution of the average velocity of water flow, according to the areas we have identified, and we know their length. Now we can determine the time when the volume of water required for the study will pass. As a result of the calculations we obtain a linear dependence of time on the length of the river bed (Fig. 3).

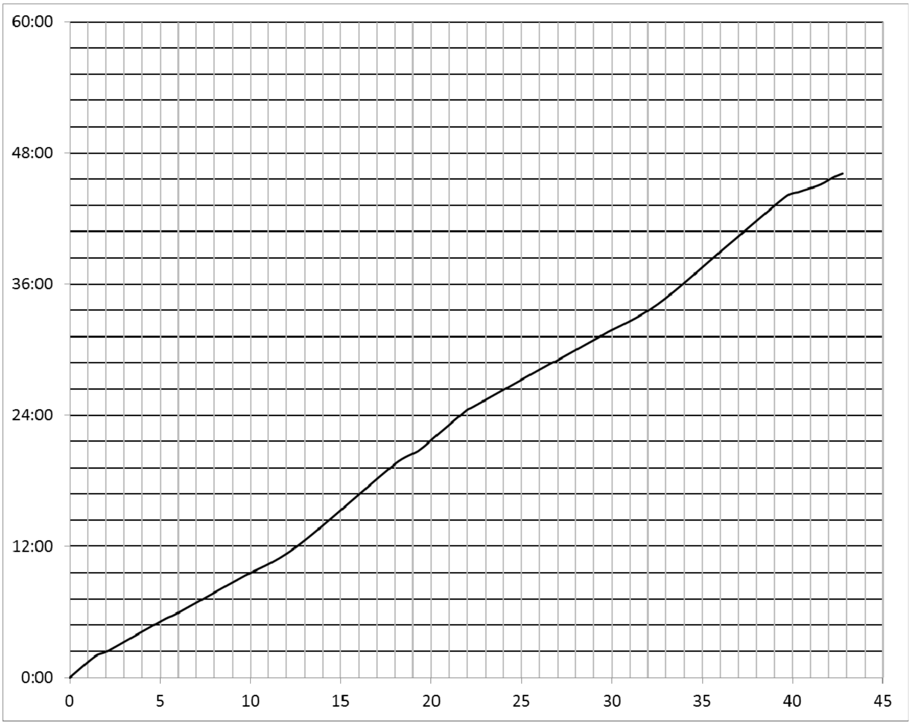

Fig. 3. Time of water sampling in the Southern Bug River on the territory of the Bugzkyi Gard NNP

The starting point is the time of sampling at the first point, which is located on the border of the park. Depending on the distance at which each control point is located, the sampling time will be different. It can be determined using the presented Figure 2. Before the reference the time indicated on the vertical axis should be added.

CONCLUSIONS

1. The study was conducted at the average long-term water level in the Southern Bug River. Therefore, it is advisable to use the information provided only under such conditions. Using this dependence during floods or in the off-season will not give reliable results. Therefore, the study should be conducted in different seasons with variable water levels in the river.
2. Checkpoints should be located at the boundaries of the plots. It may be useful to study changes in the behavior of substances presented in water and their relationship to the hydrodynamics of the river flow.
3. Additional points should be placed below the confluence of tributaries. In particular, the Velyka Korabelna River to understand the degree of their impact on water quality in the main river.

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FORMATION OF RECREATIONAL BALNEOLOGICAL COMPLEXES IN THE POST-INDUSTRIAL TERRITORIES OF THE CARPATHIAN REGION

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ABSTRACT

The research is aimed at creating a balneological medical and recreational complex around salt tailings. The healing properties of salt are increasingly revealing its recreational and tourist potential and promoting the reuse of post-industrial areas. The idea of creating a medical and recreational complex in the post-industrial area is unique. The purpose of the work is to form the foundations of medical and recreational complexes in the post-industrial territories (on the example of the Carpathian region in Ukraine). Research methods: SWOT-analysis as a method of strategic planning, content analysis of scientific areas in related disciplines (on the example of geological research), historical, urban, functional, architectural-spatial analysis, experimental modeling, prioritization. Systematic analysis of the existing sanatoriums on the basis of thermal springs made it possible to identify significant groups of factors influencing their architectural and planning organization, namely: geographical, historical, urban, ecological, socio-economic, socio-economic cultural and structure them by significance. The main directions of research of use of post-industrial territories and their objects are established: political-economic, theoretical-methodological, volume-spatial, functional-planning, social-psychological, historical-cultural, ecological. The town-planning analysis of the territory of the design object is performed. Functional-planning, compositional solutions of the problem and architectural-planning solution of the design object are established.

Keywords: post-industrial territories, tailings pond, balneological complex, recreation, system analysis.

INTRODUCTION

The beginnings of balneology appeared in the V century BC, when the ancient Greek scientist Herodotus proposed a method of consumption and indications for the purpose of mineral waters. The works of Hippocrates (V-IV centuries BC) mention the healing properties of river, salt and sea water. The first classification of mineral waters belongs to the Roman physician Archigen (I century AD) [1]. Mineral waters – groundwater (rarely surface) with a high content of biologically active mineral components. They may have specific physicochemical properties that determine the effect of mineral waters on the human body. Mineral waters contain substances that are also present in the human body. The therapeutic effect of mineral waters is to restore the disturbed balance of these substances in the human body [1].

In Ukraine, the most famous balneological resorts are Truskavets, Skhidnytsia, Morshyn, Velykyi Lyubin, Nemyriv, Khmilnyk, Myrhorod, Kuyalnyk, Nemyriv, Khmilnyk, Slovyansk, Polyana, Berehove, Shayan, Kvasy, Svalyava, Cherche, Horyn.

There is only one Subcarpathian deposit of polymineral potassium ores of sulphate type in Ukraine. These ores are characterized by a very complex and unique complex of salt minerals and an exceptionally high content of clay material. Salt tailing dumps, i.e. place for accumulation of solid salt-loamy waste of flotation beneficiation and brines generated from potassium mining, are located near extraction area. However, upon rehabilitation of territory, protective structures and dams are constructed. This comprehensively prevents the ingress of brine and salt streams into fresh water (lakes, rivers, and groundwater). There are many options and proposals for solving the problem of brine accumulation in tailing dumps. However, the best of them is the processing of brines. This would solve ecological problems and promote the development of production at the same time. Brine concentration in reservoirs would gradually decrease in the course of brine processing and would reach such a level that is suitable for arrangement of recreation areas for people. The potential of curative properties of local salts is being actively studied. However, spontaneous recreation is already developing, people bathe in salt water and feel the positive effect. Specialists from Ivano-Frankivsk National Medical University studied the effects of brines from the Dombrovsky quarry and tailing dumps on the human body. First results of this study showed that the use of water from our salt water bodies for the treatment of joints, musculoskeletal system, psoriasis and other diseases is much more effective than, for example, water from Solotvino [2].

Availability of favorable natural sources for treatment determines the planning organization of therapeutic complexes. This study is aimed at creating a unique medical and recreational complex around the salt tailing dumps since therapeutic potential of salt reveals its recreational and tourist potential and promotes the reuse of post-industrial areas. Balneological complexes have been studied both in Ukraine and abroad. However, there is little revitalization of the post-industrial territory and the use of natural resources, namely salt tailing dumps in Ukraine and around the world. The idea of creating a medical and recreational complex in the post-industrial area is unique.

Due to the conduct of comprehensive analyzes and examples of the use of post-industrial areas for recreational function, the interaction of the designed environment and its environment is determined. It is also important to understand that a person who receives treatment can also relax, using all available recreational services.

Surrounding resources create a recreational profile of a certain landscape. The needs of nature protection, economic and technical conditions of landscape development for a specific type of recreational activity contribute to its transformation, recreational development and landscaping, i.e. the creation of recreational systems [3]. Therefore, the fact of changing former industrial enterprise (factories, plants, mines) to the "industrial heritage" should be considered natural.

The aim of the work is to create medical and recreational complexes in post-industrial territories (on the example of of the Carpathian region in Ukraine).

Objectives of the study: 1) to determine the factors that influence the study of revitalization of the post-industrial area (for example, the area around the salt tailing dumps; 2) to determine the method of functional-spatial study of the revitalization of the industrial area for medical and recreational complex; 3) to form the concept of medical and recreational complex in the post-industrial territory (on the example of the territory of the salt tailing dump); 4) to propose an architectural and planning organization of the medical and recreational complex with the use of natural resources of the territory for medical purposes in the post-industrial territory (on the example of Bolekhivtsi village, Drohobych district, Lviv region).

Tailing dump is a hydraulic structure, a complex of special structures and equipment designed for storage or disposal of radioactive, toxic and other tailings from mineral beneficiation. The concentrate is obtained from extracted ore at mining and processing works (MPW) and tailing is transferred to tailing dump. The tails come in the form of pulp (sand, water).
To determine the architectural and planning features of the newly created recreational balneological complex in the post-industrial territory, the peculiarities of the formation of the recreational environment, planning organization and directions of revitalization of post-industrial territories were determined. The typology of recreational facilities is determined by number of uses, location, number of functions, etc.

METHODS AND EXPERIMENTAL PROCEDURES

The research methodology is based on the following research methods: SWOT-analysis as a method of strategic planning that comprises identifying actors of internal and external organization of the environment and dividing them into four categories (strengths, weaknesses, opportunities, threats). Content analysis of scientific directions from related disciplines (on the example of geological research), historical analysis, urban analysis, functional analysis, architectural-spatial analysis, experimental modeling, and determination of priorities are also used.

General information about studied objects.

Bolekhivtsi is a village in the Drohobych district in Lviv Region of Ukraine. The village is located seven kilometers from the district center, near the river Solonytsia. The population of village is 2351 people. Bolekhivtsi village has an advantageous location in terms of transport corridors, railways and highways. The Europe-Asia corridor, the Berlin-Kyiv transport corridor and the Kyiv-Chop international routes are located near the village (Fig. 2, Fig. 3).

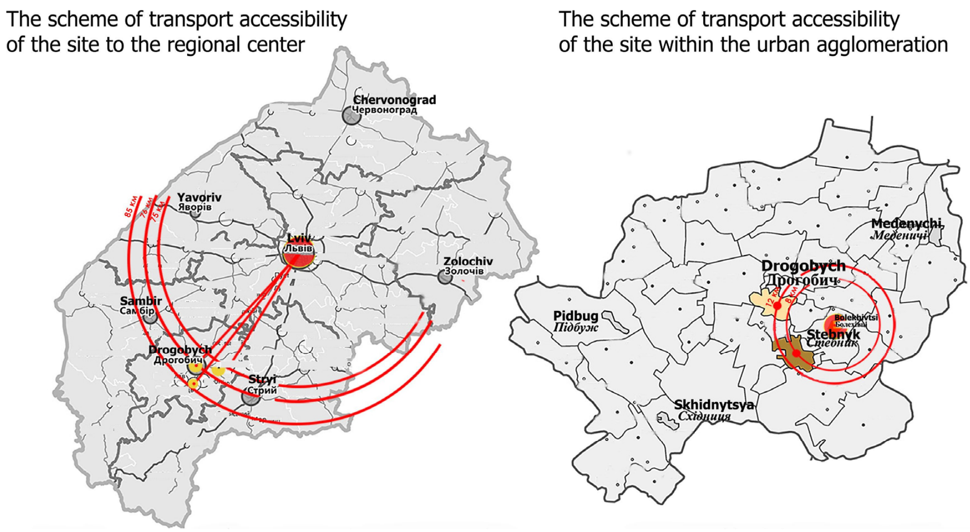


Fig. 1. Location of the design area within the region and urban agglomeration (Onufriv and Bai)

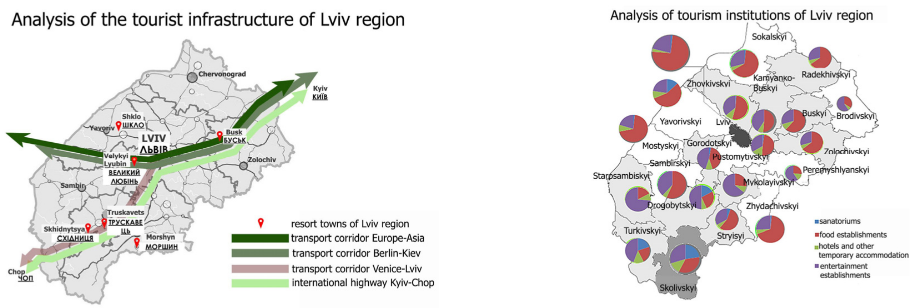


Fig. 2-3. Analysis of tourist infrastructure and tourism istitutions of Lviv region (Onufriv and Bai)

THE RESEARCH RESULTS AND DISCUSSIONS

Analysis of the problem, the level of its research.

Systematic analysis of existing sanatoriums on the basis of thermal springs made it possible to identify significant groups of factors influencing their architectural and planning organization, namely: geographical, urban, socio-economic, functional, engineering and technical, aesthetic, historical factors and structure them by significance (Fig. 4). Based on the analysis of international experience, the relevance of the cognitive and tourist potential of the monuments of mining heritage in different regions of the world and Ukraine is justified [4].

-potential for use of the reservoir for medical and recreational purposes; - landscaping of adjacent territories; -distance from highways; -plain relief of the design area; -available forest and water resources; -distinguishing different types of spaces	-insufficiently developed i nfrastructure; -poor condition of roads; - lack of land use; -wetland; -lack of engineering support of the site; -possibility of overflow of salt tailings	-development of the village and its infrastructure; -tourist and recreational opportunities; -providing jobs for the local population; -large area; -availability of valuable natural resources - salt brine, which has health-improving properties	-degradation of the ecological condition of the territory; -natural and man-made disasters; -threat of abyss formation; -threat of overflow of salt tailings in the absence of reconstruction

Fig. 4. SWOT analysis

Today, the change in the type of demand of the population for treatment and rehabilitation services is clearly visible. Previously, sanatoriums focused on elderly people, but today they attract middle-aged people, who prefer active recreation and people who have time restrictions. The number of people who maintain a healthy lifestyle and want to be in good shape and need recovery programs shows considerable increase. Therefore, sanatoriums become multifunctional centers of leisure, rehabilitation and treatment [5].

The topicality of the issues of functioning, dynamics and development of post-mining geosystems of the Western region of Ukraine is growing today. Until recently, various types of minerals were developed in the region: hard and brown coal, oil, gas, peat, mineral wax, native sulfur, sodium, potassium, magnesium salts, etc. Differences in the technology of their extraction and enrichment result in specificity and different level of anthropogenic transformation of the natural environment. It should be noted that most of the mining and processing enterprises of the Western region of Ukraine are in a critical, often emergency situation, on the verge of their liquidation and require optimization measures. Moreover, the effectiveness of these measures provide for understanding of the peculiarities of geospatial organization and functioning of post-mining geosystems, their origin, dynamics of complex natural anthropogenic processes, restoration of soil and vegetation cover, etc. [5].

The experience in designing recreational complexes and methods of revitalization of the post-industrial territory are analyzed separately. It was found that:
– the interaction of the post-industrial territory and its environment is always reversible. Depending on how it is decided to use former industrial area, it is possible to significantly increase or decrease the investment attractiveness of the territory and its environment since inflow of investment is the dominant factor that determines success of the project [6].
– main factor in territory planning is the location of the territory and the availability of natural resources.
– the most difficult problems in planning and urban reorganization of post-industrial areas arise at mining areas [7].

Basis for creation of recreational environment.

The recreational area is formed as an independent industry, a new component of the economic system. The development of the recreational industry involves a continuous search for the optimal relationship between the development of natural resources and the restoration of their properties, between the preservation of unique natural areas and meeting the needs of the population in recreation. Depending on the types of free time, the rest may be daily, short-term and long-term, each of them corresponds to certain type of area [8]:

– urbanized areas, which have large mono - or polycentric forms of settlement with a leading industrial function (for example, Donetsk recreational region), which require the organization of suburban recreation;
– recreational and urbanized areas with large recreational centers, group resettlement systems, recreational agglomerations, providing short-term and long-term recreation, tourism, treatment (for example, the Crimean recreational region);
– non-urbanized areas, having recreational settlements that are located outside influence of large cities, have dispersed settlement patter and provide long-term recreation, specialized tourism and treatment (for example, the Carpathian recreational region).

Recreational resources can be divided into three groups:
– A – intensively used due to the high degree of their readiness for development;
– B – extensively used;
– C – non-used at this time for a number of reasons, primarily due to the lack of stable transport links with populated areas [8].

The territories of the recreational area contain the following functional zones: recreational, settlement, communal and economic; organized and natural landscape, sanitary protection zone

of transport communications and pedestrian communications.
The area of organized recreational natural landscape is defined by three natural elements: green plantings; water areas and their shores; reliefs [8].
Recreational areas, differing in functional (typological) features, can be multifunctional or monofunctional, the Carpathian region can be used for sports and tourism (41% of medical and 56% of tourist facilities) [8].
In modern recreational areas, the service system is formed on the basis of urban or social concepts [9].

"SPA" is a modern trend of recovery based on mineral baths. SPA-centers offer treatment with mineral and sea waters, algae and salts, therapeutic muds and plants. Wellness is interpreted as well-being and high vitality. In general, SPA and wellness are not only physical, but also emotional, spiritual and social health. Such complexes meet the modern needs of the population in the field of health and leisure. They require architectural planning and special approach to design.

Environmental issues of Stebnyk State Mining and Chemical Enterprise "Polymineral"

The analysis of researches of environmental issues of extraction of potassium mineral fertilizers testifies to existence of a fundamental basis of the phenomenology of ecological safety of mining regions of Ukraine [10, 11], summarizes numerical, in-depth and detailed, but fragmentary and heterogeneous results of geoecological researches of salt-mining industrial complexes. Works [12–16] are devoted to landscaping, geological, geographical research of the impact of the mining industry on the environment. The issue of engineering protection of salt and sulphur deposits in the Carpathians is covered in papers [17–20]. The production of potassium-magnesium concentrate has been accompanied by the formation of a huge amount of waste in the form of sludge - "tailings". These are fairly stable fine suspensions. Their main components are salt brines, halite and sludge solid waste, which are formed as a result of potassium ore processing. The amount of waste from the production of potassium salts at the Stebnytsky State Mining and Chemical Enterprise "Polymineral" reached more than 25 million 478 thousand tons (of which 4 million 162 thousand tons is the liquid phase). The tailings pond located on the north-eastern outskirts of Stebnyk near the Solonytsia River, a right tributary of the Tysmenytsia River, is provided for their accumulation and storage almost for a limited period. A tailings pond is a hydraulic structure, a complex of special structures and equipment designed for storage or disposal of radioactive, toxic and other non-utilizable waste from mineral beneficiation. At mining and processing plants (MPPs), concentrate is obtained from the extracted ore, and processing waste is moved to tailings. The tailings come in the form of pulp (sand, water).

The tailings pond has two sections with a total area of about 125 hectares. The area of the first section is 69 hectares. The second section is filled with brine and divided by a bridge into two sections – south and north, with an area of 28.9 and 26.9 hectares, respectively. An average of 1,612,000 m^3 of precipitation falls annually on the entire area of the tailings pond, and about 572,000 m^3 evaporates therefrom, i.e., the excess water is 1,040,000 m^3 per year. The total volume of waste together with precipitation increased in the tailings by an average of 1,368 thousand m^3 per year.

Stebnykivsky tailings pond in September 1983 caused an ecological catastrophe – after heavy rain there was a breakthrough of the soil dam of the tailings pond, a huge mass of highly concentrated brine and solid waste (silt) rushed into the Solonytsia river basin, and from there - into the Tysmenytsia river, and further into the Dniester and Black Sea. The total mass of this discharge was over 5 million tons, it was a mudslide with a powerful hydraulic pressure. A huge mass of salt waste polluted the entire surrounding area (rivers, gardens, orchards, fields, forests). This caused great damage to the flora and fauna of the district, as well as to the aquatic organisms of the Solonytsia, Tysmenytsia, Dniester rivers and the Black Sea. The damage to the environment was estimated at 100 million Soviet rubles.

The negative impact of the tailings on the environment is caused by the pollution of the hydrosphere with salt water, which is due to the positive water balance in the tailings; such man-made "dead" lakes not only occupy large land plots that are withdrawn from agricultural use, but also pose a constant threat to nature and nearby settlements. Thus, the mined and unfilled mine openings and the tailings of Stebnytsky State Mining and Chemical Enterprise "Polymineral" pose a threat to technogenic safety of Lviv region.

The issues of Stebnytsky State Mining and Chemical Enterprise "Polymineral" were the cause of induced earthquake and hydraulic shock, recorded on September 30, 2017 (Fig. 5). Within a few months, water began to accumulate at the bottom of the sinkhole No. 27, and in April 2018 a subtriangular karst lake with a length of 85 m and a width of 48 m, a depth of approximately 5 meters, an area of 0.31 ha and a volume of 5000 m3, as well as a satellite lake, which is clearly visible on the Google Earth space image as of April 28, 2018 (Fig. 6) [21, 22].

After heavy rainfalls in late May - in the first half of June 2019, the water level in the karst lake rose by 1 m, and the area increased significantly. The subtriangular karst lake has taken more isometric shapes, with a length of 110 m and a width of 64 m, a depth of 7 meters, an area of 0.427 ha and a volume of 30,000 m3. The slopes of the karst hole are quite stable. Although no landslides were observed as of June 2019, but the slope and especially linear erosion has been intensified during periods of heavy rainfalls, in particular, near-surface-cut ravines have appeared to a depth of 1–1.5 m on the western slope.

Fig. 5. Sinkhole on unit № 10 of South-East mine No. 2 of Stebnytsky Mining and Chemical Enterprise "Polymineral" in the area of chambers No. 108-113, which occurred on September 30, 2017

Fig. 6. View of sinkhole No. 27 and the subtriangular karst lake on the Google Earth satellite image as of April 28, 2018

On March 15, 2020 at about 11.00 in the area of chambers 102-104 at a distance of 70 m north of sinkhole No. 27, which occurred in 2017, a new karst hole No. 30 with a diameter of about 130-150 m with very steep, almost vertical walls, which constantly slid down (Fig. 7). The new hole did not affect the level of the karst lake in sinkhole No. 27, which occurred on September 30, 2020, which is evidence of the lack of hydraulic connection between the sinkholes and the nature of the sinkholes themselves determined by us, associated with the cutting of pillars by aggressive waters and their caving over time.

In the first days after the caving, sinkhole No. 30, which occurred on March 15, 2020 was dry, despite the fact that at a distance of 70 m there was a karst lake with a water volume of more than 35 thousand m3 and a depth of about 8 m. Three months after the caving, as of June 23, 2020, a karst lake began to form, and its subvertical walls began to become more stable, but still quite steep with angles of 35 to 45 degrees, and in some places up to 60 degrees (Fig. 8).

Landslides and mudflows, especially during periods of heavy rainfall, have significantly reduced the depth of the sinkhole, which is now about 45 m from the day surface, and the size

of the sinkhole on the periphery according to the measurement results is from 143 to 167 m. In the next few years further caving of the walls to the angle of natural repose is about 30 degrees, similar to the view that is now typical of a karst lake in the sinkhole, which occurred on September 30, 2017.
The effect of karst processes is the subsidence of the earth's surface and the activation of karst phenomena with rapid development and intensity of manifestation, large areas of spread and depth. In the area of influence of underground cavities there are residential buildings of Stebnyk, high-voltage power lines, water supply networks of the cities of Drohobych and Truskavets, the national railway Kyiv-Truskavets, the highway. Underground workings reach the II-III zone of sanitary protection of the resort Truskavets. Destruction of cavities can cause induced earthquakes, which can cause damage to buildings in Stebnyk, Truskavets and Drohobych, the destruction of the tailings.

Fig. 7. Sinkhole No. 30 with a diameter of about 150 m immediately after the formation as of March 15, 2020

Fig. 8. Sinkhole No. 30 with a diameter of about 150 m immediately after the formation as of March 15, 2020

To develop constructive measures to ensure the environmental safety of the Ministry of Internal Affairs in Stebnyk, it is advisable to develop a system for monitoring karst subsidence and landslides [23, 24]. An automated information-analytical monitoring system is proposed, which includes: networks of vibroseismic sensors for registration of landslides [25]; system of data analysis and forecasting of geodynamic processes; alarm system, prompt notification and response. The objective of the monitoring system is to obtain up-to-date space-time information on karst and waste-protected processes to prevent emergencies, scaling and consequences [24]. The use of geo-information systems will allow to promptly forecast the development of the situation, to ensure risk management of possible emergencies, performing functional tasks: technological and geophysical; information-analytical; operational and managerial [25].

Directions of revitalization of post-industrial territories.

Today, the use of post-industrial buildings and areas is improved and studied more and more frequently.

The main directions of study of the use post-industrial territories and their facilities are as follows: political-economic, theoretical-methodological, spatial-spatial, functional-planning, socio-psychological, historical-cultural and ecological [6]. The economy determines the future function of the post-industrial facility. The environment, which was formed around the area used for certain type of industry, now has all chances to create new potential function for such area.

Having analyzed the natural potential, tourist infrastructure of the district and analyzed resorts with reservoirs of the region, we established the following:
– the location of the design site is advantageous in terms of easy tourist accessibility since it is

located on existing tourist routes (Fig. 9);
– based on the analysis of existing resorts with mineral waters of Drohobych district, Lviv region as a whole, it was found that currently there is no resort complex with salt pools and baths in the post-industrial areas (Fig. 10).
On the territory of the village there is a state mining and chemical enterprise that is formerly called "Stebnyk Potassium Plant". The Stebnytsia deposit of potassium salts was mined by two underground mines. The development was carried out by system of subdrifting chambers, the height of which reached 40-60 m.

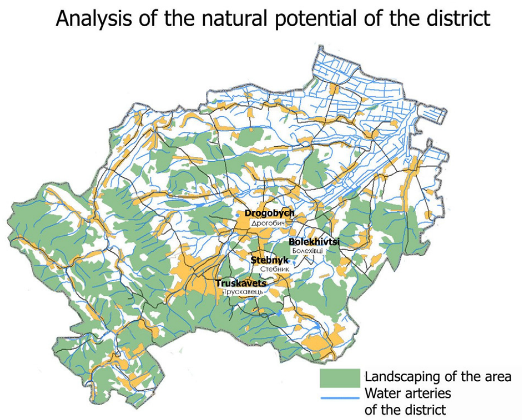


Fig. 9. Analysis of the natural potential of the district (Onufriv and Bai)

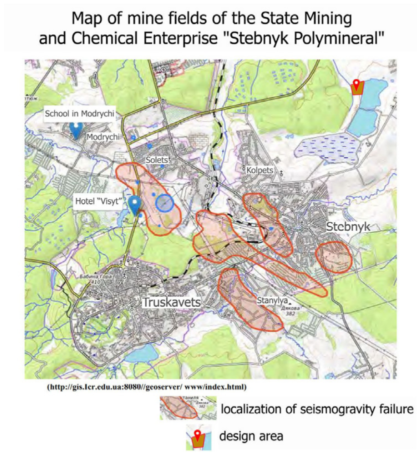
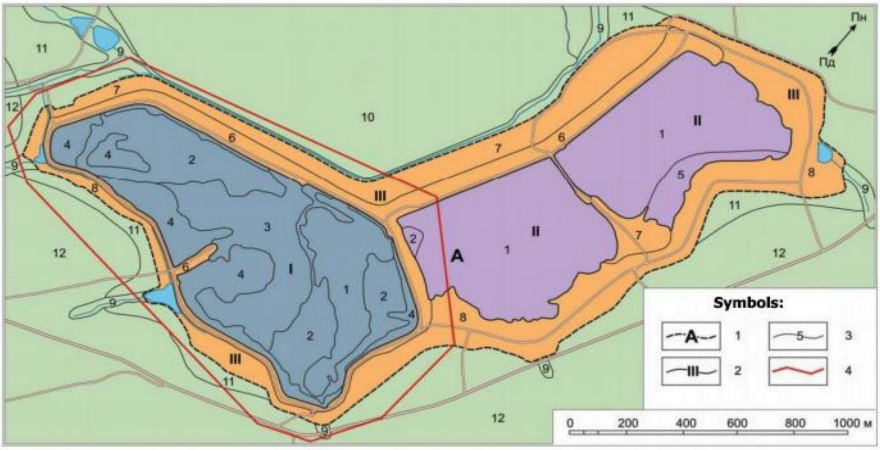


Fig. 10. Map of mine fields of State mining and Chemical Enterprise "Stebnyk Polymineral"

The tailing dumps formed on the territory contain wastes of a chemical dressing plant. They were transported by pipeline. Inefficient technology for processing of polymineral ores has led to the formation of a tailing dump, resulting in salinization of groundwater and adjacent soils [26]. The tailing dump is a man-made reservoir limited by dams, to which wastes of liquid consistency of flotation ore benefaction were transported. The tailing dump of Stebnytsya state mining and chemical company "Polymineral" consists of two sections with a total area of about 125 hectares. The first section comprises 69 ha of solid phase of salt-loamy waste of flotation beneficiation. The second section is filled with brine and divided by a bridge into two sections, southern and northern, with an area of 28.9 ha and 26.9 ha, respectively [27] (Fig. 11).
The water in the lake is weakly mineralized, hydrocarbonate-chloride-sulfate sodium-magnesium-calcium in all tested strata [28, 29].
In terms of chemical composition, the deposits of potassium salts of the Stebnytsky field belong to the sulphate salts. They are characterized by a very complex and peculiar compound of salt minerals and an extremely high content of clay material (10-15%, sometimes up to 25%). The main potassium rocks are kainite, langbeinite and kainite-langbeinite. The most common rock-forming minerals are the following: kainite, langbeinite, less common: polyhalite, kieserite, sylvite, scheonite, leonite, astrakhanite, anhydrite, rarely vanthoffite, loweite. An integral part of all potassium-containing salt rocks is halite. In the zones of hypergenesis of salt deposits the following minerals are formed: gypsum, kaluszite (syngenite), glaserite mirabilite, scheonite, epsomite, hexahydrite, astrakhanite; vanthoffite and loweite are rare.
If the mineral composition of the Stebnyk field was limited to the above-mentioned minerals, such ores would be extremely valuable: it was enough to extract, crush, sift the necessary fractions, pack or ship to consumers potassium-magnesium-sulphate, almost chlorine-free long-acting fertilizers.
However, the ores contain two other minerals that significantly degrade the quality of ores and

complicate effective beneficiation – it is halite (NaCl) with a content of 30-40% and clay minerals, clay and siltstone-sandy terrigenous material, which should also be included in the main rock-forming components. In terms of mineralogy, the "insoluble residue" is dominated by quartz, chlorite and hydromica, with subordinate values of feldspar, calcite and dolomite, their total content varies from 12 to 20%, and the K_2O content in the ores of the Stebnytsky field is only 10-12%.



Landscape structure of the tailings of the Stebnyk State Mining and Chemical Enterprise "Polymineral" and its environs. Map scale 1: 5000. (Ivanov, Rudko, 2019)

Symbols: 1 - boundaries and indices of landscape areas; 2 - borders and indices of landscape strips; 3 - boundaries and indices of landscape tracts; 4 - the limits of the model area "Stebnyk tailing"

Fig. 11. Landscape structure of the tailing dump of Stebnyk State Mining and Chemical Enterprise "Stebnyk Polymineral" [14, 15].

Brines of potassium deposits have unique therapeutic properties confirmed by studies of Balneotherapy Institute [30]. Based on this fact, it is possible to determine therapeutic properties of bathing in water with potassium salts: water or brine baths (thalassotherapy) and air baths (aerotherapy) favorably influences treatment of disturbances of gastric activity, gout, leukemia, gout, and diarrhea. This therapy is used for treatment of children who suffer from tuberculosis, and rickets. They are useful in healing wounds and cuts, skin diseases [22].

Thus, the object of study is relevant today since it has a unique direction of revitalization of the territory, namely, the use of natural resources for therapy and recreation.

Factors influencing the object of study:

- soils on the territory contain salt-loamy deposits filled with brines;
- the surrounding vegetation is halophytic and hydrophytic, partly trees and bushes. To maintain filling of the solid phase section of the Stebnytsya tailing dumps with vegetation, it is necessary to regularly reduce the level of brines or completely discharge them into the adjacent section of the liquid phase. (E. Ivanov, 2020);
- the climate in Stebnyk is temperate-continental with mild winters and warm summers. The average temperature is –4 ° C in January and + 18 ° C in June. Its location in the foothills of the Carpathians has a significant impact on the climate. The average indicators of the city's climate characteristics are obtained during long-term observations for the period from 1899 at the stationary observation station in Drohobych city [31].

According to the "Regional Report on Environment of Lviv Region in 2018" being a part of the

National Report of Ukraine on Environmental Conditions, published in 2019, the radiological condition in the Lviv region was generally stable and within the natural radiation background. Extremely high levels of radioactive contamination were not observed [31].

"The impact of post-industrial territory on the environment, depending on how it is decided to use post-industrial area, may significantly increase or decrease the investment attractiveness (and often the inflow of investment is the dominant factor determining the success of the project) of territory and its environment" [32].

Functional differentiation is mainly based on the creation of hybrid (or multifunctional) structures that complement each other. In the structure of post-industrial environment, such versatility, according to the studied examples, provides many opportunities for quality development of space, creating new challenges for the city [6].

Urban analysis of the territory of the project object.

Project area is located in Bolekhivtsi village in the Drohobych district of the Lviv region. The village is located seven kilometers from the district center, on the banks of Solonytsia River. Salt tailing dumps, created due to extraction of potassium salt, are located near the selected area. These tailing dumps are in an emergency state and pose an environmental threat to the surrounding rivers and groundwater since atmospheric precipitation rises water levels and salt brine may pour out.

Cemetery with a sanitary protection zone of 100 m is located on the opposite side of the tailing dumps are located. The sanitary protection zone around the tailing dumps is 100 m. The northern side of the site borders with sanitary protection plantings.

S. Bolekhivtsi has a very favorable location in relation to transport, railways and highways. The Venice-Lviv corridor and the Kyiv-Chop international route pass close to the village.

After analyzing the natural potential, tourist infrastructure of the district as well as resorts with medical and recreational complexes in the region, the following conclusions were made:
- the location of the design site is advantageous in terms of easy tourist accessibility, because it is located on existing tourist routes;
- The analysis of SPA resorts with mineral waters of Busk district, Lviv region shows that there is no resort complex with hot springs and outdoor pools of healing water.

The analysis of factors influencing the object of study, analysis of the territory as a sub-industrial object, analysis of medicinal properties, transport routes, tourist potential of the region and district and analysis of current state of the village were carried out in order to determine location of projected complex. It has been decided that project area around salt tailing dumps is potentially advantageous in all aspects.

Functional-planning and compositional solutions of the problem.

According to the main factors of the organization of medical and recreational complexes, it is planned to form tailing dump around existing reservoir (fig. 12).

For the selected projected object and restoration of the post-industrial territory with arrangement of medical and recreational complex on it, the following functional components of the general plan territory were selected: the existing salt tailing dumps; designed freshwater pools; designed therapeutic baths with salt water; hotel with restaurant; summer houses on the water; Spa complex; summer cafe with a pier; park area; parking lots for various purposes; sports fields (Fig. 13).

The main idea of this complex is the use of water with potassium salts, the properties of which are unique in Ukraine and around the world. Such strong healing waters are absent in Europe, Black and Azov Seas, the Mediterranean and Atlantic. Ukraine can really improve the health of its people as well as population of Europe and the world and, along with medical treatment, receive significant profits from medical tourism from the countries of the Ukrainian diaspora, Europe and Asia, the Arab world and other countries.

Interconnection between different functional areas is ensured by means of walking connections. Layout of site complies with all sanitary protection zones, deviations and gaps. It is planned to improve existing tailing dump with summer cafes and single-family houses, as well as a yacht club, with a place for storing water and boating equipment (Fig. 14).

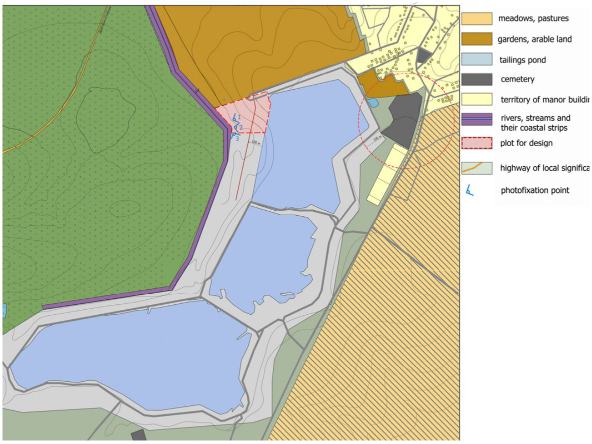


Fig. 12. Reference plan of he site "Stebnyk tailling" (Bai)

Fig. 13. Functional zoning scheme (Bai)

Fig. 14. General plan (project) (Bai)

Architectural and planning concept of projected object. The main goal that influenced the planning organization of the complex is to create a whole object in which all the functional components are harmoniously combined. The object itself must fit to environment and has modern architecture and comfortable territory (Fig. 15) [33].

This can be solved by designing open and functional spaces, simple and logical planning, which would end with the exterior.

The hotel should be four-story and designed for 100 visitors with different types of rooms, some of which will provide view of the tailing dumps, and some will provide view of green part of front area. The restaurant has 2 floors with a large terrace on the 2nd floor.

The spa complex is designed as a two-story building. The first floor comprises swimming pools, baths, spa tub, changing rooms, reception and staff room. The second floor comprises medical and salt rooms, rooms for massages and other medical procedures, rooms for short stay of visitors.

Fig. 15. Visualizations of the projected object (Bai)

CONCLUSION

The problem of using post-industrial zones as territories that have been removed from the economic and functional development of the environment is primarily relevant today. Rehabilitation of these areas is a key point for the restoration of biologically active post-industrial structure. In this case, the rational solution to this problem in the Bolekhivtsi village of Drohobych district is expedient and profitable. The availability of salt tailing dumps, favorable relief and favorable location is a good condition for work.

Peculiarities of the formation of the recreational environment, layout and directions of revitalization of post-industrial territories are determined in order to determine the architectural and planning features of the newly created recreational balneological complex in the post-industrial territory

The typology of recreational facilities is determined by number of uses, location, number of functions, etc.

All factors based on which medical and recreational complex (soils, climate, and vegetation) was designed are considered in this paper. This will allow revealing the new potential of the district and region, creating a unique recreation area for villagers and travelers from other cities or countries as well as new jobs.

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FEATURES OF THE NEUROTECHNOLOGIES APPLICATION AND GEOGRAPHIC INFORMATION SYSTEMS FOR MODELLING AND FORECASTING OF SURFACE WATER QUALITY

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ABSTRACT

The state of water bodies and water intake basins of Ukraine indicates that further economic development is no longer possible on the basis of traditional extensive methods of use state of water resource potential. To strike a balance between the demand for water and the water capacity of the water resources, ensuring the appropriate level of ecological safety in river basins there is a need to have a developed scientific-methodical basis for forecasting their condition. A Machine learning based GIS for water management is a major area of research to promote a country's economy. This research discusses application Artificial Neural Network (ANN) and Geographical Information System (GIS) models on water quality. The integration of Geographic Information Systems and Artificial Neural Networks offers a mechanism to lower the cost of analysis of landscape change by reducing the amount of time spent interpreting data. The purpose of the work is to evaluate the possibility of using neural networks and geoinformation systems to predict surface water pollution in Lviv region.

Keywords: Artificial neural networks, Geographic information Systems, water quality, Lviv region

INTRODUCTION

Water is considered one of the most important natural resources not only for a country or state but also for the entire human race [1–7]. The urgent tasks to ensure water security are to reduce pollution of water basins, ensure sustainable use of water resources, the introduction of effective regulation of extraction of aquatic resources [8–14]. The monitoring of water quality has the highest priority in the policy of environmental protection [15–18]. The major purpose of this monitor is for controlling and minimizing the incidence of pollution problems, and for providing quality appropriate for water to serve various purposes like irrigation water, drinking water supply, etc. [19–20].

Today, under the conditions of the negative effects of the influence of both natural and, especially, anthropogenic factors on the natural environment, the automated control systems of the state of the environment as a whole and its separate components become widespread. Enough known in the ecology are systems that perform only monitoring functions of certain parameters of the state of the environment, but to manage the environmental state of the environment is not enough.

The methodology of space-time modeling and prediction of surface water quality indicators consists of three main stages [20]:

1. Data Preparation – Creating an attribute relational geodatabase.

2. Data processing – prediction using neural networks.

3. Data visualization – spatial modeling using GIS technology methods and tools.

An artificial neural network (ANN) is a computational model based on the behaviour of neural networks of living organisms [21]. An artificial neural network differs from other forms of computer intelligence in that it is not rule- based, as in an expert system. An ANN is trained to recognize and generalize the relationship between a set of inputs and outputs [22].

Neural networks are used to predict outcome data through input data in a manner that simulates the operating system of the human nervous system. The basic benefit of NNs is that they don't use any mathematical model, because they can learn from data set and determine patterns in a series data of input and output without providing previous assumptions about of their type and interrelations [23]. Generally, the model is able to simulate non-linear (i.e. dynamic or static) behaviors within the assessment process and able to handle ordinal outputs like condition classes. In the case of water quality modeling, the relationship between independent variables (water quality parameters) and dependent variable (water quality index) are studied through learning from past data of water quality [24].

Geographical Information System is a set of software that allows for creating, visualizing and analyzing geospatial data. Geospatial data refers to information about the geographic location including the geographic coordinate, like a latitude or longitude value. While spatial data includes geographic data, map data, GIS data, location data and spatial geometry data, so that these data can be analyzed and integrate for deriving useful outputs and modeling [25]. GIS techniques have been developed to facilitate the integration and analysis of large amounts of multidisciplinary data, whether spatial or non-spatial within the same geographic reference. The spatial analysis of GIS can allow interpolation of water quality index at unknown location through known values for creating a continuous surface helps to understand the water quality condition scenarios of the study area. Hence, tools of the spatial analysis are used to re-classify water quality index into a various categories and each category is specified with a unique number. The spatial distribution model has been adopted for creating analytical maps for water quality index [26].

Geographic information system concepts and technologies are applied expansively in current water resources engineering, design, planning and operations and are changing the way these ehavior are accomplished.

Geographical Information Systems has become a progressively more significant means for understanding and dealing with the critical problems of water and related resources management in our world. GIS concepts and technologies help us collect and organize the data about such problems and understand their spatial relationships [26]. GIS analysis capability offer methods for modeling information that contribute to sustaining decisions for resource management over a wide range of balance, from local to global. GIS provides a way for visualizing resource characteristics and thus improving the understanding in support of decision making [25, 26].

The Machine learning technique is a swiftly emerging area of predictive odeling that is concerned with identifying structure in complex, often nonlinear, data and generating accurate predictive models. Machine learning approaches regularly demonstrate superior control for solving multifaceted relations. Machine learning approaches are not limited to the conventional assumptions normally used with traditional and parametric approaches [27].

METHODS AND EXPERIMENTAL PROCEDURES

The possibility of using artificial neural networks and geoinformation systems to simulate and predict changes in the concentration of pollutants of surface waters of the Lviv region of Ukraine is considered [28]. To analyze and forecast the indicators of surface water pollution in Lviv, a trained neural network was created using the Python programming language and the Keras library. Keras is an open source Python library that makes it easy to create neural networks. The library is compatible with TensorFlow, Microsoft Cognitive Toolkit, Theano and MXNet. Tensorflow and Theano are the most commonly used Python numerical platforms for developing deep learning algorithms, but they are quite difficult to use [29, 30].

Experimental data were obtained from the results of monitoring of the state of the environment of Lviv region. Observation of the state of surface water in Lviv is carried out by the Communal Enterprise "Administrative and Technical Administration" of the Lviv City Council. Nine water parameters were used for modelling and forecasting quality of surface water: biological oxygen demand, Total Dissolved Solids, Dissolved Oxygen, Sulphate, Chloride, Nitrate, Nitrite, Orthophosphate. In our dataset, the input is of 8 values and output is of 1 values. So the input and output layer is of 8 and 1 dimensions respectively.

Data will be represented as an n-dimensional matrix. We will stick with CSV file-format in this article. CSV (Comma Separated Values) file formats can easily be loaded in Python in two ways. One using NumPy and other using Pandas. We will use NumPy.

Below is the code to import all the necessary libraries and load the dataset (fig. 1).

Line (1-3) handles the imports to build our deep learning model using Keras.

Line (6-7) fix a seed for reproducing same results if we wish to train and evaluate our network more than once.

Line (10) loads the dataset from the .csv file. It uses an argument delimiter to inform NumPy that all attributes are separated by , in the .csv file.

Line (13-14) splits the dataset into input and output variables.

Line (17) splits the dataset into training (67%) and testing (33%) using the scikit-learn's train_test_split function. By performing this split, we can easily verify the performance of our model.

```
# organize imports
from keras.models import Sequential
from keras.models import Dense
from sklearn.model_selection import train_test_split
import numpy as np

# seed for reproducing same results
seed = 9
np.random.seed(seed)

# load pima indians dataset
dataset = np.loadtxt('dataset.csv', delimiter=',', skiprows=1)

# split into input and output variables
X = dataset[:,0:8]
Y = dataset[:,8]

# split the data into training (67%) and testing (33%)
(X_train, X_test, Y_train, Y_test) = train_test_split(X, Y, test_size=0.33, random_state=seed)
```

Fig. 1. Import all the necessary libraries and load the dataset.

Common methods of visualization the results of the analysis of any data are: graphs, charts, tables and more. However, given the specific nature of research in various applications areas, in particular in hydrologic, are not always specified methods of description results allow you to evaluate the results quickly and efficiently [31, 32]. Increasingly in various application areas for analysis and results visualization uses GIS technology. GIS are intended for the collection and storage, processing and analysis, display and distribution of space-coordinated information. The most complex solutions include expert support and allow us to obtain reasonable conclusions that needed to make decisions according to the task. The end result of GIS is the display of data in the form maps or graphics. The use of GIS software enables y map the observation data and results data analysis, modeling of technological and natural processes and more [32].

One of the main tools and purpose of GIS is data visualization. GIS contains interactive and other types of maps that operate on geographic datasets. Maps is a powerful model image for defining and standardizing how people use and interact with geographic information. Interactive maps are available on many levels: from maps for wireless mobile clients to Web-based maps in browsers and maps in powerful desk [32].

A popular enough and powerful tool for hydrological research is a line of software products from the company ESRI under the common name ArcGIS [32]. One of ESRI's software systems is ArcGISDesktop. ArcGISDesktop is a full-featured, scalable system, designed for a wide range of users. Includes three interconnected base applications: ArcMap, ArcCatalog, ArcToolbox. ArcMap is the basic ArcGISDesktop application. Used for all mapping tasks and includes map creation and analysis, editing data. There are two ways of displaying and using ArcMap work with maps: 1) in the form of geographical data and 2) in the form layout that allows you to solve a variety of GIS tasks.

ArcCatalog is designed to structure and manage data, search and view geographic data, create and view metadata, etc. Arc Toolbox is a simple application to have location processing tools. ArcGIS Desktop software components are available in the form three software products: ArcView, ArcEditor, and ArcInfo providing mapping and analysis capability, simple tools editing and geoprocessing [32].

THE RESEARCH RESULTS AND DISCUSSIONS

In Keras, a model is created using Sequential. We will create a model that has fully connected layers, which means all the neurons are connected from one layer to its next layer. This is achieved in Keras with the help of Dense function.

We will use the above Deep Neural Network architecture which has a single input layer, 2 hidden layers and a single output layer.

The input data which is of size 8 is sent to the first hidden layer that has randomly initialized 8 neurons. From here, we can easily perform trial-and-error procedure to increase the network architecture to produce good results (fig. 2).

```
1 # create the model
2 model = Sequential()
3 model.add(Dense(8, input_dim=8, init='uniform', activation='relu'))
4 model.add(Dense(6, init='uniform', activation='relu'))
5 model.add(Dense(1, init='uniform', activation='sigmoid'))
```

Fig. 2. Creation the model

Line (1) creates a Sequential model to add layers one at a time.

Line (2), the first layer expects four arguments:

– 8: No.of.neurons present in that layer.

– input_dim: specify the dimension of the input data.

– init: specify whether uniform or normal distribution of weights to be initialized.

– activation: specify whether relu or sigmoid or tanh activation function to be used for each neuron in that layer.

Line (3), the next hidden layer has 6 neurons with an uniform initialization of weights and relu activation function.

Line (4), the output layer has only one neuron as this is a binary classification problem. The activation function at output is sigmoid because it outputs a probability in the range 0 and 1 so that we could easily discriminate output by assigning a threshold.

After creating the model, three parameters are needed to compile the model in Keras.

– loss: This is used to evaluate a set of weights. It is needed to reduce the error between actual output and expected output. It could be binary_crossentropy or categorical_crossentropy depending on the problem. As we are dealing with a binary classification problem, we need to pick binary_crossentropy.
– optimizer: This is used to search through different weights for the network. It could be adam or rmsprop depending on the problem.
– metrics: This is used to collect the report during training. Normally, we pick accuracy as our performance metric.

These parameters are to be tuned according to the problem as our model needs some optimization in the background (which is taken care by Theano or TensorFlow) so that it learns from the data during each epoch (which means reducing the error between actual output and predicted output).

– epoch is the term used to denote the number of iterations involved during the training process of a neural network.

```
1  # compile the model
2  model.compile(loss='binary_crossentropy', optimizer='adam', metrics=['accuracy'])
```

Fig. 3. Compile the model

Line (2) chooses a binary_crossentropy loss function and the famous Stochastic Gradient Descent (SGD) optimizer adam. It also collects the accuracy metric for training.

The optimizer is Adam (fig. 3). Metrics is used to specify the way we want to judge the performance of our neural network.

Some advantages of Adam include:

– Relatively low memory requirements (though higher than gradient descent and gradient descent with momentum)

– Usually works well even with little tuning of hyperparameters.

After compiling the model, the dataset must be fitted with the model (fig. 4). The fit() function in Keras expects five arguments:

– X_train: the input training data.
– Y_train: the output training classes.
– validation_data: Tuple of testing or validation data used to check the performance of our network.
– nb_epoch: how much iterations should the training process take place.
– batch_size: No.of.instances that are evaluated before performing a weight update in the network.

```
1  # fit the model
2  model.fit(X_train, Y_train, validation_data=(X_test, Y_test), nb_epoch=100, batch_size=5)
```

Fig. 4. Fit the model

Line (2) chooses 100 iterations (epoch) to be performed by the deep neural network with a batch_size of 5.

The epochs parameter is the "epoch" - the number of neural network passes over all records of the dataset (selected based on how quickly the model approaches the desired predictive accuracy with each new pass), batch_size - the number of sample objects taken in one step. In the process of learning, the API will output the corresponding lines with the values of the loss function and metric for each of the eras.

After fitting the dataset to the model, the model needs to be evaluated (fig. 5). Evaluating the trained model with an unseen test dataset shows how our model predicts output on unseen data. The evaluate() function in Keras expects two arguments.

X – the input data.

Y – the output data.

```
# evaluate the model
scores = model.evaluate(X_test, Y_test)
print("Accuracy: %.2f%%" %(scores[1]*100))
```

Fig. 5. Evaluate the model

Below is the compile code of the model we have just built ((fig. 6).

```
# compile the model
model.compile(loss='binary_crossentropy', optimizer='adam', metrics=['accuracy'])

# fit the model
model.fit(X_train, Y_train, validation_data=(X_test, Y_test), nb_epoch=200, batch_size=5, verbose=0)
# evaluate the model
scores = model.evaluate(X_test, Y_test)
print("Accuracy: %.2f%%" % (scores[1]*100))
```

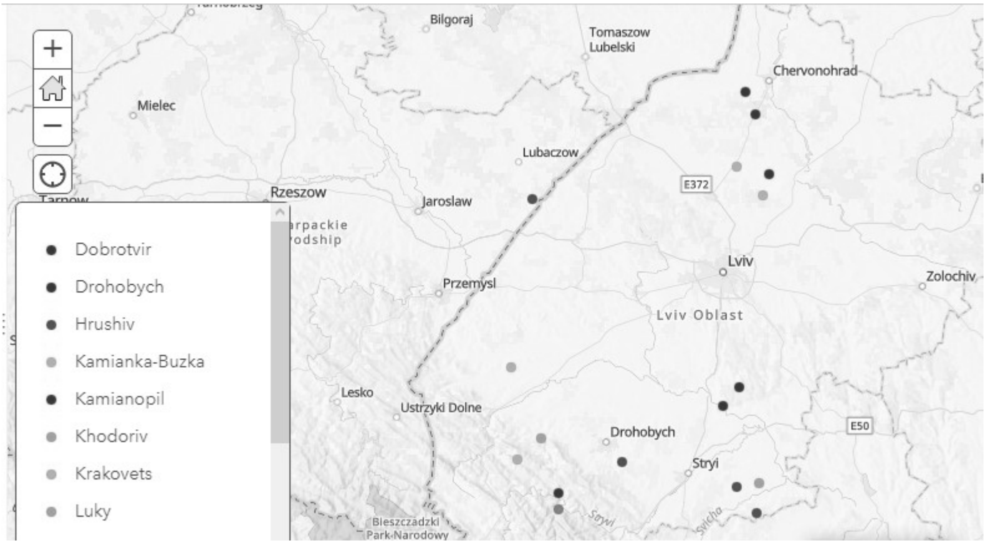
Fig. 6. Compile code of the model

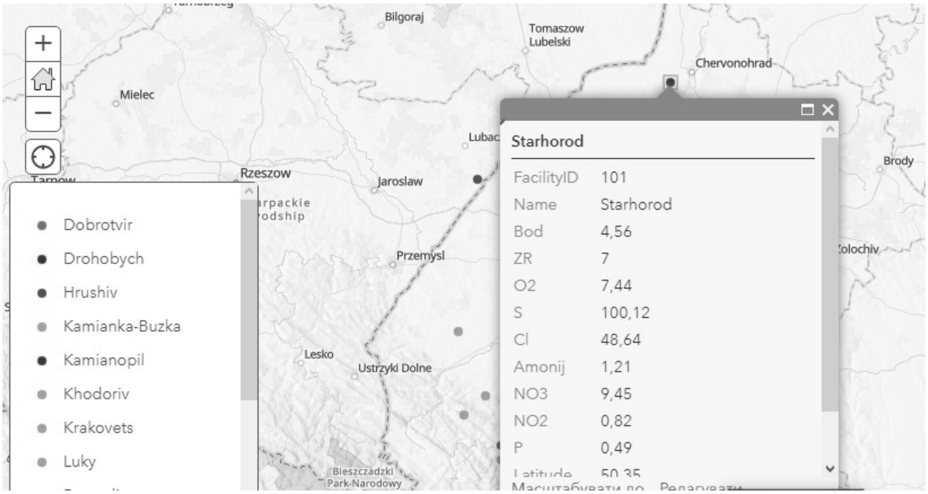
We get an accuracy of 93.5% (fig. 7).

```
acc: 93.5%
```

Fig. 7. An accuracy of model

In this study, surface water quality simulation was performed using ANN and GIS capabilities and the results were presented in a manner of geo-referenced graphic (map). Different colors indicate the multiplicity of excess standards (fig. 8)

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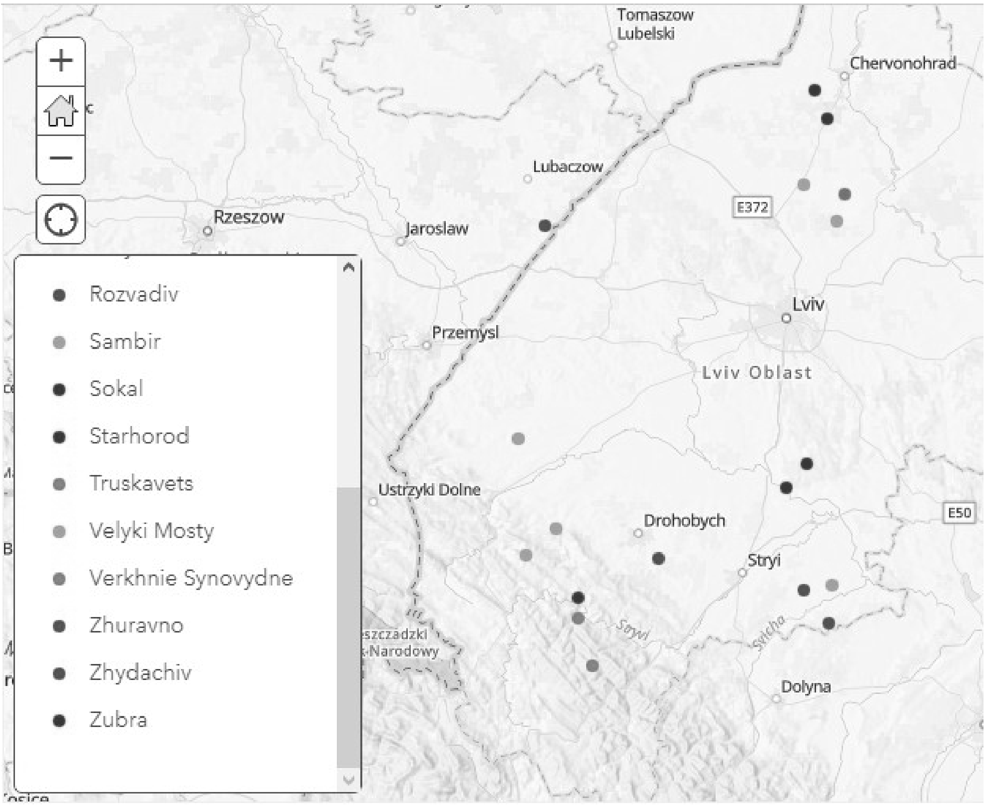
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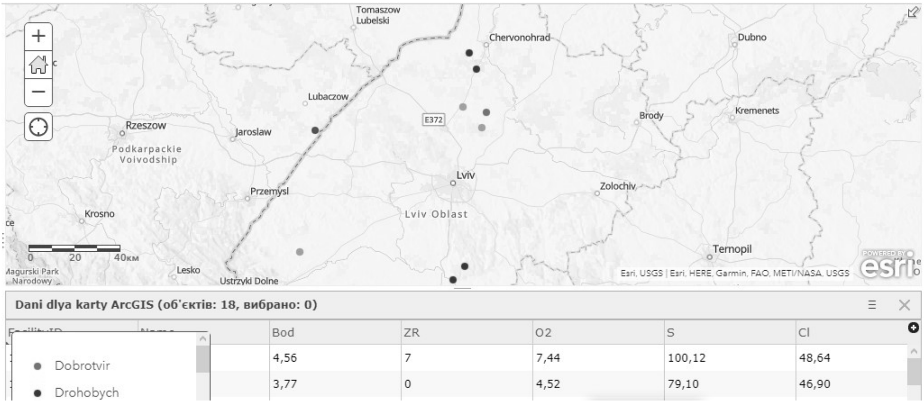

Fig. 8. Results of surface water quality modeling using ANN and ArcGis

Overload, poor technical condition, improper operation and inefficient operation of sewage treatment plants cause pollution of surface waters of the region with untreated and insufficiently treated sewage, especially at the expense of housing and communal services, enterprises of thermal power engineering, chemical and petrochemical industry, machine building and engineering industry [14]. The highest levels of pollution are recorded in the waters of the rivers of the Dniester and Western Bug basins, especially in creeks located near large settlements and administrative districts of the region.

CONCLUSIONS

The possibility of using artificial neural networks and geoinformation systems to simulate and predict changes in the concentration of pollutants of surface waters of the Lviv region of Ukraine is considered. The proposed theoretical and methodological bases for the use of GIS and neurotechnology provide an opportunity to obtain actual and predictable space-time models and patterns of distribution of surface water quality indicators with high reliability. The results of modelling have a high degree of theoretical and practical importance for increasing the level of interpretation of spatial-distribution and temporal information on the surface water status of Lviv region, which will improve the environmental safety of the region.

The analysis of results revealed that ANN model was good on water modeling. The Artificial Neural Model gave an accuracy of 93.5%. In relation to GIS, four color maps of the surface water quality of Lviv region have been constructed to give clear information of the water quality in this region of Ukraine.

Coupling ANN with GIS capabilities could provide practitioners with easily interpretable water quality maps in the management of these resources. Therefore, the presented methodology and other models can be used for prospective planning and management of sustainable water development.

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USING OF CHEMICALLY MODIFIED ZEOLITE IN WATER TREATMENT PROCESSES

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ABSTRACT

The adsorption method of water purification from pollutants has long been used in various industries of chemical, petrochemical, gas, pharmaceutical and food industries. On the territory of Ukraine there are some of the largest deposits of non-ferrous minerals in the world. Natural adsorbents occupy an important place in their structure.

The promising use of natural adapters for water purification is due to their sufficiently high adsorption capacity. At present, effective methods have been developed to improve the properties of minerals and their methods of modification. Natural adsorbents are widely used in Ukraine, these minerals have a low cost. A large number of subsoil deposits have also been deliberately removed.

The presence of a powerful Sokyrnitski field of zeolites (clinoptilolite) in Ukraine determines the profitability of its use. The directed modification of the surface and structure of the mineral makes it possible to use it in water treatment processes.

The aim of the work is to study the changes in the composition of bottom sorbents during their chemical activation, to establish the optimal conditions of the process of chemical activation of bottom cell zeolite clinoptilolite and the efficiency of its use in water processes.

To compare the efficiency of water purification from iron, chemically activated zeolite clinoptilolite and activated carbon were used.

It is established that in the process of acid activation the exchange of cations and dealumination takes place, as a result of which the Si / Al ratio increases from 3.9 to 10.5. At the same time complete removal of exchange cations is not observed and crystallinity of sorbent remains. For sorbent activated with 5.0 M HCl, the characteristic increase in coagulation capacity and specific surface area is 2.5 and 1.3 times, respectively.

It was found that according to the activity of the effect on the zeolite, the most effective method is the activation by acid in the mixing mode. The optimal activation conditions were selected 7% HC1, processing time 2 hours.

Therefore, for the purification of drinking water, natural zeolites can successfully replace activated carbon.

Chemical activation of natural fertilizer contributed to the increase of water purification indicators. The main indicator that characterizes the quality of water purification is the dynamic exchange capacity. In particular, in clinoptilolite chemically activated with 7% hydrochloric acid, the dynamic exchange capacity is 2.7 times higher than in activated carbon.

Key words: water purification, acid activation, clinoptilolite, coping capacity, dynamic exchange capacity.

INTRODUCTION

The separation method of water purification from pollutants has long been used in various branches of the chemical, petrochemical, gas, pharmaceutical and food industries. On the territory of Ukraine there are some of the largest deposits of non-ferrous minerals in the world. An important place in their structure is occupied by natural adsorbents and catalysts - aluminosilicate compounds, which are concentrated in more than several subsoils. These substances in the ground state or after a simple treatment (grinding, drying, etc.) are suitable for the purification, distribution of multicomponent compounds and mixtures.

The coping method is a well-managed process. It allows to remove the pollution of an extremely wide range of practices to any residual concentration of substances irrespective of their chemical resistance. At the same time, there is no secondary pollution. Therefore, the tendency of the development of combustion devices intended for local purification of drinking water is promising.

Adsorption methods are used in water treatment, in water treatment for the deep purification of wastewater from dissolved organic substances after biological treatment.

Also in the processes of water purification using methods of chlorination and ozonation, the method of ion exchange [6], electrocoagulation [7], simplified aeration followed by filtration [8].

The promising use of natural adapters for water purification is due to their sufficiently high adsorption capacity. At present, effective methods have been developed to improve the properties of minerals and their methods of modification. Natural adsorbents are widely used in Ukraine, these minerals have a low cost. A large number of subsoil deposits have also been deliberately removed.

The presence of a powerful Sokyrnitski field of zeolites (clinoptilolite) in Ukraine determines the profitability of its use. The directed modification of the surface and structure of the mineral makes it possible to use it in water treatment processes.

It is known that the crystals of the underlying zeolites are permeated by popes (entrance windows) with molecular poses, which are characteristic of low-molecular-weight substances. Water molecules and other substances can penetrate and accumulate on them, which occupy up to half of the total volume of crystals. All other molecules, the critical ones of which are larger than the input windows, are practically not copied by zeolite. It is obvious that the use of zeolites, the size of which is smaller than the size of the molecules of the solute, is inefficient.

To obtain natural compounds that are active in a wide range of various impurities and to eliminate the above-mentioned disadvantage, there are various connotations.

The **aim** of the work is to study the changes in the composition of bottom sorbents during their chemical activation, to establish the optimal conditions of the process of chemical activation of bottom cell zeolite clinoptilolite and the efficiency of its use in water processes.

MATERIALS AND METHODS

For research, the background zeolite clinoptilolite, extracted from the site near c, was used. Sokyrnytsia (Zakappattya, Ukraine). Clinoptilolite is an aluminosilicate mineral containing an aluminosilicate framework with alkaline earth metals of sodium, potassium and other elements.

Basic information about the processes occurring in natural sorbents during acid treatment is given by chemical analysis, in particular, the ratio of SiO2 / Al2O3, the type and quantitative ratio of exchange cations. Changes in the structure of the zeolite are confirmed by radiographic studies of acid treatment products.

Samples of chemically (acid-activated) clinoptilolite (K + HC1) were used to test bottom sorbents as purifiers of drinking water from iron ions.

The test procedure was based on the fact that the prepared sorbent was weighed and placed in a 2/3 height column. The inner diameter of the adsorption column is 0.03 m, the height is 0.47 m. To determine the cleaning efficiency, model water solutions with the content of iron ions from 5 to 9 mg are prepared. Water is supplied from the tank to the discharge column from the bottom up with a flow rate of 0.5 l / year. The speed of water supply is regulated. Water samples are reflected after 15-60 minutes and the water is analyzed for Fe3 + ions.

The transformation of the structure of zeolites during acid treatment with the increase of its concentration takes place in three stages. In the beginning, cations are removed from exchange positions without appreciable change of the cap. The second stage is characterized by the intensive removal of aluminum from the position of the tetrahedrons, while violating the Si - Al bonds, the AlO4 tetrahedron is replaced by the noses. At the third stage there is a destruction of the residual Si - O -capacity and formation of the silicon-oxygen phase. Acid activation inevitably also affects the surface-active centers, which determine the adhesion properties of zeolites.

The main factors influencing the effectiveness of action are: the mineral composition of zeolite, its acid resistance, the nature of the acid, its concentration, the durability of the coating. With increasing acid concentration and activation time, the relative content of silica in the soil increases and the molar ratio of SiO2 / Al2O3 increases.

To study the change in the composition of the natural sorbent, which occurs during its chemical activation, the natural zeolite of clinoptilolite is treated with solutions of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 M hydrochloric acid. K. Having previously determined the moisture content of the sorbent, 1.0 g (± 0.0002 g) of air-dry diatomite (fraction 0.02 - 0.06 mm) is brought into contact with 100.0 ml of the solution. Stirring for 4 hours at the set temperature. According to the kinetic experimental data, for all concentrations of hydrochloric acid, the balance in the system is reached within 4 hours. The sorbent is separated from the solution by filtration and washed with distilled water in the absence of chloride ions in the filtrate. The number of leached ions Na +, K + (by the method of flame photometry, Sr = 0.07), Ca2 +, Mg2 +, Al3 + and Fe3 + (by the method of complexation of 0.2%) is determined in the solution.

RESULTS AND DISCUSSIONS

1. Investigation of changes in the composition of bottom sorbents during their chemical activation

The order of extraction of exchange cations and the structure of atoms from these zeolites are approximately the same, and the sequence corresponding to the decrease in the bond strength of these atoms has the form: Si> Al> Mg> k> properties of ions.

The strength of the bond mainly depends on the radius of the cation and, accordingly, the size of its shell of hydrochloride.

Studies in the field of dealumination and cation of clinoptilolite [9, 10] have shown that in the course of these processes the availability of channels for molecules of heavy metals in volumes increases.

Acid activation of zeolites includes three stages: removal of exchangeable cations, delamination of the formation of the silicon-oxygen phase. The sequence and intensity of the stages is determined by the concentration of acid [11].

In the process of acid activation of the investigated sorbent, cation is observed, i.e. removal of potassium (sodium), calcium and calcium into the exchange of cation exchanges. The cationic composition in the process of treatment with an acid concentration of less than 1.0 M has the following series: Ca^{2+}> Mg^{2+}> Na^{+}> K^{+}. As the acid concentration increases, the order of cation leaching changes with Mg^{2+}> Ca^{2+}> Na^{+}> K^{+}, which makes it possible to make assumptions about the difference in the availability of the exchange rate. According to the data of the elemental analysis, the complete removal of cations during the treatment of zeolite with acid does not take place. Acid activation leads to the leaching of iron, which, as the authors suggest, [12, 13], can be used both in the structure of cellulite and in the introduction of water.

Upon contact of clinoptilolite with HCl solution, the capsule de-illuminates, which is accompanied by an increase in the Si/Al ratio (Table 1). The increase in the concentration of hydrochloric acid appears in the change of the Si/Al index from 3.9 to 10.5. According to the data of X-ray phase analysis, the extraction of aluminum with acid with a concentration of 5.0M leads to a partial amorphization of the diatomite phase.

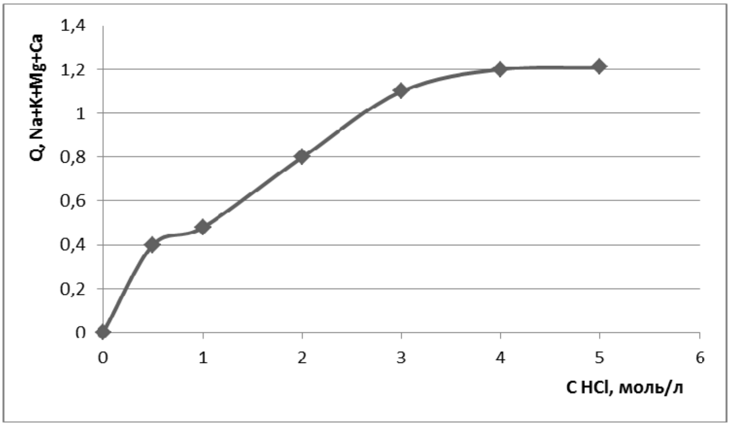

Fig. 1. Dependence of the number of cations displaced from the cobentum Na^{+}, K^{+}, Mg^{2+} i Ca^{2+} from the concentration of hydrochloric acid

Minor peak shear at 564 cm^{-1}, which corresponds to the oscillation of the chains of aluminum-silicon tetrahedrons, without changing the intensity of the bands. An analogous result was obtained by the authors of the work [12] when studying the influence of the conditions of treatment with hydrochloric acid of clinoptilolite of the Bigadic field (Turkey, containing clinoptilolite). The presence of absorption bands at 931 cm^{-1} and 928 cm^{-1}, which correspond in the sample to samples sampled with 4.0 and 5.0 M acid, characterizes the oscillations of the Si−O bond that is present bound between them by hydrogen bonds. An intense absorption band appears at 3754 cm^{-1}, which corresponds to the oscillations of the OH bond in the isolated Si−OH cyclonic groups. The oscillations of this bond in hydrogen-bonded cyanide groups are observed at 3440 cm^{-1}.

Table 1. The cations number extracted from 1.0 g of cobentum

C_{HCl}, mol/l	QCa, mmol/g	QMg, mmol/g	QNa, mmol/g	QK, mmol/g	QFe, mmol/g	QAl, mmol/g	Si/Al
0.5	0.23	0.14	0.01	0.01	0.06	0.51	3.9
1.0	0.26	0.20	0.02	0.01	0.10	0.75	7.0
2.0	0.30	0.44	0.03	0.03	0.18	0.87	8.4
3.0	0.33	0.62	0.06	0.04	0.23	0.95	9.4
4.0	0.36	0.69	0.10	0.07	0.30	1.01	10.5
5.0	0.37	0.70	0.10	0.08	0.32	1.01	10.5

The treatment of zeolite with acid leads to an increase in microflora and connecting the caps of the channel, free from exchange cations. For the sorbent activated with 5.0 M HCl, a characteristic increase in the coagulability and specific surface area, stored in methylene blue, is 1.5 times higher.

Of the known zeolites, the clinoptilolite of the Sokyrnytske field is 190 × 104 kg / m2, which is 4 times higher than for artificial 50 kg. As a result of chemical activation, the mechanical strength of the clinoptilolite of the Sokyrnytsia subsoil decreases to (150-160) × 104 kg / m2, but remains at the level, which remains the same.

Thus, due to the acid treatment of the clinoptilolite of the Sokrnytsia field, preserving high mechanical strength, such zeolites also have high adhesion properties.

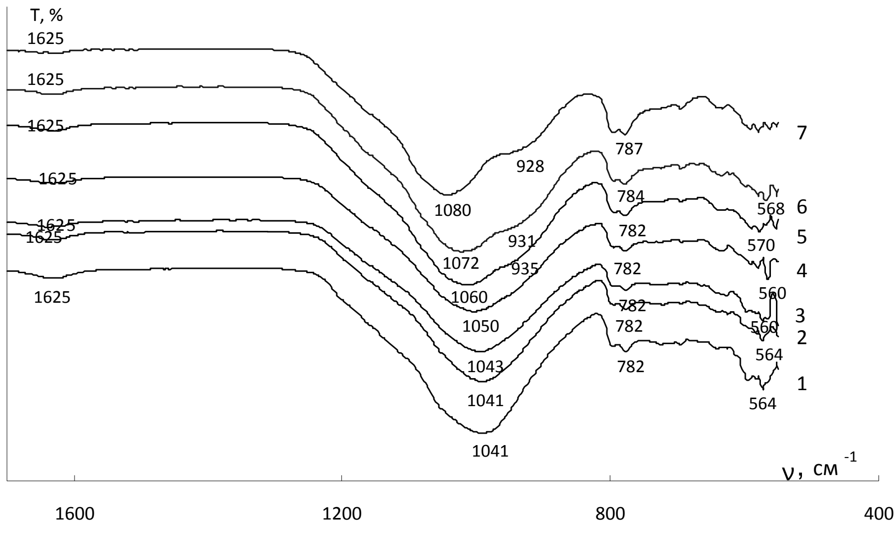

Fig. 2. IR-spectra of clinoptilolite: 1 - natural; 2 - acid-activated 0.5 M HCl; 3 - acid-activated 1.0 M HCl; 4 - acid-activated 2.0 M HCl; 5 - acid-activated 3.0 M HCl; 6 - acid-activated 4.0 M HCl; 7 - acid-activated 5.0 M HCl

It is established that in the process of acid activation the exchange of cations and dealumination takes place, as a result of which the Si / Al ratio increases from 3.9 to 10.5. At the same time complete removal of exchange cations is not observed and crystallinity of sorbent remains.

2. Influence of acid treatment on the properties of zeolites obtained by mixing and filtration methods

Acid treatment of zeolites obtained by mixing characterized by transition metal cations in solution (Table 2). With increasing concentration of acid content of Na_2O decreased by almost five times, and CaO more than doubled after treatment 10% HCl. In this case, the content of silica increases to 81%, with the most noticeable increase revealed during the treatment of 7% HCl, while a sharp increase in the molar ratio of SiO_2/Al_2O_3 (from 9.45 to 16.6) is observed.

With the SiO_2 /Al_2O_3 molar ratio increases, the ion exchange ability of the acid-activated zeolite decreases as compared to the initial zeolite, which is due to the decrease in the total number of cation exchange centers and the replacement of the exchange complex cations part into hydrogen ions. The content of monovalent and divalent metals oxides continues to decrease with increasing acid concentration. The losses during calcine practically do not depend on the concentration of the activator. An increase in the acid exposure time of 1 to 3 hours leads to minor changes in the chemical composition of clinoptilolite.

It is advisable to use hydrochloric acid for the treatment of zeolite in the ratio of solid phase: liquid (S:L) 1:2, other ratios provide incomplete development of the surface of zeolite as well as incomplete removal of cations.

For comparison, clinoptilolite was activated with sulfuric acid at concentrations of 5%, 10%, 13%, 17% and 20% for 2 hours (Table 2).

The treatment of natural zeolite with sulfuric acid was less effective: the silica content increased slightly, and the content of Al_2O_3, CaO, and K_2O oxides remained approximately the same, with only Na_2O content in acid-activated zeolite decreased by almost 2,5 times. Therefore, it should be noted that the use of sulfuric acid is not feasible. The optimal conditions for activating zeolite have been chosen: reagent - hydrochloric acid, acid concentration - 7%, treatment time - 2 hours, phase ratio S: L = 1: 2.

Table 2. Influence of acid treatment on the properties of zeolites obtained by mixing

Activation conditions	The content of oxides, %					Molar ratio SiO_2/Al_2O_3	Exchange capacity, mg - equ
	SiO_2	Al_2O_3	CaO	Na_2O	K_2O		
Zeolite	70.41	12.64	2.16	1.32	3.04	9.45	66.5
HC1 5%	72.57	10.88	2.08	0.55	3.18	11.2	39.20
HCl 7%, 1 hour	78.52	8.18	1.41	0.35	2.37	16.29	36.18
HCl 7%, 2 hours	80.74	8.25	0.99	0.26	1.46	16.61	32.35
HCl 7%, 3 hours	80.71	8.37	0.80	0.27	1.36	16.36	26.14
HCl 7%, 2 hours, without washing	78.33	9.47	1.13	0.31	1.71	14.04	29.20

HC1 10%, 1 hour	79.60	9.29	0.77	0.28	1.43	14.54	28.13
HC1 10%, 2 hours	81.63	8.78	0.90	0.28	1.38	15.78	30.16
HCl 7%, S:L=1:1	69.81	11.25	1.61	0.41	2.56	10.53	33.87
HCl 7%, S:L=1:2	80.74	8.25	0.99	0.26	1.46	16.61	32.35
HCl 7%, S:L=1:3	70.28	10.79	1.34	0.43	2.53	11.50	25.16
HCl 7%, S:L=1:6	70.40	11.00	1.25	0.42	2.65	10.86	20.18
H_2S0_4 5%	72.70	10.76	2.82	0.38	2,74	11.47	43.18
H_2S0_4 10%	72.96	10.66	2.73	0.38	2.56	11.61	40.13
H_2S0_4 13%	73.14	10.05	2.57	0.35	2.30	12.35	36.17
H_2S0_4 17%	73.92	9.39	2.48	0.53	2.20	13.36	36.3
H_2S0_4 20%	73.28	10.05	2.67	0.42	2.50	12.25	32,35

The results of the influence of acid treatment on the properties of zeolites obtained by the filtration method are shown in Table 3. The optimum acid concentration and activation time are determined. The choice of the optimal phase correlation S: L at the activation time is 96 hours and the concentration of HC1 7%. It was found that the optimum ratio of solid phase: the liquid should be considered 1:2, with the content of SiO_2 in zeolite increased to 77.08%, the molar ratio $SiO_2/A1_2O_3$ to 12.99%, and the content of $A1_2O_3$ decreased to 10,07%. Reducing and increasing the activation time and concentration of hydrochloric acid up to 10% did not lead to further improvement of the chemical composition activated by the zeolite filtration method.

Table 3. Influence of acid treatment on the properties of zeolites obtained by the filtration method

Activation conditions	The content of oxides, %					Molar ratio SiO_2/Al_2O_3	Exchange capacity, mg−equ
	SiO_2	Al_2O_3	CaO	Na_2O	K_2O		
HC1 7%, 48 hours, S:L=1:2	74.44	10.71	1.73	0.30	2.30	11.80	38.96
HC1 7%, 72 hours, S:L=1:2	74.85	10.68	1.47	0.31	2.24	11.89	33.16
HC1 7%, 96 hours, S:L=1:2	77.08	10.07	1.21	0.30	1.87	12.99	39.74
HC1 10%, 24 hours, S:L=1:2.	73.08	11.08	1.99	0.35	2.33	11.19	30.72
HC1 10%, 48 hours, S:L=1:2	74.09	10.80	1.74	0.30	2.25	11.64	29.05
HC1 10%, 72 hours, S:L=1:2	74.31	10.75	1.52	0.25	2.19	11.73	24.53

HC1 7%, 96 hours,S:L=1:2	77.08	10.07	1.21	0.30	1.87	12.99	39.74
HC1 7%, 96 hours, S:L=1:3	73.08	10.80	1.99	0.28	2.80	11.48	33.46
HC1 7%, 96 hours, S:L=1:6	75.13	10.53	1.52	0.25	2.20	12.11	30.12
HC1 7%, 96 hours, S:L=1:7	75.19	10.67	1.44	0.24	2.21	11.96	29.20
HC1 7%, 96 hours, S:L=1:8	74.95	10.00	1.87	0.28	2.22	12.72	32.14
HC1 7%, 96 hours, S:L=1:9	75.62	10.00	1.73	0.27	2.18	12.83	31.71

It was shown that decrease in the content of Al_2O_3, CaO, Na_2O and K_2O oxides leads to the decrease in the exchange capacity of clinoptilolite (Table 4).

Table 4. Comparison of the influence of methods of acid activation of zeolite on its properties

Alumo-silicate sorbent (zeolite)	The content of oxides, %					Molar ratio SiO_2/Al_2O_3	Exchange capacity, mg−equ
	SiO_2	Al_2O_3	CaO	Na_2O	K_2O		
Natural	70.41	12.64	2.16	1.32	3.04	9.45	66.5
Activated by mixing method	80.74	8.25	0.99	0.29	1.46	16.61	**32.35**
Activated by filteringя	77.08	10.07	1.21	0.30	1.87	12.99	39.74

At the same time acid activation contributes to the increase of silica content in zeolite and the molar ratio of SiO_2/Al_2O_3. By activity of influence on zeolite the method of acid activation in the mode of mixing was effective, optimal conditions of activation were selected 7% HC1, processing time 2 hours.

In table 5 data on the purity of drinking water from iron ions by thermally activated clinoptilolite (K) and chemically (acid) activated clinoptilolite (K + HC1) is resent.

Table 5. Comparative data on the purification of drinking water from iron ions by natural sorbents

Adsorbent	Contents Fe^{3+}, mg/l		Degree of purification %	Time of adsorption hours	Dynamic exchange capacity, %	pH of the medium	Mass of adsorbent, g
	before cleaning	after cleaning					
K K+HC1	9.2 6.7	0.2−3.1 0.2	64−100 100	10.25 24.25	0.017 0.052	7.4−7.7 5.8−7.5	162 149
Activated carbon	8.0	0.2−1.3	56−100	5.5	0.019	6.2−7.2	90

For comparison, the results of purification of drinking water with active carbon are shown. It has been established that for the removal of iron from ions, the most purification of sorbents is chemically active clinoptilolite. Water purification with natural zeolite is better than activated carbon, because sorption of iron ions is carried out according to the mechanism of ion exchange. Chemical activation of natural sorbents contributed to further increase of water purification rates. In particular, in clinoptilolite chemically activated with hydrochloric acid, the dynamic exchange capacity increased more than twice.

CONCLUSIONS

It is established that in the process of acid activation the exchange of cations and dealumination takes place, as a result of which the Si / Al ratio increases from 3.9 to 10.5. At the same time complete removal of exchange cations is not observed and crystallinity of sorbent remains. For cobent activated with 5.0 M HCl, the characteristic increase in coagulation capacity and specific surface area is 2.5 and 1.3 times, respectively. Optimal conditions for chemical activation of natural zeolite of clinoptilolite of Sokyrnytsia deposit (Ukraine) have been established. In the processes of water purification, natural zeolites can successfully replace activated carbon. Chemical activation of natural fertilizer contributed to the increase of water purification indicators. It was found that in terms of zeolite activity, the most effective method is activation with hydrochloric acid in the mixing mode. The optimal activation conditions were selected 7% HC1, processing time 2 hours. For the treatment of zeolite, it is advisable to use hydrochloric acid in the ratio solid phase: liquid = 1: 2. The main indicator that characterizes the quality of water purification is the dynamic exchange capacity. In clinoptilolite chemically activated with 7% hydrochloric acid, the dynamic exchange capacity is 2.7 times greater than that of activated carbon.

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COMPARATIVE ASSESSMENT OF THE QUALITY OF TRANSBOUNDARY SURFACE WATER BODIES (ON THE EXAMPLE OF THE DNIEPER BASIN)

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ABSTRACT

The article analyzes the changes in the ecological status of the water of the Dnieper basin and identifies the possible causes of this phenomenon, as well as possible ways to improve its ecological status. The change in the ecological status of surface water was determine d by carrying out a retrospective analysis of the monitoring data and environmental assessment of the water resources of Ukraine by the State Water Resources Agency of Ukraine for the period 2010-2019. The retrospective analysis was conducted according to the data of the water abstraction control within the framework of the Dnieper Basin Water Resources Management, according to 14 fence posts, taking into account the requirements of the State Standard of Ukraine 4808: 2007.

Keywords: Dnieper basin, ecological status, anthropogenic load, quality assessment, ecological improvement.

INTRODUCTION

In Ukraine, almost 80% of the population is supplied with drinking water from surface sources, in particular, almost 75% – from the Dnieper. The Dnieper is the third largest river in Europe (after the Volga and the Danube). The Dnieper is a transboundary watercourse: 20% of the river basin is located in the territory of the Russian Federation, 23% – in the Republic of Belarus and 57% – in Ukraine. The Dnieper River is the main waterway of Ukraine, its water resources make up more than 60% of all water resources of the country. The total area of the Dnieper basin is 504 thousand km2, of which 286 thousand km2 is located within Ukraine in its most economically developed part. 80% of the land area of Ukraine is fed by the waters of the Dnieper through irrigation and watering systems.

The main problems of surface waters of the Dnieper basin at this time are: high pollution of the shores; construction of coastal protection strips; deterioration of hydraulic structures, which threatens accidents and pollution of water bodies; excessive overgrowing of water area with aquatic vegetation; drainage of rainwater drainage almost without cleaning; discharge of untreated municipal wastewater from apartments that are not connected to the centralized sewerage system; weakening of state control over environmental offenses; inefficient water monitoring system; imperfection of the existing system of public administration in the field of use, protection and restoration of water resources, lack of clear delineation of functions; non–full use of domestic scientific innovations in the field of biochemistry.

METHODS AND EXPERIMENTAL PROCEDURES

Assessment of water quality was carried out taking into account the indicators: BOC_5 and O_2 as mandatory, and others – by the highest ratios to the MPC from the list: SO_4^{2-}, Cl^-, COD, NH_4^{+}, NO_2^-, NO_3^-, PO_4^{3-}, Fe total, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Al^{3+}, Pb^{2+}, Hg^{2+}, As^{3+} , synthetic surfactants. Determination of the change in the quality of the Dnieper water was carried out taking into account the change in the content of normalized parameters: the sum of anions (NO_2, NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-), converted to molar mass, in order to level the difference between the masses of different atomic anions; dissolved oxygen in water; biochemical oxygen consumption (BOC_5); phosphates PO_4^{3-} nitrites, nitrates, as well as ammonium NH_4^+.

Assessment of changes in the composition of surface water was performed by retrospective analysis of monitoring data and environmental assessment of water resources of Ukraine of the State Agency of Water Resources of Ukraine for the period from January 2010 to January 2019.

A retrospective analysis of water quality was conducted according to the samples of control water intake of the Dnieper River within the Basin Water Resources Management at 14 posts (Fig. 1): post 1: Sozh River, 32 km, p. St. Yarilovichi, Ripkin district (border with Belarus); post 2: Dnipro, 1116 km, village Kamyanka, below the village, Ripky district (border with Belarus)); post 3: Uzh river, 15 km, village Cherevach, drinking in / from Chernobyl; post 4: Dnipro, 897 km, Vyshhorod, n / b Kyiv HPP, drinking water in Kyiv; post 5: Dnipro river, 833 km, Ukrainka town, below the town, above the Bila Tserkva-Uman water supply system; post 6: Dnipro, 678 km, c. Sokirne, drinking in / from Cherkasy; post 7: Dnipro, 580 km, village Vlasivka, left bank, drinking water in Kremenchuk; post 8: Dnipro, 462 km, village Aula, drinking in / from Dnipro and Kamyanske); post 9: Dnipro, 404 km, Dnipro, SE «PdTES» PJSC «DTEK Dniproenergo», drinking water; post 10: Dnipro, 312 km, Zaporizhia, GNS of the Zaporizhia Armed Forces; post 11: Dnipro, 253 km, Energodar, influence of Zaporizhzhya NPP; post 12: Dnipro, 160 km, township Velyka Lepetykha, Rubanivska ZS; post 13: Dnipro, 65 km, village Ivanivka, Belozersky district, in the district of drinking water supply from the Nikolaev water supply system; post 14: Dnipro, 0 km, village Kizomis (Rvach sleeve).

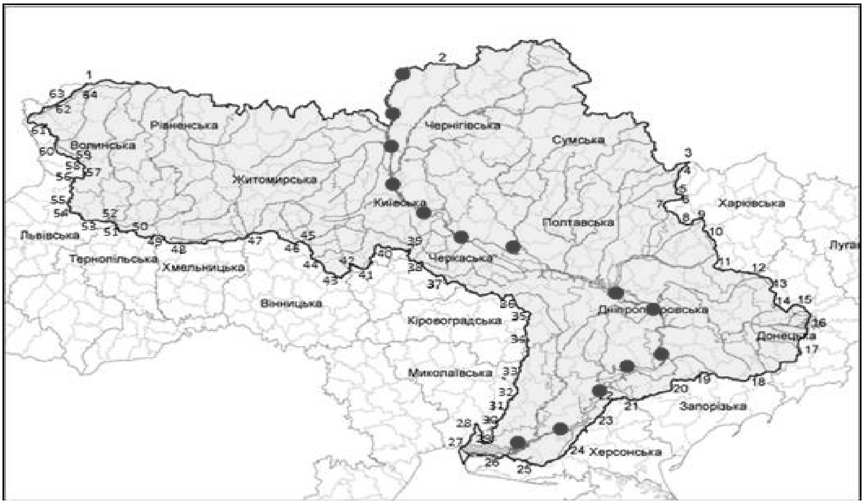

Fig. 1. Schematic layout of 14 posts of control water intake, according to which the study was conducted

THE RESEARCH RESULTS AND DISCUSSIONS

At fixed network points, the list of water quality components is determined mainly by the composition and volume of wastewater discharged into the water body, their toxicity and requirements from water consumers. These include: water temperature, suspended solids, mineralization, chromaticity, pH, dissolved oxygen, COD and BOC, odor, major ions, nutrients, and very common pollutants such as petroleum products, surfactants, volatile phenols, nutrients, heavy metals [1].

The approach to the organization of the system of observations of biological indicators in general is the same as for physical and chemical ones, ie it provides for observations and control at the established points in an agreed time and according to a single unified methodology.

To determine the program of hydrobiological observations it is necessary for some time to accumulate hydrobiological information on different species: macrophytes, phyto-, bacterio- and zooplankton, zoobenthos, neuston, periphyton [2].

Of the 17 main tributaries of the Dnieper, 15 flows into the river within Ukraine (Table 1). The largest of them are the rivers Pripyat and Desna, which carry the bulk of the water to the Dnieper.

Tributaries of the Dnieper flow through the territory of the most important industrial centres and settlements of Ukraine, creating a widely branched complex river system, which has important economic, social and environmental significance. The Dnieper, which has undergone significant changes due to the construction of a cascade of reservoirs, is no longer a river ecosystem capable of self-regulation [3, 4].

Table 1. The main characteristics of the surveyed rivers of the Dnieper basin

Name of water body (main tributaries)	Areas through which it flows	Surface water body characteristics		
		Catchment area, thousand km^2	Average annual runoff, m^3/s	Length of watercours e, km
river Sozh	Russia (Smolensk region) Republic of Belarus (Mogilev region, Gomel region) Ukraine (Chernihiv region)	41,4	207	648
Pripyat River	Republic of Belarus (Brest region, Gomel region) Ukraine (Volyn region, Rivne region, Kyiv region)	121	460	775
Teteriv river	Ukraine (Zhytomyr region, Kyiv region)	15,3	18,4	385
Irpin river	Ukraine (Zhytomyr region, Kyiv region)	3,3	173,6	162
Desna river	Russia (Smolensk region, Bryansk region) Ukraine (Chernihiv region, Sumy region, Kyiv region)	88,9	360	1130
the river Trubizh	Ukraine (Chernihiv region, Kyiv region)	4,7	3,6	113
the river Ros	Ukraine (Vinnytsia region, Kyiv region, Cherkasy region)	12,6	22,5	346

Supiy river	Ukraine (Cherkasy region, Kyiv region, Chernihiv region)	2	6,0	130
Sula river	Ukraine (Sumy region, Poltava region)	19,6	29	363
the river Tyasmin	Ukraine (Kirovograd region, Cherkasy region)	4,5	0,2	161
river Psel	Russia (Kursk region, Belgorod region) Ukraine (Sumy region, Poltava region)	22,8	55	717
Vorskla river	Russia (Belgorod region), Ukraine (Sumy region, Poltava region)	14,7	36	464
Eagle river	Ukraine (Kharkiv region, Poltava region, Dnipropetrovsk region)	9,8	13,2	346
Samara river	Ukraine (Donetsk region, Kharkiv region, Dnipropetrovsk region)	22,7	17	320
Ingulets river	Ukraine (Kirovograd region, Dnepropetrovsk region, Nikolaev region, Kherson region)	14,9	8,5	549

The results of the analysis to determine the difference in the total anion content between the posts of water intakes of the Dnieper basin are shown in table 2.

When conducting a retrospective analysis of the total anion content in the water of the Middle Dnieper, it is necessary to take into account the possible impact on the source water of the Pripyat, Teteriv, Irpin, Desna, Trubizh, Ros, Supiy, Sula, Tyasmin, Vorskla and Psel river basins and their tributaries.

Based on the obtained data (Table 2), it can be argued that there is a constant increase in the total content of anions from the fence 3 and further downstream to the mouth of the Dnieper.

Table 2. Differences in the total anion content between the posts of water intakes of the Dnieper basin

Year	$\Delta \sum_{anions}$, mmol/dm^3										
	P2–1	P4–3	P5–4	P6–5	P7–6	P8–7	P10–9	P11–10	P12–11	P13–12	P14–13
2010	–0,04				0,11	0,04	–	–	–	–	–
2011	0,18			–0,08	–0,07	0,22	–	–	–	–	–
2012	–0,04			0,14	–0,08	0,23	–	–	–	–0,08	0,62
2013	–0,09			0	0	0,2	–	–	–	–0,16	0,80
2014	–0,06			0,09	–0,07	0,02	–	–	0,01	0,06	–0,10
2015	0,02			–0,1	0,04	0,13	–	–	–0,12	–0,35	12,99
2016	0,11	0,05	–0,11	0,16	–0,07	0,21	0,07	–0,27	–0,35	–0,02	8,75
2017	0,01	0,08	–0,15	0,07	0,19	0,12	–0,67	–0,03	–0,03	0,14	1,41
2018	0,03	–0,2	–0,12	0,07	0,08	0,22	0,35	–0,32	–0,19	0,11	2,08
2019	0,01	–0,05	0,29	–0,45	0,09	–0,04	–0,36	0,06	–0,19	0,06	3,96

The total content of anions at the posts of water intakes of the Dnieper basin for 2018 is shown in Fig. 2.

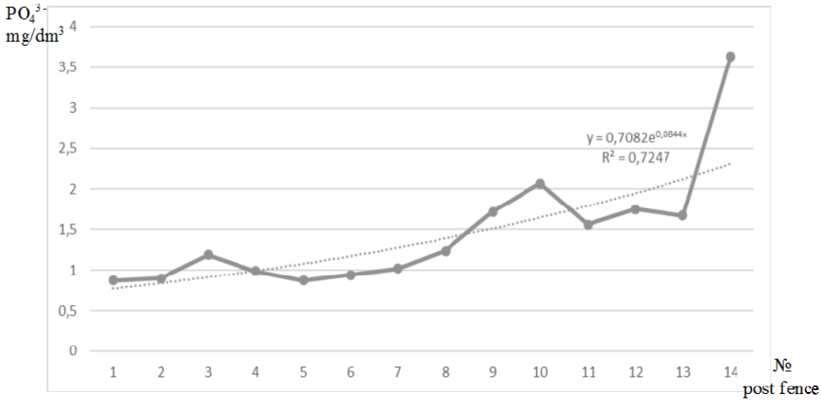

Fig. 2. T he total content of anions at the posts of water intakes of the Dnieper basin for 2018

From the data given in Table 2 and Figure 2, an increase in the total anion content along the entire course of the Dnieper River is clearly observed. And, despite the fact that in three areas (between posts 3-4-5, 10-11) a slight self-cleaning is provided, yet after them there is again a significant increase in pollution.

NH_4^+ ion is unstable, it is rapidly oxidized to nitrites and nitrates. The high content of ammonium indicates anaerobic conditions for the formation of the chemical composition of water and its unsatisfactory quality.

The analysis revealed a tendency to reduce the phosphate content of (Fig. 3) from post 1 to post 14 in the water of the Dnieper basin.

However, there is a local increase, especially between the 5th-6th posts, as well as the 7th-8th, which may be due to the influence of tributaries on them, as well as between the 12th-13th posts. A significant decrease in phosphate content is observed between 6-7th posts, as well as 11-12th (Table 3).

Table 3. Differences in the content of phosphates of ions PO_4^{3-} between the posts of water intakes of the Dnieper basin

Year	Δ PO_4^{3-} mg/dm³										
	P2–1	P4–3	P5–4	P6–5	P7–6	P8–7	P10–9	P11–10	P12–11	P13–12	P14–13
2010	–0,18	–	–	–	–0,07	–0,12	–	–	–	–	–
2011	–0,06	–	–	0,22	–0,23	0,17	–	–	–	–	–
2012	0,01	–	–	0,19	–0,15	0	–	–	–	–	–
2013	–0,03	–	–	0,11	–0,24	0,32	–	–	–	0,03	0
2014	0,01	–	–	0,09	–0,09	0,23	–	–	–0,12	0,05	0
2015	0,02	–	–	0,04	–0,19	0,03	–0,07	0,02	–0,05	0,08	–0,01
2016	–0,03	–0,04	0,15	0	–0,18	0,13	–0,07	0,06	–0,04	–0,04	0,02
2017	–0,01	0,1	0,04	0,32	–0,33	0,1	–0,12	0,07	0	0,04	–0,01
2018	0,03	0,07	0,04	0,21	–0,28	0,14	0,01	0,01	–0,14	0,15	–0,05
2019	–0,04	0,18	0,07	0,1	–0,23	0,07	0,15	–0,06	–0,14	0,1	–0,02

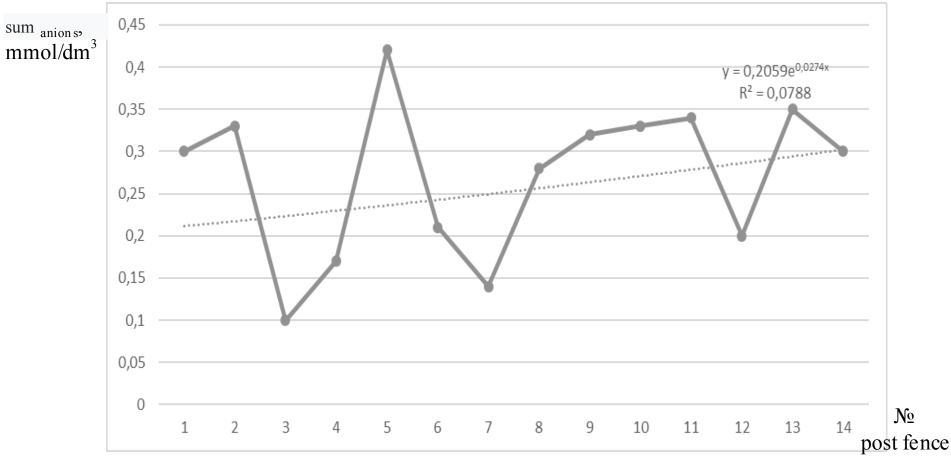

Fig. 3. The total content of phosphates of PO_4^{3-} ions – at the posts of water intake of the Dnieper basin for 2018

And, despite the fact that in five areas (between posts 2–3, 5–7, 11–12, 13–14) partial self–cleaning is provided, still between other posts there is a significant increase in pollution.

Table 4. The difference in ammonium content of NH_4^+ between the posts of water intakes of the Dnieper basin

Year	ΔNH^{4+} mg/dm^3										
	P2–1	P4–3	P5–4	P6–5	P7–6	P8–7	P10–9	P11–10	P12–11	P13–12	P14–13
2010	–0,16	–	–	–	–0,07	–0,15	–	–	–	–	–
2011	–0,06	–	–	0,18	–0,11	0	–	–	–	–	–
2012	–0,14	–	–	0,27	–0,42	–0,11	–	–	–	–	–
2013	–0,15	–	–	0,19	–0,17	–0,1	–	–	–	–0,05	–0,06
2014	–0,02	–	–	0,18	–0,25	–0,12	–	–	–0,13	–0,01	0,04
2015	–0,09	–	–	0	–0,09	–0,06	–0,03	–0,08	–0,01	–0,05	0
2016	0,04	–0,1	0	0,08	0,05	–0,1	0,13	–0,17	–0,09	–0,05	–0,01
2017	0,03	0,03	–0,09	0,14	–0,06	0,04	0,09	–0,1	–0,14	0	0,01
2018	0,06	0,07	–0,14	0,18	–0,05	–0,01	0,15	–0,12	–0,14	–0,03	0,01
2019	–0,04	–0,08	–0,05	0,19	–0,23	0,05	0,29	–0,19	–0,15	–0,17	0,02

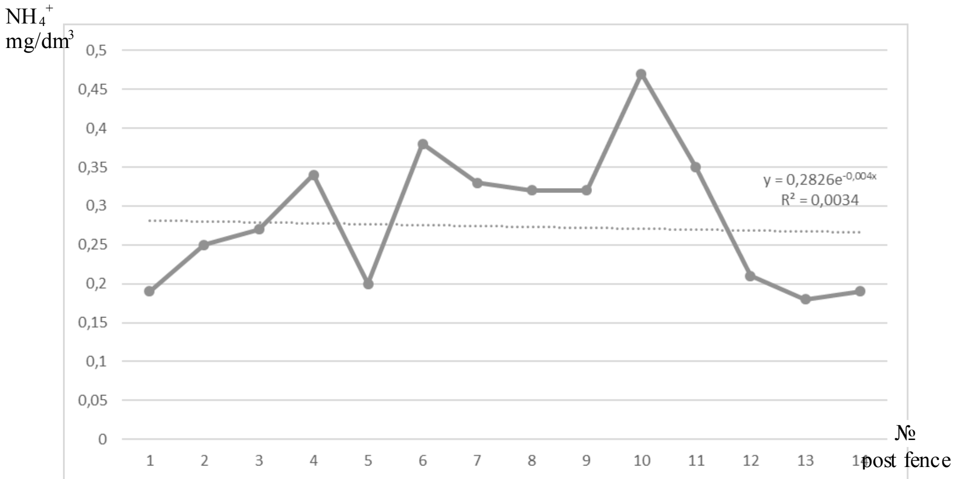

Fig. 4. Total ammonium content of NH_4^+ at water intake posts of the Dnieper basin for 2018

The ammonium content (2018) changes slightly differently from the phosphate ion content. From the data shown in Table 4 in Figure 4, a change in the ammonium content of NH_4^+ is observed along the entire course of the Dnieper River. Thus, in the areas between posts 2–3, 5–7, 10–13, partial self–cleaning is provided, yet between the other five posts there is a significant increase in pollution.

Analysis of changes in the values of the ratio of BOC5 to the concentration of dissolved oxygen in water (Table 5, Fig. 5) showed that only 4 posts of water sampling tend to improve the oxygen regime of water, the remaining 10 posts its constant deterioration, indicating loss the ability of the waters of the Dnieper basin to self–purify.

Table 5. The difference in the ratio of BOC_5 to the concentration of dissolved oxygen between the posts of water intakes of the Dnieper basin

Year	Δ BOC_5/CO_2 mg/dm^3										
	P2–1	P4–3	P5–4	P6–5	P7–6	P8–7	P10–9	P11–10	P12–11	P13–12	P14–13
2010	0	–	–	–	–	–	–	–	–	–	–
2011	–0,01	0,37	–0,39	0,2	0,09	–0,18	–	–	–	–	–
2012	–0,04	0,3	–0,41	0,07	0,09	–0,12	–	–	–	–	–
2013	–0,03	0,08	–0,11	0,11	0,02	–0,08	–	–	–	–0,03	0,03
2014	0,02	0,07	0,12	–0,16	0,02	–0,07	0,05	0,02	–0,18	0,01	–0,01
2015	0	0	–0,06	–0,09	0,15	–0,17	0,03	0,03	–0,19	–0,04	0,04
2016	0	0,04	–0,05	–0,17	0,28	–0,33	0,15	0,00	–0,15	–0,08	0,08
2017	0,01	0,11	–0,21	–0,07	0,17	–0,18	0,05	0,05	–0,19	–0,05	0,05
2018	0,02	0,53	–0,52	–0,03	0,19	–0,25	0,08	0,01	–0,23	–0,03	0,03
2019	–0,01	0,41	–0,43	–0,02	0,16	–0,13	0,08	0,11	–0,24	–0,08	0,08

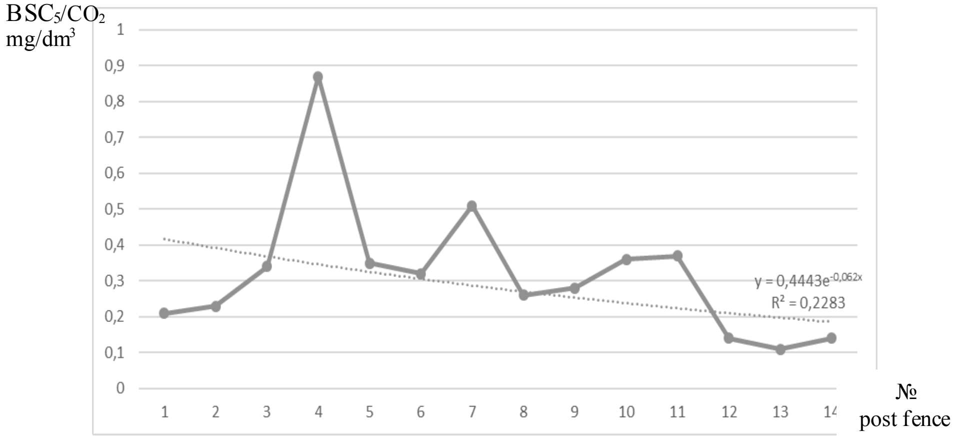

Fig. 5. Total content in relation to BOC_5 to the concentration of dissolved oxygen at the posts of water intakes of the Dnieper basin for 2018

The content of nitrates, nitrites is an important indicator of the chemical composition of natural water, which is used in environmental assessment and standardization of natural water quality. The relationship between their content, in addition to assessing water quality, can be used as an indicator in addressing the balance of nutrients, the relationship between the life processes of aquatic organisms and the chemical composition of water. Therefore, it was advisable to establish a correlation between the content of nitrates and nitrites at the studied fence posts (Fig. 6).

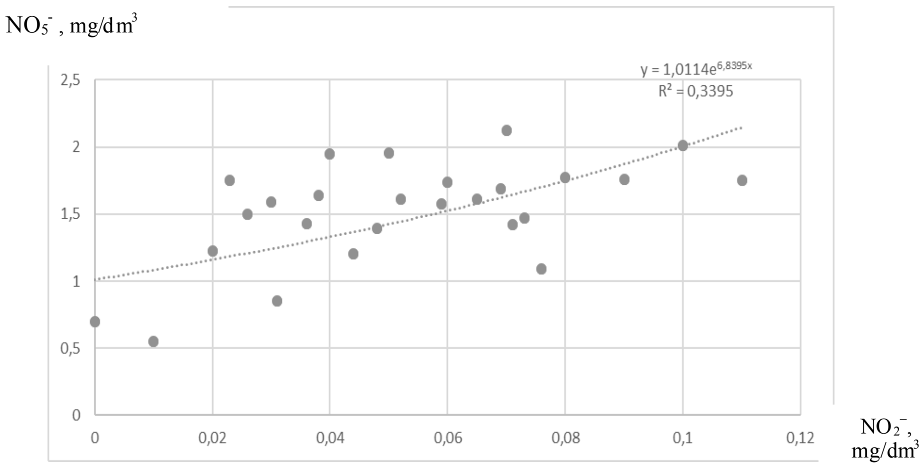

Fig. 6. Correlation between the average annual concentrations of nitrite and nitrate ions in the water of the Dnieper for the period 2010–2019.

In addition, it should be taken into account the fact that the rapid development of bioplankton of blue–green algae provokes water blooms in the shallow waters of the Dnieper reservoirs, which make up more than 30% of their territory.

Under conditions of supersaturation of the Dnieper water with organic and biogenic substances, the processes of extinction, putrefaction, decomposition of algae and bioplankton intensify, which causes deterioration of the oxygen regime, lowering the pH of water in the bottom layer and, consequently, increasing manganese ion concentration. The concentration of manganese in the period July – August increases, compared to the winter period, in 3–10 times and is about 1.9 ÷ 7.0 mg/dm^3.

First of all, it should be noted that the manganese ion $Mn^{2+}$is part of a fairly strong reducing agent. The reaction MnO_2 + 4H + 2e– = Mn^{2+} + $2H_2O$ is characterized by the value of Red–Ox potential E_0 = 1,23 V. But in the summer, when the concentration of oxygen in the water of surface sources decreases significantly, it as a natural oxidant in water is not enough to to convert the highly water–soluble manganese ion Mn^{2+} to the sparingly soluble compound MnO_2.

Based on the survey of the Dnieper river basin and the results of hydrochemical analyzes, using the developed integrated matrix assessment of the state, a ranked series was compiled according to the selected sections along its length (Table 6).

Table 6. Ranked number of areas for the inflow of pollutants between the posts of water intakes of the Dnieper

№ by order	Areas between posts	The contribution of the site
1–2	Sozh river, 32 km, village St. Yarilovichi, Ripkin district (border with Belarus) – Dnieper, 1116 km, s. Kamyanka, below the village, Ripkin district (border with Belarus)	0,09
3–4	Uzh River, 15 km, village Cherevach, drinking water in the city of Chornobyl – Dnipro, 897 km, Vyshhorod, n / a Kyiv HPP, drinking water in the city of Kyiv	0,32
5–6	Dnipro River, 833 km, Ukrainka, below the city, above the water supply line Bila Tserkva–Uman – Dnipro River, 678 km, p. Sokirne, drinking in / from Cherkasy	0,23
7–8	Dnipro, 580 km, village Vlasivka, left bank, drinking water supply station, Kremenchuk – Dnipro river, 462 km, township Aula, drinking in / from Dnipro and Kamyanske	0,09
9–10	Dnipro, 404 km, Dnipro, SE «PdTES» PJSC «DTEK Dniproenergo», drinking water – Dnipro, 312 km, Zaporizhia, GNS Zaporizhzhya Armed Forces	0,18
11–12	Dnipro, 253 km, Energodar, influence of Zaporizhzhya NPP – Dnipro, 160 km, town Velyka Lepetykha, Rubanivska ZS	0,06
13–14	Dnipro, 65 km, village Ivanivka, Belozersky district, in the district of drinking water supply station of Mykolayiv water supply system – Dnipro river, 0 km, village Kizomis (Rvach sleeve)	0,03
Amount		1

Thus, the results of the research allow us to claim a significant deterioration of the ecological condition of the Dnieper, which today, due to man–made impact, leads to a deterioration of water quality and its river runoff.

The use of the proposed interpreted methodological approach to determine the assessment of water pollution in the Dnieper basin makes it possible to assert the nature and degree of its pollution; at the same time in the future requires a more detailed study of the impact of 15 tributaries of the Dnieper, which, flowing into the river within Ukraine, to change its ecological status.

The reasons for the constant increase in the total anion content in the waters of the Dnieper may be municipal sewage, as well as sewage of enterprises, especially against the background of insolvency, due to over–regulation of the construction of the Dnieper reservoir cascade, to its self–treatment.

An exception was the part of the water area between the 5th and 4th posts, the possible reason for which may be the dilution of the Dnieper water with the waters of the Desna and Trubizh rivers, the total water flow of which is more than 400 m^3/s.

However, it should be noted that in the water area between the 10th and 12th posts of the fence there is a process of self–cleaning; this can be explained by the fact that there are no tributaries between these posts (Fig. 2). This fact can be a confirmation of the Dnieper's ability to self–clean, and its tributaries can be the main source of pollution.

The revealed tendency to change the content of phosphate ions and ammonium, in the direction of their increase, can be explained by the fact that along with the intensification of bioproductive processes in reservoirs and the introduction of nitrogen and phosphorus fertilizers in water may increase the concentration of ammonium and phosphate ions. The influence of phosphate ions and ammonium on the qualitative ecological state of the surface source is explained by their ability to act as chemical catalysts for the process of man–made eutrophication of surface waters, which is characterized by a sharp increase in algal biomass, higher aquatic vegetation, phytoplankton due to nutrient nutrients.

As a result of biochemical decomposition of this biomass in river water and reservoirs, oxygen deficiency can occur, especially in summer, which is accompanied by fatigue and poses a significant threat to the life of many aquatic organisms. In addition, the decomposition of plant organisms releases toxic substances into the water that are dangerous for both animals and humans (toxoids, aphantotoxins, microcystins, metabolites and biologically active substances – hydrogen sulfide, methane, ammonia, phytohormones and enzymes).

An additional reason for the increase in phosphate content may be the inflow of untreated and insufficiently treated wastewater from municipal, industrial and agricultural enterprises into the Dnieper waters against the background of constant population use of various detergents and other household chemicals. points, including country settlements, the area under construction along the river banks is increasing every year without compliance with water protection zones.

Of particular concern is the increase in phosphate (as well as ammonium) content between intake posts 5 and 6, given the fashion trend and prestige of private sector buildings on the banks of the Kaniv Reservoir and given the main sources of surface water; the reasons for this increase have a logical explanation and allow us to assert the projected increase in their content in the future.

Additional sources of ammonium ions in water bodies can be livestock farms, domestic wastewater, as well as wastewater from the food, coke, forest chemical and chemical industries.

The concentration of dissolved oxygen in water directly depends on the degree of contamination of surface waters. The content of dissolved oxygen in water determines the life of aquatic organisms that use oxygen for respiration, the intensity of oxidation and decomposition of organic residues, self–purification of water bodies.

Elevated levels of BOC_5 indicate an insufficient amount of dissolved oxygen, which is spent on aerobic biochemical oxidation of unstable organic compounds to CO_2, H_2O, NH_3. In addition, BOC_5 also characterizes the total content of organic matter in water and the state of pollution of water bodies, the main indicators of which are the content of organic matter and ammonium compounds, on which largely depend the conditions to ensure the required oxygen content in rivers.

The source of high nitrate content in surface water can be surface water due to intra–reservoir nitrification processes of ammonium ions under the action of nitrifying bacteria, with precipitation, discharges of industrial and domestic wastewater, runoff from agricultural lands containing nitrogen.

Decreased nitrate levels are associated with their consumption by phytoplankton and denitrifying bacteria (aquatic plants). It is a known fact that today, due to the widespread use of mineral fertilizers in many parts of the world there are cases of contamination of surface waters with nitrates.

The danger of drinking water with a high content of NO_3^- is that nitrates, getting with water into the human body, are restored by the microflora of the digestive tract and tissue enzymes to nitrites, the toxicity of which is 10–20 times higher than NO_3^-, and react with amino acids , forming carcinogenic compounds nitrosoamines.

Nitrites NO_2^- is an intermediate form in the chain of bacterial processes of oxidation of ammonium to nitrates (nitrification – in aerobic conditions) and, conversely, the reduction of nitrates to nitrogen and ammonia (denitrification – in the absence of oxygen). Nitrates enter surface waters when nitrites are used as corrosion inhibitors in process water treatment, with wastewater discharges from the food industry, and runoff from agricultural lands.

Increasing concentrations of nitrites indicate increased decomposition of organic matter under conditions of slower oxidation. The increased concentration of nitrites indicates the intensity of decomposition of organic matter and delayed oxidation of NO_2^- to NO_3^-, which clearly indicates the pollution of the reservoir.

Additional evidence of the deterioration of the ecological condition of the waters of the Dnieper basin was revealed as a result of studies of increasing trends in the concentration of manganese ions in the form of Mn^{2+} due to the rapid development of blue–green algae bioplankton and water blooms due to their presence.

CONCLUSION

The proposed interpreted methodological approach to assessing the quality of surface water allows us to state that the aquatic ecosystem of the Dnieper River, as the main waterway of Ukraine, and the transboundary water body, under constant man–made influence, tends to permanent and persistent deterioration of its ecology. In the future, it is possible to use the proposed approach to analyze changes in the ecological status of other surface water sources. Given the results of the analysis, further change in the ecological status of surface waters of the Dnieper basin in the direction of its improvement can not occur without the development and implementation of a reliable and effective model for forecasting its ecological status, and the only possible way to solve the deterioration of the Dnieper control levers of the basin directorate.

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ALGAE AND CYANOBACTERIA OF THERMAL SPRINGS IN VYSNE RUZBACHY SPA (SLOVAKIA)

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ABSTRACT

Algae and cyanobacteria occur in very different aquatic habitats, ponds, lakes, hot springs, on moist barren soil, tidal flats and cliffs. In general they provide much Earth's oxygen and foods base for almost all aquatic life. These organisms are an original source of petroleum products and provide foods and industrial elements for humans. Their R&D plays an important role for the future existence of man.

There are more than 1,300 mineral sources in Slovakia that are used like curative water and high quality mineral water for drinking. The Spis Spa of Vysne Ruzbachy [GPS: N 49°18'23"; E 20°33'33", its altitude: 623 m] , which is situated in eastern Slovakia on the boundary between two national parks – the High Tatras National Park (TANAP) and the Pieniny National Park (PIENAP), has become well-known mainly thanks to its mineral thermal springs. They are in algology fields represent very interesting localities. The thermal springs, which from travertine, are based on the local natural waters – hydro-carbonic, calciferous-magnesium and hypotonic water with low mineralization and temperatures up to 26 ºC.

Observations on thermophilic algal communities at 8 thermal springs and one cave have been analysed during seasons 2014 and 2015. The purpose was evaluated the distribution of species in thermal streams relative to temperature and competitive interactions. 14 genera of cyanobacteria with 22 species, 21 genera of diatoms with 39 species, 12 genera of green algae with 14 species and 4 interspecific taxa from different groups of algae were recorded. Totally 79 species of algae and cyanobacteria were determined. Algae flora consisted mainly of thermophilic, halophilic and species which prefer unpolluted environment. In regard to taxonomic diversity with similar thermal springs in Slovakia, the research showed distinctive and specific algae and cyanobacteria species, f. e. taxa of diatoms *Luticola nivalis*, *Pinnularia borealis*, *P. subgibba*, *P. viridiforis*, *Diploneis Krammer*, *Navicula amphiceropsis*, *N. digitoconvergens*, *Ropalodia rupestris*, green algae *Klebsormidium rivulare* and cyanobacteria *Oscillatoria rupicola*, *Phormidium crustaceum*, *Gloeothece rupestris* and *Gloeocapsa alpina*.

Temperature appears was the most important physical factor affecting the distribution in alkaline springs, interspecific competition for space also influences the distribution. Diatoms and cyanobacteria species commonly occurring above 14.3 ºC are noted, along with the apparent tolerance by certain species of temperatures in excess of 24.3 ºC. The diversity of the diatom and cyanobacteria flora increases as the water cools. Despite thermal and chemical constancy, the growth rate of the algae is negligible during the winter months when light is

minimal. It is the first significant study in the issue of algal species diversity in the Vysne Ruzbachy localities in Slovakia.

Key words: algae, biodiversity, cyanobacteria, thermal springs, thermophilic, Vysne Ruzbachy

INTRODUCTION

Cyanobacteria are ancient photosynthetic microorganisms, which have been involved in creating an oxygen atmosphere in the planet Earth. They dominated in the period 2.5 to 0.6 billion years ago. The oxygen concentration increased to the current value during this long time. On the other hand, they have adapted to almost all habitats on climatic conditions and therefore we still find them in many thermal springs and other extreme habitats [6].

The body of consists of single cells, short filaments, tidal flats and cliffs. Cells almost always encased in mucilaginous envelope. They contain chlorophyll a, β-carotene, and 2 water-soluble pigments – phycocyanine and phycoerythrine [15]. The name blue-green algae are derived from its colour. As a reserve they accumulate cyanophyte starch. No flagellated cells occur and sexual reproduction has been established. Their reproduction is carried out by fragmentation in filamentous forms or by cell division. Filamentous genera produce thick-walled cells – heterocyst, can fix aerial nitrogen (N_2), and acinetes to withstand adverse conditions. Cyanobacteria have ecological importance in global carbon and nitrogen cycles as well as evolutionary significance. They are the most abundant group of organisms on the earth and found in a diverse environment, especially in the marine and freshwater. Taxonomic belongs to the empire of *Bacteria* (prokaryotic organisms) and the division of *Cyanophyta* [18].

Algae are a very diverse group of all photosynthetic (eukaryotic) organisms. Eukaryotic algal cells contain 3 types of double membrane bound organelles: nucleus, chloroplast and mitochondria. Many algae consist of only 1 cell, other have 2 or more cells, and the largest have millions of cells. They have many types of life cycles, from simple to complex.

The major groups of eukaryotic algae are the diatoms, red algae, brown algae and dinoflagellates, which are classified in empire *Chromista* and the group of green algae is in empire *Plantae* [18]. Diatoms and green algae with their large prevalence are important for our study of life in thermal springs.

Each diatom has a cell wall made of glass that is very finely etched with a species specific pattern of dots and lines. The patterns on the diatom cell walls are so precise that they are used for many years to test the optics of new microscopes (picture 1 and 2). Diatoms are also the most abundant algae in the open ocean and responsible for one-quarter of all oxygen production on the earth each year.

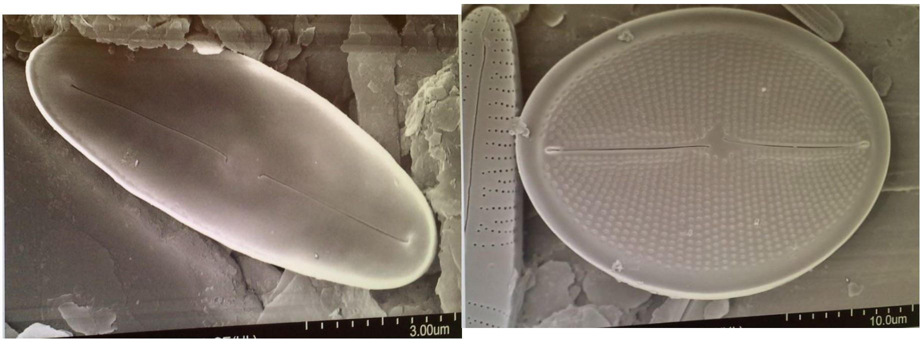

Fig. 1 and 2: Micrographs of diatoms [3.00 μm and 10.00 μm] taken on scanning electron microscope show the characteristic depth of fields, dots and lines (photos: Salamon, I., Rzesow University, Poland, 2018).

Green algae have the same pigments (chlorophyll a, b and carotenoids), the same primary and secondary metabolites, the cellulose cell walls and the same storage product, starch, as the plants. They may be unicellular of form filaments, nets, sheets, spheres, or complex moss like structures.

The economic and ecological importance of algae is huge [14]. They are played important function in marine, freshwater, and some terrestrial ecosystems. Algae are the base of the aquatic food chain. The photosynthesis done by this group of organisms is very important to biosphere because it reduces the amount of carbon dioxide (CO_2) and increases of amount of oxygen (O_2) in the atmosphere.

The primary interest is in the habitat of thermal springs as living conditions for cyanobacteria and green algae. Some springs are heated by subterranean magma or other heat sources and emerge at temperatures much greater than the surrounding ambient water and atmospheric temperatures. These hot or thermal springs are unique to the point of rarity, but are found throughout the world, mostly near fault and tectonic zones and near volcanoes [4].

Hot springs are as varied as the ground chemistry and heat sources that define them. Some are acidic, characterized by sulphur (S) fumes and low productivity. Others are basic, characterized by high concentrations of salts and precipitates. Many thermal springs support colonies of algae and cyanobacteria that mesh together to form mats [16].

The temperature is greatest at the source of hot springs, but it cools as a function of distance from that source, along the spring runoff. A succession of life is found along this thermal gradient. Species of algae and cyanobacteria occupy niche spaces defined by temperature, chemistry, and competitive exclusion, sometimes in a predictable pattern. The largest number hot springs are protected in the Yellowstone National Park in North America (picture 3 and 4). Many research projects studied thermophilic algae and cyanobacteria in this part of the USA for at least 70 years [32].

Fig. 3 and 4: Yellowstone National Park and its thermal springs, one with a geyser (photos: Salamon, I., Wyoming State University, WY, USA, 2014).

The majority of research has focused on several hot springs in the national parks. However, only few studies of thermal springs have consisted of surveys of large geographic areas. Such investigation could answer whether thermophilic species of green algae and cyanobacteria are truly cosmopolitan or could find new species [5].

The aim of this study was of the taxonomic determination of photosynthetic microorganisms, algae and cyanobacteria, which were occurring in the thermal springs in Vysne Ruzbachy Spa area, the Eastern Slovakia. The complex aspects of our research at this same time included abiotic environmental factors, comparison of these springs with other Slovakian thermal waters and their occurrence of cyanobacterial and algal species.

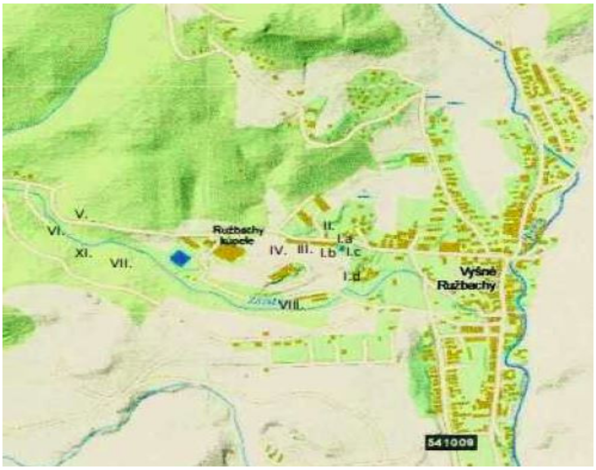

Fig. 5: 12 phytoplankton sites, which were monitoring: I. Karolina: I.a Krater, I.b Bazen 1, I.c Bazen 2, I.d Vodopad, II. Stastny, III. Ondrej, IV. Vojtech,

METHODS AND EXPERIMENTAL PROCEDURES

Microalgae were collected by scraping, brushing, or suctioning material from all periphyton microhabitats present in the sampling reach and placing algal collections from each microhabitat into a separate container. Samples of cyanobacteria and algae were taken in winter on January 28, 2014/January 31, 2015 and in summer on July 14, 2014/July 31, 2015 from 11 springs and one cave in Vysne Ruzbachy Spa [GPS: N 49°18'23"; E 20°33'33", its altitude: 623 m]. A total of 12 localities were monitored during 2 years, from which 49 samples were taken (picture 5). The same procedures, numbers and types of samples were followed for both samples.

Qualitative phytoplankton samples were preserved with formalin (4 %) and were identified with a sample label and with information recorded on the field data sheet. Samples were transported and stored in boxes containers that they protect from exposure to light.

Physical and chemical parameters of water, namely conductivity, temperature and pH values, were measured at individual sites using a Hanna Combo HI 98129 multifunction device.

The determination of organisms was carried out at the Department of Botany, Faculty of Science, University of South Bohemia in Ceske Budejovice, Czech Republic. The samples were microscopically fresh, and fixed samples and cultures were used in addition.

An Olympus BX51 light microscope was used to determine the cyanobacteria and algal species.

The type BX51 is the microscope, which allows reflected light observation as well as transmitted light observation. Reflected light mode offers dark field, where the angle of sample illumination is 90°, and bright field, where the sample is illuminated sideways, observation. The microscope is equipped with a colour digital camera with a resolution of 5 megapixels and connected to a powerful computer system. The system as a whole is designed to provide accurate colour reproduction of the observed sample. The type BX51 is suitable for observation of defects on the film surface, impurities, and corrosion of the substrate, effect pigments and film thickness. Its specifications are as follows: - transmitted light: LBD (sunlight spectrum filter), ND25 and ND6 (grey filters); - reflected light: BF (bright field), DF (dark field); - magnification: ocular 10×; objective lenses 5×, 10×, 20×, 50× in 100×; - maximum sample height: 25 mm; and - maximum sample dimensions: 150 mm × 150 mm.

The Olympus DP73 camera was used for documentation together with the computer program Cellsens standard. The program is designed to capture digital photos from a microscope. The camera settings allow you to save, edit and measure parameters such as circumference, length, angles, areas and counts objects. The advantage of the documentary apparatus is also the rotating head, which adjusts the orientation of the image as it necessary.

The phytological literature for the period last 30 years was reviewed and used. In order to check the habitats and described taxa, some localities studied previously were visited during the period January 2013 – November 2013. All the analyses were made using the taxonomic system of Hindak (1978): Freshwater Algae; and (2008): Colour Atlas of Cyanophytes; with some additions according to the taxonomical works by Komarek and Anagnostidis (1999, 2005), Komarek (2013), Lange-Bertalot (2011) and Sladecek and Sladeckova (1996).

Characteristics of the studied area

The Spis Spa of Vysne Ruzbachy, which is situated in eastern Slovakia on the boundary between two national parks – the High Tatras National Park (TANAP) and the Pieniny National Park (PIENAP), has become well-known mainly thanks to its mineral waters. The spa is located at 623 metres above sea level, forms part of the village of Vysne Ruzbachy with its coordinates: N 49°18'23"; E 20°33'33".

The therapeutic effects of the earthy carbonate mineral water springs were also well known in the Middle Ages when the first spa was founded here. The oldest written reference to the existence of springs is from the captain of the Spis Castle from 1549. Polish and Hungarian nobility liked to visit this spa in the next few centuries.

Therapeutic and preventive effects of the spa are based on the local natural healing waters - hydro-carbonic, calciferous-magnesium and hypotonic 14 springs with low mineralization and temperatures up to 26 ºC. The healing properties of these natural carbonic springs are ensured through the absorption of carbon dioxide into human skin during bathing, which leads to the dilatation of skin capillaries and better skin blood flow [3]. The most productive spring Izabela feeds the outdoor swimming pool. At the centre of the swimming pool is a small round island with greenery [17].

The geological characteristics of the Ruzbasske foothills are in Mesolithic limestones, quartzites and dolomites. Travertines form a relatively complex system of terraced hills, cascades and craters [3]. Travertine is a common continental limestone that is formed during the precipitation and accumulation of calcium carbonate ($CaCO_3$) and is largely due to aquatic plants, algae and cyanobacteria. The vegetation removes carbonate oxide (CO_2) from the water, thus forming a $CaCO_3$ precipitate [17]. Algae and cyanobacteria have a positive effect on limestone deposition due to the suitable physic-chemical microenvironment in which controlled biochemical and photosynthetic processes take place [23]. In the springing mineral water, the precipitates are mainly located on the edge of the crater, on the edge of the pools and by the waterfall. They form a white spring, which gradually hardens and thus creates new layers of travertine.

Biotopes (appendix 1)

Spring Karolina includes the localities: I.a Krater, I.b Bazen 1, I.c. Bazen 2, and I.d Vodopad. The water from all localities comes from one source, which is the Karolina spring. The spring is located near the entrance to the spa area, where it creates a natural formation - a crater. The crater formed by the fall of a travertine pile, which is an intra-crater cavity [1]. The spring stems in the middle of travertine crater, which is deep about 3 m with a diameter of about 20 m. The origin of the Karolina spring is in the Belianske Tatras, where this water is mineralized in layers of limestone and dolomites. The water temperature is approximately 23 ° C during year [24]. The water flows through a canal into two reservoirs (I.b Bazen 1, I.c Bazen 2). In front of the mouth, the spring from the crater is considered by a steep slope and creates a waterfall (Id. Vodopad). The reservoir is used as a natural swimming pool. The spring water is not drinkable [24].

II. Spring Stastny is located to the left of the Travertine spa house [24]. It is introduced into a travertine sculpture. The water is not drinkable.

III. Spring Ondrej and IV. Spring Vojtech: springs regulated into 2 fountains are located in the middle spa area. They spring from one source. Splashing water from fountains affects the entire perimeter of the artificially modified environment in which it is captured. The composition of water is earthy, it contains a lot of sulphates and acid carbonates per litter. Water is not for drinking.

V. Spring Svateny 1 is located in west orientation of the spa area. Hot mineral water flows out of the slope. It contains minerals – magnesium (Mg), calcium (Ca) sulphates, carbonates and a small amount of rare gases. This mineral water is possible to use for drinking purposes. The spring with a small well is protected by a wooden shelter [17].

VI. Spring Svateny 2 opposite the Svateny 1 on the right bank. Mineral water is trapped in a concrete shaft. Its composition is earthy carbonated. In the past it was used for drinking treatment. Today water is not drinkable.

VII. Spring Jan – the west of the spa area about 50 m in the forest is a lake with a diameter about 3.5 m. The hot water springs directly from the ground. In the pond it is possible to observe the release of gases from the sediment, which causes a slight bubbling on the surface. All space is located in a very nice environment, protected by forest and is faintly observable. This old crater was once used for swimming. The water is lukewarm earthy, surface polluted, currently not used and not drinkable [24].

VIII. Spring Jozef is located near the post office building in the village of Vysne Ruzbachy Spa. It is used for drinking purposes and its deep is up to 220 m deep. People from close surroundings the village know it and use this spring for its beneficial effects on health. A protective shelter has been built above the spring [3].

IX. Cave, Jaskyna – a small cave with one longitudinal 3 m long and 0.15 m high was found in the west of the spa area. Water flowed through this small calcium cave and there were also stalagmites in it. Despite its small size, it is a very nice natural formation [24].

RESEARCH RESULTS

The differences among cyanobacteria species in different thermal springs are shown in Table 1. The largest biodiversity in regard to this division is in the spring Karolina, the part I.d. Vodopad. The cyanobacteria species: *Calothrix parietina* (Nägel) Thuret, *Gloeocapsa alpina* (Nägeli) Brand, *Leptolyngbya* sp. and *Phormidium* sp. 2 were found in most thermal springs. The rare species were occurred one by one in the hot springs were these: *Aphanothece smithii*

Kom.-Legn. et Cronberg, *Cyanobacterium minervae* (Copeland), *Geitlerinema splendidum* (Grev. ex Gom.) Anagnostidis, *Gloeothece rupestris* (Lyngbye) Bornet, *Nostoc minutissimum* Kützing ex Bornet & Flahault and *Pseudanabaena galeata* Bocher.

Table 1. Cyanobacteria species of the springs in Vysne Ruzbachy Spa.

Empire: ***Bacteria***	**Habitat**											
Division: ***Cyanobacteria*** Species	**I.a**	**I.b**	**I.c**	**I.d**	**II.**	**III.**	**IV.**	**V.**	**VI.**	**VII.**	**VIII.**	**IX.**
Aphanothece smithii Kom.-Legn. et Cronberg									×			
*Calothrix parietin*a (Nägel) Thuret	×			×	×	×		×	×			×

Cyanobacterium minervae (Copeland)				×								
Geitlerinema amphibium (Ag. ex Gom.)							×					
Geitlerinema splendidum (Grev. ex Gom.) Anagnostidis											×	
Gloeocapsa alpina (Nägeli) Brand	×		×	×	×		×	×				×
Gloeothece rupestris (Lyngbye) Bornet				×								
Heteroleibleinia sp.				×								×
Chroococcus minutus (Kütz) Nägeli			×			×	×					
Leptolyngbya sp.	×		×	×	×	×			×	×		×
Limnothrix sp.	×			×								
Nostoc minutissimum Kützing ex Bornet & Flahault								×				
Nostoc sp.				×			×			×		
Oscilatoria rupicola Hansgirg						×						
Phormidium crustaceum Voronichin				×	×							
Phormidium sp. 1										×		
Phormidium sp. 2	×		×	×	×	×		×		×		
Pseudanabaena cf. *catenata* Lauterborn				×				×				
Pseudanabaena galeata Bocher								×				
Pseudanabaena limnetica (Lemmermann) Komarek	×		×									
Pseudanabaena sp.					×							
Rivularia haematites (DeCandole)		×		×								
Total number of species	**6**	**1**	**5**	**12**	**6**	**5**	**4**	**6**	**3**	**4**	**1**	**4**

Legend: I. Karolina: I.a Krater, I.b Bazen 1, I.c Bazen 2, I.d Vodopad, II. Stastny, III. Ondrej, IV. Vojtech, V. Svateny 1, VI. Svateny 2, VII. Jan, VIII. Jozef, IX. Jaskyna

Table 2 presents the diatom diversity of 12 thermal springs. Diatoms have only unicellular thallus. It is composed of two overlapping cell halves. Cell wall is impregnated by silicon dioxide (SiO_2). Cell wall made of glass is very finely etched with a species-specific pattern of dots and lines. It was very important in determination differences among species. It is the largest group of organisms in terms of numbers. The huge number of species of diatoms was determined in hot springs: VI. Svateny 2, Karolina: I.d Vodopad, V. Svateny 1, III. Ondrej and VII. Jan. The species most occurring in individual hot springs were as follows: *Achnanthes thermalis* (Rab.) Schoen. var. *thermalis*, *Achnanthidium exile* (Kütz.) Roun d& Bukhtiyarova, *Amphora coffaeformis* (Agardh) Kützing, *Caloneis alpestris* (Grunow) Cleve, *Caloneis silicula* (Ehrenberg) Cleve, *Cymbella cymbiformis* C. Agardh, *Navicula amphiceropsis* Lange-Bertalot & Rumrich, *Nitzschia palea* (Kütz.) W. Smith var. *palea*, *Pinnularia brebissonii* (Kützing) Rabenhorst and *Planothidium lanceolatum* (Bréb. ex Kütz.) Lan-Bert. The rare diatom species were following: *Cocconeis placentula* Ehrenberg, *Cyclotella meneghiniana* Kützing, *Navicula lanceolata* (C. Aghard) Ehrenberg, *Nitzschia fruticosa* Hustedt, *Pinnularia gibba* Ehrenberg and *Tabellaria flocculosa* (Roth) Kützing.

Table 2. The occurrence of the diatoms in different habitats of Vysne Ruzbachy Spa.

Empire: ***Chromista***	**Habitat**											
Division: ***Chromophyta*** Class: ***Bacillariophyceae*** Species	**I.a**	**I.b**	**I.c**	**I.d**	**II.**	**III.**	**IV.**	**V.**	**VI.**	**VII.**	**VIII.**	**IX.**
Achnanthes thermalis (Rab.) Schoen. var. *thermalis*		×	×	×	×	×		×	×			
Achnanthidium exile (Kütz.) Roun d& Bukhtiyarova		×	×	×	×	×		×				×
Achnanthidium minutissimum (Kützing) Czarnecki				×		×		×				×
Amphora coffaeformis (Agardh) Kützing		×		×		×			×	×	×	×
Caloneis alpestris (Grunow) Cleve				×	×	×		×		×	×	
Caloneis silicula (Ehrenberg) Cleve		×		×	×	×			×	×		×
Cocconeis placentula Ehrenberg									×			
Craticula buderi (Hustedt) Lange-Bertalot				×								
Cyclotella meneghiniana Kützing									×			
Cyclotella ocelata Pantocsek								×				
Cymbella cymbiformis C. Agardh	×	×	×	×	×	×		×	×	×		×
Cymbella sp. 1				×								
Diploneis krammeri Lange-Bertalot & E.Reichardt								×		×	×	
Encyonopsis				×					×			

microcephala (Gronow) Krammer												
Epithemia argus var. *alpestris* (W.Smith) Grunow									×	×		
Epithemia turgida (Ehrenberg) Kützing		×				×		×	×	×		
Gomphonema parvulum (Kützing) Kützing				×		×	×	×	×			
Luticola nivalis (Ehrenberg) D. G. Mann								×				
Melosira varians C. Agardh									×			
Navicula amphiceropsis Lange-Bertalot & Rumrich	×	×		×	×	×			×		×	
Navicula lanceolata (C. Aghard) Ehrenberg		×										
Navicula sp. 1				×				×		×		
Navicula digitoconvergens Lange-Bertalot										×		
Nitzschia palea (Kütz.) W. Smith var. *palea*		×	×	×	×	×						×
Nitzschia fruticosa Hustedt						×						
Nitzschia sinuata (W. Smith) Grunow										×		
Nitzschia solgensis Cleve - Euler									×	×		
Nitzschia sp. 1				×								
Nitzschia sp. 2						×					×	
Nitzschia sp. 3									×			
Pinnularia borealis Ehrenberg var. *borealis*								×				
Pinnularia brebissonii (Kützing) Rabenhorst		×		×		×	×	×	×	×	×	
Pinnularia gibba Ehrenberg								×				
Pinnularia subgibba Krammer var. *subgibba*								×			×	
Pinnularia viridiformis Krammer										×		
Planothidium lanceolatum (Bréb. ex Kütz.) Lan-Bert.		×		×	×	×		×	×	×		×
Ropalodia rupestris W.						×			×	×		×

Smith (Krammer)												
Tabellaria flocculosa (Roth) Kützing									×			
Ulnaria ulna (Nitzsch) P. Compere				×		×		×	×			
Total number of species	**2**	**9**	**4**	**18**	**8**	**17**	**2**	**17**	**19**	**15**	**7**	**8**

Legend: I. Karolina: I.a Krater, I.b Bazen 1, I.c Bazen 2, I.d Vodopad, II. Stastny, III. Ondrej, IV. Vojtech, V. Svateny 1, VI. Svateny 2, VII. Jan, VIII. Jozef, IX. Jaskyna

Species (table 3) of class *Xanthophyceae* can occur in nature, none are known to be of practical importance. They are characterized by possession of chlorophylls a, c_1, and c_2 and a range of xanthophylls, but not fucoxanthin, in generally yellowish-green, discoidal, parietal chloroplasts. Thylakoids are in groups of three, and most species investigated have a single thylakoid forming a girdle band around the periphery of the chloroplast. Chloroplasts are surrounded by chloroplast endoplasmic reticulum [27].

Table 3. Stramenopilan photoautotrophs single species of class *Xanthophyceae* in Vysne Ruzbachy Spa springs.

Empire: **Chromista**	**Habitat**											
Phylum: ***Chromophyta*** Class: ***Xanthophyceae*** Species	**I.a**	**I.b**	**I.c**	**I.d**	**II.**	**III.**	**IV.**	**V.**	**VI.**	**VII.**	**VIII.**	**IX.**
Tribonema vulgare PASCHER									×			
Vaucheria geminata D.C.	×			×	×					×		
Total number of species	**1**	**0**	**0**	**1**	**1**	**0**	**0**	**0**	**1**	**1**	**0**	**0**

Legend: I. Karolina: I.a Krater, I.b Bazen 1, I.c Bazen 2, I.d Vodopad, II. Stastny, III. Ondrej, IV. Vojtech, V. Svateny 1, VI. Svateny 2, VII. Jan, VIII. Jozef, IX. Jaskyna

The majority of aquatic green algae are freshwater forms and their occurrences in various hot springs in Vysne Ruzbachy Spa are shown in Table 4. The species of *Chlorophyta* occurring most of them in the hot springs of these localities were *Klebsormidium flacidum* A. Braun and *Spirogyra* sp., only. The richest icidence of species of this phytoplankton group was in the Karolina: I.d Vodopad habitat.

Table 4. The number of green algae species and their diversity in hot springs

Empire: ***Plantae***	**Habitat**											
Phylum: ***Chlorophyta*** Species	**I.a**	**I.b**	**I.c**	**I.d**	**II.**	**III.**	**IV.**	**V.**	**VI.**	**VII.**	**VIII.**	**IX.**
Cosmarium botrytis Meneghini					×							
Chaetophora pisiformis (Roth) Agardh				×								
Chlorophyta 1				×								
Chlorophyta 2									×			

Klebsormidium flacidum A. Braun	×		×	×	×	×	×					
Klebsormidium rivulare Kütz.							×	×				
Microthamnion structissimum Rabenhorst												×
Misrospora sp.		×				×	×					
Mougeotia sp.				×								
Oedogonium sp.				×						×		
Spirogyra sp.				×		×	×	×				
Trentepohlia aurea (Linnaeus) C. F. P. Martius	×								×			
Ulothrix sp.					×							×
Zygnema sp.					×							
Total number of species	**2**	**1**	**1**	**6**	**4**	**3**	**4**	**2**	**2**	**1**	**0**	**2**

Legend: I. Karolina: I.a Krater, I.b Bazen 1, I.c Bazen 2, I.d Vodopad, II. Stastny, III. Ondrej, IV. Vojtech, V. Svateny 1, VI. Svateny 2, VII. Jan, VIII. Jozef, IX. Jaskyna

The very interesting taxa group is euglenas, which comprises unicellular flagellates with 2 flagella. They contain the same chlorophylls (a + b) and carotenoids as green algae and land plants. The reserve polysaccharide is paramylon. Some species are colourless and heterotroph. The name of phylum is derived from red eyespot (stigma) at the anterior end of the cell [28]. 2 species of *Euglenophyta* were determined in the thermal springs of locality Karolina – I.a Krater and I.d Vodopad (table 5).

Table 5. The euglena occurrence in different habitats of Vysne Ruzbachy Spa.

Empire: ***Protozoa***	Habitat											
Phylum: ***Eugelenophyta*** Species	**I.a**	**I.b**	**I.c**	**I.d**	**II.**	**III.**	**IV.**	**V.**	**VI.**	**VII.**	**VIII.**	**IX.**
Colacium physeter Fott				×								
Euglena sp.	×											
Total number of species	**1**	**0**	**0**	**1**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

Legend: I. Karolina: I.a Krater, I.b Bazen 1, I.c Bazen 2, I.d Vodopad, II. Stastny, III. Ondrej, IV. Vojtech, V. Svateny 1, VI. Svateny 2, VII. Jan, VIII. Jozef, IX. Jaskyna

The richest in regard to species diversity (appendix 1) was locality I.d Vodopad with up to 37 species. This site had representation of all determined phytoplankton taxonomical groups. There was also large diversity in habitats – III. Ondrej and VI. Svateny 2 with the number of species 26 at each thermal spring. The total species abundance of algae and cyanobacteria in 11 springs and 1 cave of Vysne Ruzbachy Spa are 79. Several species were interesting because they did not occur at other Slovakian localities (f. e. diatoms: *Luticola nivalis*, *Pinnularia borealis*, *P. subgibba*, *P. viridiforis*, *Diploneis krammeri*, *Navicula amphiceropsis*, *N. digitoconvergens*, *Ropalodia rupestris*, green algae: *Klebsormidium rivulare* and cyanobacteria: *Oscilatoria rupicola*).

The colour photographic illustrations of some freshwater cyanophytes, diatoms and green algae occurring in the hot springs of Vysne Ruzbachy Spa (pictures 6,7,8,9).

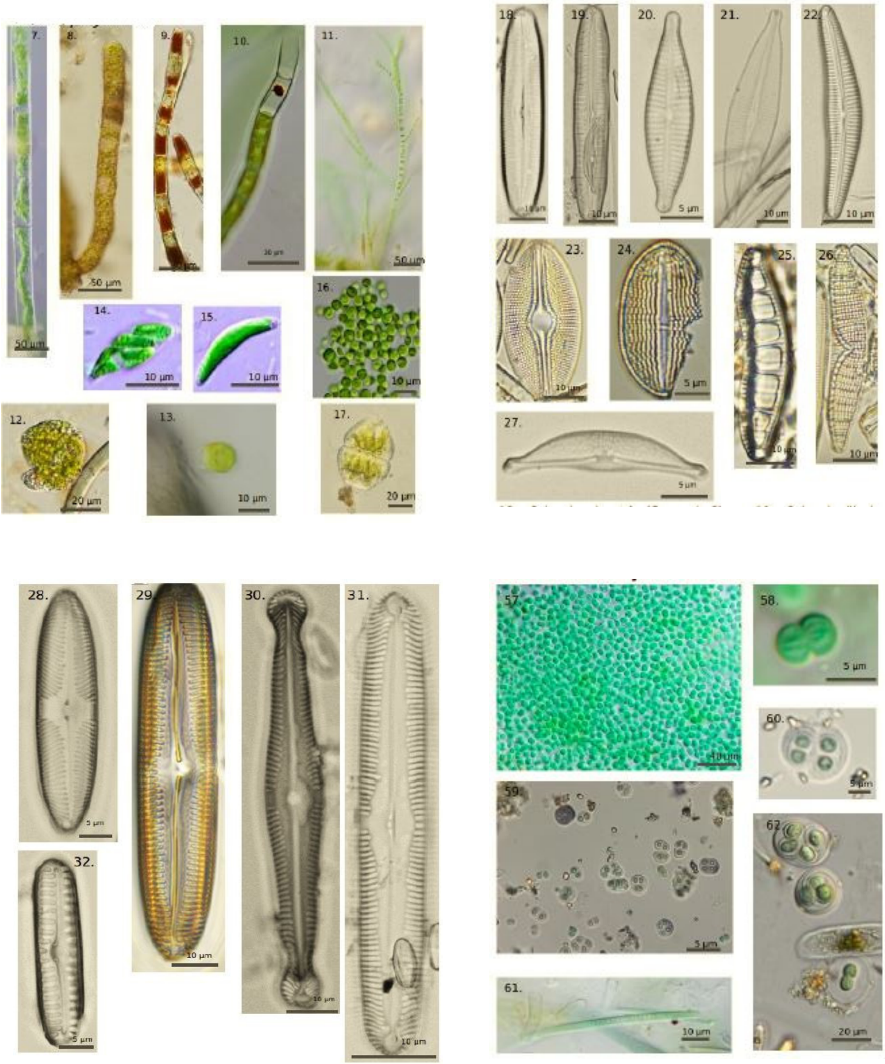

Fig. 6, 7, 8, 9: Species of phytoplankton in thermal springs of Vysne Ruzbachy Spa.

7. *Mougeotia* sp., 8. *Vaucheria geminate* D.C., 9. *Trentepohlia aurea* (L.) C.F.P. MARTIUS, 10. *Tribonema vulgare* PASCHER, 11. *Chaetophora pisiformis* (Roth)Agardh, 12. *Euglena* sp., 13. *Colacium physeter* Fott., 14.-15. *Chlorophyta* 1, 16. *Chlorophyta* 2, 17. *Cosmarium botrytis* Men., 18. *Caloneis alpestris* (Grunow) Cleve, 19. *Caloneis sicicula* (Ehrenberg) Cleve, 20. *Gomphonema parvulum* Kutzing, 21. *Craticula buderi* (Hustedt)Lange-Bertalot, 22. *Cymbella*, 23. *Diploneis krammeri* Lange-Bertalot, 24. 28. *Pinnularia brebissonii* (Kutzing) Rabenhorst, 29. *Pinnularia viridiformis* Krammer, 30. *Pinnularia gibba* Ehrenberg, 31. *Pinnularia subgibba* Krammer var. *subgibba*, 32. *Pinnularia borealis* Ehrenberg var. *borealis*, 57.-58. *Cyanobacterium minervae* (Copeland Komarek, 59.-60. *Gloeothece rupestris* (Lyngbye) Bornet.

Cocconeis placentula Ehrenberg, 25. *Epithermis argus* var. *alpestris* (W.Smith) Grunow, 26. *Epithemia turgida* (Ehrenberg)Kutzing, 27. *Amphora coffaeformis* (Agardh)Kutzing.

Physical Parameters

Winter spring temperatures ranged from 14.3 ° C to 19.9 ° C in years 2014 and 2015. Summer temperatures ranged from 16.6 ° C to 24.3 ° C (picture 10). Sites exposed to sunlight, unstoppable, showed a temperature more than 2 ° C higher compared to shaded ones.

The springs maintained their constant temperature in winter, which was much higher than the atmospheric temperature more 8 °C in the end of January both years. The temperature of the springs measured in winter was lower in all localities compared to summer measurements (picture 10). The largest temperature difference was recorded at the III. Ondrej spring, Where in winter the water temperatures reached 14.3 °C and in summer the temperature was higher more than 10 °C (24.3 °C).

The conductivity above 2000 µS.cm^{-1} was measured at most habitats of Vysne Ruzbachy Spa. The highest registered conductivity (2778 µS.cm^{-1}) was at IX. Jozef hot spring in January and in July (2589 µS.cm^{-1}) in 2014. The lowest measured conductivity values of 1600 µS.cm^{-1} were at site IX. Jaskyna and IV. Vojtech with 1744 µS.cm^{-1}. The values in summer were always slightly higher in order to winter season in both years. In regards to biotope observations this physical parameter was very stable during all 2 years. The average conductivity was higher than 2000 µS.cm^{-1}. The winter conductivity curve copies the summer one (picture 10).

The highest pH values of hot water about 8.66 were recorded in the I.d Krater spring. In contrast, the lowest measured pH values of 6.42 were in winter at springs V. Svateny 1 a VI. Svateny 2. The pH values all habitats were neutral to slightly basic in 2014 and 2015. The graph curves are copied with minimal deviations (picture 10).

In general, it was showed a confirmation of the stability of conditions by measured physical characteristics at the thermal springs in Vysne Ruzbachy Spa during 2 years. Slight deviations of graph curves from the average values are tolerance and they were mainly caused by the weather and climate created by geographical location. In our cases, there was no danger of the formation of eutrophic waters that would produce large amounts biomass. The water bloom did not formed and it was not toxic and dangerous for animals and humans alike.

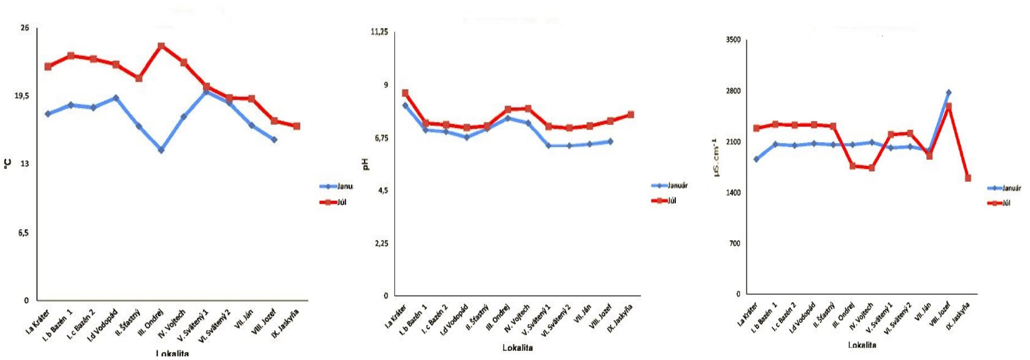

Fig. 10. Biotopes and their physical parameters (temperature, pH, conductivity).

DISCUSSION

Data on the distribution of cyanobacteria and algae in Slovakia are incomplete. Many localities are completely unexplored and need new observation. At the same time, the low level of information on the spread of phytoplankton does not allow us to fully assess the state of threat.

Due to few specialists in algology only, it is necessary to continue to address the issue of algal and cyanobacterial diversity.

The research was focused mainly on algae and cyanobacteria biodiversity on the thermal springs in Vysne Ruzbachy Spa. The premise was that the species of the phytoplankton in these springs were different from other Slovak Spa places.

The thermophilic algoflora in Piestany Spa has been studied in the past by Bily (1934), who determined 96 taxa and Rehakova (1976) with a total of 214 species found. Finally, Hindak and Hindakova studied the diversity of phototrophic microorganisms in thermal waters in Piestany Spa in 2006. They determined 20 species of cyanobacteria and 217 species and interspecific taxa from different groups of algae. The dominant feature was diatoms with 197 species and 16 intraspecific taxa. They were blue-green, green, reddish, violet, yellow, brown to dark brown or nearly black in colour.

In regard to comparison the results of the algae and cyanobacteria organisms of the hot springs from Piestany Spa and Vysne Ruzbachy Spa, it was found agreement in 20 species. Cyanobacteria were the same in 3 species (*Cyanothece minervae*, *Chroococcum minutus* and *Pseudanabaena galeata*). In both sources they found the same centric diatoms, halophilic species (*Amphora coffaeformis*), thermophilic species (*Achnanthes thermalis*) and other cosmopolitan species. The thermal baths in Vysne Ruzbachy Spa represented a greater species richness of cyanobacteria, but a smaller diversity of diatoms. The number of taxa of other groups of green algae was approximately the same, with only some genera matching.

In the past, only one paper has been published on the phytoplankton of the thermal springs of Sklene Teplice Spa. Hindak (1978) published only 4 coccal species of cyanobacteria. From several years of research observing the diversity of algae and cyanobacteria in this spa area, Hindak and Hindakova (2007) report 80 species of diatoms and 30 species of cyanobacteria.

The temperature of the springs in Sklene Teplice Spa is higher than in Vysne Ruzbachy. However, plankton organisms had aquatic environments with similar physical and chemical characteristics. In regard to comparing the diversity from both places, in Sklene Teplice Spa the species composition is slightly richer [12]. The same species were determined in only 2 taxa of cyanobacteria (*Cyanothece minervae* and *Geitlerinema amphibium*) and 8 diatoms (*Achnanthes thermalis*, *A. exile*, *Caloneis silicula*, *C. alpestris*, *Planothidium lanceolatum*, *Navicula amphiceropsis*, *Gomphonema parvulum*, *Ropalodia rupestris*).

The study of cyanobacteria and algae in the vicinity of the hyalothermal geyser in Gánovce was studied in the past by Vilhelm (1924) and Prat (1929), who determined 21 taxa. Hindak and Hindakova (2013) measured temperatures at the spring up to 25 ° C. The mentioned species, 8 are identical, of which 1 cyanobacterium (*Rivularia haematites*), 2 green algae and 5 diatoms (*Achnanthes minutissimum*, *Planothidium lanceolatum*, thermophilic *A. thermalis*, as well as purebred sap *Caloneis silicula* and halophilic *Craticula buderi*).

A similar habitat as the hot spring in Ganovce is the live travertine mound with name: Siva Brada. The phycological survey and published results from this hot water are still incomplete. Only one species, *Achnanthes thermalis* was occurred in a comparison to Vysne Ruzbachy springs. The temperature of the Siva Brada spring is around 20 ° C [9, 11].

The total species biodiversity of algae and cyanobacteria in the springs of Vysne Ruzbachy was 79. This species abundance was slightly higher after the application of modern molecular methods and a longer period of research on the springs. Due to the temperature of the springs, which was not extremely high as in the eurythermal and acrthermal springs, they assumed the largest diversity of the class *Bacillariophyceae,* which was confirmed. The second most abundance group was cyanobacteria with 22 species, 14 species of green algae, 2 species of red-algae and 2 euglenas. Among the species that were present only sporadically or did not occur at all in the mentioned habitats are diatoms – *Luticola nivalis*, *Pinnularia borealis*, *P. subgibba*, *P.*

viridiforis, *Diploneis krammeri*, *Craticula buderi*, *Navicula amphiceropsis*, *N. digitoconvergens*, *Ropalodia rupestris*, green algae – *Klebsormidium rivulare*, *Microthamnion strictissimum* and cyanobacteria – *Calothrix parietina*, *Oscilatoria rupicola*, *Gloeothece rupestris* and *Gloeocapsa alpina*.

CONCLUSIONS

The study summarizes the literature data and our own knowledge about the occurrence of cyanobacteria, green algae, *Xanthophycea*, *Euglenophyta* in the thermal springs in Vysne Ruzbachy Spa. In the past, any attention was paid to the study of phytoplankton in this area of Slovakia.

The investigation of thermophilic algal communities at 8 thermal springs and one cave have been analysed during seasons 2014 and 2015. The purpose was evaluated the distribution of species in thermal streams relative to temperature and competitive interactions. 14 genera of cyanobacteria with 22 species, 21 genera of diatoms with 39 species, 12 genera of green algae with 14 species and 4 interspecific taxa from different groups of algae were recorded. Totally 79 species of algae and cyanobacteria were determined. Algae flora consisted mainly of thermophilic, halophilic and species which prefer unpolluted environment. In regard to taxonomic diversity with similar thermal springs in Slovakia, the research showed distinctive and specific algae and cyanobacteria species, f. e. taxa of diatoms – *Luticola nivalis*, *Pinnularia borealis*, *P. subgibba*, *P. viridiforis*, *Diploneis krammer*, *Navicula amphiceropsis*, *N. digitoconvergens*, *Ropalodia rupestris*, green algae – *Klebsormidium rivulare* and cyanobacteria – *Oscillatoria rupicola*, *Phormidium crustaceum*, *Gloeothece rupestris* and *Gloeocapsa alpina*.

The most common species on the hot springs were diatoms – *Achnanthes thermalis*, *A. exile*, *Amphora coffaeformis*, *Caloneis alpestris*, *C. silicula*, *Cymbella cymbiformis*, *Epithemia turgida*, *Gomphonema parvulum*, *Pinnularia brebissonii*, *Planothidium lanceolatum* and Cyanobacteria – *Calothrix parietina*, *Gloeocapsa alpina* and species from genus of *Phormidium*, occurred mainly in many observed biotypes.

The world of thermal springs is fascinating and beautiful. Many of the colours in hot springs are caused by thermophilic microorganisms, which include certain types of bacteria, such as cyanobacteria, and species of archaea and algae. Many thermophilic organisms grow in huge colonies called mats that form the colourful scums and slimes on the sides of hot springs.

The geochemistry, the temperature and pH of hot springs play a central role in determining which organisms inhabit them. Cyanobacteria and algae are the most successful and sustained organisms during the course of evolution [30]. Their biomass can also be used for the large scale production of food, energy, biofertilizers, secondary metabolites, cosmetics and medicines [29].

Hopefully the research will promote further endeavours to study and document the variability of form, colour and beauty of these unique organisms.

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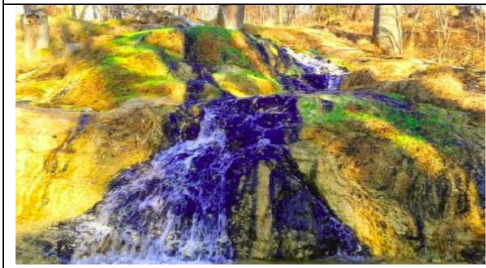
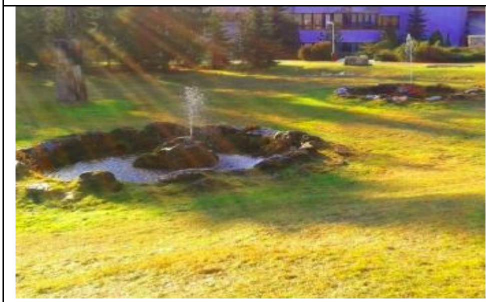
SUPPLEMENT

Appendix 1: Biotopes of observation in Vysne Ruzbachy Spa (Slovakia)

rich species phytoplankton abundance	low species diversity of chlorophytes
 I.d Vodopad (+++)	 I.a Krater (-)
 III. Ondrej (++)	 I.c Bazen (- -)
 VII. Jan (++)	 VIII. Jozef (- - -)

Algae and cyanobacteria abundance: +++ > ++ > - > - - > - - -

GEOINFORMATION SYSTEMS IN MONITORING OF WATER PROTECTION ZONES

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ABSTRACT

The article analyzes the scientific basis of monitoring water protection zones through the use of cartographic and aerospace information in order to obtain quantitative and qualitative information about water bodies that are not available during field research or measurements.

The possibilities of the geoinformation system of the water object are analyzed, which provides opportunities to monitor the situation regarding the state and dynamics of water protection zones in space-time dimension. It is indicated that it is possible to navigate the map, edit data, operate with vector layers of the map, to implement spatial analysis. The possibilities of the geoinformation system of the water object are analyzed, which provides opportunities to monitor the situation regarding the state and dynamics of water protection zones in space-time dimension. It is indicated that it is possible to navigate the map, edit data, operate with vector layers of the map, to implement spatial analysis. Emphasis is placed on the priority of forming a geographic information system of a water body as a management tool for government and community. It is stated that it is a convenient platform for ensuring the functioning of the monitoring system, accumulation of databases, their systematization and storage of the state of the basin system, water management facilities and water resources.

Keywords: water safety, water protection zones, monitoring of the state of the water body, geographic information system of a water body, geospatial data

INTRODUCTION

Anthropogenic load significantly affects the state of hydroecosystems of Ukraine. Climate change over the past 50 years has significantly affected the water supply of all regions of our country and determines the need to improve the strategy of prevention of dangerous phenomena, cataclysms. The Carpathians have lost much of their forest cover in recent decades and are unable to retain moisture. The loss of at least one spruce aged 40-50 years leads to the release into the free flow of 5 tons of water during the season, which causes a rapid, avalanche flow of water from the mountains, rapid runoff into river basins, causing large-scale environmental disasters. Floods most often occur in foothills and mountainous areas during spring floods on rivers and prolonged summer rains.

It should be noted that the state of water resources at the present stage of development of Ukraine directly depends on the quality of their management, environmental policy, determining its role in the system of administrative relations in the field of environmental protection, monitoring their condition. The concept of European integration, which is declared by Ukraine, provides for the transition to a qualitatively new level in all areas of natural resources management, including water, adaptation of the principles of legislation in this area to the standards of European Union legislation.

Today in Ukraine the period of reforming the management system continues: the system of subject composition is changing, new principles are being introduced, including the basin principle, which is the basic principle of state water cadastre, on which all activities (stages) of state water cadastre are based.

The priority task of the state water policy is the introduction of monitoring of hydroecosystems with the use of geographic information systems on the basis of the basin management principle. Nine areas of the main river basins have been established in Ukraine, within the territories of which comprehensive integrated water resources management is being implemented: the area of the Dnieper basin; the area of the Dniester basin; the area of the Danube basin; the area of the Southern Bug basin; the area of the Desna basin; the area of the Western Bug basin; the area of the Seversky Donets basin and the areas of the Ros and Tisza river basins. Sub-basins can be identified within the areas of the main river basins.

The main attention is paid to the monitoring of water bodies with the use of geographic information systems in order to implement an integrated approach to water resources management. These are modern technologies for obtaining information about the state and dynamics of water bodies development.

Water safety is focused on the monitoring of water protection zones on a geoinformation basis, which is carried out in order to:

- timely detection and forecasting of the development of negative processes affecting water quality in water bodies and their condition, development of the coastal zone, development and implementation of measures to prevent the negative consequences of landslides, shallowing;

- assessment of the effectiveness of measures taken to protect water bodies;

- information support of management in the field of use and protection of water bodies, including for the purpose of the state control and supervision over use and protection of water objects.

In recent decades, significantly increased the impact of factors that lead to the occurrence and development of floods, thereby increasing the frequency and severity of the latter, as well as the scale of destruction. The danger posed by floods lies in the high levels of water from the river to the floodplain and the flooding of houses, land, communications and other facilities, which are often built in the floodplain of the river. It is clear that natural disasters cannot be completely averted, but they can be mitigated, localized and, provided timely warning, minimize material losses. This is achieved in the context of organizational land management measures on the basis of operational monitoring and forecasting of the flood situation, construction and strengthening of water dams, timely notification of the possibility and scale of floods.

METHODS AND EXPERIMENTAL PROCEDURES

The theoretical and methodological basis of the study were the works of leading scientists on the analysis of the organization of the monitoring system of water protection zones on a geoinformation basis, which directly correlate with the tasks of water safety. The research methods such as analysis and synthesis are used in the paper to theoretically generalize modern research on the topic of substantiation of the components of the water management mechanism, namely land resources of the water protection zone, according to the basin principle, which is the basis for state water cadastre; method of strategic management - for the formation of topographic and cartographic databases, their analysis and monitoring in order to improve the strategy of prevention of dangerous phenomena, cataclysm in the context of sustainable development; graphic - for visual results of scientific research; abstract-logical - for theoretical generalization and formation.

THE RESEARCH RESULTS AND DISCUSSIONS

Recently, the problems related to research, use of water resources and monitoring of the state of water bodies of Ukraine and water protection zones have become much more relevant. To solve the state problem of forming a strategy for normalization of anthropogenic pressure on aquatic and near-water ecosystems, geoinformation technologies are used in the monitoring of water bodies. The development of scientifically sound recommendations for management decisions requires a system of sequential observations, collection, processing of data on the state of water bodies, coastal strips, forecasting their changes. Space images and cartographic materials, analysis and comparative characteristics of available cartographic information, field observations with satellite information will allow to trace changes and development of channel, coastal transformations and erosion processes of water bodies, areas of flooded lands.

The procedure for state water monitoring was approved by the Cabinet of Ministers of Ukraine dated September 19, 2018 № 758 and defines the basic requirements for the organization of state water monitoring, interaction of central executive bodies in the process of its implementation and providing information to state authorities and local governments for adoption. decisions on water status [1].

In accordance with the Procedure, the following subjects of state water monitoring provide information on ensuring full monitoring of water bodies, including on ensuring monitoring of the dynamics of water protection zones:

- State Geocadastre provides topographic, geodetic and cartographic information and geospatial data in the manner prescribed by law;

- The State Space Agency of Ukraine provides archival and operational aerospace information for remote sensing of the Earth on the territory of Ukraine.

Depending on the goals and objectives of state monitoring of water bodies, including monitoring of water protection zones, the following procedures are established:

- procedure for diagnostic monitoring of surface and groundwater massifs;

- procedure of operational monitoring of surface and groundwater massifs;

- procedure of research monitoring of surface water massifs;

- sea water monitoring procedure.

During the implementation of state monitoring of water bodies, special attention is paid to monitoring the condition of the bottom and shores of water bodies, as well as the condition of water protection zones.

The only legal mechanism for determining the size and boundaries of water protection zones and the regime of economic activity in them is specified in the Procedure for determining the size and boundaries of water protection zones and the regime of economic activity in them in accordance with the Cabinet of Ministers of 08.05.1996 № 486 [2]. Also in the Procedure the purpose of creation of water protection zones is specified. It is stated that they are installed to create a favorable regime of water bodies, prevent their pollution, clogging and depletion, destruction of aquatic plants and animals, as well as reducing runoff fluctuations along rivers, seas and around lakes, reservoirs and other bodies of water.

Water protection zones are zones created in order to ensure a favorable regime of water bodies, prevent their pollution, clogging and depletion, reduce runoff fluctuations along rivers, near seas, around lakes, reservoirs, etc. reservoirs, conservation of aquatic plants and animals [3].

The legal regime of water protection zones is determined by parts 3-5 of Art. 87 of the Water Code of Ukraine [4]. They are in state and communal ownership. Within the water protection zones, economic activity is allowed in accordance with the legislation and land management documentation, but land privatization is prohibited. The following is prohibited on the territory of water protection zones: use of resistant and strong pesticides; arrangement of cemeteries, cattle burial grounds, landfills, filtration fields; discharge of untreated wastewater using the terrain (beams, lowlands, quarries, etc.), as well as in streams.

The size and boundaries of water protection zones are determined by the project on the basis of regulatory and technical documentation. The water protection zones must include the river floodplain, the first floodplain terrace, curbs and steep slopes of the banks, as well as adjacent beams and ravines. The boundaries of water protection zones are set taking into account the purpose of the lands that are part of the water protection zone, as well as the terrain, flooding, inundation, the intensity of shore destruction, the design of shore protection engineering.

In accordance with Articles 88-91 of the Water Code of Ukraine within the water protection zones are allocated lands of coastal protection strips and drainage strips with a special regime of their use in width:

- for small rivers, streams and streams, as well as ponds with an area of less than 3 hectares - 25 meters;

- for medium rivers, reservoirs on them and ponds with an area of more than 3 hectares - 50 meters;

- for large rivers, reservoirs and lakes - 100 meters.

- along the seas and around sea bays and estuaries, a coastal protection strip at least two kilometers wide from the water's edge shall be established.

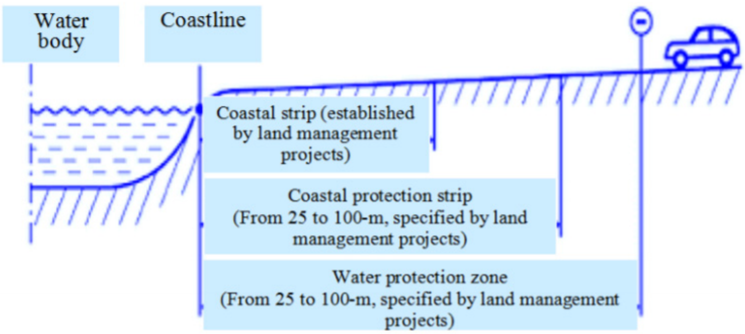

Fig. 1. Spatial location of the water protection zone, coastal protection and coastal strip within the city land use

URL: file:///D:/Downloads/13875-32069-1-PB.pdf [5]

Some of these areas are also periodically flooded by the river. These lands should be left under natural grass cover, trees and shrubs should be planted, which often grow due to the presence of moisture.

In order to address the organization of the territory and avoid floods, it is advisable to develop land management projects for the organization and establishment of boundaries of water protection zones of water bodies.

The customers of land management projects in water protection zones must be water management bodies and "other specially authorized bodies". In practice, due to the lack of budget funding, the customers of the relevant projects are increasingly other entities, primarily local governments or businesses that plan to carry out any activities near water bodies and fear that in the absence of an established water protection zone relevant project documentation will not be agreed. This practice of the law does not contradict and in itself does not affect the compliance of the developed documentation of the law. That is, water authorities and "other authorized bodies" must order project documentation, but this in no way prohibits other entities from acting as customers [6].

Until 2001, there was no practical experience in establishing water protection zones along the seas, in particular, in cities and towns.Today, there is practical experience in establishing water protection zones and coastal protection strips along large and small rivers, around reservoirs, lakes, ponds and other bodies of water outside settlements and within rural settlements. Such works were performed by the UAAS Institute of Land Management, Vodproekt Institute, and other design organizations. One of the first examples of such works is the installation of coastal water protection strips along the Black Sea on the territory of the Odessa Plant of Agricultural Engineering OJSC "Odessilmash", which were performed at the request of the Odessa City Council by the Institute of Land Management of UAAS within the framework of an experimental project.

Monitoring of water protection zones of river systems requires preliminary work, namely the study of catrographic and topographic materials, scanning of available materials, research in the dynamics of shoreline changes, abrasion processes in the treadmill, the presence of unauthorized landfills, improper use of water protection zone lands. In many cases it is necessary to create the necessary image from separate fragments.

Organizational measures that precede the creation of GIS in the system of monitoring water protection zones [7]:

- scanning paper documents and maps
- sbinding of cartographic materials
- digitization
- filling the GIS database

Consider in detail each of these stages.

Scan maps and plans. To ensure the process of forming a fund of electronic raster maps or their subsequent digitization, scanning of materials from paper media is performed. Long and flatbed scanners are used to scan materials. The maps are scanned from the environment of the graphic editor, which allows you to save and initially convert the received electronic copy (figure 2):

- trimming of frame design;
- stitching or cutting into smaller parts;
- geometric correction of the scanned copy;
- increase the clarity of the raster image, etc.

Fig. 2. Scan maps and plans

URL: https://magneticonemt.com/geoprostorove-koordinuvannya-zobrazhe/ [6]

In order to obtain the highest quality scanned cartographic material, the following technical requirements are set:

- palette for monochrome cards - greyscale;

- palette for color cards - color;

- resolution - 300-600 dpi;

- output file format - JPEG, TIFF.

This stitching is carried out in the form of merging individual images into one and even assembling "mosaics" of a large number of files. The fragments are stitched together by defining several common points in the plane of the image, so that the stitched fragments largely overlap each other.

The technical requirements are set taking into account that the data to be converted into electronic form are contained on different media and have different distortions. Scanned and glued cartographic materials for the purpose of systematization of data are named according to the nomenclature or identification number.

Spatial mapping is the next step in creating a geoinformation system in the field of water protection zone monitoring, where developers face the problem of transferring spatial data from paper media (separate sheets of urban planning documentation or tablets of river systems, etc.) to vector format. The solution to this problem can be achieved by scanning raster images and their subsequent geospatial coordination, ie spatial reference of raster information to a given coordinate system.

At the stage of creating a geographic information system in the field of monitoring water protection zones, developers face the problem of transferring spatial data from paper media (separate sheets of urban planning documentation or tablets of river systems, etc.) in vector format. The solution to this problem can be achieved by scanning raster images and their subsequent geospatial coordination, ie the spatial binding of raster information to a given coordinate system.

Spatial binding of maps, maps and plans in the software environment of geographic information systems is carried out in order to further unify their use and is to bring the source materials to the real geographical location. The binding process is a comparison of reference points that connect the coordinates on the raster images of water bodies with the coordinates of the spatially bound information layers.

Binding of cartographic materials is performed in the following ways:

- comparison of reference points with the subsequent introduction of their spatial coordinates;
- binding to the information layer with certain spatial coordinates.

The next preparatory stage in the system of monitoring of water protection zones is the procedure of *digitization of documents* - an important step in optimizing the work in order to organize the archive and create a convenient system of access to documents. Digitization of documents involves the transfer from paper to electronic format (digitization) of various types of cartographic documents, allows to carry out the comparative characteristic of localization of water protection zones.

Creating an interactive map. In order to develop a strategy for the management of water protection zones on the basis of monitoring data on their condition, there is a need to create interactive web maps for the needs of public authorities in the field of water use.

An interactive map is an innovative web resource that allows users to view, edit, and analyze spatial data using a standard web browser. To work with the interactive map, the user does not need specialized software and the qualification of a GIS specialist, it is enough to have a web browser and an Internet connection.

The interactive map presents cartographic information, the content of which is laid out in layers with the ability to connect to display different layers of thematic information and edit the content. The efficiency of using interactive maps is achieved due to the flexible database. It can contain reference information in the form of text descriptions of objects, numerical data, photographs, graphs, charts, etc. Interactive maps of water resources contain the most complete set of functions available in desktop GIS: map navigation, data editing, manipulation of vector map layers, spatial analysis, address search, geocoding and much more.

Advantages of using interactive maps by the State Agency of Water Resources of Ukraine, Basin Councils, statistical departments, other interested government agencies are focused on developing effective management decisions in the field of water use, land use, environmental protection.

Monitoring of water protection zones requires a combination of thematic layers of the interactive map in order to identify cause-and-effect relationships and patterns. The interactive map attribute data is used to identify important features of water bodies, including water protection zones. It is possible to analyze space-time data and control access to cartographic information on the Internet.

Filling the GIS database. The main task of GIS in the monitoring of water protection zones is to ensure the functioning of the water cadastre, namely the ability to collect data, create databases, enter them into computer systems, store, process and convert, and then issue at the request of the user. Information should be presented in cartographic form or in the form of tables, graphs, charts.

All the identified stages precede the creation of a *geographic information system of a water body*, which is extremely relevant and in demand today. It is a cartographic web resource that allows you to observe in spatio-temporal dimension of the water body, including to reflect the current state and dynamics of water protection zones around some objects (figure 3):

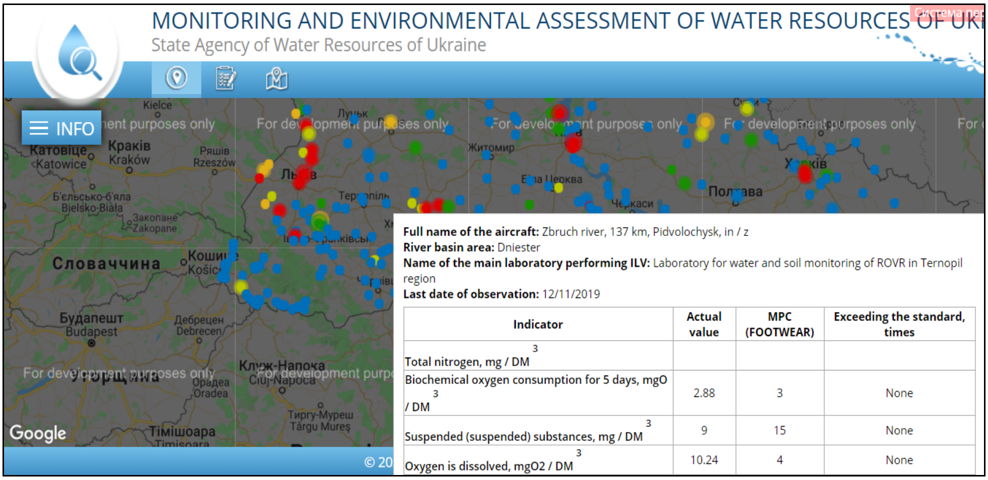

Fig. 3. Geoinformation system for monitoring and environmental assessment of water resources of Ukraine [8]

A geographic information system of a water body is a cartographic web resource designed for effective water resources management. The main task of the geographic information system is to monitor the structure of the river network, collect, record, process, store and display data on the state of water bodies, forecast their changes and develop scientifically sound recommendations for management decisions that may affect water status.

In the geographic information system, spatial data are laid out in layers with the ability to connect to display different layers of thematic information and edit the content. Each layer of the map contains a group of the same type of elements, combined into separate catalogs: the actual hydrographic network, terrain, boundaries of settlements, utilities, transport routes, forests, boundaries of districts and regions, and so on. It is also possible to display water protection zones, the degree of their erosion, afforestation, unauthorized construction, abrasiveness of slopes, etc.

Monitoring of water protection zones on the basis of geographic information system of a water body allows:

- to observe in the current state reference information (technical characteristics, documentation, etc.) when given by the navigator to water bodies in accordance with the information support of the register of water and water management facilities;

- to carry out operative monitoring of a condition of a coastal strip (operatively displays data on qualitative and quantitative changes of a coastal zone in a water cut line, level of pollution, afforestation, change of water level in dynamics on seasons;

- create and display electronic thematic maps of water management facilities by areas of activity, depending on the needs of individual departments and specialists;

- to carry out operational management in emergency situations (floods, floods), to model and forecast flood zones, etc.;

- provide data collection on violations in water protection zones and adjacent territories (within water protection and coastal protection zones) in the field in real time using a mobile application synchronized with the geographic information system;

- ensuring the protection of the water protection zone and the reflection of planned measures to regulate and improve the state of basin systems.

- introduction into the structure of the GIS database of the information block on the observation of water protection zones and improvement of the informative component of the water cadastre

- filling of basic geoinformation resources (cartographic basis): digital topographic basis, digital orthophotoplans, digital terrain model, register of geographical names;

- expansion of thematic information resources: network of water bodies (rivers, lakes, canals, reservoirs, etc.), places of water sampling, localization of hydraulic structures within the coastal strips, etc.;

- updating and supplementing complex or problem-oriented information resources, which are a set of basic and thematic resources that are combined into a system with the formation of a new resource to solve the problem of land management, such as restricted areas within water protection zones , flood zones, etc.

- a wide range of analytical capabilities (display of information in the form of graphs, spatial and statistical analysis);

- constant readiness of the resource to work from a mobile device (tablet, smartphone) connected to the Internet;

- collection and editing of data in the field in real time using a mobile application.

Geographic information system of a water body is a management tool for the government and the community, which allows to obtain a convenient platform for storage and systematization of data on the basin system, water management facilities and water resources.

CONCLUSION

The current state of monitoring of water protection zones is characterized by an imperfect mechanism of coordination and interaction of state structures. The situation is complicated by the lack of a single methodology for collecting, processing, accumulating and transmitting data. Accordingly, there is a subjective assessment of the state of the lands of the coastal strip, which leads to further inappropriate decisions to eliminate or reduce the anthropogenic impact on the land resources of the water protection zone. In addition, for most water bodies there are no projects to establish the boundaries of coastal protection zones and water protection zones, which leads to an uncertain type of land use.

The introduction of geoinformation monitoring of water protection zones must be performed taking into account current trends in the development of geoinformation technologies based on the use of high-resolution aerospace systems to obtain information about the water body. Unification of geospatial models of water bodies should be achieved based on the requirements of the international standards of the ISO 19100 series: Geographical information / geomatics.

The automated geographic information system of the water body can be used to promptly provide government agencies, enterprises, institutions, organizations, citizens with the necessary data in the form of catalogs. It contains spatial data, layered with the display of different layers of thematic information and content editing. Access is provided to the hydrographic network, the relief of the coastal strip, boundaries of settlements, utilities, transport routes, forests, boundaries of districts and regions, and should reflect water protection zones, the degree of their erosion, afforestation, unauthorized construction, abrasive slopes.

The decision support system in the management of water and land resources of water bodies is based on modern advances in geographic information technologies and web cartography. The practical aspect of using GIS for water cadastre allows to facilitate and automate the work, significantly expand the use of topographic and thematic maps, which contain a large amount of information needed to monitor and analyze the protection of water protection zones, hydrological regime of water bodies.

The perspective of advanced digital methods of image processing and geospatial information is focused on the transition from the paradigm of digital map layers as a modeling tool to the use of full-fledged relational models of geospatial data in the environment of relational databases with appropriate spatial extensions.

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FUNCTIONING OF LANDSCAPE COMPLEXES OF THE SOUTHERN BUH RIVER BASIN

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ABSTRACT

The study of the exchange of matter, energy and information between landscape complexes in the riverbed and floodplain can be carried out in two aspects: as a manifestation of paragenetic relations (if they are common in origin) and as a manifestation of paradynamic (if they are adjacent but different in genesis). In paragenetic landscape complexes, the main role is given to the "central place", in relation to which the direction of mass and energy flows between the components of the system is determined. There is an active connection between channel-floodplain paradynamic landscape complex and the adjacent valley-watershed divide landscapes, which determines the functioning of the basin paragenetic landscape complex. Taking into account the peculiarities of such relationships will enable effective implementation of regional environmental policy in the Southern Buh basin.

***Key words**:* landscape complexes, the Southern Buh river basin, transition zones, water-coastal landscape, geoecotons.

INTRODUCTION

Riverbeds and floodplains hold a specific place in the structure of modern landscapes and human life in any region of the Earth. This is due to the peculiarity of their hydrological and climatic conditions, dynamics of metabolic processes, diversity of flora and fauna, high soil productivity. River exploration is one of the top priorities in modern geographical science. However, the question of river beds and floodplains in terms of landscape is open. Identification and functioning of paradynamic and paragenetic relations, which determine the specifics of the development of channel-floodplain landscape complexes, remain outside the view of modern physio-geographers and landscape scientists and are the basis for the development of measures for their optimization, rational use and protection.

The suggested study is a result of years of detailed exploration of the landscapes of the Southern Buh valley and basin by the authors. The vast majority of issues covered in this paper are new, problematic, and can provoke scientific debate, as there is almost no similar research in contemporary geographical and landscape literature.

RESEARCH METHODS

The unique model region for solving these scientific problems is the Southern Bup valley, whose catch basin is the largest of all, completely located within Ukraine. Over the past centuries, landscapes and floodplains of the Southern Buh have been altered as a result of active and diversified economic development. Construction of ponds, water reservoirs, reclamation and drainage canals, dams, bridges, mills and hydroelectric power stations almost destroyed natural river and floodplain tracts. In this regard, research into the anthropogenic landscapes of the Southern Buh riverbeds and floodplains is relevant and will contribute to the improvement, reproduction and conservation of the river valley as a whole.

RESEARCH AND DISCUSSION RESULTS

Peculiarities of natural channel-floodplain landscape complex functioning. Riverbed and floodplain as a paragenetic landscape complex. River basins are characterized by a natural change of landscape complexes from outer divide line to riverbed. All geo complexes that are located here are connected by a common origin – laying of the river, formation of its valley and basin – form a basin paragenetic system (a kind of paradynamic). This system consists of two subsystems: valley and watershed [15]. The first subsystem includes riverbed, floodplain, terrace above flood-plain and root slopes. Valleys are characterized by transverse and longitudinal paragenetic relations with the prevailing tendency to transport matter and energy from top to bottom – from root slopes to riverbed, from the source to the mouth [15]. The peculiarities of geological structure, relief and vegetation of the drainage ditch in the upper reaches of the river are reflected in costs, chemistry, solid waste, the composition of alluvium floodplain many kilometers below the current [16].

The nucleus (core complex) of the valley-river subsystem is river bed. It is the river channel that serves as the carrier of information about ecological state and landscape features of the entire basin. The specificity of riverbed is determined by its dynamics, fluidity and constant updating of matters. The most elemental river paragenetic complexes are riffles and reaches. Due to longitudinal natural paragenetic relations, these aquatic areas merge into a single inseparable whole along the entire path of the stream (Fig. 1 A). The processes of transferring alluvium of different sizes predominate on riffles. In particular, in the tracts of rapids with high (3–4 m/s) flow velocities, fragile material is transported to a diameter of 5–6 cm. At the same time, the accumulation of alluvium takes place between the outcrops of crystalline rocks, which eventually leads to the formation of islands. Due to the process of active mixing of liquids on the rapids, the water of the Southern Buh is characterized by high oxygen saturation [3]. On the brink of riffles and reaches there is a postponement of large-scale alluvial material and the transport of small and medium-sized particles continues. In the tract with slow (up to 1 m/sec) flow velocities, intensive deposition of the material takes place, aggradation in the coastal partial floodplains and partial transfer of small particles downstream.

Along with the movement of matters and energy from the top downstream (direct relations), there are movements from the bottom up – against the current (reverse realtions), which are manifested in valley winds, moving of fish for spawning, spring and autumn migrations of birds [16].

While riverbed is an active complex in the valley-river subsystem, floodplain plays a passive role here. It arises in the process of channel deformation and is formed under the influence of channel forming mechanisms. The floodplain influences riverbed indirectly (performs the function of its boundaries, determines the velocity and direction of the water flow during the flood). In accordance with the principle of contrast [17; 19] heterogeneity of the environments (water – land) causes an active exchange of matter, energy and information between the stream and the floodplain. This makes it possible to distinguish a complex channel-floodplain natural paragenetic landscape complex (NPGLC) in nature, in which the constituent elements complement each other.

Channel-floodplain NPGLC of the Southern Buh is characterized by spatial and temporal contrast. Spatial contrast (Fig. 1 B) is manifested in the alternation of water tracts with terrestrial, the diversity of mesorelief forms and changes in short distances of one type of vegetation to others (thickets of bushes, meadows, and forests) [16]. The change in aquatic tract by terrestrial is particularly important, since thick wetland plant associations (reed, sedge, bulrush, duckweed) with peculiar to them fauna (grass snake, frogs, beavers, muskrats, numerous species of birds) are formed.

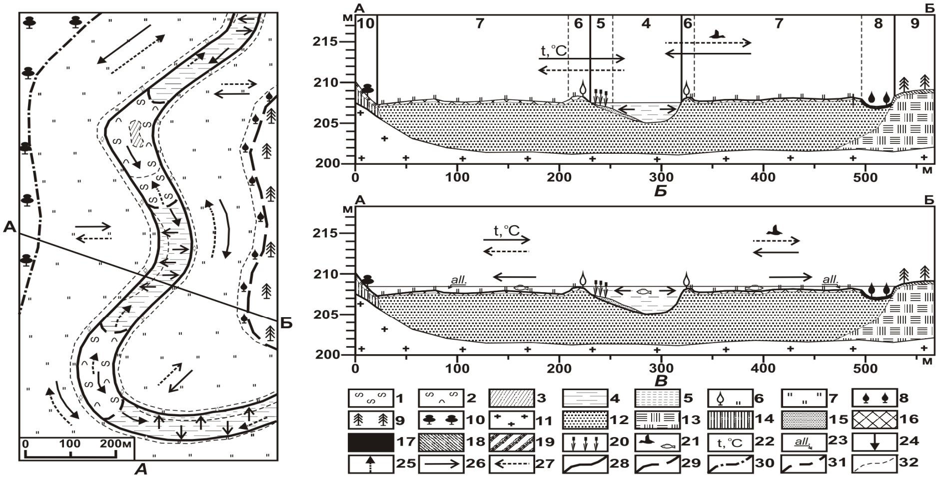

Fig. 1. Generalized charts of paragenetic in the channel-floodplain NPGLC of the plain river

A. Longitudinal and transverse paragenetic relations between riverbed and floodplain.

Б. Spatial and temporal (constant) contrast of NPGLC "riverbed – floodplain".

B. Temporal (seasonal) contrast of NPGLC "river bed – floodplain".

Natural landscapes. Channel. Riffles. Tracts: 1 – central channel; 2 – rapids; 3 – natural island. Reaches. Tracts: 4 – central deep water; 5 – coastal shallow waters. Floodplain. Tracts: 6 – natural levees with thickets of willow and meadow-cereal vegetation on meadow sandy soils; 7 – central floodplain with uneven surface and meadow-cereal vegetation on meadow sandy soils; 8 – back marsh with alder stands on wetlands. Supra-floodplain. Tracts: 9 – the first supra-floodplain terrace with a wavy surface and a pine forest on light gray and gray forest sandy soils. Sloping. Tracts: 10 – flat (6–8º) slope with hornbeam-oak forests on gray weakly-formed forest soils.

Landscape profiles: 11 – Precambrian crystalline rocks: granites, gneisses; 12 – sandy floodplain alluvium; 13 – fluvioglacial sands; 14 – loess-like loams; 15 – silty channel alluvium; 16 – meadow soils; 17 – waterlogged soils; 18 – sod-medium and strongly-podzolized soils; 19 – gray weakly-eroded forest soils; 20 – wetland vegetation; 21 – animals; 22 – cold and warm air masses; 23 – alluvium that is transported and sedimented during the flood.

Paragenetic relations: 24 – longitudinal direct relations; 25 – longitudinal feedback; 26 – transverse direct relations; 27 – transverse reverse relations.

Boundaries. Types of terrain. Natural: 28 – channel and floodplain; 29 – floodplain and supra-floodplain; 30 – floodplain and sloping. Aquatic areas: 31 – riffles and reaches. Tracts: 32 – natural.

Temporal contrast determines functioning of transverse PGR between landscape complexes of riverbed and floodplain. It can be constant and seasonal. Constant contrast (Fig. 1 B) is manifested through concaving banks and shore spread (meandering of riverbed in the floodplain); redistribution of heat and moisture day and night; day migrations of animals, etc. Seasonal temporal contrast (Fig. 1 C) is characterized by a change in water regime, in which the floodplain is flooded in the spring for several weeks by water, and by mid-summer it dries. During the flood accumulation of alluvial material occurs on the surface of the floodplain. In short-term flooding, this results in the rapid growth of meadow grasses and the diversification of phytocoenoses, in long-term – inhibition of their growth and the replacement of meadow-grass associations by water-marsh. Each beginning of the flood determines the directed migration of animals in the direction from the channel to the watersheds. Land animals change habitats to the adjacent to the floodplain area, representatives of aquatic fauna carry out pendular movement – from the riverbed to the floodplain and vice versa. After the flood decline, animals return in the opposite direction to their usual habitat. Separate specimens of the fish that have not migrated to the channel may stay in flooded rectangular depressions or old lakes. During the drought season plants that had time to develop on fertile alluvial soils, would be negatively affected by solar radiation. At the same time, the growth of moisture-loving plants is suppressed on elevated sections of the floodplain, and over time – on the middle ones. Gradually they are replaced by dry-resistant species. In modern conditions of regulation of the Southern Buh with ponds and water reservoirs, the Southern Buh riverbed is characterized by constant temporal contrast. The manifestation of seasonal contrast is possible only in the form of partial and not annual flooding floodplain in the lower reaches of hydro systems.

Spatial and temporal contrast are closely interrelated. Due to the contrast of the environments, the boundaries of tracts of the riverbed and floodplain vary from flood to drought season. This is one of the reasons for high productivity of channel-flood biocenoses and the separation of channel-floodplain as the most dynamic complex of valley-river subsystem.

Riverbed and floodplain as a paradynamic landscape complex. Riverbed and floodplain have been formed and function not isolated, but interact with all structural elements of the Southern Buh basin as a paradynamic landscape complex. The combination of channel, floodplain, supra-floodplain, sloping, upland, and interfluvial undrained types of terrain together form a single paradynamic system of the orographic type. The interaction of the channel-floodplain paradynamic landscape complex and the adjacent LC of the river basin is carried out through internal and external paradynamic relations (Fig. 2).

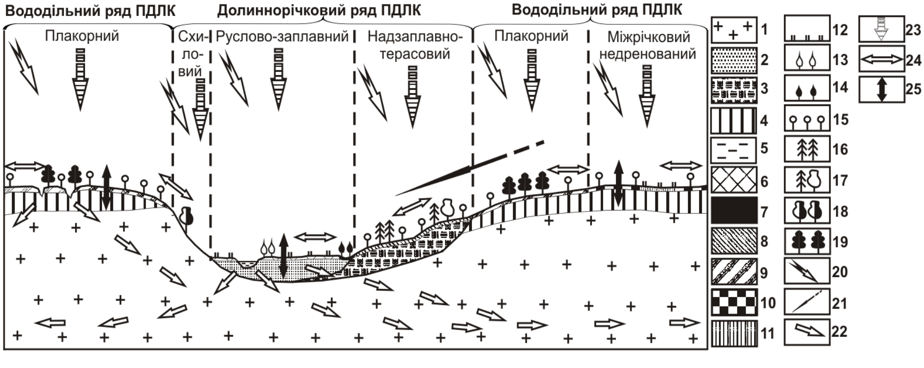

Fig. 2. Generalized chart of interaction in paradynamic system “channel-floodplain NPGLC – adjacent valley-watershed NPGLC”

Landscape profile: 1 – indigenous rocks (granites and gneisses); 2 – modern alluvial deposits; 3 – fluvioglacial sand and sand clay; 4 – loess-like cover and cover loams; 5 – surface waters (river); 6 – floodplain meadow soils; 7 – waterlogged soils and peatlands; 8 – sod-medium and strongly-podzolized soils; 9 – clear gray and gray forest soils; 10 – podzolized chernozems; 11 – over moistened chernozems (mochary); 12 – grass-cereal meadows; 13 – willow stands; 14 - sticky alder forests; 15 - agrophytocenoses; 16 – pine-spruce forests; 17 – pine-broadleaved forests; 18 – ravine forests; 19 – broad-leaved (hornbeam-oak) forests. Paradynamic relations. Outer: 20 – thermal; 21 – mechanical; 22 – water; 23 – social. Inner: 24 – biotic; 25 – biocos.

External PDR include influence of solar radiation on lanscape (thermal), gravitational influence of watersheds on low-lying complexes of the channel and the floodplain (mechanical), the influence of surface and ground waters on chemical composition of water and nutrition of rivers (water), as well as relations caused by economic activity of people (social). The direction of these relations is mostly one-sided, so their reverse effect is negligible and can be neglected. Internal PDR are manifested in the interaction of living and inanimate substances (biokosnye) and between the components of biocenosis (biotic).

Adjacent watershed areas receive a little less heat than low-lying channel-floodplain. During the warm period of the year, the difference in the sum of the temperatures in these areas is 35–50° C [6, p.79]. In the winter, wind blows snow from unforested upland to the floodplain, the wetlands of which are characterized by high humidity and frequent fogs.

Due to the considerable vertical differentiation of the landscapes of the watersheds (340–320 m n.r.m.) and the channel-floodplain PDLC (220–180 m n.r.m.), the development of linear and plane erosion increases. Thus, within Upper Pobuzhzhia, the intensity of the flat-flush on the slopes of the plowed land is from 5 to 20 t/ha, and in some plots – up to 50 t/ha a year [12, p.155]. At the same time, a layer of soil with the in thickness from 1.1 to 3.7 mm/a year is washed [13, p.209]. Sloping and supra-floodplain PDLC play the role of peculiar “transit corridors”, through which the eroded material enters the floodplain, which causes sedimentation of its surface and lowering the water level in the channel.

Modern canalization of the Southern Buh riverbed and its tributaries with ponds and water reservoirs leads to a stable water regime, which significantly reduces mass and energy exchange between channel-floodplain and adjacent basin landscape complexes.

The increasing influence of economic activity on the exchange of matter, energy and information makes social PDR one of the leading factors in the functioning of the paradynamic system “channel-floodplain PDLC adjacent valley-watershed PDLC”. The role of the SPDR will be considered in more detail in the next section.

Biocos relations [22] in landscape complexes of the river basin are manifested through biological matter cycling that covers the soil and representatives of flora and fauna. The combination of processes of photosynthesis, breathing of living organisms, the decomposition of their dead remains and the accumulation of deluvial-alluvial deposits causes accumulation of humus in floodplain soils. Biotical relations are first and foremost traced in trophic feeding chains and animal migration. Thus, during the feeding of the offspring of a white stork (*Ciconia ciconia* L.) can make up to a hundred of flights from the nest which is located on the upland to the riverbed and the floodplain.

Located on different altitudinal levels, the channel-floodplain PDLC and the adjacent valley-watershed paradynamic landscape complexes are characterized by the process of increased matter and energy exchange and information transmission. A complex set of paradynamic relations is formed between them, which together form natural PDLC "Southern Buh basin".

Due to paragenetic and paradynamic relations, natural channel-floodplain landscape complex is the most sensitive to human activity in the river basin and vulnerable in the case of its ill-considered economic development. The specificity of channel-floodplain nature management is that each specific terrain or tract depends on adjacent (upstream river) complexes and at the same time affects those that are downstream [20].

Transition zones between river-floodplain and adjacent anthropogenic landscape complexes. Relations of water anthropogenic floodplain landscapes with dry land landscapes. After flooding of the floodplain during the construction of water reservoirs and ponds of the Southern Buh, re-formation of interrelations with the landscapes of the dry land was due to increased flow of substances and energy. As a result, water-dry land anthropogenic paradynamic landscape complexes (WDAPLCs) were formed, which include water reservoirs, ponds, their intra-aquatic landscape complexes and adjacent landscapes.

The development and functioning of (WDAPLCs) determine direct and reverse natural PDRs. These relations within the interacting landscape complexes are carried out with the help of moving components that form them: surface and underground waters, solid runoff, snow cover, migration of chemicals, animals, plant seeds, etc. The most active interaction of inner aquatic and transient LCs with landscapes of dry land is due to horizontal flows of substances and energy. Vertical relations are local in nature. Changes in inner aquatic relations and properties of each LC are transmitted as direct relations to adjacent landscapes [28].

The pecualirities of the interaction of the transformed landscapes of the riverbed and the floodplain with the landscapes of the land should be considered in two directions: 1) the impact of anthropogenic reservoirs on the landscape complexes of the land (direct PDR); 2) the impact of landscape dry land complexes on anthropogenic water bodies (reverse PDR) (Fig. 3).

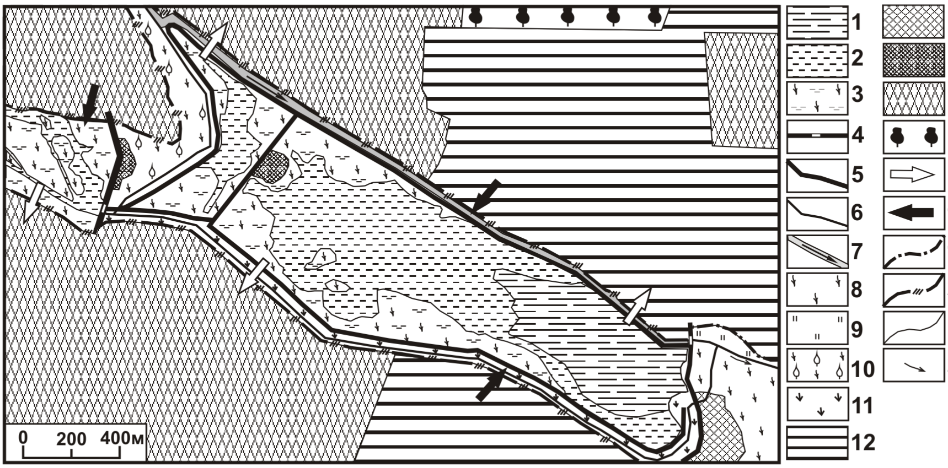

Fig. 3. Relations between landscape complexes of Marianivka water reservoir (the city of Chornyi Ostriv, Khmelnytskyi region) and adjacent territories

Water anthropogenic landscapes. Water reservoir. Floodplain-water reservoir. Tracts: 1 – dam deep water (3–4 m) with concave bottom and silty sediments (0.3–0.4 m), overgrown with small duckweed; 2 – central shallow water (1.5–2.5 m) with flat bottom and silty sediments (0.3–0.8 m), overgrown with small duckweed; 3 – shore shallow water (up to 1 m) with flat bottom and silty sediments (0.5–0.6 m), overgrown with water-marsh vegetation; 4 – stone-earthen dams with the height of up to 3 m, overgrown with grass-cereal vegetation and planted around with aspen and poplar; 5 – earth dams up to 3 m high, overgrown with grass-cereal vegetation; 6 – drainage canals with the depth of 1.5–2 m and the width of 5–7 m; 7 – deep (up to 5 m), 15–30 m wide canal – transformed Southern Buh riverbed.
Agricultural landscapes. Meadow-grazing. Floodplain. Tracts: 8 – flat surfaces with meadow-bog vegetation on meadow-marsh soils under hayfields and grazing; 9 – gently sloping (1–3°) surfaces with meadow-cereal vegetation on meadow-marsh soils under grazing. Floodplain-water reservoir. Tracts: 10 – hilly surfaces with willow stands and meadow-bog vegetation on meadow-marsh soils for grazing; 11 – flat surfaces with meadow-marsh vegetation on meadow-marsh soils for grazing. Field. Sloping. Tracts: 12 – sloping (10–15°) slopes, composed of loess-like loams with gray forest soils under field crop rotations.
Residential landscapes. Town. Floodplain. Tracts: 13 – flat surfaces under low-rise buildings on meadow-marsh soils. Floodplain-water reservoir. Tracts: 14 – bulked stone-earthen surfaces under low-rise buildings on meadow-marsh soils. Sloping. Tracts: 15 – sloping (10–15°) slopes under low-rise buildings, gardens on gray forest soils.
Forest anthropogenic landscapes. Derivatives. Sloping. Tracts: 16 – sloping (10–15°) hills with hornbeam-oar forests on gray forest soils.
Paradynamic relations: 17 – direct PDR of landscapes of water reservoir with landscapes of the land (hydrological and climatic impact); 18 – reverse PDR of landscapes of the land with the landscapes of water reservoir (silting, accumulation, overgrowth).
Boundaries. Types of terrain. Natural: 19 – floodplain and sloping. Anthropogenic: 20 – floodplain-water reservoir. Tracts: 21 – anthropogenic.
Other keys: 22 – direction of the current.

Due to direct NPDR of water reservoirs and ponds on the landscapes of the dryland, zones of hydrological, climatic and hydrogeological influences are formed. The first manifestations of direct paradynamic relations can be traced in the shore zone of water reservoirs and ponds. Two processes prevail here: 1) filtration of water to the shore; 2) support of groundwater in the coastal strip from the side of water objects. The width of the zone of hydrological influence depends on geological and geomorphological conditions of the coast [5, p.36]. Within the zone of climate impact of water reservoirs in autumn, the frost-free period extends from 1 to 5 days, respectively, in the summer – cooling [5]. In summer, the air temperature in the daytime is 0.5–1.5º C lower than outside of the influence of the water reservoir (500m) in the outskirts of Shchedriv water reservoir during daytime breeze movement. The most pronounced climatic influence of water reservoirs is at a distance of 200–250 m, further its borders vary depending on the direction and strength of the wind, features of the relief and the underlying surface. The zone of hydrological influence of water reservoirs forms belt of permanent and periodic flooding, considerable flooding and moderate flooding [21]. LC of the floodplain have undergone radical changes in the area of Ladyzhyn water reservoir in places of considerable flooding. Thus, floodplain meadows with grass-cereal vegetation have turned into aquatic complexes that extend for several kilometers. Unlike water reservoirs, the activity of natural pond densities is much lower, which is due to the small size of these water bodies.

Reverse NPDR are manifested through entrance of liquid and solid waste waters, chemicals, biomass, etc. from the landscape of dry land to water reservoirs. Water reservoirs and ponds of the Southern Buh are powerful accumulators of matters transported from adjacent territories due to erosion processes and coastal abrasion [5]. As a result, anthropogenic water reservoirs are getting intensely muddy, forming wetlands. Such processes are especially intensified due to the action of anthropogenic factor, which is determined by the level of intensity of economic load on adjacent to the water reservoirs of landscapes [28]. Thus, in the spring, during snow melting, migration of dissolved mineral fertilizers and pesticides from fields that are confined to the slopes or supra-floodplains of the valley is intensified. As a result of NPDR, intensive process of overgrowing takes place in shallow waters of anthropogenic water reservoirs. All water anthropogenic LC of the Southern Buh feature groupings of reed, cattail, cane, calamus and sedge of various species. Unlike water reservoirs, ponds become overthrown faster due to their lower parameters and active economic activity in adjacent LC. One of the manifestations of reverse PDR are landslide processes, for example, landslide, which was formed as a result of continuous erosion of the left bank (the floodplain terrace) of Ladyzhyn water reservoir within the village of Stepashky, Vinnytsia region. Vertical movements of matter and energy (evaporation, filtration, ascension and downward displacement of water masses) also affect functioning of WDAPLCs. In arid years, due to evaporation and filtration, water losses increase, hydrodynamic, biochemical and thermal processes are violated, which leads to the transformation of the landscape complex itself.

Relations of road landscapes with landscape complexes of riverbed and floodplain. Laying of roads over the channel and the floodplain of the Southern Buh caused the formation of APDLCs of “bridge – riverbed – floodplain” type. First of all, the interaction of bridges with the riverbed is carried out through direct PDR, which are transmitted from the supports to aquatic landscape complexes. Due to frequent transitions of vehicles through the bridge, there is vibration that scares animals that inhabit the area of the transformed canal. Fixed in the bottom supports divide the river bed into 2–3 or more sleeves, which leads to an accelerated flow of water (up to 0.5 m/s) at short distances. At the sites of the reaches between the bridges, alluvial material is moved more quickly, which sediments 10–20 m below the current. Access embankments of roads and bridge settlements, located on the surface of the floodplain hinder the movement of valley winds and vice versa – in the intervals between the bridge supports air masses flow accelerates, which adds energy to the water flow. V.M. Samoilenko’s research [24] of toxic contamination of the ichthyofauna of surface waters of Ukraine shows that aquatic organisms are active storages of chemical elements that enter water reservoirs. Exhaust gases of cars cause migration of heavy metals in bottom sediments and their accumulation in bodies of representatives of aquatic fauna. Thus, D.V. Lukashev [14] notes the accumulation of Pb in shells and soft tissues of duck mussel (*Anodonta anatina L.*) in the Southern Bug riverbed (the bridge on the 274th kilometer of Kyiv – Odesa highway) and an increase in the concentration of the chemical element by 2.4–2.7 times in specimens below the current. The elevated content of Fe and Mn in molluscan organisms in samples taken near the bridge explains the release of these heavy metals from structural materials of the facility.

Reverse relations of the riverbed LC on the bridges are manifested in the continuous washing of the supports and the destruction of the foundation underneath. In the course of the conducted research it was discovered that there is a washed layer of bottom alluvium 0.5–1 m thick between the supports of the bridge in the village of Voroshylivka, Vinnytsia region. Bulky islands that remained after the construction around the supports of the railway bridge in Pervomaisk, become gradually overgrown with water-marsh vegetation. In the spring period of thawing, the supports of bridges (the upper course of Southern Buh) can prevent the movement of large debris of trees, beds of reeds and sedge, etc.

Relations of mining landscapes with landscape complexes of riverbed and floodplain. Public PDR (Fig. 4), which are conditioned by the need for building materials, and natural PDR in the form of several streams of mineral and nutrient substances: terrestrial (mineral, biogenic and water migration), air and technogenic take part in forming paradynamic relations of mining landscapes with adjacent LC.

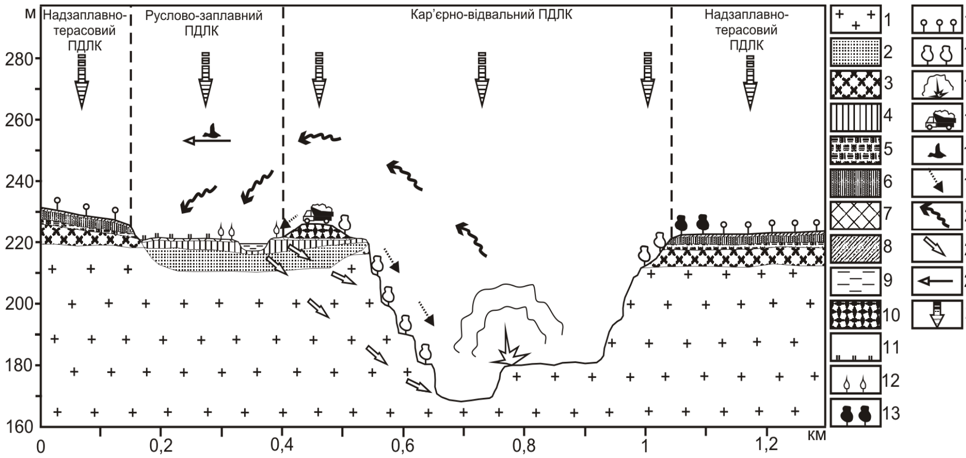

Fig. 4. Relations between channel-floodplain PDLC of the Southern Buh and Hnivan-Vitavsk quarry-stocker PDLC (the outskirts of the city of Hnivan, Vinnytsia region)

Landscape profile: 1 – granites; 2 – alluvial sands of the floodplain; 3 – kaolins; 4 – floodplain loams; 5 – fluvioglacial sands of supra-floodplain; 6 – loess-like loams; 7 – meadow-marsh soils; 8 – gray forest podzolized soils; 9 – waters of the Southern Buh; 10 – dam of granite-loamy rocks; 11 – meadow-cereal vegetation; 12 – thickets of willow stands; 13 – ash-oak plantations; 14 – agricultural crops; 15 – plantations of common birch; 16 – blasting operations; 17 – transport works; 18 – animals. Paradynamic relations: 19 – mechanical (landslides, taluses, creeps, erosion); 20 – aerodynamic (dust transfer, spreading of vibration and sound); 21 – water; 22 – biotic; 23 – social.

The ground flow is manifested in the early unstable stage of the development of the GPL. Migration of mineral matter (mechanical PDR) at this stage actively take place in mining LC, which are confined to sloping and floodplain types of areas. Thus, in 1975, as a result of the erosion and collapse of the freshly-formed part of the dam of Vitovsk deposit of granites in the Southern Buh riverbed, about 1.5 million tons of opening rocks were carried. The island formed by them (length 26 m, width 8 m) divided the channel into two sleeves [4, p.192]. Getting to the riverbed, the products of erosive erosion of opening rocks change its configuration, direction and velocity of the flow, causing silting and shallowing.

An important role in the relations of GPL with the riverbed and the floodplain is played by water migration (water PDR). The developments of peat and granite after the cessation of mining operations during the year are filled with water. Former granite quarry in the outskirts of the village of Myhiia of Mykolaiv region, which was confined to upland and separated from the Southern Buh floodplain by a natural slope, was filled with water to the depth of 15 m in one night. Around the newly formed water complexes of sand and peat quarries, there was waterlogging of the territories in the floodplains of rivers Vovk on the plot between the town of Derazhnia and the village of Haiky and the Southern Buh – between the village of Oleshyn and the city of Chornyi Ostriv [4].

Biogenic migration (biotic PDR) is manifested through the settlement of former mining developments with new plant species. Typically, wetlands are characterized by sedge-reed-cattail associations. Water reservoirs of trench-wetlands in the floodplain of the Southern Buh become gradually overgrown with green and blue-green algae, duckweed, sedge and reed. Here, new habitats of snakes, frogs, beavers, muskrat and waterfowl are formed.

The transfer of air masses (aerial-paradynamic relations) from mining LC to the riverbed leads to the migration of rock particles that rise up during blasting in quarries. According to the production department of Hnivan-Vitavsk granite quarry, in the second quarter of 2010 6.5 tons of dust was released into the air. In this case, the concentration of silicon dioxide of the crystalline (SiO_2), which is part of the granite dust, often exceeds the norm. In the air of the working area of Pervomaisk Quarry "Granite", which is confined to the right bank slope of Syniukha valley (10.5 km to the Southern Buh), the amount of SiO_2 is 8.1 mg/m^3 (4.1 GDC) [23, p.3]. Part of this material enters the riverbed and, along with the alluvium is transported downstream. Dusts, sedimenting on the surface of the leaves of plants that grow in the floodplain, hamper the processes of photosynthesis and transpiration and inhibit their development. Sound fluctuations from bursts in quarries extend over a considerable distance. Regular harvesting leads to scaring animals, especially birds, whose habitats are floodplain meadows and sloping forests.

Technogenic flow of matter is associated with the process of reclamation, when PDR of mining landscapes with adjacent LC are weakened. However, in case of inappropriate use of re-cultivated territories, negative processes are restored. For Pobuzhzhia region, such processes may include re-flooding and bogging of reclaimed floodplains where peat was previously mined.

Patterns of formation and functioning of anthropogenic landscape complexes of the river basin. Relations in landscape complexes which appeared as a result of the construction of located near a dam HEPS. Due to a significant role of construction of located near a dam HEPS and water reservoirs in the transformation of natural geocomplexes of the riverbed and the floodplain of the Southern Buh, the interaction in paragenetic landscape complexes should be considered on the example of APGLC of the type "located near a dam HEPS – water reservoir – modified landscape complexes of the lower reach" Fig. 5). According to the principles of development and functioning, APGLC "dam – pond – modified landscape complexes of the lower reach" are similar to the mentioned above, but differ only in their parameters and absence of an HEPS building. However, APGLC of the second type are rare (partly in the upper part of the current) and more characteristic of river tributaries.

APGLC of both types are formed and function due to social and natural PDR and PGR. In the first case, the manifestation of SPDR is the need for HEPS, dam and water reservoir for electricity production, in the second – the need for a dam and a pond – for fish breeding or recreation [31]. Natural PDR are manifested through the transfer of matter, energy and information downstream water flow.

In APGLC "dam HEPS – water reservoir – modified landscape complexes of the lowe reach" the "central location" [30] role belongs to LES "dam HEPS", which forms a peculiar framework, around which the entire landscape complex is formed through the operation of direct and inverse paragenetic bonds. Direct PGR are found in the construction of the HEPS and constant maintenance of its optimal state by man. Reverse PGR are more diverse, their manifestation is due to natural factors in the headrace and the tail bay of water reservoirs.

In the dam part of the upper reaches, transporting capacity of the river flow decreases, which leads to silting of the bottom of the water reservoir. And vice versa – in the lower reach, where the force of transfer of matter increases – the bottom of the riverbed is blurring and deepening, which causes lowering of the longitudinal equilibrium profile.

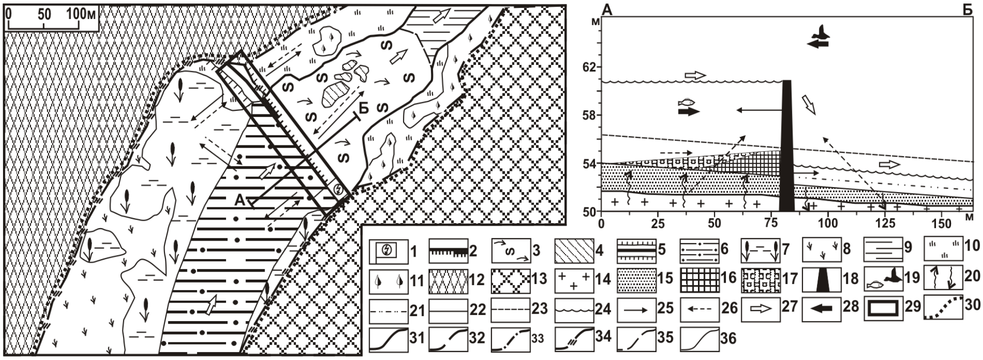

Fig. 5. Relations in APGLC "dam HEPS – water reservoir – modified landscape complexes of the lower reach"(the city of Pervomaisk, Mykolaiv region)

Water anthropogenic landscapes. Water reservoirs. Channel. Tracts: 1 – concrete and brick building of Pervomaisk HEPS; 2 – complex of reinforced concrete dam structures of overflow type; 3 – central stream with the depth of 1–1.5 m and velocity of water flow 2–3 m/s with outcrops of crystalline rocks flooded by waste waters of the water reservoir; 4 – islands with the area of 0.1–0.3 ha with uneven surface, overgrown with willow and sedge on alluvial sediments. Floodplain-water reservoir. Tracts: 5 – water-retaining earth dam of trapezoidal profile (width – 20 m, length – 74 m, height – 7.60 m) with grass-cereal vegetation; 6 – dam deep water (6.7 m) with sandy-silty trough-like bottom and water masses used for the needs of HEPS; 7 – gently sloping (3–5°) loamy surface of the floodplain with reed-sedge associations on marshy meadow soils; 8 – gently sloping (3–5°) loamy surface of the floodplain with over moistened meadows on meadow soils.

Residential landscapes. Urban. Water-recreational. Channel. Tracts of the reaches: 9 – central deep water with the depth of 2–3 m and flow velocity 0.2–0.3 m/s for fishing. Floodplain. Tracts: 10 – flat loamy surface of the floodplain with meso-xerophytic meadow-cereal vegetation on meadow soils under natural beaches; 11 – plantations of crack willow on loamy meadow soils used for recreation. Low-rising. Sloping. Tracts: 12 – sloping (10–12°) loess surfaces under low-rise buildings and gardens on common medium-humus chernozems. Multi-storeyed. Supra-floodplain. Tracts: 13 – true loess surfaces under multi-storeyed buildings on common medium-humus chernozems.

Landscape profile: 14 – Precambrian crystalline rocks: granites, gneisses; 15 – sand channel alluvium; 16 – body of sedimentation of the water reservoir by small sediments; 17 – body of accumulation of the water reservoir with large loads; 18 – concrete dam; 19 – animals; 20 – underground waters; 21 – the previous level of the bottom of the riverbed; 22 – the current level of the bottom of the riverbed; 23 – previous water level; 24 – current water level.

Interrelations: 25 – direct PGR; 26 – reverse PGR; 27 – direct PDR; 28 – reverse PDR.

Boundaries. PGLC: 29 – central site of APGLC; 30 – APGLC "dam HEPS – water reservoir – modified landscape complexes of the lower reach". Types of terrain. Natural: 31 – channel and floodplain; 32 – floodplain and supra-floodplain; 33 – floodplain and sloping. Anthropogenic: 34 – floodplain-water reservoir. Aquatic areas: 35 – riffles and reaches. Tracts: 36 – anthropogenic.

Thus, in the upper reach of Myhiia water reservoir, the thickness of alluvial deposits in front of the overflow dam is 0.9–1.3 m. Due to the fact that water does not spill over the crest for most of the year, and velocity of the current is 0.1–0.2 m/s, in the dam part of the water reservoir the association of coontail and yellow water-lilly have formed. As a result of maintenance of a persistent level of water-retaining horizon, accumulation of various polyutanes that enter the

Southern Buh as polluted waste water of populated areas takes place in the headrace. Studies [29] confirm this by the lowest (64 species) indicators of the phytoplankton species diversity of in the area of Sabarivska HEPS, compared to the sites located upstream near the city bus station (94 species) and outside the city of Vinnytsia (151 species). At the same time, intensive development of blue-green algae (*Microcystis pulverea* (Wood) Forti and *Snowella lacustris* (Chodat) Komárek & Hindák) was observed, which is the result of organic pollution of the river. Thus, Southern Buh water within Vinnytsia region are characterized by the following one-time values of BSKp = 3.4–14.6 mgO_2/dm^3 (maximum limit allowed = 3,..0 mgO_2/dm^3) are characteristic in 47 samples out of 63 selected.

During the interaction of water and soil components of LC, paragenetic relations have a vertical multidirectional character. Saturation of soils of the floodplain with waters of the water reservoir leads to a rise in the groundwater level (up to 1 m and higher), resulting in the development of tracts of wet and moist meadows in the shore part of headrace. In the lower reach, due to lowering of the groundwater level below 2–2.5 m [8; 25], there is dewatering of floodplain meadows and new vegetative groups that were not previously peculiar here develop. In the works of V.S. Zaletaiev [11], H.I. Denysyk [8] it is proved that all the tracts of the lower reaches meadows of the Southern Buh water reservoirs without exception have signs of xerophytization.

In comparison with the upper reaches, geoecological situation is also changing in the lower reaches of the water reservoirs. From 1993–1995, after the beginning of “blowdown” of the water reservoir-cooler of the Southern Ukrainian HEPS to the Southern Buh riverbed, which is a kind of a lower reach of Tashlyk water reservoir, significant concentrations of radioactive elements get it. Thus, according to Yu.A. Tomilin [9; 246], in the area of the area of the discharge of “blowdown” waters in the riverbed and near the village of Buzke, Mykolaiv region, value ^{90}Sr increased to 30–50 mBq/l, and ^{137}Cs – 10–15 mBq/l, during flood, these levels increased by 2–3 times. An increase in the concentration of ^{137}Cs has affected its accumulation in the bottom sediments, seaweed and fish 2-3 times. The activity of ^{3}H in the river water increased 8-10 times. Migration of radioactive elements from the Southern Buh riverbed to the watersheds of the basin continues through the canals of Southern-Buh irrigated massif [10]. As a result of watering soils with contaminated water, active accumulation of ^{90}Sr, ^{137}Cs, ^{3}H in crops takes place [7].

Relations in landscape complexes, which appeared as a result of construction of mills. Construction of the riverbed and the floodplain of the Southern Buh with the mills with drainage canals led to the formation of APGLC of the “mill – canal – island” type. Continuous interaction between the components of APGLC was provided by the control of their condition on the part of man. The cessation of control meant destruction of the mill and disappearance of the whole complex. However, in some cases complexes, left without human control, continued to function due to NPDR. Let us consider the peculiarities of relations on the example of spatial-temporal process of formation of such APGLC in the village of Sokiltsi of Vinnytsia region (Fig. 6).

The construction of Sokilets mill in 1894–1898 was initially conditioned by social PDR, which were manifested in: 1) the need of the local population to process grain for flour and groats; 2) convenient location of the mill buildings on the surface of the left bank floodplain and in the river bed at the site of the riffle; 3) a close delivery of building materials (granites were mined in a quarry confined to the right bank slope of the village of Pechery).

The role of the "central place" in APGLC was played by the mill building with a turbine, where the process of grain processing was coordinated. In relation to the mill, direct PGR with it had a drainage canal and a newly formed island, the state of which was supported by people for the most effective operation of the whole complex. The mill was connected with the Southern Buh riverbed by direct NPDR, which manifested themselves through the canal in the form of downstream flows of matter (water, rock and soil particles, plant seeds, animals), energy and information. Due to the mentioned NPDR, the components of the mill complex were united into a single anthropogenic paragenetic system "mill – dam – canal – island".

Reverse mechanical NPDR were manifested in the processes of watering the banks of the canal and the island.

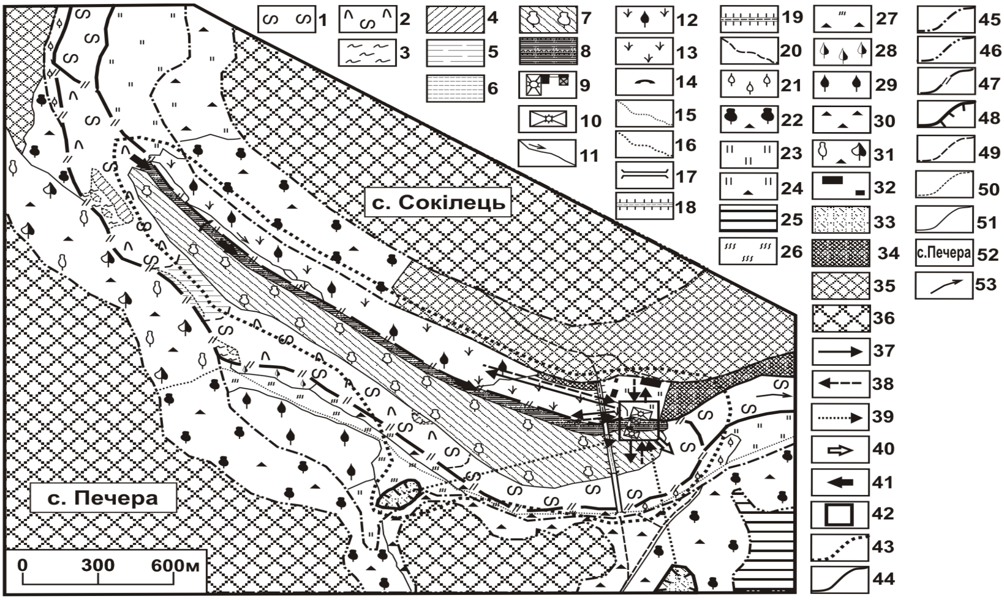

Fig. 6. Relations in APGLC "inactive HEPS – inactive mill – dam – banked earth with a bridge – bottom of a drained water reservoir - island" (the villages of Sokilets and Pechera of Vinnytsia region)

Water natural landscapes. Riffles. Tracts: 1 – central riverbed; 2 – rapids; 3 – shallow water sleeves; 4 – natural islands. Reaches. Tracts: 5 – central deep water; 6 – bank shallow waters.

Water anthropogenic landscapes. Canals. Channel-canal. Tracts: 7 – an island with uneven surface, overgrown with various bush and woody vegetation on floodplain loams; 8 – shallow (1–1.5 m) drainage canal with the width of 11–12 m with "opust"; 9 – granite dam (length – more than 30 m, width–2.5 m, height – 3 m), inactive gristmill and hydroelectric power station. Floodplain. Tracts: 10 – stone building of a former roller mill; 11 – shallow (0.5–1 m) inflow of the canal; 12 – flat surfaces with sticky alder forests and sedge-grassy vegetation on silty sediments; 13 – even surfaces with over moistened meadows with sedge-grassy vegetation on silty sediments.

Road landscapes. Pedestrian. Soil-wood. Channel-canal. Tracts: 14 - a wooden bridge without supports 13 m long. Highway. Soil-gravel Floodplain. Tracts: 15 – low (0.5–1 m) clay-schistose embankments with the width of 2.5–3 m without vegetation. Sloping. Tracts: 16 – field road with the width of 2.5–3 m on sloping (10–12°) loess surfaces with gray forest soils. Asphalt-concrete. Channel-canal. Tracts: 17 – reinforced concrete bridges on 1 and 5 supports (44 and 121 m long, width of the carriageway – 6 and 7 m, load capacity – 30 and 80 t); 18 – high (1.5–2 m) loamy-stone embankment with steep (40–45°)

slopes, planted with box-elder and crack willow, on the surface of the island. Floodplain. Tracts: 19 – high (1.5–2 m) loamy-stone embankment with steep (40–45°) slopes, planted with box-elder and crack willow, on the surface of the floodplain. Sloping. Tracts: 20 – high (1.5–2 m) loamy-stone embankment with steep (40–45°) slopes, planted with box-elder and crack willow, on sloping (10–12 °) surface of the slope.

Forest anthropogenic landscapes. Derivatives. Floodplain. Tracts: 21 – channel alder-willow thickets on loamy meadow soils. Sloping. Tracts: 22 – steep (25–30°) slopes with outcrops of crystalline rocks and oak-hornbeam forests on gray podzolized soils.

Agricultural landscapes. Meadow-pasture. Floodplain. Tracts: 23 – flat loamy surfaces with fresh meadows with meadow-cereal vegetation on meadow soils for grazing. Sloping. Tracts: 24 – steep (25–30°) slopes with outcrops of crystalline rocks and fresh meadows with meadow-cereal vegetation on gray podzolized soils for grazing. Field. Upland. Tracts: 25 – sloping (6–8°) surfaces on eroded gray forest soils under field crop rotations.

Recreational landscapes. Floodplain. Tracts: 26 – flat loamy surfaces with fresh meadows with meadow-cereal vegetation on meadow soils under natural beaches; 27 – situated near the river channel uneven surface of the floodplain with outcrops of crystalline rocks and meadow-grass and wetland vegetation on loamy meadow soils for recreation; 28 – situated near the river channel thickets of willow stands on loamy meadow soils for recreation; 29 – alder plantation on loamy meadow soils for recreation. Sloping. Tracts: 30 – steep (30–45°) slopes with outcrops of granite rocks and meadow-cereal vegetation on washed gray soils for recreation; 31 – park on sloping (10–15°) slopes with the outcrops of crystalline rocks and oak-birch and spruce stands on clear gray soils.

Industrial landscapes. Actual industrial. Floodplain. Tracts: 32 – gently sloping (1–3°) loamy surfaces with additional mill buildings on meadow soils. Mining. Quarry-stocker. Granite variant of the type of terrain "stony badland". Tracts: 33 – small (up to 0.5 hectares) granite quarries overgrown with ruderal vegetation.

Residential landscapes. Rural. Floodplain. Tracts: 34 – true loamy surfaces under low-rise buildings, gardens on meadow soils. Sloping. Tracts: 35 – sloping (10–12°) surfaces under low-rise buildings, gardens on washed gray forest soils. Upland. Tracts: 36 – sloping (8–9°) surfaces on eroded gray forest soils under low-rise buildings.

Interconnections: 37 – direct immediate PGR; 38 – reverse immediate PGR; 39 – direct intermediated PGR; 40 – direct PDR; 41 – reverse PDR.

Boundaries. PGLC: 42 – central site of APGLC; 43 – APGLC "inactive HEPS – inactive mill – dam – banked earth with a bridge – bottom of a drained water reservoir – island". Types of terrain. Natural: 44 – channel and floodplain; 45 – floodplain and sloping; 46 – sloping and upland. Anthropogenic: 47 – channel-canal; 48 – types of terrain "stony badland". Aquatic areas: 49 – riffles and reaches. Tracts: 50 – natural; 51 – anthropogenic.

Other keys: 52 – names of populated areas; 53 – direction of the current.

During the spring floods, water, filling over the canal, blurred the surface of the left bank floodplain, resulting in a shallow channel of river Fosa. The channel is directed in parallel to the drainage canal. The total length of river Fosa is more than 600 m, it is connected with the canal several times, forming three islands in the left bank of the floodplain. The width of the channel is 2–3 m, the depth – 0.5–1 m.

Reverse biological NPDR were manifested in the overgrown of the newly-formed island with wood and bush vegetation. The forested island became a habitat for water-loving animals. In the course of the long-term functioning of APGLC, the projective coverage of the island by the tree-plant increased, which predetermined the emergence of the phenomenon of climatic contrast.

Thus, at the forested surface of the island, the air temperature in the summer is 10–12% lower compared to the shore landscape complexes, the relative humidity of the air increases by 10–40%, and the wind speed decreases by 11 times.

In 1924 a small hydroelectric power station with the capacity of 240 kW was added to the roller mill building. A dynamo machine, whose current illuminated the villages of Pechera and Sokilets, was installed at the station. Direct public PDR, manifested in the provision of settlements with electric power, led to the conditional change of the previous paragenetic landscape complex on APGLC of "HEPS – mill – dam – canal – island" type. Fundamental changes in this complex occurred in 1951, when the HEPS and the dam were reconstructed in order to increase the capacity, and a water reservoir was built for its normal functioning.

The emergence of APGLC of "HEPS – mill – dam – water reservoir – island" type caused reverse water NPDR. As a result of flooding, the surface of the left bank floodplain with wet meadow-cereal biocenoses came under water. Groundwater dam within the water reservoir increased by 1–1.5 m. Water-marsh vegetation belts began to appear in the coastal parts of the water reservoir.

Biological NPDR were manifested in stocking of a new water reservoir with fish populations that migrated from the riverbed. Wild ducks, water hens, muskrat, etc. settled in the coastal thickets. Mechanical PDR in the form of the process of erosion in the coastal part of the island intensified. During one of the floods, the water broke through the mound within the middle part of the island and formed a drop-off. It has a winding character, its depth is 1–1.5 m, its width is 2–2.5 m. The erosional drop-off crosses the island from northwest to southeast and is connected to the riverbed.

In 1964, two reinforced-concrete bridges were built over the Southern Buh riverbed between the cities of Nemyriv and Mohyliv-Podilskyi in order to provide better transport connections (the manifestation of SPDR). The first (121 m long) connects the village of Pechera with the island, the second (44 m long) – the island with the village of Sokilets. Soilets bridge was built in the upper reach of the water reservoir on one support. In order to dampen the level of Sokilets bridge with Pechera bridge, part of the island and of the laeft bank floodplain were elevated by means of embanked earth. Construction of Sokilets bridge led to drainage of the water reservoir, whose waters washed the access embankment and the support, and stopped the operation of the HEPS. As a result, the APGLC of "inactive HEPS – a mill – a dam – banked earth with a bridge – the bottom of a drained water reservoir – an island" type.

In the process of functioning of a new APGLC, water and biotic NPAR played a major role. After the water drainage, the bottom of the former water reservoir, enriched with alluvial sediments, began to be actively overgrown with moisture-loving plants. On the surface of the floodplain, which is located closer to the bridge, a tract of overmoistened meadows was formed, herbs of which are represented by 27–30 species of plants. The grouping is dominated by greater pond sedge, carex acuta, common reed, broad-leaved cattail, narrow-leaved cattail, nettle, snakeweed, throatwort. On the other part of the floodplain the tract of alder-willow thickets develops.

The stop of the mill in 1992 led to "attenuation" of direct public PDR and transformation of landscape complex in APGLC "inactive HEPS – inactive mill – a dam – banked earth with a bridge – the bottom of the drained water reservoir - island", which now continues to operate due to natural PDR.

Water-coastal landscape geoecotons. Paragenetic landscape complexes of the riverbed and the floodplain are physiologically and qualitatively different. In the framework of their contact, due to direct and reverse relations, peculiar transition bands – geoeoctons are formed. Field studies show that water-bank landscape geocotones (WBLG), represented by wetland landscape complexes, are specific transition lanes from the riverbed to the floodplain of the Southern Buh.

According to landscape features, WBLG are radically different from contacting landscape complexes, since they occupy an intermediate position between terrestrial and amphibian variants of landscape sphere [18]. The basis of WBLG is the contact of solids and water, coastal zone and coastal shallow water. Within its limits, the upper component of the cycle of substances, which is directed from land to the water surface, and the lower (underground) in the form of a stream of ground waters, which provides hydromorphy of soils and vegetation in the coastal zone, are well distinguished [1, p.32]. Geocotons are characterized by their own flora and fauna. Due to the principle of contrast (water – soil) here and now, in conditions of anthropogenic loading, relict representatives of flora and fauna can live.

Geoeocontos of anthropogenic origin are of great importance for forming modern river landscapes. WBLG, formed in the conditions of natural hydrological regime of the river, change as a result of the construction of HEPS, dams, ponds and water reservoirs. During the flooding of landscape complexes of the riverbed and the floodplain by water reservoirs, natural WBLG are destroyed and new anthropogenic ones, located on a higher hypsometric level and have larger areas for distribution, appear (Fig. 7).

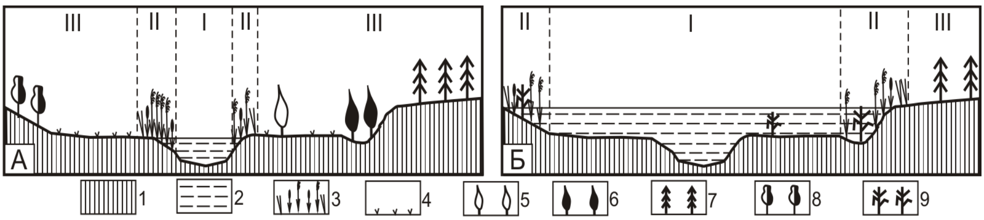

Fig. 7. Generalized charts of the Southern Buh WBLG

A. I – natural riverbed; II – natural water-marsh landscape complex; III – landscape complexes of the dry land.

B. I – riverbed and floodplain, flooded by water reservoir; II – anthropogenic water-marsh landscape complex; III – landscape complexes of the dry land.

Landscape profiles: 1 – indigenous rocks and soils; 2 – water masses; 3 – reed-sedge-cattail associations; 4 – meadow-cereal associations; 5 – willow stands; 6 – sticky alder forests; 7 – pinewoods; 8 – hornbeam-oak forest; 9 – flooded vegetation.

The peculiarity of anthropogenic WBLG is its instability. In its development between the aquatic environment and the land, a process of constant and gradual increase of geoeoconus territory is observed by means of shallowing of ponds and water reservoirs, which promotes the spread of wetland vegetation [27].

Thus, in Marianivka water reservoir (the town of Chornyi Ostriv of Khmelnytsk region) in the period from 2008 to 2011, the width of WBLG increased from 74 to 86 m. The main vegetative groups, due to which its width increased, are small duckweed, common cane, broad-leaved cattail and acute sedge. In the future there is a steady tendency of complete overgrowth of the water reservoir. Already, the entire surface of the water reservoir is 90% covered by a population of small duckweed (Fig. 3).

Now, due to predominance of river landscape-engineering systems in the structure of the Southern Buh valley, natural WBLG are rare. As a rule, they are common in the form of narrow (1–3 m) water-marsh landscape complexes in lower reaches of ponds and water reservoirs.

CONCLUSIONS

The study of the exchange of matter, energy and information between landscape complexes in the riverbed and floodplain can be carried out in two aspects: as a manifestation of paragenetic relations (if they are common in origin) and as a manifestation of paradynamic (if they are adjacent but different in genesis). In paragenetic landscape complexes, the main role is given to the "central place", in relation to which the direction of mass and energy flows between the components of the system is determined. There is an active connection between channel-floodplain paradynamic landscape complex and the adjacent valley-watershed divide landscapes, which determines the functioning of the basin PDLC. Taking into account the peculiarities of such relationships will enable effective implementation of regional environmental policy in the Southern Buh basin. As a result of direct and reverse relations of landscapes of water bodies with dry land, transitional water-marsh stripes, geocotones, appear. As a result of the flooding of the riverbed and floodplain by water resevoirs, anthropogenic geocotones have become widespread, which differ from natural ones by their altitude and latitude location within the valley and constant increase of areas.

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CHALLENGES OF DRINKING WATER SECURITY IN THE WEST OF ENGLAND

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ABSTRACT
The purpose of this paper is to introduce readers to common approaches to drinking water treatment used in the UK through examination of a large drinking water treatment works in the west of England. In addition to discussing key stages in the primary, secondary and tertiary phases of water treatment we discuss attendant challenges, such as the management of disinfection by-products. Finally we discuss emerging challenges for drinking water treatment related to climate change, population change (including behaviour and expectations) and social justice.

KEYWORDS
Drinking water treatment processes, sustainability, challenges, engineering

INTRODUCTION

The purpose of this paper is to introduce readers to common approaches to drinking water treatment used in the UK in general and the west of England in particular. The next section of the paper outlines, step-by-step, the treatment process for transforming raw water from a relatively low-quality source (an ex-industrial canal) into clean and stable drinking water in full compliance with regulatory standards. We also discuss some current and emerging challenges to drinking water security related to climate change, population change, and emerging contaminants.

DRINKING WATER SERVICES IN THE WEST OF ENGLAND

In England (each of the constituent nations of the UK organises water services slightly differently), water companies are private companies, though they are heavily regulated.

There are government regulators: Ofwat for economic regulation of the privatised water and sewerage industry, the Drinking Water Inspectorate for drinking water quality, and the Environment Agency for environmental standards [1]. Primary legislation governing the privatised water companies, particularly the Water Act (1989, revised 2014) and the Water Industry Act (1991, revised 1999) and the Water Resources Act (1991, revised 2016) set the basic legal framework for water services. These acts have been updated and augmented several times since 1989, in particular by the Flooding and Water Management Act (2010) and a major revision to the Water Act in 2014. Among other things these more recent acts bar water companies from disconnecting domestic customers (even if they are in significant debt) and impose on water companies a ‘resilience duty’, which we will explore towards the end of this paper [2]. Though essential regional monopolies, since April 2018 non-domestic customers have been able to shop around for the best available deal on water services, leading to the entry of new providers (often middleman resellers) into the market place. Debates about extending this model to domestic water customers are ongoing.

Bristol Water is one of roughly two dozen water services companies (as of 2021) serving customers in England, Wales, Scotland and Northern Ireland (Map 1). One of the smaller water companies, Bristol Water was founded in 1846 – it celebrates its 175th birthday in July 2021 - by a group of philanthropists who wanted to supply safe and clean water to the people of Bristol [3]. That remains the main reason for Bristol Water’s existence to this day as it only supplies drinking water. Wastewater services for the Bristol region are provided by another company. As we will see towards the end of this chapter, the company is currently reframing its corporate mission in terms of a new ‘social contract’ with its service community.

Bristol Water supplies 1.2 million customers located in an area of roughly 1,000 square miles, centred on Bristol in the west of England. Raw water sources include both groundwater and surface water, treated in 17 water treatment works (WTWs) producing an average daily total of 264 megalitres (Ml). Two of the three largest WTWs (Purton and Littleton) abstract surface water from the Gloucester and Sharpness canal, treat it to acceptable legal standard and then distribute it to customers via more than 6,000 kms of pipe network. Purton WTW has a peak output of 165Ml/d and Littleton WTW up to 65Ml/d. Bristol Water has 165 service reservoirs, which store water after it is treated, before it reaches customers.

Bristol Water’s service area runs from the Purton WTW (slightly outside the supply area) and Tetbury in the north, to Bridgewater, Street and Glastonbury in the south. This area is split into 207 water supply zones, which is a way of dividing up the larger service area into manageable sub-units.

All potable water supplied by Bristol Water must comply with the Water Supply (Water Quality) Regulations 2000, as amended in 2016, which requires service providers to provide water that is “wholesome.... for such domestic purposes as consist in or include, cooking, drinking, food preparation or washing”. The 2016 amendment to Regulation 26 further requires water companies to “design, operate and maintain the disinfection process so as to keep disinfection by-products as low as possible without compromising the effectiveness of the disinfection process” [4]. These regulations are overseen by the

Drinking Water Inspectorate (www.dwi.gov.uk), which publishes annual reports on company performance.

PURTON DRINKING WATER TREATMENT WORKS: AN EXAMPLE OF A MODERN DWTW

Officially opened by HRH the Prince of Wales on 16 October 1973, Purton is Bristol Water's biggest water treatment works, and sits on the banks of the Gloucester and Sharpness Canal just outside the company's service area in Gloucestershire. From this plant, treated water is pumped 30 kms to the ring mains at Pucklechurch. It can take half a day for the water to travel there from Purton. Norit Activated Carbon, a carbon regeneration company, is also based at Purton, and as we shall see they provide a key service during the treatment process.

There are more than a dozen separate steps in the treatment process at Purton, making it one of the more complex and expensive water treatment plants – necessitated by the relatively low quality of the input raw water and persistent non-point source pollution issues related to agricultural nutrients. This section of the chapter will focus on a selection of these treatment stages, as well as discussing some of the resilience challenges related to raw water supply and distribution, i.e. upstream and downstream from the plant itself, in the west of England.

The Gloucester and Sharpness Canal provides the raw (untreated) water inputs into Purton WTW. Initially, larger debris is removed from the water by belt screen before it is settled in raw water storage tanks for around half a day. The water is then pumped up into the treatment works. The process involves quite high energy use – water is heavy, and there are several stages of pumping required to get it into the treatment works.

The storage tanks provide four essential benefits to the plant:

1. They offer a buffer in case of brief interruptions of supply, which can occur when the canal is periodically dredged. Each tanks has a capacity of 55,000m^3.
2. They offer initial 'treatment' of raw water through unaided settlement (heavier materials sink when the water is still) and off-gassing of any undesirables such as H_2S or CO_2.
3. They offer the possibility of lowering incoming pollution levels (especially nitrates – discussed below) through controlled blending with water of higher purity.
4. Since 2015, they have incorporated mechanical aeration to reduce levels of trihalomethanes (THMs, discussed below) which are themselves a consequence of the initial dosing of raw water with chlorine to kill invasive Zebra mussels (*Dreissena polymorpha*) which proliferate in the intakes.

As noted above, raw water abstracted from the Gloucester and Sharpness canal is dosed with chlorine to prevent Zebra mussel colonisation of the inlet works of Purton and Littleton WTWs (Figure 1). Many water companies are reporting having problems with their water-treatment plants because of these mussels, and also the equally invasive Quagga mussel (*Dreissena rostriformis*), attaching themselves to pipeworks, interrupting mechanisms and decreasing the throughput capacity of pipes. Quickly reproducing, there are documented cases of populations rising from densities of 200 individuals/m^2 to 700,000 individuals/m^2 in only a year to two [5]. Elsewhere in the world, there have been many instances of mussel propagation completely compromising water treatment works and hydroelectric power plants. UK water companies spend millions of pounds each year managing this problem [6][7].

Raw water chlorination is used as sparingly as possible due to concerns over THM formation. THMs, one group of disinfection by-products, are formed when chlorine reacts with natural organic matter (NOM) present in the raw water and if present it must be removed before the treated water goes into distribution. The Drinking Water Inspectorate (DWI) assesses how well companies are meeting the disinfection by-product rule by reviewing the THM concentration in treated water. An annual average value of <50ug/l (50% of the maximum limit) is taken as a broad indicator that the company is minimizing disinfection by-products effectively. Reduction of THM risk was the primary driver for commissioning of the water settlement pond aeration scheme in 2015.

Figure 2 is a screenshot from Bristol Water's telemetry system. In the top left, the raw water tanks are in green. Following the green pipes, there are notations indicating pip pressure (in bar) and flow rates (in Ml/d). The groupings of three and four circles indicate pump sets. Water is pumped to the pre-ozonation tanks, at a rate, as indicated, of 79.7 Ml/d. Before the water flows through the pre-ozone tanks, Bristol Water adds acid to reduce pH. Most of the source waters used by Bristol Water are somewhat alkaline (i.e., pH higher than 7 on a scale of 0 to 14) and in order to get the next stage of treatment to work properly, the water needs to be slightly acidified. They use highly concentrated 96% sulfuric acid, since this requires less volume to be stored on site and added to achieve target changes in pH. At Purton, incoming water fluctuates between pH values of about 7.4 and 8.4, and the pH needs to reduce to around 6.8 for subsequent treatment stages to work effectively.

Ozone (O_3) has been used in water treatment since the late 19th century [8][9]. Today it is applied for the disinfection of drinking water, for the removal of effluents from wastewater treatment plants in a process called ozonation (or ozonisation), as well as for the degradation of organic and inorganic pollutants in wastewater.[1] When there is stable control of the acid dosing, and the pH of the water is at the correct value, ozone is applied to the water. Ozone is a very powerful oxidant which is applied as a gas and diffused into the large concrete tanks through bubblers (Figure 3). The ozone gas will grab onto material such as dissolved metals, pesticides and organic material and help it degrade more rapidly. It also has some benefits for improving taste and odour. Bristol Water produces its own O_3 on site by converting liquid oxygen.

Clarification refers to the sequence of operations used to remove *suspended* solids (mineral and organic) from the now partly processed raw water, together with a

[1] One of the original 19th chemical water treatment processes involved using 'Fenton's Reagent', a combination of Hydrogen Peroxide and Ferric sulphate. It is still used in different applications around the world, although not at Purton.

proportion of the *dissolved* organic matter (this latter through the associated process of flocculation). Depending on the specific concentrations of the various contaminants present, different combinations of coagulation, flocculation, sedimentation or flotation can be used to achieve the desired effects. Also relevant is the type of filtration that is used in subsequent treatment steps [10].

The clarification step used at Purton combines coagulation and flocculation (see Figure 4) and involves a chemical water treatment technique typically applied prior to sedimentation and filtration (rapid sand filtration) to enhance the ability of this sequence of treatment steps to remove suspended and dissolved contaminants. Coagulation is a process used to neutralise charges and form a gelatinous mass to trap (or bridge) particles thus forming a mass large enough to settle by gravity or be trapped in the filter. Chemicals used for coagulation are usually higher valence cationic salts (Al^{3+}, Fe^{3+}, etc.). Flocculation essentially refers to the gentle stirring or agitation to encourage the particles thus formed to agglomerate into masses large enough to settle or be filtered from the solution. Long chain polymers may also be added to facilitate binding together of larger flocs.

During this step Bristol Water doses the incoming water with liquid aluminium. This requires good flash mixing to intensively mix the chemical into the water. The aluminium then changes from a soluble form into a particulate, but this conversion only works if the pH is at the right level (once again we see the importance of careful pH regulation). If the water was dosed when the pH was too high, it would have no effect. The injected aluminium would stay as a liquid, and would just travel through the treatment works, giving no benefit at all. By reducing the pH to just below seven through acidification, the aluminium becomes activated. It forms a small fluffy particle and starts binding together with other particles that are also present, and forming solids which can then settle under their own weight. As well as the aluminium coagulant, Bristol Water also uses polyelectrolyte, which is a very heavy long-chain molecular substance that binds together with, and adds weight to, all of the flocs of aluminium. Throughout the process aluminium and pH levels are continuously monitored to ensure the correct values for both are maintained. Ideally, the aluminium and polyelectrolyte will settle out entirely, bringing with it the target suspended and dissolved contaminants.

Bristol Water uses ‘Hopper-bottomed’ clarifiers with a V-shaped cross-sectional profile and vertical baffles to facilitate settlement. The Hopper-bottomed clarifiers’ shape is commonly used throughout the water industry because it allows the floc, as it rises up through these settlement tanks, to slow down as it reaches the outer edges of the Hopper. When water is pumped into the clarifier, the floc rises up, but it gets to a certain point where the floc is too heavy to rise, so it tries to settle again. But it cannot settle because there is water flowing into the tank, so it tries to rise up, but it cannot rise because it is too heavy. The end result is the formation of blanket of accumulated floc sludge part way up the water column, with cleaner water on top, free to flow off the top through decanting. Also, as the water flows through the structure, the floc gets intercepted by these plates. The floc will build up on the plates and it will gradually slide off and sink to the bottom of the tank, and can then be removed. As with the other type of clarifier, the clean water, known as supernatant, accumulates at the top of the tank. Periodically, the accumulated solids will need to be removed from the clarifier because otherwise the whole structure would eventually fill with sludge and become completely congested. This is usually done on a timer, where solids are removed and sent down into the waste system.

The sludge sent to the waste system is concentrated into 'cake' via a dewatering process. This is completed through pressure filtration, whereby the sludge is pressed between filter cloths at high pressure, carried by slowly revolving drums. Despite the environmental effects of particular elements within sludge waste, since 2001 effluent sludge is sent straight into the Severn estuary via pipeline from Purton and Littleton. This reduces disposal costs related to common industry practices of transportation and land fill.

Once the water has been settled, the clean supernatant is moved from the clarifiers to the next stage of the process, which is filtration via rapid gravity filters, also known as sand filters (at right on Figure 3). These filters use an anthracite carbon media and consistently reduce remaining turbidity to below 0.01 NTU.[2] As with other filtration media, these filters will clog up, or 'blind', over time and must be periodically taken offline and backwashed to restore filtration efficacy [11]. There are seven rapid gravity filters at Purton, each with a carbon media filter about 1.5 metres thick.

Figure 5 shows the final stages of water treatment at Purton prior to the pumping of the treated water into distribution via the Pucklechurch reservoir (bottom centre). The remaining treatment steps involve post-ozonation (a second ozonation step), ultraviolet treatment, granular activated carbon and final chlorination. It is apparent from the process flow diagram that at all stages, key parameters of interest continue to be carefully monitored to ensure that the treatment steps are delivering the required treatment benefits.

Ozone has already been applied earlier in the treatment process. This second application of ozone is aimed particularly at pesticide removal as well as addressing potential taste and odour issues related to geosmin and methylisoborneol (also known as MIB). The concentrations are not high, but they are above the threshold at which a human would be able to taste them, which is around five nanograms, depending on a person's sense of taste or smell. Because Bristol Water is not permitted to vent unused ozone to the atmosphere it has been necessary to invest in a plant for capture of unused ozone and convert it, by pyrolysis, to CO_2, which can then be safely vented to the atmosphere.

The final stages of water treatment are known generally as 'polishing' stages because the water is now mostly clean and remaining issues are about taste, odour, and management of risks of treatment by-products such as bromates and THMs. Polishing has become increasingly important also as a function of the generally deteriorating quality of raw input water and the demand for stability in treated water even in the face

[2] NTU stands for 'Nephelometric Turbidity Unit' and is an alternative way of assessing the cloudiness of water to suspended solids. 1 mg/l (ppm) suspended solids is equivalent to 3 NTU, so 300 mg/l (ppm) of SS is equivalent to 900 NTU. According to the World Health Organization, the turbidity of drinking water should never exceed 5 NTU [1].

of elderly (and often lead-based) customer supply pipes. The water industry has not used lead pipes in decades, but very many homes and businesses in the UK have old lead-based connectors taking water from their property lines (where water company responsibility ends) onto their premises so it is necessary to adjust water chemistry to prevent solution of lead into the water during distribution.

Granular activated carbon (GAC), essentially a bed of small pellets of carbon through which water must pass before moving on to later stages of treatment, is a key stage in the polishing process. This step is simply a larger version of that used universally in freshwater fish tanks. ‘Activated carbon’ comprises a family of substances, whose members are characterized primarily by their sorptive and catalytic properties [12][13]. Activated carbon can be made from a variety of carbonaceous materials and processed to enhance its adsorptive properties. Some common materials that are used to make activated carbon are bituminous coal, bones, coconut shells, lignite, peat, pecan shells, petroleum-based residues, pulp mill black ash, sugar, wastewater treatment sludge, and wood. Whatever material is used, particle size and GAC bed design – for example, using downflow (most common), upflow or other designs – are the critical variables. The key mechanism here is adsorption which results from the interaction of the molecular structure of an adsorbent, such as activated carbon, with an adsorbate, such as a taste- and odour-causing compound like geosmin.

Disinfection is very nearly the last stage in the treatment process. In order to be effective, disinfection must be carried out on good quality water. The suspended solids content must be kept below 1 mg/L. Were this not the case, bacteria and especially viruses could collect on suspended solids which can protect them from the effect of disinfectants.

UV disinfection is now an established disinfection process that is recognised to be an effective treatment against a range of waterborne pathogens, including certain chlorine-resistant pathogens (for example, cryptosporidium, and also Klebsiella, poliovirus type 1, Giardia lamblia, rotavirus SA-11 and others), although it is less effective than chlorine against some viruses at the doses most commonly applied in drinking water treatment [14][15]. To work effectively UV transmissivity (UVT), which indicates the clarity of the water, must be high. Bristol Water’s UVT is typically around 98.4, which is very good.

Whilst some people believe that all water companies add fluoride to treated drinking water, in fact this is relatively rare in the UK where the Water Act 1991 stipulates that a water company can only add fluoride where required to do so by the Strategic Health Authority [16][17]. Most measured fluoride levels in UK water are the result of natural environmental fluoride levels. The best available evidence suggests that fluoridation of drinking water supplies does reduce caries prevalence over and above fluoride contained in toothpaste, etc. On average, between 2005 and 2015, 72% of the population received a water supply with a low concentration of fluoride (less than 0.2mg/l). The EC drinking water directive (Directive 80/778/EEC) sets a level of 1.5mg/l for fluoride in drinking water. This is in line with the WHO guideline which represents a concentration which “does not result in any significant risk to the health of the consumer over a lifetime of consumption”. Artificial fluoridation is only operated in a handful of Strategic Health Authority areas, including West Midlands, East Midlands, East of England and Northwest.

CHALLENGES OF ENSURING ADEQUATE QUALITY AND QUANTITY OF WATER AT PURTON

With a growing population and the deepening climate crisis, there is considerable concern that water shortages could emerge in coming years, so Bristol Water is investing heavily in supply augmentation (mostly through optimisation and interconnection schemes rather than new reservoirs) and demand management. Bristol Water's *Water Resources Management Plan* [18] outlines the key elements of the company's strategy for ensuring that they can supply sufficient water:

- Reducing leakage to a baseline position of 39.33 Ml/d by 2024/25.
- Reducing bulk export to Wessex Water from 11.37 Ml/d to 4.37 Ml/d after 2024/25, as agreed with Wessex Water.
- Continuing to actively promote their free meter option and to meter households on change of occupier, increase meter penetration rates from 66% at the end of 2019/20 to 87% by 2044/45.
- Enhancing water efficiency activities to complement the metering programme to reduce average dry year PCC down to at least 129.4 litres/person/day by 2044/45 as well as continuing research and innovation to help drive PCC down to the long-term ambition of 110 litres/person/day by 2050.

Note that there are no plans currently for new reservoir development – it seems that new reservoirs are no longer the first-choice option for redressing supply shortages. Optimising existing supply assets, such as Purton WTW and also the Line of Works, are preferred options.

In Bristol Water's catchment area, the southern sources of water are in the Mendip Hill region. There are several reservoirs of various shapes and sizes. The biggest is Chew Valley Lake, followed by Blagdon Lake, and Cheddar reservoir – together there is almost 40,000 Ml of storage. Despite being quite close geographically, the quality of the water in these sources varies immensely. Blagdon is plagued by significant algal blooms in summer and also gives Bristol Water considerable problems with manganese. Chew does not suffer the same problems. These sources all have their own microclimates, and various inflow sources creating unique water treatment challenges, especially in the context of climate change [19].

In the northern part of the Bristol Water catchment area, there is the Gloucester and Sharpness Canal, which taps in to the River Severn. In terms of water quality, the canal is very different to the surface waters sources. As a source, it is very volatile and it can change from very low sediment and colour to the complete opposite within 48 hours. Whereas Bristol Water's southern treatment works get more gradual seasonal changes, the Purton treatment works in the North has to respond extremely quickly to sudden changes in quality.

In the area surrounding the Gloucester and Sharpness Canal, there is extensive agriculture including raising dairy cattle (suggesting a potential water quality problem related to ammonia from slurry as well as microbiological contamination) and pollution from cash crops such as oilseed rape and wheat. As a result, Bristol Water faces considerable challenges from microbiological contamination: pesticides, herbicides, molluscicides, sediment, colour, and some algae. In the previous section we discussed the treatment train engineered at Purton to deal effectively with these challenges.

Also linked to climate change, since surface run-off is an important part of keeping water storage reservoirs topped up, the pollutants that can come with the run-off are also important. In both northern and southern supply areas, there is considerable agriculture and therefore managing nutrient and pesticide run-off into reservoirs is a key issue. We have already seen how Purton WTW removes pollutants including pesticides, but the company has long believed that it is better to prevent pesticide pollution in the first place and has therefore worked extensively with local land managers to reduce the use of harmful pesticides. In their 2019 *Water Resource Management Plan* [18] they say:

> We work alongside farmers and other stakeholders to implement catchment management to manage the risk of raw water quality. This not only provides resilience benefits from reduced outage but also provides a sustainable and cost-effective approach in comparison to traditional treatment approaches. We have also worked with the Environment Agency to identify catchments where pollution is likely to require increased levels of treatment, and we are working across these catchments to control and where possible reduce these risks.

In 2014, Bristol Water set up the Mendip Lakes Partnership to bring together organisations working to reduce the impacts of diffuse pollution from agriculture. The Partnership works with farmers across a number of catchments to protect and improve water quality in the reservoirs and associated watercourse, and to enhance wildlife habitats. As part of the project, Bristol Water has implemented a comprehensive water quality monitoring programme in order to understand risk areas and identify improvements over time. Measures underwritten by the company include investing in better slurry management for individual farms and other on-farm mitigations.

Managing algal growth is a key consideration. Even when storage time is relatively short (a few days), algae and actinomycetes may proliferate and their metabolites can impart unpleasant taste and aroma. Longer residence time can allow useful zooplankton to develop, but can also create ideal conditions for hazardous phytoplankton, especially where there are excessive nutrients available [20][21][22]. The deaths in the 1980s of several dogs and lambs that had consumed algal-laden water from the margins of water storage reservoirs raised the question of possible risks to health via drinking water. At that time, cyanobacteria were known to produce a range of toxins, some of which are of concern for human health. Toxigenic cyanobacteria, including *Anabaena*, *Cylindrospermopsis*, *Microcystis*, and *Oscillatoria* (*Planktothrix*), tend to dominate nutrient-rich, freshwater systems due to their superior competitive abilities under high nutrient concentrations, low nitrogen-to-phosphorus ratios, low light levels, reduced mixing, and high temperatures. The health risks arising from contact with toxic algal blooms via recreational activities were well understood but little was known about the persistence of the toxins in water or whether the toxins were removed or inactivated by water treatment processes. Suitable analytical techniques for drinking water analysis were not available and there was insufficient toxicological data to set health-based guidelines or standards for drinking water.

Raw water quality in Bristol Water reservoirs does not show high concentrations of algae when compared to other reservoirs or natural lakes, though the frequency of instances is growing. The treatment process at Purton requires settlement in order to sink the solids to the bottom, so the clean water is at the top. Algae, by their nature, love to spend a lot of time floating around near the surface of water, soaking up the UV, so this causes Bristol Water a challenge.

The reduction of nitrogen and phosphorus inputs into water has been identified as one of the most important measures to be taken in the River Basin Management Plans (RBMPs) prepared for each River Basin District under the Water Framework Directive. In the UK, the principle control measures in water supply catchment areas have been to reduce nutrient inputs to watercourses by, for example, applying phosphate removal processes in sewage treatment (which in turn improves raw water quality at downstream drinking WTWs) and modifying agricultural practices to reduce the run-off of nutrients. In large water supply reservoirs, physical measures are applied to reduce the growth of algae, for example, aeration by blowing compressed air through a network of perforated tubes laid on the reservoir bed (DAF systems), or re-circulating pumped water through inclined jets to induce mixing within the water column.

Reduction in the algal load on water treatment processes is also achieved by the use of multiple draw-off levels in a reservoir, where a number of outlet valves are provided at different depths on the draw-off tower. By monitoring algal concentrations against water depth, it is possible to ensure that high concentrations of algae are avoided. Unfortunately, this option is not available at Purton, where the reservoir is a three-metre deep by 10-metre wide canal.

Microbiological pollution of water is usually equated with sewage, or faecal coliform pollution. Two common coliform measures are E. Coli and Total Coliform. Evaluation of water quality by measuring faecal coliform is a standard technique undertaken in major river systems and along the UK's coastline. There are over 400 beaches subject to regular (approximately weekly) faecal coliform assessment. This type of assessment differs from others inasmuch as results are not instant (by whichever technology you are using), but rather are produced over 12-18 hours through growing visible coliform communities in a special medium. Samples must meet the following standards as specified in the EU Directive 98/83/EC Quality of Water Fit of Human Consumption: total coliforms less than or equal to 500 total coliforms per 100ml, less than 100 faecal coliforms per 100ml, and less than 100 faecal streptococci per 100ml [1]. E. Coli is a problem in Bristol Water's source water, and that is understandable given the surrounding land use, but the treatment train is designed to remove coliforms entirely and the control values for the process are strictly designed to ensure this.

As discussed earlier, during summer periods, there is a lot of algal growth. This is an area where there is liquid nitrogen and phosphate, which are common constituents that favour algal blooms. Alongside these algal blooms, there are also zooplankton 'grazers', such as *Daphnia*, *Asellus* and *Nauplius*. Such zooplankton occupy the centre of the open-water food web of most lakes [20]. They eat bacteria and algae that form the base of the food web and, in turn, are heavily preyed upon by fish, insects and other zooplankton. Because zooplankton eat algae, it has been proposed that it may be possible to control algal blooms by increasing zooplankton grazing. This method is called biomanipulation, and is usually done by reducing predation on zooplankton by planktivorous fish, either by directly removing these fish or adding a fish predator such as pike. Results of trials of such biomanipulation have been mixed to date.

The problems associated with zooplankton can be divided into two main categories:

- the risk that micro-invertebrates will penetrate into and develop in the mains networks, an aesthetic problem but one which creates many user complaints;
- the health problems posed by parasitic protozoan cysts of which *Cryptosporidium* is the most dangerous and the most difficult to eliminate as we have already seen in this paper.

Metaldehyde is a molluscicide for the control of snails. It is dosed onto fields and quite commonly used in the UK, particularly in areas growing oilseed rape, which is often used to produce oils for cooking, industrial lubricant and animal feed. However, metaldehyde is a contaminant that was regarded as incredibly hard to treat out of water. There was some public concern and media stories about it potentially reaching the tap, albeit in a very tiny, trace amounts [23]. Toxicity data for metaldehyde indicates a health-based seven-day suggested no adverse response level (SNARL) of 300 μg/l and a 24-hour SNARL of 600 μg/l [24]. The World Health Organization (WHO) classifies metaldehyde as "moderately hazardous" [25] but provides no guideline values for water supply and there is no prescriptive standard for metaldehyde in the USA [24]. Nonetheless the drinking water standard (DWS) for individual pesticides in potable water set in UK legislation is 0.1μg/l, whilst the standard for pesticides as a whole, i.e. total pesticides, is 0.5 μg/l, both of which are derived directly from the EU Drinking Water Directive (DWD).

Bristol Water was the first in the industry to test for metaldehyde, with other water companies following their lead. Although the levels of metaldehyde in the Bristol Water area are not as high as they are for Anglian Water, for example, which is in the east of the UK where they have more flat lands and intensive agriculture, it still causes some problems. Bristol Water established a working group, and went out into the catchment, liaising with farmers with a view to understanding how the metaldehyde was being applied onto the land and to explore alternative products for use [26]. They ended up with a product called Slux, which is a ferrous-based substance, and a big part of this project was winning the hearts and minds of the farmers and trying to get them to put their trust in an alternative product. These farmers are trying to protect their livelihood from ravenous slugs and snails, so to put their trust in another product is a difficult sell, potentially. However, Bristol Water got the farmers on board, and there has been a gradual reduction in metaldehyde in the water and, as of 2020/21, it is at the minimum detectable value. Figure 6 shows elements of the community education-based approach taken to metaldehyde and the reductions achieved.

Another challenge for drinking water supply is the complex web of conservation designations that apply to the estuary, and the potential impacts of climate change on water quantity and quality. Figure 7 shows that the entire estuary is managed under one or more conservation designations as far up as the Arlingham Bend, upstream of the water treatment facility. Immediately adjacent the facility and the canal, the foreshore is simultaneously subject to three different conservation designations including RAMSAR, SAC and SSSI. Moreover, these designations apply notwithstanding the environmental legacies of more than a century of heavy industrial use of both the estuary and the canal (which was built to create a safer route for barges around the dangerous Arlingham Bend). There has been a long history of pollution in the Severn Estuary coming from many sources such as steelworks, electroplating, chemical industry, nuclear, mine and sewage discharges into the River Severn and its many tributaries [27][28]. Water quality sampling in the foreshore around the village of Purton in 2016 revealed persistent pollution relating to shipping and the use of decommissioned boats to stabilise the foreshore (the so-called ‘Purton Hulks’), local heavy industry and industrial accidents, such as the collision, and subsequent burning, of two fuel barges in 1960.

Both climate change and population growth mean that it is increasingly important for Bristol Water to fully understand and optimise the interconnections within its water production and distribution system. Figure 8 offers a systemic overview of the system of reservoirs, groundwater pumping points, treatment works and interconnecting distribution mains that makes up the system developed over the course of the 175 years since the company was founded. Purton is at the top of the schematic (the yellow boxes), and they are pumping the water down a 46-inch main, all the way to Pucklechurch, 35km away. From Pucklechurch, they have the option of allowing the water to go further south, down into the Mendip region of their network. This is the Barrow part of the system, which is the second largest treatment works, and treats the majority of the water from the Cheddar and Barrow reservoirs.

Over the course of nearly two centuries, Bristol Water has used a variety of different materials for its distribution network including rolled steel (used on the Line of Works), cast iron, pre-formed ferrocement and most recently plastic. Unsurprisingly different materials used at different times come with different vulnerabilities. A problem unique to cast iron pipework, tuberculation is the corrosion and build-up of iron modules within the water main. This can cause restrictions but also these nodules can burst and result in discoloured water. The iron materials also result in a lot of rust collecting at the bottom of the water mains, which under normal operations do not cause any problems, but a sudden change in pressure or flow might result in these materials being lifted and carried through the system.

CONCLUSION

Overall, water companies in the UK provide a very high standard of drinking water supply that rarely fails. As we have seen drinking water treatment works such as Purton are highly technical facilities for managing water quality across a large number of physical, chemical and biological contaminant parameters. This challenge is further compounded by the age of the network and by the combined impacts of climate change, population growth and urbanisation, and changing customer perception and demand.

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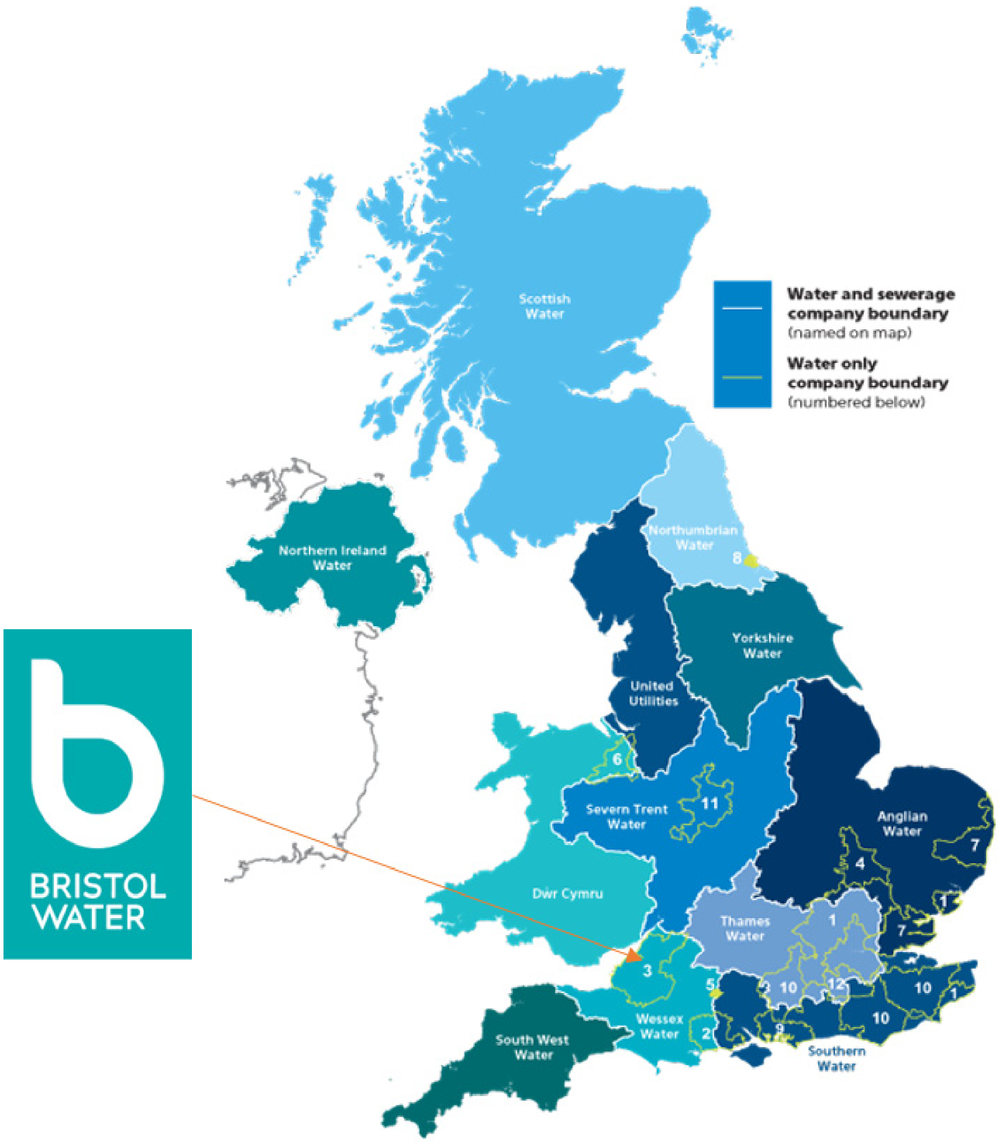

Map 1: Bristol Water in the context of the UK's network of public and private water services providers (Source: Bristol Water)

Fig.1. Zebra and Quagga Mussels colonising water intakes (Source: Bristol Water)

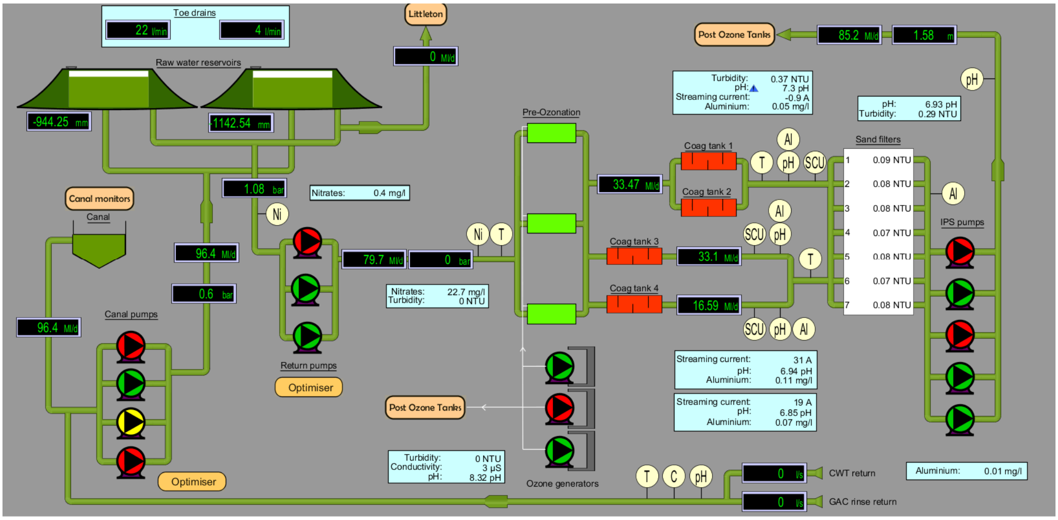

Fig. 2. Schematic of initial part of drinking water treatment train operated at Purton WTW (Source: Bristol Water)

Fig. 3. Ozone bubblers in operation at Purton WTW (Source: Bristol Water)

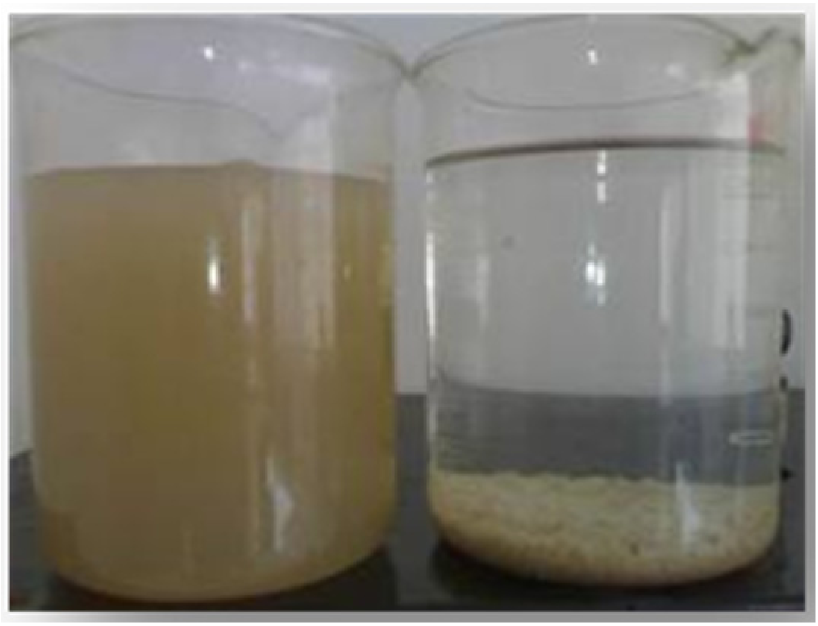

Fig. 4. Water sample before Coagulation/Flocculation treatment step and after (Source: Bristol Water)

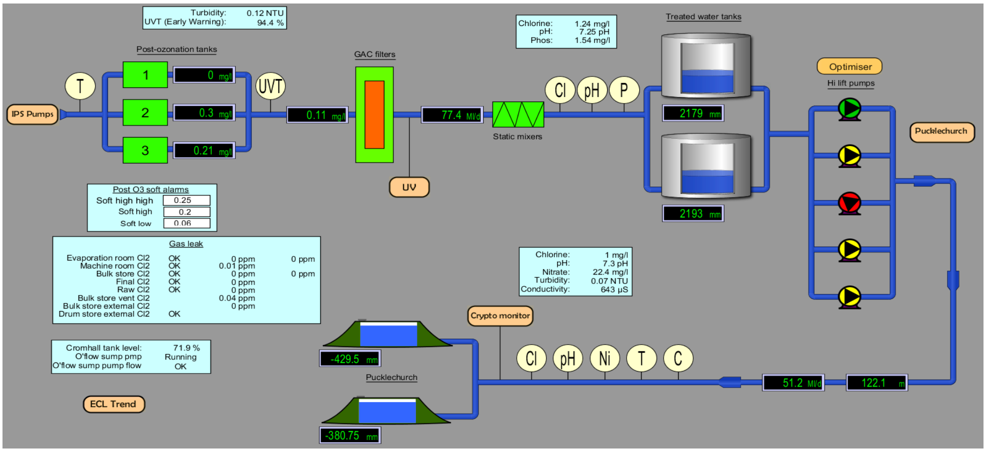

Fig. 5. Final Treatment Steps at Purton WTW (Source: Bristol Water)

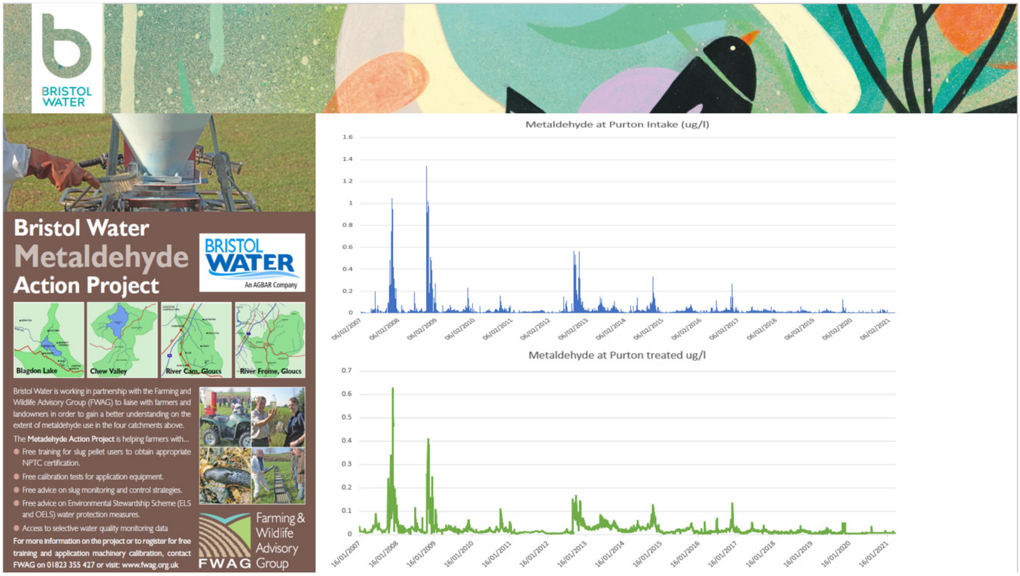

Fig. 6. Successful reduction in metaldehyde levels achieved through stakeholder engagement (Source: Bristol Water)

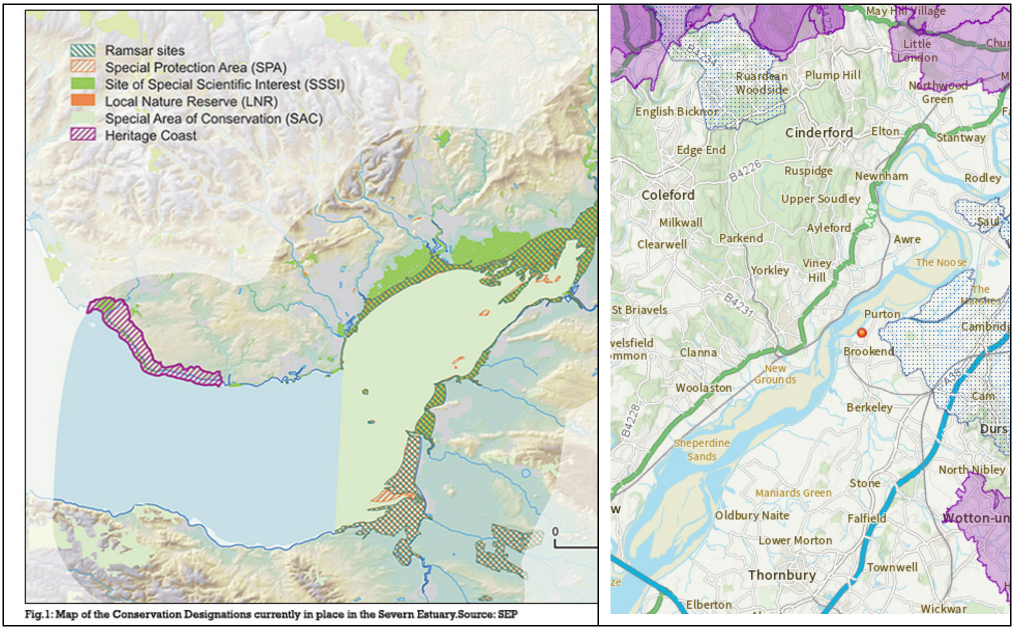

Fig. 7. Map of On-shore and Off-shore Conservation Designations (Source: Severn Estuary Partnership)

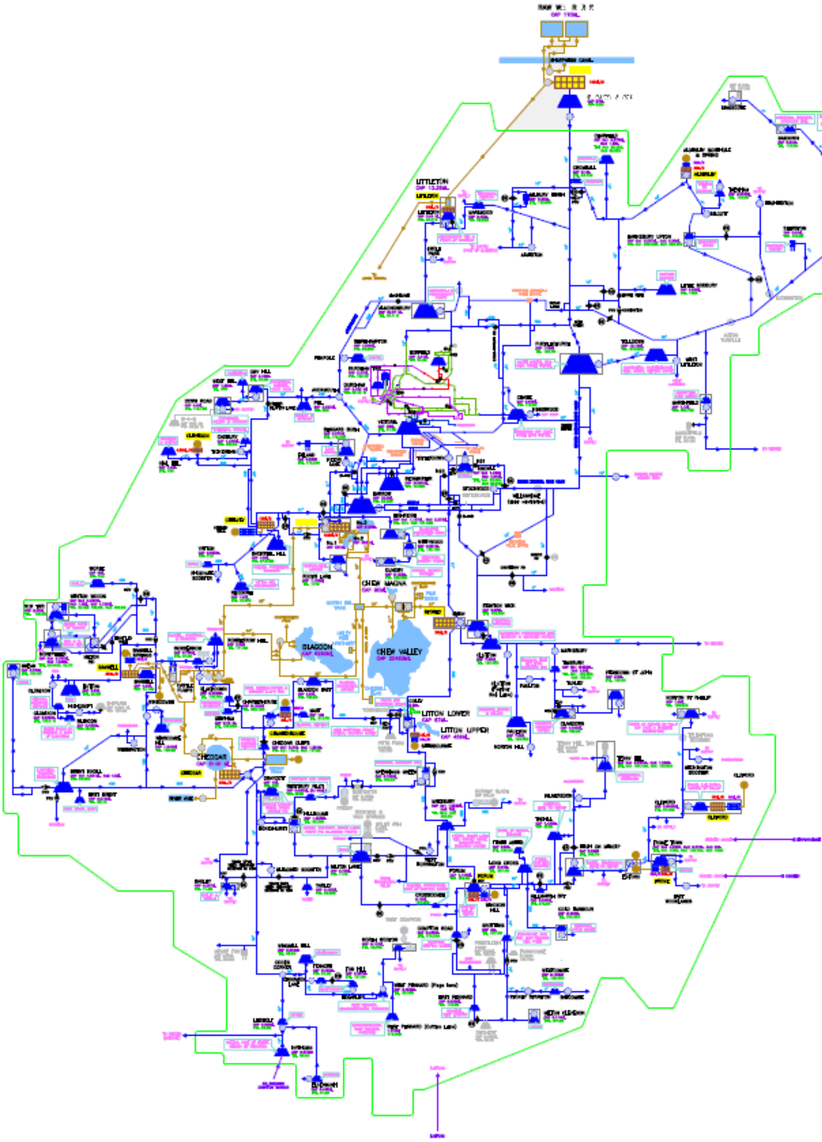

Fig. 8. Schematic of water supply system operated by Bristol Water (Source: Bristol Water)

pH	The scale used to describe the concentration of acid or base is known as pH, for power/potential of the Hydrogen ion. A pH of 7 is neutral whilst pHs above 7 are alkaline and below 7 are acidic.
Dissolved oxygen	Dissolved oxygen is one of the best indicators of general water quality. As a general rule, the higher the DO, the better the water quality. DO between 6 & 15 ppm is considered desirable.
Turbidity	Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates. The more total suspended solids in the water, the murkier it seems and the higher the turbidity. Turbidity is considered as a good measure of the quality of water – less turbid water is usually cleaner in most other respects than more turbid water.
Hardness	Hardness refers to the amount of calcium and magnesium in the water. The natural source of hardness is usually limestone rock. Drinking water with a total hardness under 250 ppm is best. Over 250 ppm usually leads to limescale and other problems.
Nitrates/nitrites	The presence of excessive amounts of nitrogen (nitrate/nitrite) compounds in water presents a major pollution problem and can be harmful to humans. Nitrates in conjunction with phosphates can also cause algal blooms and resultant eutrophication.
Phosphates	Phosphates in water stimulate the growth of algae. This in turn can lead to accelerated eutrophication of a body of water.
Biochemical Oxygen Demand	Biochemical oxygen demand, abbreviated as BOD, is a test for measuring the amount of biodegradable organic material present in a sample of water. The results are expressed in terms of the mg/L of oxygen which microorganisms, principally bacteria, will consume while degrading these materials. Unpolluted water =< 2 mg/l 0_2; raw sewage ~ 600 mg/l 0_2; treated sewage effluent ~ 20 - 100 mg/l 0_2
Total and Faecal Coliform	Coliform bacteria normally live in the intestines of mammals and are excreted with the faecal wastes. Some (but not all) forms are pathogenic. If they are present in a water sample this indicates that the sample has been through an animal intestine.
Cryptosporidium	Cryptosporidium is a widespread protozoan parasite encased in a leathery shell, or oocyst, which can be ingested by animals and humans and cause a diarrhoeal disease known as cryptosporidiosis. Most healthy people will recover from the disease in 4-6 weeks. However those with comprised immune systems may be more seriously affected and fatalities are known to occur.

Table 1. Common Water Quality Indicators (Source: adapted from Staddon, 2010)

CIRCULAR ECONOMY APPROACHES TO WASTEWATER TREATMENT IN THE WEST OF ENGLAND

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ABSTRACT

In this paper we discuss the design and operation of a large wastewater treatment plant, Avonmouth, located in the city of Bristol, as a typical example of modern wastewater treatment and attempt to peel back some of the layers of social, environmental, cultural and technical operation that can be discerned from analysis of this one site. In particular we focus on key sustainability and circular economy challenges including energy efficiency in process optimisation, resource recovery (especially biogas) and challenges related to improper use of the wastewater network.

KEY WORDS
Wastewater treatment, sewerage, circular economy, bioenergy, sustainability

INTRODUCTION

The story of sewage is, as no less a literary giant than Victor Hugo points out, the story of urban life:

> "The history of men is reflected in the history of sewers...it has been a sepulchre, it has served as asylum, crime, cleverness, social protest, the liberty of conscience, thought, theft, all that the human law persecute or have persecuted is hidden in that hole" [1, p.5254]

Most of what we need to survive and even to live comfortably eventually finds its way into our waste streams, especially wastewater. How we have come to deal with these ever-growing streams of domestic and industrial wastewater is intimately linked with the story of urban growth itself. Yet, because it is 'dirty', people mostly prefer to pretend that it does not exist and by adolescence most have learned that sewers and what goes into them are not topics for polite conversation.

In this paper we discuss the design and operation of a large wastewater treatment plant, Avonmouth, in the city of Bristol, as a typical example of modern wastewater treatment and attempt to peel back some of the layers of social, environmental, cultural and technical operation that can be discerned from analysis of this one site.

Before turning to Avonmouth directly, it is worth briefly noting some of the key drivers for wastewater development in England and Western Europe. As with drinking water supply, a key driver for systemic change were the early 19th century cholera epidemics, which led to a series of increasingly histrionic government inquiries into, as one title put it, the “sanitary conditions in English cities”. But there were other drivers too. The emergence of an urban middle class, especially large in cities like Bristol that depended on trade more than industry, brought an ever-increasing demand for water: for bathing, laundering and heating as well as for drinking and waste removal. But it was the proliferation of indoor toilets, especially after the 1851 Great Exhibition in London, using waterborne waste removal technologies that really created the necessity for an integrated water and sewerage system. Paid public flush toilets installed at the Great Exhibition greatly boosted the popularity of the indoor toilet and successive Acts and regulations favoured water-borne sewerage over dry alternatives [2]. With domestic cesspits frequently overflowing it is perhaps unsurprising that sanitary engineers took to bypassing them entirely and plumbing households straight into sewers (originally designed only for storm water removal – a reality that caused difficulties later on) and then into larger rivers such as the Avon and the Frome. As Geels [3], Smith [4] and Allen [5] have shown for various European cities, technologies of personal and domestic hygiene co-evolved with changing social and cultural mores. As household sanitary provisions spread through working class neighbourhoods during the late 19th and early 20th centuries, demand for urban water services continued to rise.

In the UK, the vast majority of the population is connected to at least primary wastewater treatment and indeed the proportion connected to secondary and tertiary treatment is relatively high too, even compared with European and North American cities [6]. In western-central Europe, for example, the connection rate is 97%. In southern, south-eastern and eastern European countries, it is generally lower, although it has increased over the last 10 years to reach about 70% [7]. At Minworth Treatment Works, near Birmingham, England, more than 500 megalitres of effluent are treated every day to at least advanced secondary standard with a recently extended capacity for activated sludge treatment and odour control, given that the works is located adjacent residential communities. Tertiary treatment generally involves treatment of wastewaters to a higher overall standard as well as removal of specific targeted pollutants such as nitrates, ammonia and phosphates as well as disinfection through UV light exposure. At this stage treatment methods can be very high tech and, indeed, expensive and so are used only as required by governmental regulation.

Depending on the technology applied we may distinguish the following types of wastewater treatment works (WWTW):

1. Mechanical, where larger easily removable solids, suspended matter, oils, fats and greases are removed through screening on grids and sieves to remove larger solids, sedimentation in grit chambers and settling tanks to remove easily

depositing pollutants, flotation in oil and grease traps and flotation chambers to separate grease, oils, petrols and organic solvents.
2. Biological, where biological decomposition processes are used at sufficient oxygen supply; microorganisms causing biodegradation of pollution are suspended in the wastewater mass (activated sludge) or are fixed to a solid grain material and sprinkled with wastewater (biological bed); the decomposition by activated sludge is followed by clarification in settling tanks; biological treatment is usually preceded by mechanical treatment; biological WWTW may additionally be equipped with a module for enhanced reduction of nitrogen compounds (denitrification module, where specialised bacteria groups convert nitrates generated in the process of mineralisation of pollutants into ammonia or free nitrogen); the last step should consist of disinfection of effluent to remove pathogens.
3. Chemical, using physical and chemical processes to change the reaction of wastewater, separation of specific substances, oxidisation or reduction of wastewater substances; processes used in chemical WWTW: chemical precipitation, allowing removal of certain substances from wastewater due to their nuisance or recuperation (e.g., heavy metals and phosphorus compounds), coagulation allowing the removal or suspended matter and colloids, neutralisation of wastewater reaction, extraction consisting in adding solvents to insoluble wastes to dissolve such substances which we want to remove from the wastewater (used e.g., to remove phenols), electrolysis by DC (e.g., to remove chromium), chemical oxidation with the use of chlorine or ozone (e.g., removal of phenols, humus acids, compounds generating colour and odour), ion exchange consisting in the use of special substances capable of exchanging their ions for ions comprised in the effluent (e.g., removal of copper, chromium, zinc, dissolved salts).

Commonly used water quality parameters that are often used to regulate the treatment process are included in Table 1.

WASTEWATER TREATMENT AT AVONMOUTH WTW

Across its entire system, Wessex Water treats 863 million litres of sewage from 2.8 million customers every day. They also maintain 34,820 kilometres (21,637 miles) of sewers, 409 water recycling centres (or wastewater treatment works, WWTW) and 1,660 sewage pumping stations – and that is just the wastewater side of the business.

Avonmouth WWTW is Wessex Water's principal wastewater treatment works. As well as providing secondary treatment for approximately 1.1 million people, the works accounts for more than 50% of the region's sludge treatment. It is designed to process approximately 300 Ml through full secondary treatment conveyed to the plant through a system of sewerage mains constructed incrementally over the last century and a half.

Table 2 shows influent and effluent contaminant levels and indicates the efficiency of the wastewater treatment train operated at Avonmouth. Biological oxygen demand (BOD) is the amount of oxygen that would be required to oxidize biological materials in a sample of wastewater. Chemical oxygen demand (COD), like BOD, is a measure of the amount of oxygen that would be required to oxidize chemical constituents. Ntot is total nitrogen, and Ptot is total phosphorus. Both nitrogen and phosphorus are important for managing wastewaters because they are nutrients that can contribute to eutrophication in natural water bodies. There is a direct positive correlation between the amount of nitrogen and phosphorus in the water body and its risk of eutrophication. Reducing eutrophication risk means reducing Ntot and Ptot. It is clear that the Avonmouth system is very effective at removing most pollution, although as we have noted in our consideration of drinking water treatment [8], nitrogen is much harder to remove, so the usual solution here is mixing or dilution in compliance with the plant's discharge consents. At other plants, like Minworth in Birmingham which discharges inland, there is more emphasis on removing more nitrogen and phosphorus.

The wastewater sewer system was originally designed as what is called a 'combined sewerage system', meaning that it also collects rainwater and surface run-off and transports it to the treatment plant. In heavy rain events this creates the potential for 'combined sewer overflow' (CSO) events, whereby the sewers overspill into the natural environment—not pleasant but a preferred alternative to sewers backing up completely into homes and businesses or overwhelming downstream treatment plants. To reduce CSO incidents, UK water companies have invested in considerable onsite temporary storm water storage tank capacity over the last two decades. At Avonmouth, the storm tanks (noted in Figure 1) are capable of coping with at least another 12,500m^3 each, or 25,000m^3 in total. This is in addition to other investments in stormwater storage around the Bristol area where local sewer flooding risks are highest.[3]

Incoming water is raised using two Archimedes Screws to a level that gives it the hydraulic head to then progress by gravity only through the initial processes without appreciable additional pumping. As the name suggests, this is an ancient technology used for lifting water up to a higher level, dating back to at least the 3rd century BC. Archimedes Screws can also be used in reverse as a hydroelectricity generating turbine. For example, there are numerous pumped storage power systems, such as Dinorwig in North Wales and Belmeken in Bulgaria that use these technologies to refill higher altitude storage reservoirs at night when electricity is cheap only to release it to drive screw turbines during peak load hours when power is expensive [6, p. 150].

The initial challenge at all wastewater works, including Avonmouth, is removal of what is euphemistically called 'rags and plastics' (Step 2 in Figure 1). Most of this material should not have been put down the toilet and into the system in the first place. Incoming water is initially strained by 19 mm rake strainers, which remove most of the larger rag and plastic material. There are a lot of sanitary products and wet wipes, which have replaced nappies as the biggest problem from WWTW. More recently, the Covid pandemic has seen a rapid rise in the volume of masks being flushed into the sewer system, which are removed by the rake screens at this stage. This solid waste material is diverted to another part of the plant for further treatment which we will discuss shortly.

[3] Due to hydraulics, risk of sewer flooding is often quite localised.

Once the rags and plastics have been removed, the water moves through a penstock. The next item that needs to be dealt with is grit: the stones and gravels that have been washed off from the roads and people's gardens into sewers. The grit channel operates by allowing the treatment water to briefly slow down so that grit can sink naturally. Vacuum hoses suck cleaner water off the top, leaving the heavier grit behind. The grit tank is V shaped which means that the grit sinks to the very bottom, further out of the way of the suction hoses. As with the rags and plastics, the grit gets some further treatment elsewhere on site before being recycled.

The removed rags, plastics and grit do not go to landfill. It is dumped on site in long rows and left for a couple of months to compost. It is turned over with JCBs occasionally to improve aerobic processes. The grit is loaded into skips and mixed with composted rags and plastics (larger plastics are removed) and added to agricultural soils or used for industrial fill purposes. One large consumer of processed rags, plastics and grit are the China Clay quarries in Cornwall which use the material as fill when they decommission open cast mines and quarries. Dried sewage sludge is also sent to agricultural users, once it has been used for biogas production elsewhere on-site.

There will still be some debris remaining in the wastewater, even though the majority of the rags, plastics and the grit have been removed. For Step 3 in the treatment process, the wastewater goes through 6mm screens which separate out nearly everything else that should not be in there. After this, the water is now free of solid materials, but it is very murky (the technical term for this is 'turbidity').

Industrial wastewater from commercial operations is added to the wastewater stream at this stage. In England and Wales, companies must either develop their own on-site treatment or have an agreement with a company such as Wessex Water who will treat their wastewaters for them. Many industrial producers may be required by government regulators in the Environment Agency and Defra to treat their own wastewaters on-site rather than relying on being able to tanker it to the nearest wastewater treatment plant, like Avonmouth, for treatment. That usually happens if the kind of contamination that is typical of that effluent is unique or more effectively treated locally, like washing waters in the dairy industry or dye contaminated waters from textiles manufacture. In other cases, industrial wastewater producers may find that on-site treatment to a certain threshold followed by transfer to a larger wastewater treatment plant is most effective and cost beneficial. In this case WWTW typically use what is called the 'Mogden formula' to calculate the cost to the customer of these wastewater treatment services.[4]

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[4] The Mogden Formula calculates the charges water companies apply to industry for the conveyance and treatment of effluents discharged to the public wastewater network.
The Mogden formula for biological treatment of effluents is: R + [V+VB] + [B x (Ot/Os)] + [S x (St/Ss)] X volume of effluent (in m3) where
R = Reception Charge 57.16 p/m3
V = Primary Treatment Charge 52.68 p/m3
B = Biological Oxidation Charge 92.75 p/m3
Ot = Average effluent settled COD Variable mg/l
Os = COD of average of settled sewage 744 mg/l
S = Sludge treatment charge 55.42 p/m3
St = Average effluent suspended solids Variable mg/l

The dairy and beverage industries use a lot of water for washing, and that water is contaminated with detergents [9]. The favoured, most cost-effective way for dairy effluent treatment is a substantial sized lagoon for biological treatment, with a holding capacity of 2-3 weeks and substantial aeration, to avoid anaerobic conditions. Dissolved air flotation (DAF) is used to ensure suitable oxygen for oxidation can occur over the planned residence time. The plants use a settlement system for decanting clear effluent and removing sludge. The sludge can then be used for agricultural benefit by spreading to land. This is a very similar process to the domestic wastewater treatment processes used in the UK and discussed in this paper.

Primary treatment of sewage is removal of floating and settleable solids through sedimentation. Clarifiers reduce the content of suspended solids as well as the pollutant embedded in the suspended solids. Because of the large amount of reagent, preliminary chemical coagulation and flocculation are generally not used (as they are in drinking water processing). However, coagulation and flocculation can be used in a compact treatment plant (sometimes also called a 'package treatment plant'), or for further polishing of the treated water, perhaps where discharge consents (especially inland) are stricter. Sedimentation tanks called 'secondary clarifiers' remove flocs of biological growth created in some methods of secondary treatment including activated sludge, trickling filters and rotating biological contactors.

Seen from the air, the primary and secondary settlement tanks are usually easy to pick out. At Avonmouth there are six primary settlement tanks arranged in a compact circle formation (Figure 1). Though coagulants such as Alum can be used at this stage, at Avonmouth nothing is added and the basic treatment mechanism is just gravity. The highly turbid wastewaters are simply left for between 4 and 8 hours for the sand and dust-like particles that make up much of the remaining turbidity to sink to the bottom. Less turbid water is then decanted off the top of the settlement tank and sent on to the next stage of treatment. In a conventional wastewater plant the remaining particulate matter, called 'sludge', is sent for sterilisation (usually by hydrolysis) before final disposal. At Avonmouth however, the sludge is used for biogas generation before being sterilised and disposed of, to mostly agricultural users.

Wastewater now goes into whichever one of the six settlement tanks is available. These six tanks are approximately four meters deep and the sewage will sit there for between two and six hours. The sewage comes up from the middle and works its way around the tank. There is a metal bridge with scrapers that continually removes the sludge that has sunk to the bottom of the tank. The majority of the sludge is automatically removed to another part of the process and the water moves on to secondary treatment.

At Avonmouth, secondary treatment involves a technology called sequence batch reaction (SBR). SBR is comprised of one or more tanks that can be operated in series or parallel. The tanks use a flow through system, with raw wastewater (influent) coming in at one end and treated water (effluent) flowing out the other [10][11][12]. In systems with multiple tanks, while one tank is in 'settle/decant' mode, another can be aerating

Ss = Suspended solids in crude sewage 489 mg/l and filling. In some systems, tanks contain a section known as the 'bio-selector', which consists of a series of walls or baffles which direct the flow either from side to side of the tank or under and over consecutive baffles. This helps to mix the incoming influent and the returned activated sludge (RAS), beginning the biological digestion process before the liquor enters the main part of the tank.

Due to the requirements of the 2003 Urban Wastewater Treatment Directive, there are now eleven of these SBR units at Avonmouth. They are very good at dealing with large volumes of water, as each one holds 13 million litres. Wastewater goes through a four-stage treatment process. First the tank will fill up, and then some of the biological sludge is added. After one hour – these processes tend to take about an hour each - air bubbles are pumped in, and this encourages the bio sludge in the water to react. The third process involves turning off the air injection so it will stop bubbling, and this allows the sludge to settle to the bottom of the tank as dissolved oxygen levels decline. The fourth process is decanting, where the clean water is removed and the sludge will go on to the next process. If, for whatever reason, the treated water is not yet achieving appropriate pollution reduction levels, it can be directed back into SBR for another round of treatment.

When Wessex Water planned to invest in additional treatment, they argued that the originally-designed SBR units were under increasing pressure through rising volumes of wastewater. Whilst the system was felt to be working fine, it was just not big enough for anticipated wastewater volumes or rising pollutant loads. For example, although there were always fluctuations in biological oxygen demand of wastewater, there was a rising trajectory and from 2014 onwards, there were occasional exceedances of maximum allowable values. In which case, the water is actually routed back through the system again for a second go, but of course that limits system throughput. The same was increasingly starting to happen by 2015 for chemical oxygen demand, so there was a clear argument that more capacity was needed, which could mean building more tanks, or it might involve additional treatment steps using different processes.

Wessex Water and other water and sewerage companies are given discharge permits which say they are allowed to release a certain volume of treated wastewater, and that treated wastewater must meet certain quality conditions. Figure 3 shows the progressive improvement of water clarity (and by implication cleanness) with the sample furthest right having been taken immediately after treatment in the SBR unit. While not achieving drinking water standards, this water is clean enough to be released into the Severn Estuary in accordance with Wessex Water's discharge permits.

Each year, a report is prepared on compliance levels. All water and sewage companies in the UK are very good at this, because they have been doing it for a long time, with 99% compliance in 2017. That 1% of non-compliance will be separately investigated by regulators, usually in consultation with the company, because it does not necessarily mean that something has gone wrong. It could be as a result of a single rain event, probably not at a site like Avonmouth, which is very large and has had a lot of investment. It is more likely related to one or more of the 160 other wastewater treatment plants in the system, most of which are much smaller and less complex.

Once the water has left the SBRs, it will then go through pipes that discharge back into the natural environment. Because of the very high tidal range in the Severn Estuary (second highest tidal range in the world) constructing and maintaining this pipe system is relatively difficult. First, it must be constructed so that the outlet is below commonly experienced low tides. Second, and as noted earlier, it is designed (with Archimedes Screws) to prevent back-flow that could occur during periodic Severn Bore events.

Every day, 16 million litres of this final effluent is also piped directly to a company called Seabank, who run a gas-fired power station just up the estuary from the Avonmouth WWTW. That water is used for the cooling process or for washing down areas at the power plant. This is one of many examples of how wastewater can be used in a circular economy context. At Avonmouth, most of the treated effluent, once it is it is tested and guaranteed to be within discharge permit limits, goes out into the Severn estuary. Wessex Water's discharge consents at this site do not require a disinfection step, due essentially to there being no designated bathing waters nearby. At other WWTW, for example Seafield near Edinburgh, the proximity of bathing waters means that water needs to be disinfected through UV treatment prior to release into receiving waters (the River Tay for Seafield). This somewhat different treatment train is noted in Figure 4.

ENERGY FROM ANAEROBIC DIGESTION OF SLUDGE

Over the last two decades, Wessex Water have also been developing its energy generation capacity, particularly through biogas-based energy derived from digestible sludge solids and related digestible solids from kitchen waste. While this started as a side concern, it is now quite a substantial business operated by GENeco, a spinoff company from Wessex Water.

Currently there are two separate but connected processes for treating sewage sludge created by wastewater treatment, and food waste brought directly to the biogas facility at Avonmouth. Wessex/GENeco started with biogas production from sewage sludge using a process called 'mesophilic acidic digestion' (MAD) to produce biogas/methane, which could then be used in a number of ways. Once they became skilled at this line of biogas production, they realised that they could do something similar, but with a few technical modifications, with other bio digestible solids, in particular the liquid food wastes and collected food scraps of the million or so people who live in the Bristol city region.

Although separate, the two processes run on quite similar principles: collect together the bio digestible solids, process them such that they can then be put into a state where the digestion process which relies on bacteria can release the maximum amount of energy from them, and then render remaining waste biosolids safe for return to the land, either as a soil conditioner or as an in-fill product (as in quarrying). We will deal with each in turn, starting with the biogas from sewage sludge process.

In the first step, the sewage sludge goes onto a gravity belt where it is thickened up with a polymer (similar to the long chain polymers used in some clarification processes, particularly for drinking water treatment) to make it easier to handle and process. It is also put through a process called 'biological hydrolysis', which breaks down sludge into short-chained acids which then becomes ready feedstock for the mesophilic digesters that produce the methane. Treated sludge stays in these digesters for between 12-14 days and is heated up to between 32-42°C. With heat, water, and sludge as their food, introduced bacteria thrives, multiplies and produces methane.

There about a half a dozen different bacteria that are used for very specific processes at different stages of the biogas production process. Some bacteria are methanogenic, meaning they eat sludge and then discharge methane. Other bacteria are used to change the characteristics, chemically, of the sludge to maximise gas production. In 2007, Wessex Water introduced in an Acid Phase Digestion (APD) plant upstream of the MADs, using different bacteria to slightly change the character of the influent sludge, to further increase methanogenesis. The APD also provides heat and electricity for the site and is sold to around 8,300 homes in the area.

There are a number of microbial groups involved in digestion:

1. Hydrolytic Bacteria: produce extra-cellular enzymes to break down carbohydrates, proteins, and lipids.
2. Acid Forming Bacteria: break down products of hydrolysis are fermented to acetate, propionate, butyrate, and hydrogen by the acid-forming bacteria. There are two-groups of acid-forming bacteria:
   i. Acidogenic Bacteria: metabolise amino acids and sugars to the intermediary products acetate, hydrogen, and carbon dioxide.
   ii. Acetogenic Bacteria: Two distinct groups of acetogenic bacteria can be distinguished on the basis of their metabolism. The first group, the obligate hydrogen producing acetogens (OHPA) produce acetic acid, carbon dioxide (CO2) and hydrogen (H2) from the major fatty acid intermediates (proprionate and butyrate), alcohols and other higher fatty acids (valerate, isovalerate, stearate, palmitate, and myristate). The second group are homoacetogens catalyzing the formation of acetate from hydrogen and carbon dioxide.
3. Methanogenic Archea are divided into two groups:
   i. Acetoclastic Methanogens: which cleave acetic acid into methane and carbon dioxide.
   ii. Hydrogen Utilising Methanogens: which utilise hydrogen and carbon dioxide to produce methane.

The process for treating imported liquid in food waste is very similar, in broad terms. It is trying to take digestible material and process it through a series of steps so the maximum amount of methanogenesis, the maximum amount of CH_4 methane production, is produced. Currently, approximately 35,000 tons of food waste are processed per year – and this is increasing. This is food waste from people's homes collected by the Council. GENeco also have two 'Bio-Bee' trucks that will go to restaurants, cafes and places that are open to the public, such as National Trust properties, and collect food waste. On-site, collected food waste is scooped up into a hopper. It goes into a shredder that is able to remove packaging and the plastics. The food that has gone into the hopper is called 'soup'. It is heated to about 17 °C and that kills off any harmful bacteria. After an hour, it is then put through the MAD biodigestion process just like the sewage sludge.

Over the last decade or so both biodigestion lines have become increasingly efficient at realising much of the potential energy latent in the incoming sewage sludge and food waste. However, the produced gas still needs to be further processed by having propane added, to bring it into line with the regulatory standards for gas that can be distributed to domestic and other users via existing pipeline systems [13][14].

GENeco recycles more than 230,000 tonnes of biosolids from sewage treatment works across the Wessex Water region each year. The biosolids are brought to the centres as liquid waste from sewage treatment works or as food waste. The GENeco food waste plant is based on the Monsal plant design in Deerdykes Scotland which is one of only two plants in the UK to have successfully obtained the PAS 110 certification for the digestate end product. This certification serves as a quality hallmark for the fertiliser produced at the end of the process and offers farmers independent reassurance that the digestate has been converted from a waste into a soil conditioning product.

Gas-to-grid is an established technology used throughout Europe. The process acts to upgrade raw biogas to a quality that is equivalent to natural gas which can be injected and exported into the gas grid. A water washing and filtration process is used to remove impurities and carbon dioxide from the biogas before injection into the grid.

This biogas can fuel cars, like the GENeco 'Bio-Bug', for about 250 miles on one full tank. However, as the only way to refuel the biogas was at GENeco's Avonmouth base, it was also able to run on standard unleaded petrol if the gas ran out. As with electric vehicles, the lack of filling/recharge stations around the country is a constraint on proliferation of this technology. GENeco has also designed a bus to run on biogas, as part of Bristol's year as the European Green Capital in 2015. The emissions were nil, and there was no smell. There were seven tanks at the top of the bus - sufficient for a normal day's operations - and it was put into service on the existing 'Number 2' route (of course!).

CURRENT CHALLENGES IN WASTEWATER TREATMENT

It is important for operators to always be mindful of future challenges that may require modifications to their current operations, in particular related to climate change, scientific advancement and population dynamics. These are represented in Figure 5 under the general categories of "Challenges, Solutions and Opportunities".

Climate change poses at least two immediate challenges/risks for wastewater treatment operators. First, the increased likelihood of large flood events could create conditions for both CSO events, where raw sewage is routed straight to the natural environment in order to avoid backing up into premises and causing health hazards. Wessex has addressed these challenges through a three-pronged approach: creating significant on-site stormwater storage capacity, increasing sewer capacity and working with the City of Bristol to carefully monitor CSOs. City authorities are also attempting to decrease flood risk by increasing green infrastructure provision throughout the city, but particularly in areas of highest risk [15].

The second climate-related challenge involves the growing imperative to reconceive of industrial processes, including wastewater treatment, as parts of circular economies. Not only can wastewater yield new values such as biogas and soil conditioners for agriculture, but there is certainly much more potential for development of potable and non-potable wastewater reuse. At WWTW like Avonmouth, we have seen significant developments in resource extraction and reuse from materials recently thought of only in terms of waste, but as yet relatively little planned wastewater reuse. Given its location in an industrial zone there may be opportunities for expanding the number of industrial customers for treated wastewater beyond the nearby power station. Other large WWTW that are, like Minworth, closer to residential communities may more quickly develop into sources for managed wastewater reuse, as has happened in in Beijing [16], Singapore [17], in Windhoek, Namibia [18] and elsewhere. Paranychianakis et al. [19] suggest that although there are many examples of successful non-potable wastewater schemes, regulators need to agree common standards and provide clear direction and incentives.

Second, scientific advancements are continually identifying either new contaminants of concern or demonstrating that currently allowable concentrations need to be further reduced. One example of a relatively new contaminant of concern is metaldehyde, the principal active ingredient in slug and snail control pellets used in agriculture and horticulture in the UK. When in 2010 a specific test for metaldehyde became readily available, it was immediately apparent that there were significant pollution issues related to this compound. Since then water companies have worked with the agricultural and horticultural industries to adjust pesticide practice to protect water sources, as well as trialling alternative slug control products such as Ferrous Sulphate (known by the trade name Slux). Another example of an emerging class of contaminants involves pharmaceuticals and especially those containing antibiotics and hormone compounds [20][21][22]. Their presence is of concern due to impacts on human health and the environment, though research suggests that monitoring systems need to change to ensure that these are adequately assessed [23] and that technologies exist for their effective removal [24]. And finally, wastewater managers have, during the global Covid pandemic, learned that wastewater also contains significant viral load which can be used for epidemiological and public health purposes [25].

Third, as urban and suburban areas continue to expand, facilities like Avonmouth and Minworth are increasingly becoming sources of local noise and odour complaints which may create pressure for changes to wastewater processing operations. At Minworth in suburban Birmingham, the proximity of residential development has forced investment in technologies for improving odour control including covering over certain treatment stages to avoid venting directly to local air, better control an issue with insect propagation, and suppress noise.

With respect to Avonmouth and similar facilities in the Bristol/West of England region, Wessex is continuing to work in partnership with Bristol City Council to develop increasingly sophisticated surface water management plans, focussing particularly on

CSOs, which cause significant pollution in the city during high rainfall periods, and network resilience. Short and medium term activities include:

- Completing the North Bristol Strategic sewer project to support future development and reduce flood and pollution risk.
- Working with the West of England Combined Authority to twin the sewer network as a part of the Metrobus scheme, to improve performance and resilience of the network.
- Assessing flooding incidences and potential solutions to reduce flood risk.
- Increase capacity at the major water treatment works to accommodate development in the catchment and climate change mitigation measures.
- Further investigating a number of recurring local sewer flooding issues and if required, carry out improvements.
- Reline priority sewers to reduce risk of collapse.
- Investigating and, if applicable, identifying solutions for addressing particular CSO-related pollution risks.

Important tools for promoting circular economy and resilience approaches in wastewater management include the specific resilience duty included in the 2014 Water Act which applies to both water supply and wastewater operations and the adoption of 'Drinking Water Safety Plans' as a common approach to integrated water cycle management [26].

CONCLUSION

In this paper we have examined the wastewater treatment process at a large facility in the west of England. We have examined all steps from the moment that wastewater arrives at the Avonmouth WWTW, to the moment that treated wastewater is returned to the natural environment, or sold on to non-potable water users (such as power plants). We have also discussed examples of circular economy approaches in wastewater processing including the biogas energy recovery system that has been developed in stages over the last 20 years at Avonmouth. Through a series of investments in power generation from biogas, wind and solar PV, wastewater plants like Avonmouth have rapidly transformed themselves from single-function wastewater treatment plants into multidimensional water treatment and energy generation plants. Finally, we have discussed some key challenges that the plant's operator, Wessex Water Plc, must consider related to climate change and population growth.

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pH	The scale used to describe the concentration of acid or base is known as pH, for power/potential of the Hydrogen ion. A pH of 7 is neutral whilst pHs above 7 are alkaline and below 7 are acidic.
Dissolved oxygen	Dissolved oxygen is one of the best indicators of general water quality. As a general rule, the higher the DO, the better the water quality. DO between 6 & 15 ppm is considered desirable.
Turbidity	Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates. The more total suspended solids in the water, the murkier it seems and the higher the turbidity. Turbidity is considered as a good measure of the quality of water – less turbid water is usually cleaner in most other respects than more turbid water.
Hardness	Hardness refers to the amount of calcium and magnesium in the water. The natural source of hardness is usually limestone rock. Drinking water with a total hardness under 250 ppm is best. Over 250 ppm usually leads to limescale and other problems.
Nitrates/nitrites	The presence of excessive amounts of nitrogen (nitrate/nitrite) compounds in water presents a major pollution problem and can be harmful to humans. Nitrates in conjunction with phosphates can also cause algal blooms and resultant eutrophication.
Phosphates	Phosphates in water stimulate the growth of algae. This in turn can lead to accelerated eutrophication of a body of water.
Biochemical Oxygen Demand	Biochemical oxygen demand, abbreviated as BOD, is a test for measuring the amount of biodegradable organic material present in a sample of water. The results are expressed in terms of the mg/L of oxygen which microorganisms, principally bacteria, will consume while degrading these materials. Unpolluted water =< 2 mg/l 0_2; raw sewage ~ 600 mg/l 0_2; treated sewage effluent ~ 20 - 100 mg/l 0_2
Total and Faecal Coliform	Coliform bacteria normally live in the intestines of mammals and are excreted with the faecal wastes. Some (but not all) forms are pathogenic. If they are present in a water sample this indicates that the sample has been through an animal intestine.
Cryptosporidium	Cryptosporidium is a widespread protozoan parasite encased in a leathery shell, or oocyst, which can be ingested by animals and humans and cause a diarrhoeal disease known as cryptosporidiosis. Most healthy people will recover from the disease in 4-6 weeks. However those with comprised immune systems may be more seriously affected and fatalities are known to occur.

Table 1. Commonly used water quality parameters (Source; Staddon, 2010)

	Influent t/a	Effluent t/a	Removal rate
BOD	23,143	393	98%
COD	53,636	4,312	92%
Ntot	1,850 (estimate)	1, 480	20%
Ptot	585	260	66%

Table 2. Quality of incoming and Outgoing Water at Avonmouth WwTW (Source: Wessex Water)

Fig. 1. Schematic of Avonmouth WwTW, including the Bioenergy facility (Source: Wessex Water)

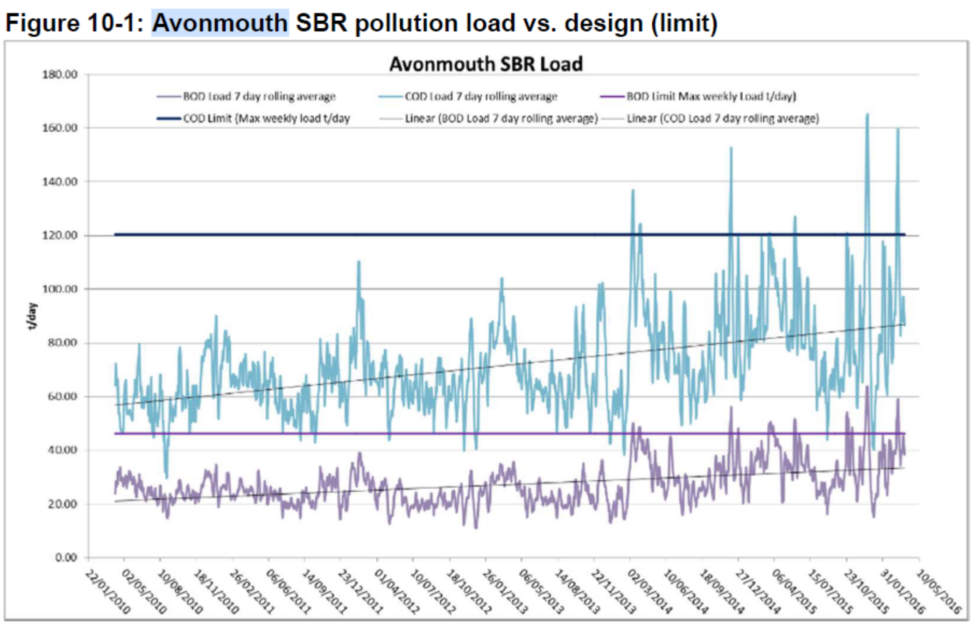

Fig. 2. Control curves for SBR units 2010 – 2016 (Source: Wessex Water)

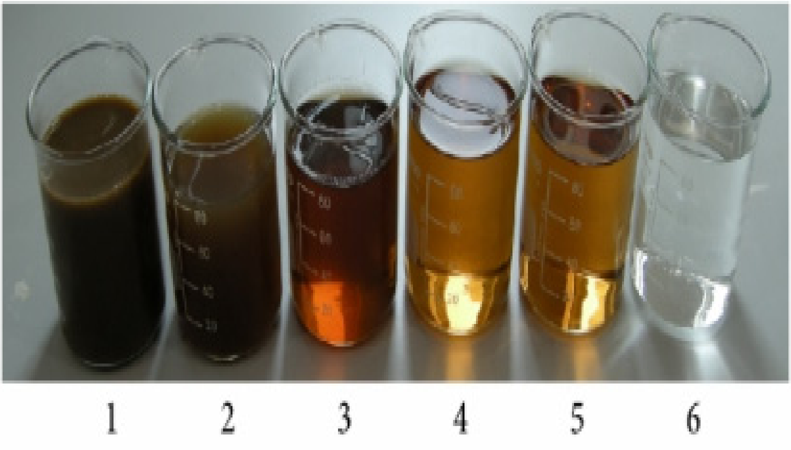

Fig. 3. Progressive Improvement of Water Quality through Treatment Stages (Source: Wessex Water)

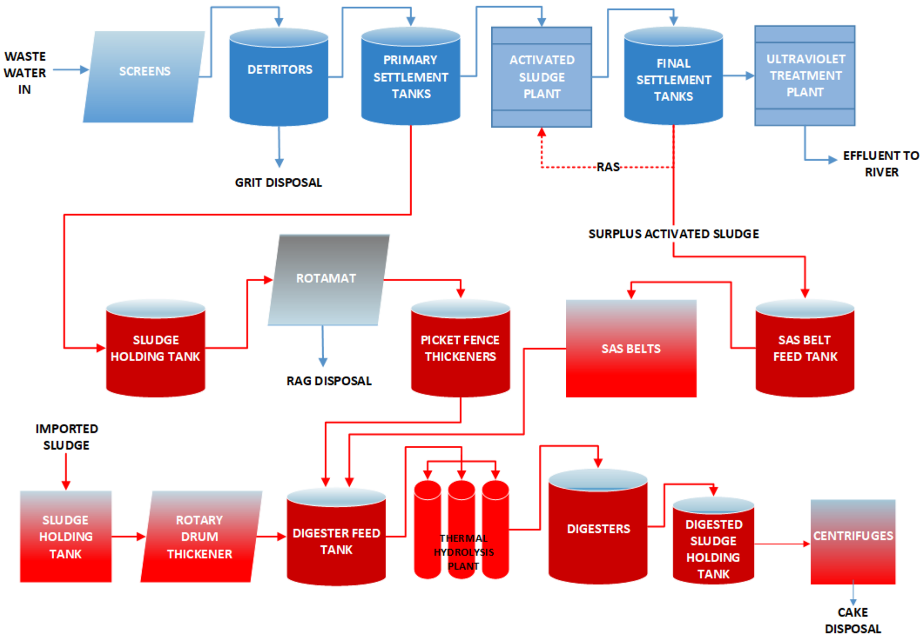

Fig. 4. Alternative Wastewater Treatment Train Operated at Seabank, Edinburgh, Scotland (Source: Seabank WwTW)

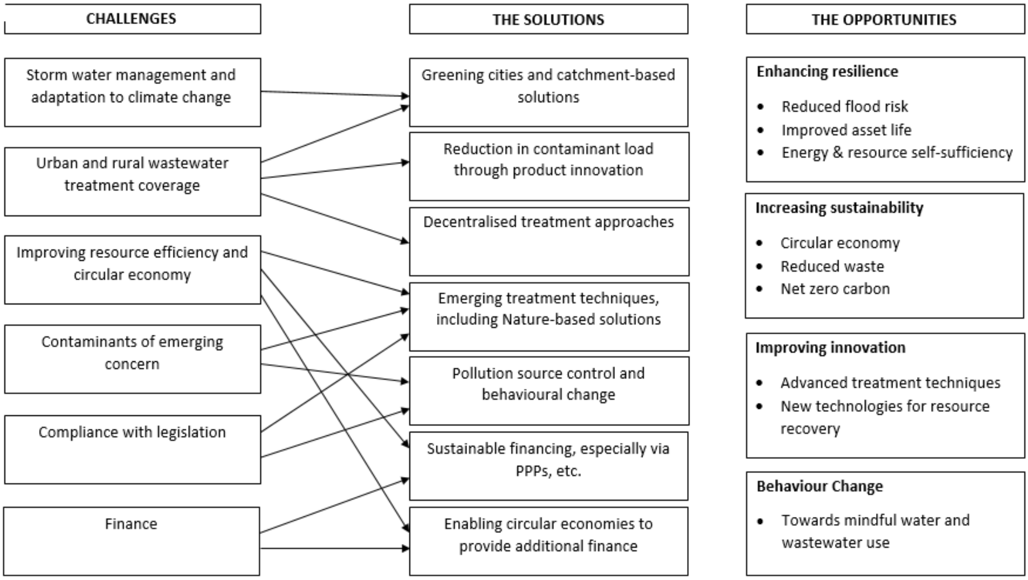

Fig. 5. Challenges, Solutions and Opportunities in Wastewater Management (adapted from Shah et al, 2020)

WASTEWATERS TREATMENT FROM NITROGEN IN BIOREACTORS USING BIOFILM MODELS

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ABSTRACT

The mathematic model and calculations of the wastewaters cleaning parameters from the compounds ammonium nitrogen (nitrification) in bioreactors with additional using in theirs volume the fixed biocenosis as the biofilm are presented. The valuation of the different influence factors on the waste waters cleaning parameters is given. The kinetics of reaction according to Monod nonlinear equation is used that allow to calculate the nitrogen concentrations on the external and in the interior biofilm surfaces and to evaluate the efficiency of the biofilm work of the given thickness relative to penetration character of the nitrogen pollutions in it. As showed the biofilm thickness and the flow in it are decreasing as the tearing off velocity of the biomass from its surface is increasing and at increasing of the nitrogen concentrations these parameters are increasing too. At this the substrate flow and the penetration depth into the biofilm are the functions of the substrate concentration on the biofilm surface, velocity of the reaction within it and the diffusive masstransfer. For evaluation of the oxygen influence for control of the process of ammonium oxidation to nitrite the relation of the concentrations oxygen to ammonium nitrogen is proposed. The specific examples and calculations have showed the given relation may be better alternative for control of the nitrification processes in reactor in comparison with oxygen concentration.

Key words: biofilm, bioreactor, model, nitrogen compounds, oxygen, water treatment

INTRODUCTION

It is known that one of the main pollutants which are the part of the wastewaters of different origin are the nitrogen compounds of predominantly ammonium form [1], [2], [5], [7]. According to the existing regulatory requirements these waters are subject to significant treatment before discharge into different reservoirs. In the practice of wastewater treatment from nitrogen compounds as well as pollutants of organic origin biological treatment methods have become the most widespread. The classic scheme of such treatment inclusion as a main construction the bioreactor-aeration tank. In the aeration tank takes a place an extraction (biooxidation) of activated sludge sorbed on floating flakes which in this case consists of the autotrophic microorganisms suspended or dissolved in water nitrogen contaminants. However especially in connection with the increasing in regulatory requirements for water cleaning such treatment does not provide the required degree and quality of removal of nitrogen contaminants by suspended (floating) biocenosis and requires an additional treatment. The analysis showed that the efficiency of nitrogen contamination removing in aeration tanks can be significantly increased if simultaneously with the suspended biocenosis (activated sludge) to provide additional loading in the volume of the aeration tank (various sorbents, devices, nozzles, etc.) on the surface of which a biofilm with high concentration microorganisms is formed. Such combined biological wastewater treatment in the plants with fixed biocenosis (biofilm) according to experts opinion has a number of significant technological advantages and can be widely used in practice the removal of contaminants of various origins.In the general case the extraction of ammonium nitrogen consists of the several processes namely: from the process of oxidation of ammonium to nitrites (first stage of nitrification), oxidation of nitrites to nitrates (second stage of nitrification) and from almost anaerobic denitrification - reduction of these nitrogen compounds to molecular nitrogen.

AIM OF RESEARCH

Aim of the work consists on the development of the mathematical model and calculation methods for the case of the nitrogen removal at the first stage of nitrification and extraction of ammonium nitrogen when it occurred according to zero order reaction and more accurate nonlinear one on the base of Monod equation for conditions of the sufficient supply of the treatment process by the oxygen with the aerobic bacteria Nitrosomonas participation in the process of purification.

THE RESEARCH RESULTS AND DISCUSSIONS

In some early publications the analysis and the features of joint biological wastewaters treatment from organic pollutions (OP) and nitrogen compounds (N) by the different biocenosis (microorganisms) which are formed as a biofilm on the loading elements surface in bioreactors such as aerotanks or submerged filters were provided and designated [1], [3], [5], [7], [8], [9]. At this was established that during joint aerobic treatment and sufficient oxygen quantity the removal the nitrogen in biofilm takes a place if only when the OP removal was occured almost completely by the more active heterotrophic microorganisms. As a result the removal of OP and N may be considered in two stages namely: at first one the removal OP and N is occured without nitrification and on the second one the nitrification process is optimized only. At small transition period time from first to second stage almost full removal of OP and some insignificant nitrogen removal are occured which in practical calculations may be fail take into account. Nitrogen in wastewaters predominates as ammonium nitrogen and for it removal the biological processes nitrification-denitrification are used most often and at this ammonium nitrogen turns into molecular nitrogen. In the given paper the simplified calculation methods of removal ammonium nitrogen are proposed which may be used in engineering practice. That to obtain an engineering estimates and analysis consider a bioreactor-aeration tank-mixer in which nitrogen is extracted by suspended (activated sludge) and fixed biocenosis in the form of a biofilm with a high concentration of microorganisms which is formed on the surface of the additional loading. When forming the model of nitrogen extraction by biofilm it is necessary to take into account the fact that the concentration of nitrogen entering the biofilm from the aeration tank liquid for utilization passes in the form of a flow through the boundary layer. Due to the fact that different transformations take place in the boundary layer due to the processes of mass exchange and mass transfer the concentration of nitrogen on the outer surface of the biofilm will differ from the concentration of nitrogen in the aeration tank. As a result of the analysis it was found that in this case the flow of nitrogen in the boundary layer will be equal to the flow of nitrogen on the surface which was accepted in the implementation of biofilm models. Thus under conditions of sufficient provision of the aerobic process of nitrogen extraction with oxygen the general balance mathematical model of nitrogen extraction which is recorded with respect to changes in ammonium nitrogen concentration N in wastewater treated in bioreactor (aeration tank- mixers), biofilm and liquid film of a boundary layer will be:

$$W_p \frac{dN_a}{dt} = Q_a(N_0 - N_a) - F_{\delta_e} I_N - R_{a_0} W_p. \tag{1}$$

In practical calculations it is sufficient to consider equation (1) in stationary conditions and bring it to this form:

$$N_0 - N_a - F_{\delta_n} T_a I_N - R_a T_a = 0, \tag{2}$$

where

$F_{\delta_n} = \frac{F_{\delta_e}}{W_p}$, $T_a = \frac{W_p}{Q_a}$, $I_N = K_n(N_a - N_{\delta_0})$, $W_p = W_a \varepsilon$, $N_{\delta_0} = N|_{z=0}$,

$R_{a_0} = R_a - R_c$, $\varepsilon = 1 - \frac{W_\delta}{W_a} = \frac{W_p}{W_a}$, R_a, R_c - rate of reactions of nitrogen utilization by suspended biocenosis (activated sludge) and isolated substances during sludge death, I_N - flow (transport) of nitrogen compounds N through the surface of the biofilm for their utilization by the fixed biocenosis (biofilm), N, $N_{\delta 0}$, N_0, N_a – concentrations of nitrogen N in the biofilm, on the biofilm surface , on the enter and in the aeration tank respectively; W_a , W_p ,W_δ - working volume of the aeration tank, the volume of liquid in the aeration tank, the volume of the installed load (nozzle) with fixed biocenosis respectively; Q_a - the flow rate of liquid in the aeration tank, $F_{\delta e}$ - the total surface area of the biofilm, K_n – mass transfer coefficient nitrogen pollutions in the liquid film (through the boundary layer); δ, δ_n - respectively the thickness of the biofilm and liquid film (boundary layer). According to (2) at known (specified concentrations of N in wastewater entering to bioreactor N_0 and treated in wastewater by suspended biocenosis (activated sludge) N_a , the duration of aeration T_a to ensure the oxidation process will be:

$$T_a = \frac{N_0 - N_a}{F_{\delta_n} I_N}, \tag{3}$$

where F_{δ_n} - the specific surface area of the biofilm in the bioreactor.

Since in the present case the extraction of nitrogen is mainly takes place in biofilm and is determined in particular according to the equation (2) by the flow of nitrogen I_N into the biofilm through its surface then its determination is based on the implementation of the following biofilm models: a) in the general case in conditions of elements of possible loading on which forms a biofilm in the bioreactor-aeration tank

$$\frac{\partial N}{\partial t} = D_N \frac{\partial^2 N}{\partial z^2} - R_N; \tag{4}$$

b) in the conditions of loading from elements of the cylindrical form (nozzles, grids, etc.) on which the biofilm is formed

$$\frac{\partial N}{\partial t} = D_N \left(\frac{\partial^2 N}{\partial r^2} + \frac{1}{r} \frac{\partial N}{\partial r} \right) - R_N, \tag{5}$$

where R_N - the reaction rate in the biofilm which in the complete absence of inhibited effect is described by the known Monod equation [3], [5]

$$R_N = \frac{\rho_m N}{K_{m_N} + N}, \qquad \rho_m = \frac{\mu_m X_N}{Y_N}. \tag{6}$$

The solution of equations (4) and (5) allows to determine the concentration of nitrogen along the thickness of the biofilm δ and what is most important for further calculations of the concentration of nitrogen on the outer and inner surfaces of the biofilm and the value of the flow into the biofilm which is written in the following dimensionless form as:

$$\frac{d^2 N}{d\bar{z}^2} - \alpha_N \frac{\overline{N}}{\overline{K}_{m_N} + \overline{N}} = 0, \tag{7}$$

whose solution is executed under the next boundary conditions:

$$\text{at } \bar{z} = 0, \ \frac{dN}{d\bar{z}} = \gamma_N \left(1 - \overline{N}\right); \qquad \text{at } \bar{z} = 1, \ \frac{dN}{d\bar{z}} = 0 \tag{8}$$

here $\bar{z} = \frac{z}{\delta}, \quad \overline{N} = \frac{N}{N_a}, \quad \alpha_N = \frac{\mu_m X_N \delta^2}{Y_N D_N N_a}, \quad \gamma_N = \frac{K_N \delta}{D_N}, \quad \overline{K}_{m_N} = \frac{K_{m_N}}{N_a}.$

Note that the boundary condition at $z = 0$ is accepted under the condition that the value of the flow in the boundary layer is equal to the flow on the surface of the biofilm. In this case the general dependence for determining the flow into the biofilm will look like this:

$$I_N = K_N N_a \left(1 - A_N\right), \qquad A_N = \frac{N_{\delta_0}}{N_a}. \tag{9}$$

For the convenience of further calculations the dependence (9) is presented in the form

$$I_N = \bar{I}_N \lambda, \qquad \lambda = \frac{D_N}{\delta} N_a. \tag{10}$$

As a result of the analytical solution of equation (7) under boundary conditions (8) carried out to determine the relative flow I_N we obtain the following equation:

$$\bar{I}_N = \sqrt{2\alpha_N} \sqrt{\overline{N}_{\delta_0} - \overline{N}_{\delta_1} - \overline{K}_{m_N} \ln\left(\frac{\overline{N}_{\delta_0} + \overline{K}_{m_N}}{\overline{N}_{\delta} + \overline{K}_{m_N}}\right)}, \tag{11}$$

and an equation that relates the concentrations on both the outer and inner surfaces of the biofilm:

$$\overline{N}_{\delta_0} = \overline{N}_{\delta_1} + \overline{K}_{m_N} \ln\left(\frac{\overline{N}_{\delta_0} + \overline{K}_{m_N}}{\overline{N}_{\delta_1} + \overline{K}_{m_N}}\right) + \eta\left(1 - \overline{N}_{\delta_0}\right)^2, \tag{12}$$

where $\eta_N = \frac{\gamma_N^2}{2\alpha_N} = \frac{K_N^2 N_a}{2 D_N w_N}, \quad w_N = \frac{\mu_m X_N}{Y_N}.$

When at $N_{\delta 0} >> N_{\delta 1}$ it is possible to neglect the concentration $N_{\delta 1}$ in dependences (11) and (12) which allows in practical calculations to determine the flow I_N and nitrogen concentration at which the transition from partially permeable to fully permeable biofilm at given initial reaction parameters and biofilm thickness is occured. Since in practice the nitrogen concentration will be preferably much higher than the half-saturation parameter $N>>K_{mN}$ the extraction of nitrogen by the biofilm in bioreactors can take according to the reaction kinetics of zero order:

$$R_{N_0} = w_N, \qquad w_N = \frac{\mu_m X_N}{Y_N}. \tag{13}$$

Then when solving the equation

$$D_N \frac{d^2 N}{dz^2} - w_N = 0, \tag{14}$$

in depending on the penetration of nitrogen into the biofilm the following two cases should be considered. In the first case which corresponds to the complete penetration of nitrogen into the biofilm ($L_{\delta 1}$) the solution of equation (14) is performed under the following boundary conditions:

$$I_N = -D_N \frac{dN}{dz} = K_N \left(N_a - N_{z=0}\right) \quad npu \quad z = 0,$$
$$\frac{dN}{dz} = 0 \quad npu \quad z = \delta. \tag{15}$$

In this case that to determine the values of concentrations N, $N_{\delta 0}$ and $N_{\delta 1}$ we obtain

$$N = N_a - \frac{w_N}{D_N}\left(\frac{\delta D_N}{K_N} + \delta z - \frac{z^2}{2}\right), \tag{16}$$

$$N_{\delta_0} = N_a - \frac{w_N \delta}{K_N}, \tag{17}$$

$$N_{\delta_1} = N_{\delta_0} - \frac{w_N}{2D_N}\delta^2. \tag{18}$$

For further analysis we write the equation (18) in the form:

$$N = N_{\delta_0}\left[1 - \left(\frac{2z}{\delta \beta_N^2} - \frac{z^2}{\delta^2 \beta_N^2}\right)\right], \tag{19}$$

where $\beta_N = \sqrt{\dfrac{2N_{\delta_0} D_N}{w_N \delta^2}}$ or $\beta_N \delta = \sqrt{\dfrac{2N_{\delta_0} D_N}{w_N}}$. The parameter β_N characterizes the change in the concentration of nitrogen in the biofilm and in this case according to (19) when $\beta_N > 1$ $N_{\delta_1} > 0$ and at $\beta_N = 1$ $N_{\delta_1} = 0$ .In the case when there is a partial penetration of nitrogen into the biofilm ($\beta_N < 1$) that its extraction occurs at the site $z = \beta_N \delta$ and at the solution of equation (14) takes the boundary conditions $dN/dz = 0$ and $N = 0$. Under the boundary condition dN/dz at $z = \beta_N \delta$ for to determine the value of the concentration in the area $0<z< \beta_N \delta$ we obtain the equation

$$N_z = N_{\delta_0} - \left(z\beta_N \delta - \frac{z^2}{2} \right) \frac{w_N}{D_N}, \tag{20}$$

$$N_{\delta_0} = N_a - \frac{w_N \beta_N \delta}{K_N}. \tag{21}$$

In the case of the boundary condition $N = 0$ at $z = \beta_N \delta$ when solving equation (14) we obtain

$$N_Z = N_{\delta_o} \left(1 - \frac{2z}{\beta_N \delta} + \frac{z^2}{(\beta_N \delta)^2} \right), \tag{22}$$

$$N_{\delta_o} = \frac{N_a - w_N \cdot \beta_N \delta}{\left(1 - \frac{D_N}{\beta_N \delta K_N} \right)}. \tag{23}$$

If the ratio (D_N / β_N δ K_N) << 1 than in both cases the concentration $N_{\delta 0}$ can be found by formula (21).

According to equation (20) the flow into the biofilm at $\beta_N > 1$ will be

$$I_N = w_N \delta, \tag{24}$$

and in the second case at $\beta_N < 1$ we have

$$I_N = w_N \beta_N \delta. \tag{25}$$

Since the parameter β_N depends on the concentrations the dependence (24) can be written as

$$I_N = \sqrt{2 D_N w_N} \cdot \sqrt{N_{\delta_o}}. \tag{26}$$

Thus the flow ratios for zero-order reactions for a partially permeable biofilm and for a fully permeable biofilm will be determined by a parameter β_N. As mentioned above the efficiency of nitrogen extraction by biofilm using the proposed calculation methods will largely depend on the accepted thickness of the biofilm δ. Recall that in this case under conditions of extraction of one substrate by autotrophic microorganisms (nitrification process) a homogeneous structure of the active biofilm is formed. However it should be noted that on the formation of the biofilm is influenced the various processes which in this case can be taken into account on the basis of the implementation of the following general equation according to [5], [6]:

$$\frac{d\delta}{dt} = \int_0^{\delta} \frac{\mu_m N}{K_{m_N} + N} dz - b_s \delta - u_{ds}. \tag{27}$$

In the accepted models of the biofilm to determine its thickness δ equation (27) is preferably solved in stationary conditions at $d\delta/dt$ = 0. In some cases it is proposed to use a more simplified balance equation [5], [6], [7]:

$$\frac{Y_N}{X_N} I_N - b_s \delta - u_{ds} = 0. \tag{28}$$

In the accepted equations b_s - the coefficient that takes into account the processes of decay of the biofilm, u_{ds} - the rate of separation of biomass from the surface of the biofilm that to determine of which is recommended the dependencies presented in [5], [6]:

$$u_{ds} = b_d \delta, \tag{29}$$

$$u_{ds} = K_d \delta^2. \tag{30}$$

So for example if we take for the reaction of zero order the value of the flow by formula (11) then on the basis of the solution of equation (28) taking into account formula (30) we obtain

$$\delta = \frac{\mu_m - b}{K_d} . \tag{31}$$

As an example based on the solution of numerical methods of equation (27) in the table 1shows the values of the thickness of the biofilm δ depending on the change in concentration Na, parameter b as well as the accepted values of the initial parameters recommended in [5], [6], [7].

$$\mu_m = 0{,}95\, day^{-1}, Y_N = 0{,}22 \frac{gCPK}{gN}, K_{mN} = 1\frac{gN}{m^3}, X_N = 10000\frac{gCPK}{m^3}, K_N = 0{,}10\, m/hr,$$

$$\delta_{\min} = 10 mkm, D_N = 1{,}70 \cdot 10^{-4}\, m^2/day.$$

Table 1

Values of active thickness of a biofilm δ, mkm ,in stationary conditions at various values b and concentrations N_a , g/m^3

b, hr^{-1}	$N_a, g/m^3$					
	1	3	5	7	9	11
0,01	100	260	410	570	680	750
0,02	-	130	210	290	350	390
0,03	-	-	90	160	200	250

According to equation (27) and the data of table1 it follows that with increasing parameter b (K_d) the nitrogen flux and the thickness of the biofilm decrease while with increasing nitrogen concentration in the bioreactor these characteristics increase. As mentioned above the extraction of nitrogen by the biofilm takes place under aerobic conditions with the provision of oxygen in the required sufficient amount which is necessary for the growth and activity of autotrophic microorganisms. On the base of provided analysis in the practical calculations of the parameters of the oxygen regime consider the case when the extraction of nitrogen in the biofilm occurs by the reaction of zero order during oxidation (oxygen consumption) which also occurs by the reaction of zero order:

$$R_C = \alpha_1 R_1 + \alpha_2 b_c X_N . \tag{32}$$

As a result of solving the next equation

$$D_C \frac{d^2 C}{dz^2} - R_C = 0 \tag{33}$$

under boundary conditions

$$-D_C \frac{dC}{dz} = K_C \left(C_a - C_{\delta_0}\right) = I_C \quad при \quad z = 0$$

$$\frac{dC}{dz} = 0 \quad при \quad z = \delta \qquad (34)$$

we obtain the following equations to determine the concentration C_δ and flow I_C

$$C_{\delta_o} = C_a - \frac{w_c \delta}{K_C}, \qquad (35)$$

$$I_C = w_c \delta, \qquad (36)$$

where

$$w_c = \alpha_1 R_N + \alpha_2 b_c X_N. \qquad (37)$$

As it will be recalled above the consumption of oxygen for utilization (self-oxidation) of the dying biocenosis in the biofilm is taken into account by the parameter $\alpha_2 b_c X_N$. In the general case the value of the flow of oxygen entering the biofilm is determined by equation (35). However for the zero-order reaction without taking into account the processes determined by the parameter b_c in the case $b_c = 0$ for determining the flow I_C taking into account the required stoichiometric coefficients after some transformations we obtain the following dependences:

$$I_C = \left(4{,}57 - Y_N\right) I_N, \quad I_N = \frac{I_C}{\left(4{,}57 - Y_N\right)}, \quad Y_N \approx 0{,}22 \quad , \qquad (38)$$

that is in this case the value α_1 will be $\alpha_1 = \alpha_N - Y_N, \quad \alpha_N = 4{,}57 \frac{гO_2}{гN}.$

The processes of nitrogen extraction by biofilm under aerobic conditions are controlled by oxygen penetration. Therefore the determination and comparison of the parameters of penetration into the biofilm of the contaminants and oxygen are the most important result of kinematic studies in biofilms as it allows to determine which of them will limit the process of utilization of the substrate (nitrogen). In the general case this question can be solved by comparing and analyzing constructed in the biofilm epures of the change in concentrations nitrogen and polutions in the thickness of the biofilm. In this case as a rule nitrogen may be present throughout the thickness of the biofilm but can not be removed in areas where oxygen can not penetrate in it in sufficient quantities. A number of criteria have been substantiated and proposed in the literature for different reaction kinetics using stoichiometric coefficients. Thus under conditions of zero-order kinetics by comparing the values of concentrations N_δ and C_δ and flows I_C and I_N as well as known penetration parameters β_C and β_N it is possible to determine which of the substrates limits the conversion processes within the biofilm [5], [10]. For example the results of calculations showed that in most cases namely in the conditions $N_\delta > 0.3C_\delta$ and $\beta_C < \beta_N$ the extraction of ammonium is limited by oxygen especially along the thickness of the biofilm which must be taken into account in engineering calculations of biofilm cleaning. The processes and mechanisms of ammonia nitrogen extraction from wastewaters by the fixed biocenosis are influenced by temperature, pH (alkalinity) and the presence of other substances [1], [2], [8], [11]. The influence of these factors in the proposed models can be taken into account by correction coefficients f_T , f_{pH} , f_i. The kinetics of biooxidation as well as the processes of mass transfer are affected by temperature but this effect in the conditions of the fixed biocenosis will be less than in the conditions of suspended biocenosis (activated sludge). It is known that for practical calculations the effect of temperature is taken into account by correcting some constants and coefficients for a known temperature factor [10], [11]. In particular it is shown that under conditions of limiting the process of nitrogen extraction by oxygen the change in temperature in the range from 14^o C to 27^o C almost does not affect on the nitrification process [8], [11]. The effect of pH (alkalinity) is especially evident in the processes of nitrification mainly in the extraction of ammonium. Analysis of the evaluation of the influence of various parameters, examples of calculation of alkalinity values required to maintain a given pH and other factors in the oxidation of ammonium are considered in particular in [8]. The value pH <6.0 can practically lead to inhibition of the process. Specific recommendations for pH as well as the parameters f_{pH} and degree of their influence on the processes of nitrogen extraction are given in [8], [10], [11]. Thus in particular for determination f_{pH} the next dependences are proposed to the correction factor:

$$f_{ph} \approx 0 \quad npu \quad ph < 6{,}0 \, , \tag{39}$$

$$f_{ph} = 1 - 0{,}833(7{,}2 - ph) \quad npu \quad 6 < ph < 7{,}2 \, , \tag{40}$$

$$f_{ph} = 1 \quad npu \quad ph \geq 7{,}2. \tag{41}$$

It is known that in the presence of toxic and other substances in wastewater the reaction rate can be significantly reduced due to their inhibitory effect [2], [8]. In the general case the effect of different substances can be taken into account by using the well-known Chaldean equation instead of the Monod equation to describe the biooxidation process as well as other equations of kinetic reactions. The specific data which allow to estimate the inhibitory effect of various metals and other substances on nitrification processes are presented in [3], [8]. On the further the follow theoretical researches of nitrogen purification in the conditions of the second stage of nitrification are provided. In particular at first a theoretical substantiation of the processes and construction of mathematical models will be carried out which describe the conversion of ammonium during oxidation into nitrites and then oxidize them to nitrates under the action of other bacteria. Note that under conditions of a rather complex anaerobic denitrification process and under the action of a special kind of bacteria nitrate is converted into free nitrogen [2],[4].

CONCLUSIONS

The methods of calculations of organic contaminations and ammonium nitrogen removal by biofilm which are obtained on the base of created and realized mathematical biofilm models are proposed. They are validated enough and may be used at the valuation on the processes of the simultaneous wastewaters treatment in different bioreactors. The results of solutions of the methodic problems by numerical methods on the base of the simplified analytical dependences showed that the developed methodic allows to simplify the practical calculations at the forecasting of the wastewaters treatment processes and projecting of the corresponding treatment plants.

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STUDY OF THE IMPACT OF SURFACE AND GROUNDWATER POLLUTION ON PUBLIC HEALTH

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ABSTRACT

The pollution of the region was researched and the medical and ecological parameters of the pollution of the territory as an important factor of public health were characterized. The statistical dependence between concentrations of microelements in water resources and morbidity and mortality of the population was established. Functional dependences were found that adequately model these connections on the basis of the created mathematical model. An information analytical computer system for environmental services was created and a computer program EcoForecast was developed. Results allow predicting changes in public health depending on the concentrations of chemical elements in the habitat. The conducted medical and ecological analysis has showed that the level of morbidity and mortality of the population largely depends on landscape and geochemical features of the territory (content of macro- and microelements, alkaline-acid and redox conditions, degree of technogenic pollution and self-cleaning, content of mineral elements in food products. etc.

Keywords: monitoring, ecological safety, remote sensing, geographic information system, population health.

INTRODUCTION

The sustainable development of each country determines the quality of human life and health, which depends on the level of economic development [1,2], the state of the environment [3-10], the quality of food and drinking water [11, 12].

Water is one of the most important elements necessary for the existence of different ecosystems including the existence of humanity. Both lack and excessive amounts of water may lead to extreme changes in any areas of the national economy. Therefore, the detection of water bodies and their subsequent control is an important process in academic and practical environmental research. Control over fresh water on the surface of the Earth is gaining special topicality as its volumes decrease every year. Therefore, monitoring of surface water bodies which controls the changes in the number of bodies of water, their area, shoreline, and other characteristics is carried out.

The urgent tasks to ensure water security are to reduce the pollution of water basins, ensure the sustainable use of water resources, the introduction of effective regulation of extraction of aquatic resources [13, 14].

The majority of the population of Ukraine uses low-quality water, which poses a danger to health. The problem of the environmental state of water objects is important for all pools and rivers in Ukraine. One of the main components of environmental security towards sustainable development is monitoring the quality of water [15–18]. Ukraine is one of the few water resources countries in Europe. Under the influence of economic load, about 70% of surface and part of groundwater in Ukraine have lost their importance as sources of drinking water supply.

One of the most important monitoring component of any object is to determine its pollution degree. In t the first place, operational and accurate information about the quality of water facilities and soils is the basis for water and land users activities regulation, ensuring measures for the rational use of nature, informing the relevant authorities and the public about possible hazardous situations.

The work of many researchers was proven the association between the chemical composition of soils, surface and groundwater and the incidence of diseases named as environmental markers. The content of certain chemical elements in the soils of human habitats through water, food, respiration is reflected in the balance of trace elements in the human body. There are almost no completed studies with adequate analytical modeling of the relationship between the intake of micronutrients in humans and the occurrence of diseases. Therefore, statistical studies are important, which in the first approximation can characterize the processes that are closely related to the environmental safety of human habitat. They will significantly increase the effectiveness of environmental policy, which is impossible without the priority of public health in the focus of adverse environmental impacts. In Ukraine a comprehensive approach and a single methodology for monitoring the state of ecosystems and public health [19–24], their accocoations in the organizational-technical and information-analytical sense were not yet been created [25–28].

METHODS AND EXPERIMENTAL PROCEDURES

Estimation of surface and groundwater pollution levels. The spatial and territorial unit within which the environmental safety of geosystems is managed is the river basin. The basin concept makes it possible to coordinate measures for the optimization of geosystems with the characteristics of catchment areas, starting with the smallest (elementary) catchments. The functioning and relative stability of all geosystems is largely determined by the speed of certain processes in different parts of the basin. The river basin (basin geosystem) is a paragenetic ecological, hydrological and economic unit with clearly defined boundaries. It is based on a set of geomorphological, soil and climatic conditions [29, 30]. They determine the intensity of flows of substances and energy, which allows to justify the structure and optimal ratio of geosystems, their rational spatial location, as well as to determine the types and calculate the parameters of the necessary reclamation elements [31–33].

The rivers of the territory belong to the basins of the Dnieper, Dniester, Western Bug. The chemical composition of fresh water, calcium bicarbonate. Surface water is contaminated with nitrates, to a lesser extent - nitrites. Contamination is caused by the use of mineral fertilizers on agricultural land.

Groundwater is confined to sediment and has varying degrees of protection. Groundwater is the first unprotected from the surface of aquifers, which are used for commercial water supply [34, 35]. Interstratal aquifers of the Neogene, Cretaceous, Devonian on the watersheds are protected, on the slopes are conditionally protected. Natural and social approach to assessing the quality of the environment involves, first of all, assessing the stability of human habitat, which means a set of natural conditions and anthropogenic and natural factors that exclude the onset of any psychological, mental, physiological, genetic and other effects for human health throughout his life. It also requires the development and compliance with certain environmental safety standards – environmental quality standards [35–37]. The latter are now understood as uniform norms, rules or regulations aimed at ensuring the level of environmental safety in combination with improving public welfare, which are the maximum allowable levels of pollutants or other harmful anthropogenic impacts [38]. However, this approach seems imperfect. It is important to study the environment in the context of living comfort, human development. Water sampling was carried out according to the methods taking into account the water, landscape and geomorphological maps of the Ternopil region for coverage by a uniform network. The data of the State Ecological Inspectorate and the Sanitary Epidemiological Station were also taken into account [39].

Territorially, the samples covered the entire area (Fig. 1). The analysis was performed by X-ray fluorescence method with a NAT device (toxic element analyzer).

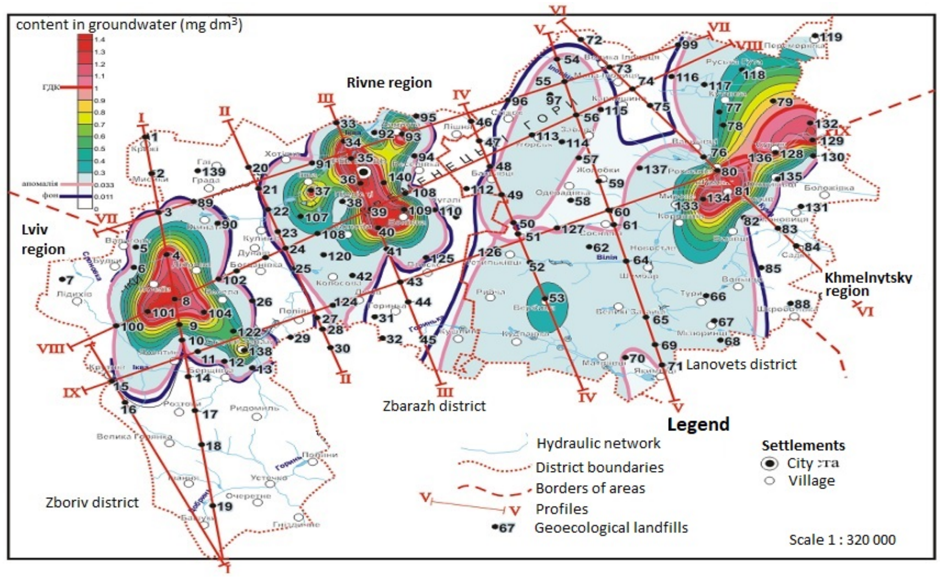

Fig. 1. Map of copper (Cu) distribution in groundwater of the northern part of Ternopil region

The chemical composition of water is mainly hydrocarbonate, less common sulfate-hydrocarbonate, chloride-carbonate calcium, magnesium-calcium with a mineralization of 0,4-3 g/dm^3.

In groundwater, increased mineralization (g/dm^3) is determined in the following wells: 134 (village Stryivka) – 3,0; 140 (village of Velykyi Khodachkiv) – 2,6; 85 (Chistopadi village) – 1,8; 68 (village of Luchkivtsi) – 1,4; 141 (village of Panasivka) – 1,4; 144 (village of Piznanka) – 1,3; 24 (village of Pochapyntsi) – 1,3; 147 (village of Ilavche) – 1,3; 78 (village of Mshanets) – 1,3; 48 (village of Snihurivka) – 1,2; 38 (Mykulyntsi township) – 1,2; 112 (village of Pohribtsi) – 1,2; 49 (village of Zalisty) – 1,2; 145 (village of Hlibiv) – 1,2; source 68 (the village of Yastrubove) – 1,3.

The main components of groundwater pollution are nitrates. Increased content (mg/dm^3) of nitrates is available in wells 140 (village of Velykyi Khodachkiv) – 884,76 (19,7 MPC), 134 (village of Stryivka) – 741,13 (16,5 MPC) and chlorine 471,75 (1,4 MPC), 85 (Chistopady village) – 615,57 (13,7 MPC), respectively, the level of pollution is dangerous. The average content of nitrates was determined in the following wells: 37, 147 (village Sinozhaty, Ilavche) –

318,17, 317,75 (7,1 MPC), 49 (village Zalistsi) – 279,76 (6,2 MPC), 112 (Pogribtsi village) – 265,52 (5,9 MPC). Contamination in other wells, the MPC of which is from 8,7 to 3,1, corresponds to a moderately dangerous level. Nitrite contaminated (mg/dm^3): well 145 (village of Hlibiv) – 5,0 (2,5 MPC), source 68 (village of Yastrubove) – 2,0 (1 MPC); phosphates - wells: 78 (village Mshanets) – 7,47 (2,1 MPC), 83 (village Bzovytsia) – 5,6 (1,6 MPC). The level of pollution is moderately dangerous.

Testing of groundwater intakes revealed varying degrees of pollution. Bromine and copper contents (in μg/dm^3), exceeding the MPC, were found in water intakes: Verkhno-Ivanivskyi, village Horishniy Ivachiv: bromine 180 (1,8 MPC); Ternopil, village Bila: bromine - 560 (5,6 MPC), copper – 3,2 (1,1 MPC); Vyshnivets township, KKP: copper – 5,5 (1,8 MPC), bromine - 170 (1,7 MPC); Zaliztsi township, distillery: bromine - 420 (4,2 MPC); Pidkamin township, hospital: bromine - 12100 (12,1 MPC), copper – 4,7 (1,6 MPC); village. Velyki Birky, CCP: bromine - 1580 (15,8 MPC); Mykulyntsi township, CCP: bromine - 800 (8 MPC); with. Konopkivka, sanatorium "Medobory". Comparing the data on the manifestations of industrial bromine waters, we conclude that bromine contamination is of natural origin [4–6]. The content of microelements (in dry residues) exceeding the MPC (according to the above-mentioned regulations) was recorded (in mg/dm^3): barium – 1,1 (11 MPC), 0,9 (9 MPC), 0,49 (4,9 MPC) – village Kozliv; well 28, p. Sorotske, well 37; titanium – 0,27 (2,7 MPC) – village Zalistsi.

According to the results of water pollution monitoring from 1995 to 2020, it was established that water quality is deteriorating every time. Groundwater is distributed throughout the territory very unevenly due to the difference in structural-geological and physical-geographical conditions of formation of resources and chemical composition of the underground hydrosphere of different zones of the southern part of the region. Enterprises significantly affect the quality of groundwater. Chortkiv district ranks 2nd among the districts of the region in terms of industrial production. The quality of groundwater in the Chortkiv district is most affected by the metalworking industry, machine building and light industry. The largest polluters of groundwater in the district are: SE "Marylivsky distillery", OJSC "Chortkiv plant" Agromash ", LLC" Wawryk and company LTD", OJSC "Chortkiv cheese factory", SE "Chortkiv bakery", SE "Chortkivmyasprom". At these plants, in most cases, the wastewater does not go into the general municipal sewage system or there are no appropriate treatment facilities. The level of groundwater pollution is defined as acceptable and moderately dangerous.

Study of the impact of surface water pollution on public health. The study of the main ecological living conditions of the population of Ternopil region began with sampling and analysis. According to the administrative division of the region, we identified 17 ecological sites, which were characterized by numerical values of concentrations of individual chemical elements, surface water (Table 1) and morbidity (Table 2).

Table 1. Results of instrumental and laboratory quality control of surface waters of Ternopil region for 2019

№	District	Chemical elements							
		Zn	Cd	Ca	Co	Mn	Mg	Cu	Ni
1	Berezhansky	0,192	0,001	54,11	0,001	17,02	0,076	0,0020	0,003
2	Borshchivsky	0,221	0,003	56,1	0,046	29,2	0,0228	0,0006	0,0021
3	Buchatsky	0,214	0,006	92,2	0,0176	10,94	0,0462	0,0033	0,0076
4	Gusyatynsky	0,198	0,006	78,2	0,002	15,5	0,133	0,013	0,0038
5	Zalishchytsky	0,164	0,006	78,2	0,007	20,7	0,035	0,005	0,004
6	Zbarazh	0,266	0,002	66,2	0,004	13,38	0,083	0,009	0,0056
7	Zborivsky	0,219	0,003	56,1	0,001	21,9	0,143	0,0072	0,0021
8	Kozivsky	0,131	0,004	84,2	0,012	25,54	0,0383	0,008	0,005

9	Kremenets	0,197	0,007	66,1	0,003	21,88	0,029	0,065	0,0071
10	Lanivetsky	0,241	0,002	50,1	0,001	14,59	0,049	0,0046	0,0015
11	Monastic	0,205	0,005	79,2	0,006	18,24	0,008	0,005	0,003
12	Podvolochysky	0,256	0,006	110,2	0,008	21,9	0,057	0,011	0,0123
13	Pidhayetsky	0,128	0,003	68,1	0,006	23,1	0,105	0,002	0,0031
14	Terebovlya	0,249	0,002	80,2	0,020	52,29	0,046	0,0018	0,0015
15	Ternopilsky	0,169	0,003	56,1	0,0126	18,24	0,0057	0,014	0,006
16	Chortkivsky	0,03	0,005	98,2	0,0146	12,16	0,046	0,009	0,003
17	Shumsky	0,102	0,004	55,1	0,031	34,05	0,064	0,025	0,009

Table 2. Morbidity rates of residents of Ternopil region in 2019

№	District	Morbidity per 100 thousand population	
		blood circulation	breath
1	Berezhansky	775	239
2	Borshchivsky	705	247
3	Buchatsky	778	272
4	Gusyatynsky	736	168
5	Zalishchytsky	857	187
6	Zbarazh	768	177
7	Zborivsky	703	257
8	Kozivsky	740	168
9	Kremenets	637	146
10	Lanivetsky	772	176
11	Monastic	803	293
12	Podvolochysky	873	357
13	Pidhayetsky	742	260
14	Terebovlya	761	170
15	Ternopilsky	689	278
16	Chortkivsky	72	357
17	Shumsky	775	212

The correlation coefficient between the concentration of zinc in surface waters and diseases of the circulatory system was 0.655, which indicates the possibility of such a statistical relationship (Table 3).

Since the sample size is 17, then the estimation of the correlation coefficient of the general population can be improved by equation (1):

$$r^* = r\left[1 + \frac{1 - r^2}{2(n-3)}\right], \qquad (1)$$

where r^* - is the estimate of the correlation coefficient of the general population, r - is the correlation coefficient, n - is the sample size. The corrective calculation estimate of the correlation coefficient of the general population showed 0.66849647. The 95% confidence interval is found for r = 0.67 and n = 17. It is [0,3; 0,85], which suggests a correlation between the concentration of zinc in the surface waters of the habitat and diseases of the circulatory system. In our opinion, this connection is explained by the chain of surface water - domestic animals - food.

Table 3. Correlation coefficients

Chemical elements	Circulatory organs	Respiratory organs
Concentrations in surface waters		
Zn	0,6551	-0,2551
Cd	-0,0970	0,1331
Ca	-0,1995	0,4468
Co	-0,0961	0,1214
Mn	0,2173	-0,2848
Mg	0,0556	-0,1159
Cu	-0,1309	-0,3089
Ni	0,2268	0,2444

The approximate dependence was selected as the most accurate of the functions:

$y_1(x) = a_0 + a_1 \cdot x$, $y_2(x) = a_0 + \dfrac{a_1}{x}$; $y_3(x) = a_0 + a_1 \cdot \ln(x)$; $y_4(x) = a_0 \cdot e^{a_1 \cdot \ln(x)}$;

$y_5(x) = a_0 e^{a_1 \cdot x}$; $y_6(x) = \dfrac{1}{a_0 + a_1 \cdot x}$; $y_7(x) = a_0 \cdot e^{a_1 \cdot x^2}$; $y_8(x) = \dfrac{x}{a_0 \cdot x + a_1}$;

$y_9(x) = a_0 + a_1 \cdot x^3$; $y_{10}(x) = a_0 + a_1 \cdot x^2$ and selection of coefficients and degree of polynomial $Q(x) = a_0 + a_1 x + a_2 x^2 + ... + a_m x^m$. As a result, the more accurate of the functions is y_2 з coefficients a_0=882,146 і a_1= –23,342.

Polynomial **(Fig. 1)** gives the best accuracy of the model of the dependence of circulatory diseases K (cases per 100 thousand population per year) and the concentration of Zn (mg/kg) in the surface waters of the habitat. This is a polynomial of the 5th order with coefficients a_0= –763.332, a_1= $3.606 \cdot 10^4$, a_2= $-3.044 \cdot 10^5$, a_3= =$1.097 \cdot 10^6$, a_4= $-1.516 \cdot 10^6$, a_5=$3.360 \cdot 10^5$.

The established dependence will be used to predict changes in the health of the circulatory system depending on the concentrations of zinc in the surface waters of habitats. Such prediction is possible only within the studied concentrations, which are for zinc [0,03; 0,266] mg/kg.

The calculations (Table 4) revealed statistically significant relationships, namely the direct relationship between the concentration of Zn in surface waters and the incidence of circulatory system (significance level $\alpha = 0{,}005$), the inverse relationship between the concentration of Co in surface waters and the incidence of pneumonia (significance level α=0,025), direct relationship between Ca concentration in surface waters and total morbidity (significance level $\alpha = 0{,}05$), direct relationship between Ca concentration in surface waters and respiratory disease (significance level $\alpha = 0{,}05$), a direct relationship between the concentration of Mg in surface waters and the incidence of pneumonia (significance level $\alpha = 0{,}05$).

For correlation analysis with gross content in surface waters of Ternopil region (Table 5) Ca and Mg can be used normal distribution, for others – no.

The degree of statistical relationship between the concentrations of chemical elements and the morbidity of the population using parametric methods is the Pearson correlation coefficient [40–42]. Analysis by nonparametric methods was performed using Spearman's rank correlation coefficient.

EcoForecast is designed for use by computers running MS Windows software.

Table 4. Correlation characteristics

	Morbidity per 1000 population		Morbidity per 100 thousand population		
	Total	primary	circulatory system	respiratory organs	pneumonia
Gross content in surface waters					
Cu	-0,1543	-0,0635	-0,2555	-0,1339	0,0583
Zn	-0,0436	-0,0388	0,6551	-0,2551	-0,0302
Ni	0,1195	0,14710	0,1877	0,2443	0,1230
Co	0,0400	-0,0537	-0,0566	0,1906	-0,4898
Ca	0,4163	0,0500	0,1820	0,4469	-0,2366
Cd	0,1534	0,0188	0,0554	0,0068	0,1967
Mn	-0,1913	-0,2811	-0,0276	-0,2848	-0,0626
Mg	0,0582	0,0585	0,0920	-0,1159	0,4249

Table 5. Statistical characteristics of the results of instrumental and laboratory control of surface waters for 2012

	Gross content							
	Zn	Cd	Ca	Co	Mn	Mg	Cu	Ni
Kurtosis	1,2502	-1,2429	-0,2979	3,4158	5,0345	0,3468	11,1846	1,300
Asymmetry	-1,0937	0,0725	0,64509	1,7953	1,9645	0,9241	3,1758	1,2211

The program interface (Fig. 3.) consists of one window, which indicates the concentration of zinc in the surface waters of the habitat. After clicking on the "Run" button, the forecast of the number of cases out of 100 thousand population per year is calculated. The "Clear" button deletes the numbers, after which you can calculate the forecast for another concentration.

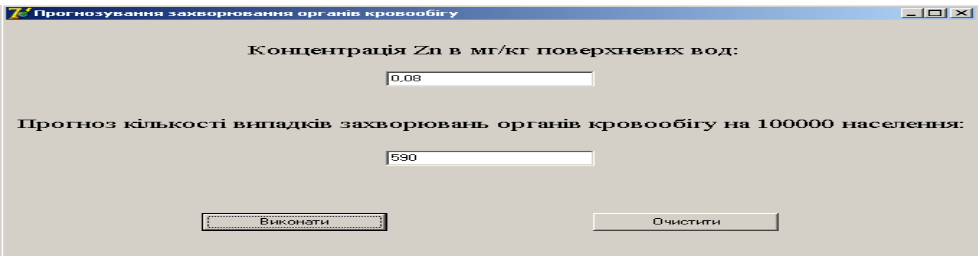

Fig. 3. Forecasting program window

The research of concentrations of certain chemical elements of surface waters and the state of morbidity of the circulatory and respiratory systems of people of Ternopil region showed the relationship between the concentration of zinc in surface waters and diseases of the circulatory system (Fig. 4). The identified dependence was modeled by an analytical function. A software was developed to predict changes in the health of the circulatory system depending on the concentrations of zinc in the surface waters of habitats.

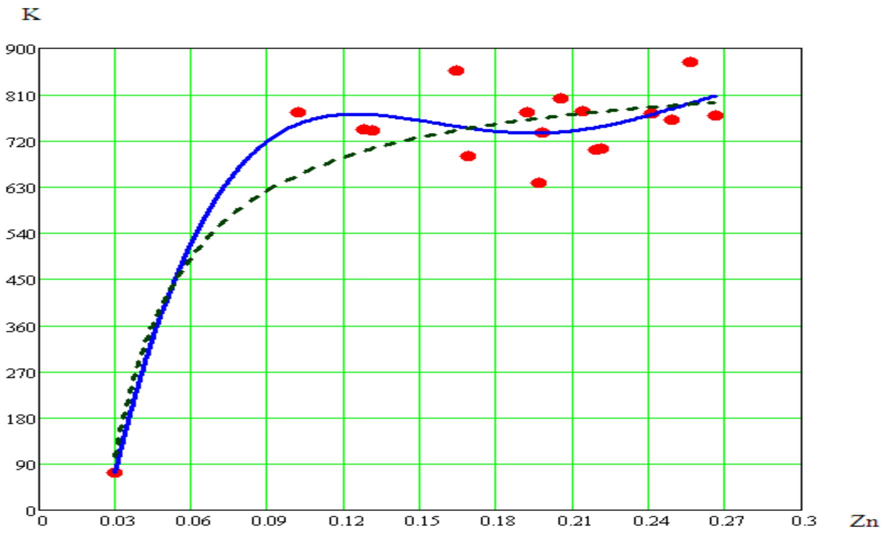

Fig. 4. Dependence of diseases of the circulatory system on the concentration of zinc in surface waters: points – simulated values; dotted line – function; solid line – polynomial.

CONCLUSION

The study of concentrations of certain chemical elements of surface waters and the state of morbidity of the circulatory and respiratory systems of people of Ternopil region showed the lack of connection between the concentration of zinc in surface waters and diseases of human circulatory system. The identified dependence was modeled by an analytical function. A software was developed to predict changes in the health of the circulatory system depending on the concentrations of zinc in the surface waters of habitats.

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QUANTITATIVE ASSESSMENT OF WATER RESOURCES AND EVALUATION OF WATER QUALITY (ON THE EXAMPLE OF SUMY REGION)

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ABSTRACT

The study is devoted to the development and testing of the methodology for assessing water resources, which involves a combination of their quantitative assessment, determination of water quality and taking into account the basin principle, which is a modern approach to water resources management. A step-by-step algorithm for estimating water resources of Sumy region in the context of the basins of the main rivers of the region is created. The first step is to estimate the quantitative indicators of water resources (water supply of total runoff, local runoff and underground predicted resources per capita, as well as drainage into surface water bodies, volumes of discharged polluted return waters in the main river basins of the region). The second step is to assess the quality of water resources (stability of surface waters, water pollution index, anthropogenic pressure on river basins). This methodology was tested in the assessment of water resources of Sumy region in terms of basins of the main rivers of the region. It is established that water resources of the Desna river basin within Sumy region are characterized by a level "above average", which is associated with high water supply of total and local runoff, predicted groundwater resources and maximum surface water stability in the region. Water resources of the Vorskla, Seim and Sula river basins are characterized by an average integrated value. The water resources of the Psel river basin have a low value due to low water supply, which can be explained by such factors as densely populated area of the basin, high drainage rates, high water pollution and significant levels of anthropogenic pressure on natural complexes of the river basin.

Keywords: water resources, water supply, water use, stability of surface waters, water pollution index, anthropogenic pressure.

INTRODUCTION

Water resources (suitable for the use Earth's water) are an important part of the national wealth, and preservation of their volume and quality is the most important problem today. Water is the basis of human life, because a sufficient number of quality water resources determines the standard of living and health of the population [17, 19]. Water supply in the world and in Ukraine is quite uneven. In Sumy region it is 1-2 thousand m^3 per capita per year, which is higher than the average in Ukraine, but it is more than 2 times less than in Europe and 4 times less than the world average. Therefore, the problem of assessing water resources, their quantity and quality is extremely important, and its solution is necessary for the conservation and rational use of water resources.

METHODS AND EXPERIMENTAL PROCEDURES

In today's world, the use of water resources is increasing, which in turn requires their adequate assessment. To assess the country's water supply per capita per year in the world practice is used the Falkenmark water stress indicator [8]. The level of water scarcity in a given country was determined on the basis of threshold values. If the amount of renewable water resources (river runoff) in the country per capita is less than 1700 m^3/year – the country experiences water stress; less than 1000 m^3/year – there is water shortage in the country; less than 500 m^3/year – the country has an absolute shortage of water. Ukraine's water resources (river runoff) per capita are about 1800 m^3/year, which is one of the lowest in Europe and, according to the Falkenmark indicator, the country is on the verge of water stress. However, it should be borne in mind that not only the quantity of water resources is important, but also their quality. Today in the world an acute problem is reduction of water resources due to the loss of their quality, which is a greater threat than their quantitative depletion.

In addition to the assessment of specific indicators of water supply per capita, there is a methodology of assessing natural waters by determining their suitability for practical purposes, which is based on state standards and regulations.

Analysis of the methodologies for assessing water resources suggests that they are all reduced to two areas: economic (taking into account the quantitative indicators of runoff) and ecological (taking into account indicators of water quality). Economic assessment of water resources, in addition to the assessment of "physically available" water resources (surface, groundwater), specific indicators of water supply per capita, Ye. V. Obukhov [15] provides a cost estimate of water resources, determines the total cost of the resource with the calculation in the economic plane, which is discussed in the works of M. A. Hvesyk [13], L. V. Levkovska, A. M. Sunduk [11], M. M. Tsependa [18] and others.

Ecological assessment of surface water quality carries information about the state of water bodies and reflects its changes under the influence of natural and anthropogenic factors. One of the simplest methodologies for assessing the quality of water resources is assessment of the water pollution index (WPI), described in the works of V. K. Khilchevsky [16], S. I. Snizhka [17]. Other widely used methodologies are assessment of surface water quality by hydrochemical parameters [19] and ecological assessment of surface water quality by relevant categories [14].

Our own vision of the region's water resource assessment algorithm combines quantitative resource assessment and water quality evaluation, taking into account the basin principle – a modern approach to water resources management, where the main subject of management is the river basin. Implementation of the assessment of water resources of the region in the context of the basins of the main rivers is carried out by successive realization of two stages of the study: 1) assessment of quantitative indicators of water resources; 2) assessment of water quality indicators (Fig. 1).

Assessment of quantitative indicators of water resources. At the first stage of the assessment, the water supply was analyzed. The analysis was conducted by calculating the specific indicators of water supply (surface water: total runoff, local runoff, as well as predicted groundwater resources) per capita in terms of basins of the main rivers of the region. Since statistical information (population, groundwater reserves) is usually presented by administrative-territorial units, and their boundaries do not coincide with the boundaries of river basins, we have listed these indicators for the basins of the main rivers of the region, taking into account the share of administrative districts within river basins. Also, at this stage, there was conducted an analysis of water use, including drainage into surface water bodies, its volume and the amount of polluted return water discharged into water bodies in the region.

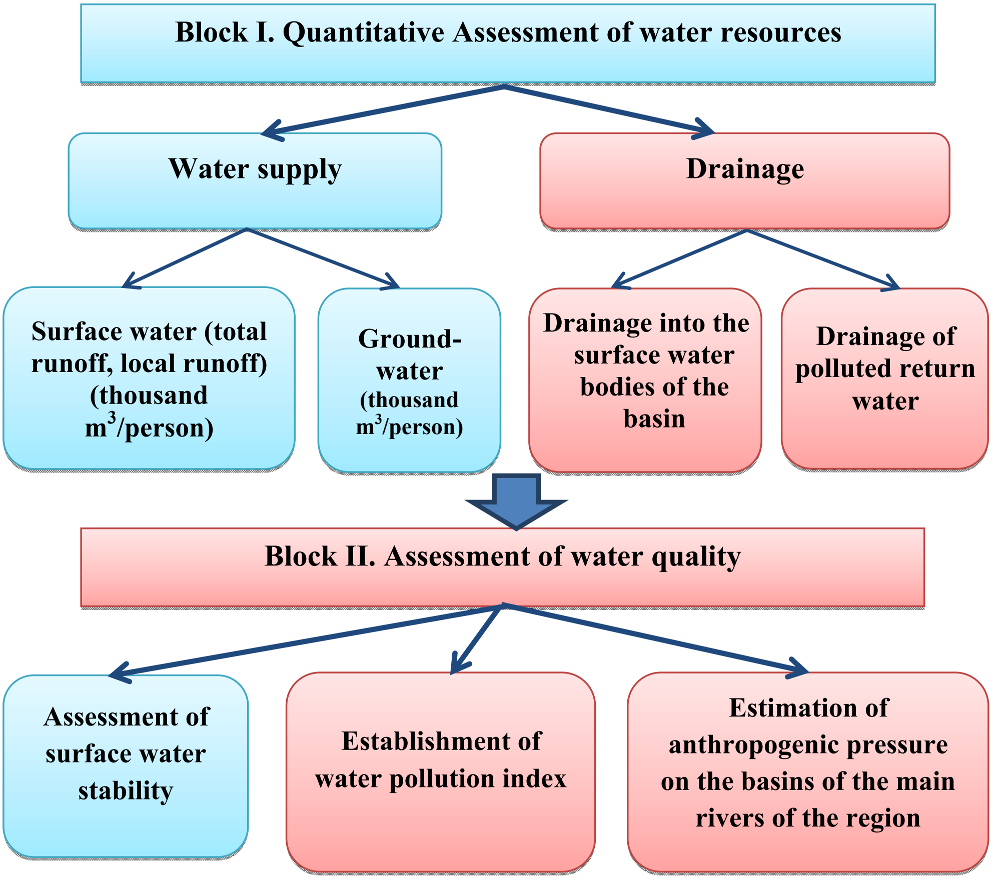

Fig. 1. Algorithm for assessing water resources of the region in terms of main river basins

Assessment of water quality indicators. When assessing the quality of water resources, the resistance of water (natural self-purification potential) to anthropogenic pressure is taken into account, because the aquatic environment can easily change its quality in different ways at low or high stability indicators. Methodological aspects of determining the stability of the natural environment were developed by V. A. Baranovskyi, M. A. Hlazovska and others [1, 9], but there are no universal methodologies for assessing the resistance of geosystems to anthropogenic pressure. Regarding the assessment of surface water stability, M. A. Hlazovska identifies the processes necessary to neutralize pollutants in various ways, namely mechanical, chemical and biological [9]. They include transparency and chemical composition of water, flow rate, temperature, biodiversity, etc. Aquatic stability is a complex process of biochemical and biological self-purification of water. It is influenced by different groups of factors: temperature and color of water, hydrological characteristics of water flow. In this paper, the stability is calculated as the product of the biotic potential of water self-purification (which, in turn, depends on the temperature and color index of water) and the coefficient of water flow (the ratio of water consumption indicator of a water meter to its average value) [12] (formula 1).

$$W = B \times h = \left(\frac{a}{365}\right) \times j \times h, \quad (1)$$

where W – stability of surface waters, B – biotic potential of water self-purification, h – coefficient of water consumption, a – number of days during the year with water temperature above 16ºC, j – index of water chromaticity (makes 1 – at chromaticity to 30º; 0,9 – at chromaticity of 30-60º; 0,8 – 60-90º, 0.7 – 90-120º and 0.6 – at chromaticity above 120º).

The next step is to assess the quality of water resources in the region, which is carried out through the establishment of the average value of WPI for the basins of the main rivers of the region. For surface waters, the number of indicators taken for the calculation of the WPI should be at least 6 [16, 17]. These indicators include ammonium nitrogen, nitrite nitrogen, petroleum products, phenols, dissolved oxygen, biochemical oxygen demand (BOD_5). The sum of the values of all six indicators, expressed in terms of MAC (ammonium nitrogen, nitrite nitrogen, petroleum products, phenols) or standard (BOD_5, dissolved oxygen) is divided by the number of indicators (formula 2). In the absence of some pollutants in the water, the total value is still divisible by 6.

$$WPI = \sum \frac{C}{MAC} / n \quad (2)$$

where WPI – water pollution index, MAC – maximum allowable concentration (value) of the indicator; C – actual concentration (value) of the indicator; n – number of indicators.

The next step involves calculating the average value of anthropogenic pressure on the basins of the main rivers of the region, because according to the methodology that we have used [2], the levels of anthropogenic pressure on the basins of small rivers are calculated, which must then be averaged. This methodology involves: 1) assessment of factors of anthropogenic impact by calculating the appropriate coefficients: forest cover – Kf, bogging of the basin – Kb, plowing – Kp, settlement – Ks, soil erosion – Ks, over-regulation of the riverbed – Kover, drainage in the river basin – Kd, pollution of the basin by pesticides – Kpp, plowing of the coastal protection strip – Kpcps; 2) since the calculated coefficients have different dimensions, their normalization is carried out according to formulas (3-4), for factors that have a direct and inverse effect on the level of anthropogenic pressure, respectively;

$$Y_i = \frac{X_i - X_i^{min}}{X_i^{max} - X_i^{min}} \quad (3)$$

$$Y_i = 1 - \frac{X_i - X_i^{min}}{X_i^{max} - X_i^{min}} \quad (4)$$

where X_i – non-normalized value of the indicator *i*; X_i^{min} – minimum value of the indicator *i*; X_i^{max}– maximum value of the indicator *i*; Y_i – normalized value of the indicator *i*.

The weight of each coefficient as a result of normalization is expressed in tenths and hundredths of a unit, except for the minimum and maximum values (0 and 1.0 points, respectively).

All normalized coefficients are summed and the integrated coefficient of anthropogenic pressure (K_{an}) is determined (formula 5):

$$К_{an} = \sum_i^9 У_n \quad (5)$$

where K_{an} – integrated coefficient of anthropogenic pressure on the river basin, $У_n$ – normalized values of the corresponding coefficients.

An important stage of the study is to determine the integrated indicator of water resources assessment, which is carried out through a number of procedures. At the first stage, the normalization of quantitative indicators of water resources (water supply and water use) and indicators that determine their quality (stability of surface waters, WPI, and anthropogenic pressure). Integrated assessment of water resources of the region is calculated as the sum of normalized values of indicators according to formula 6:

$$О_{w.r.} = \sum_{i}^{8} У_n \quad (6)$$

integrated assessment of water resources, $У_n$ – normalized values of indicators (direct effect: $У_1$ – stability of surface waters of the basin, $У_2$ – water supply of total runoff, $У_3$ – water supply of local runoff, $У_4$ – water supply of groundwater; inverse effect: $У_5$ – drainage in the surface water objects, $У_6$ – drainage of polluted return waters, $У_7$ – index of water pollution, $У_8$ – integrated coefficient of anthropogenic pressure on the river basin.

At the final stage of the study, the levels of comprehensive assessment of water resources are established. Possible values of the integrated indicator of such an assessment according to the proposed methodology are in the range from 0 to 8. Within this range, the following assessment levels: low (<2.0), average (2.01-4.0), above average (4, 01-6.0) and high (6.01-8.0) have been determined.

THE RESEARCH RESULTS AND DISCUSSIONS

Water resources of Sumy region include surface (rivers, lakes, reservoirs, ponds, swamps) and ground waters. The main share in the structure of water resources of the region falls on rivers. As of January 1, 2020, 1,543 rivers with a total length of 8,020 km flow through the region. The only large river that is part of the hydrographic network of Sumy region is Desna. In addition, there are 6 medium rivers (Seim, Kleven, Sula, Psel, Khorol, Vorskla) and 1536 small rivers and streams. The most flooded river in Sumy region (except the Desna) is the Seim with an average long-term runoff of 3.15 km^3, an average total surface runoff in the region is 5.79 km^3. A significant number of watercourses in the region is transit. First of all, these are such rivers as the Desna, the Seim, the Kleven, the Psel and the Vorskla and a large number of small rivers. Therefore, transit runoff accounts for 60 % and only 40 % for local runoff. There are 537 lakes in the region, with a total water volume of 25 million m^3 and a water surface area of 2,042 hectares. The number of reservoirs is relatively small, there are 42, with a total area of 4,366 hectares and a total volume of 94.57 million m^3. There are 2,192 ponds, with a total area of 11,386.6 hectares and a total water volume of 121.3 million m^3. Wetlands of Sumy region are quite uneven; the total area of bogs is 46.6 thousand hectares. According to rough estimates, about 1.35 km^3 of water is concentrated in the swamps, which is 25 % of the total surface runoff of the region and can be a promising, backup source of water resources [4]. The swampiest is the northern part of the region where the share of wetlands is about 4 %, with an average swamp of the region 1.4 %.

The assessment of water resources of Sumy region was carried out in the context of the basins of the main rivers of the region, namely: the Desna (without the Seim river basin), Seim, Sula, Vorskla and Psel. As the Desna river flows along the border of Sumy and Chernihiv regions for only 37 km, the indicators of the average annual perennial runoff of the Desna river were not taken into account in the calculations.

Assessment of quantitative indicators of water resources of Sumy region. Water supply. The maximum water supply indicators of the total runoff are set in the Seim basin (12.87 thousand m^3/person per year), which is quite logical, as the Seim is the deepest river in the region, the minimum – in the Psel river basin (2.4 thousand m^3/person per year), due to the significant population of the basin (Table 1). The maximum indicators of water supply by local runoff are set for the Desna river basin (3.1 thousand m^3/person per year), the minimum – for the Psel river basin (0.85 thousand m^3/person per year).

Table 1. Water supply of surface waters in terms of the basins of the main rivers of Sumy region

Basins of the main rivers	Volume of total long-term annual runoff (thousand m^3)	Population (as of 01.01.2020)	Water supply with total runoff (thousand m^3/person per year)	Local average annual runoff (thousand m^3)	Water supply by local runoff (thousand m^3/person per year)
Desna (without Seim)	500200	161298	3,1	500200	3,1
Seim	3267500	253741	12,87	618400	2,4
Sula	334000	125335	2,66	334000	2,66
Psel	987000	408616	2,4	347100	0,85
Vorskla	599000	117065	5,1	258600	2,2

In hydrogeological terms, the territory of the region is located within the Dnieper-Donetsk artesian basin, where almost half of all operational reserves of groundwater in Ukraine are concentrated. Indicators of drinking and technical groundwater reserves in Sumy region are considered to be one of the highest in Ukraine. The total predicted groundwater resources in the region are 1251.5 million m^3 per year, approved operational reserves – 210.8 million m^3 per year. Water supply of groundwater (artesian) per capita in the region is 0.177 thousand m^3 per year, the number of deposits – 25, the number of sites – 50, the exploration of predicted resources – 18 % [4]. Water supply of predicted groundwater resources on average per capita of the region is 1,174 thousand m^3 per year. The maximum is for the Sula river basin (2.55 thousand m^3/person per year), the minimum is for the Vorskla river basin (0.12 thousand m^3/person per year) (Table 2).

Table 2. Water supply of groundwater in terms of the basins of the main rivers of the Sumy region

Basins of the main rivers	Predicted resources thousand m^3/year	Population (as of 01.01.2020)	Groundwater water supply (thousand m^3/person per year)
Desna (without Seim)	261035	161298	1,6
Seim	218085	253741	0,85
Sula	320480	125335	2,55
Psel	319830	408616	0,78
Vorskla	132070	117065	0,12

Water use. Water consumption in the region is quite uneven. The maximum values (48.32 million m^3 per year) of water intake were recorded in the basin of the Psel river, which is explained by its flow through the regional center, where water consumption is many times higher than in other settlements due to the concentration of industrial facilities and larger population. The basins of the Seim and Sula rivers have significant indicators – 19.45 million m^3 and 10.22 million m^3, respectively. The minimum value of water intake and use is represented in the basin of the Vorskla river and is 4.441 million m^3 per year [4]. Since drainage directly depends on water consumption, both maximum and minimum data have a corresponding trend, namely the Psel river basin has the highest rates of drainage and discharge of polluted return water, and the Vorskla river basin – the lowest (Fig. 2).

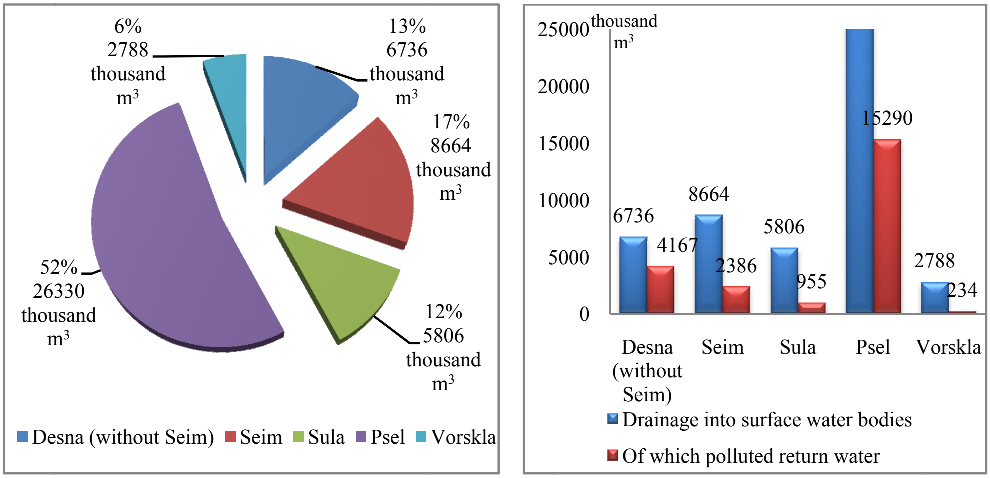

Fig. 2. Water drainage in terms of the basins of the main rivers of Sumy region

Assessment of water quality indicators of the Sumy region.

Stability of surface waters of the region. To establish the stability of the surface waters of Sumy region, 23 rivers were selected, which, in our opinion, are representative for this study. The initial information within the main river basins of the region is accepted according to the data of the Regional Office of Water Resources in Sumy Region. Having analyzed the information on the water temperature, color and average long-term water flow on selected rivers, we found that the average value of average long-term water flow for rivers in the region was 16.8 m^3/s. The stability of surface waters of the region was calculated with the help of the above methodology. The obtained results allow to distinguish the levels of surface water potential of the Sumy region (corresponding to the levels of surface water stability on the map of Ukraine [12]). The maximum values of surface water stability index were obtained for the Desna river and the Seim river – 3.342 and 2.008, respectively, which are identified as “very high level” of stability. The “high level” is typical for the Psel and Vorskla rivers – 0.582 and 0.351, respectively. The “average level” of surface water stability corresponds to the Sula river and the Kleven river – 0.199 and 0.116, respectively. The rivers Khorol, Romen, Vyr and Ivotka with the indicators – 0.055, 0.057, 0.075 and 0.061, respectively, belong to the “low level” of stability potential. Most of the studied small rivers in the region are characterized by a “very low” stability potential with an integrated value of less than 0.05. In general, large and medium-sized rivers in the region are characterized by very high, high and average levels of stability, and small rivers – by low and very low, ranging from 0.019 (for small rivers of the Psel basin) to 0.047 (for small rivers of the Sula basin).

In terms of the basins of the main rivers of the region, the situation is as follows: the maximum indicators of surface water stability are typical for the rivers of the Desna basin (0.867 average) and the Seim basin (0.45), the minimum – for the rivers of the Psel basin (0.091) [5, 6] (table 3).

Table 3. Stability of surface waters of the Sumy region

Basins of the main rivers	River	Dates of transition t of water through +16 °C	a	Chromaticity of water, deg.	J	Q, m³/s	h	B	W
Desna (without Seim)	Desna	29.05-25.09	114	24	1	180	10,7	3,342	0,867
	Znobivka	01.06-30.08	91	51,5	0,9	2,94	0,18	0,04	
	Ivotka	01.06-30.08	91	33,6	0,9	4,6	0,27	0,061	
	Shostka	28.05-20.09	116	37,6	0,9	1,4	0,08	0,023	
Seim	Seim	27.05-22.09	119	24,4	1	103,5	6,16	2,008	0,45
	Kleven	07.06-25.08	80	28,2	1	9.8	0,53	0,116	
	Yezuch	25.05-25.09	123	34,1	0,9	2,3	0,14	0,042	
	Vyr	10.05-20.09	133	38	0,9	3,9	0,23	0,075	
	Chasha	30.05-15.09	108	35	0,9	0,44	0,03	0,008	
Sula	Sula	25.05-30.09	128	34,9	0,9	10,6	0,63	0,199	0,097
	Tern	30.05-27.09	121	33,6	0,9	2,02	0,12	0,036	
	Romen	25.05-30.09	128	32,1	0,9	3,02	0,18	0,057	
Psel	Psel	20.05-15.09	118	27,7	1	30,2	1,80	0,582	0,091
	Khorol	05.05-25.09	143	29,7	1	1,48	0,09	0,055	
	Sumka	18.05-10.09	115	40	0,9	1,16	0,07	0,02	
	Vilshanka	30.05-15.09	108	30,7	0,9	0,48	0,03	0,008	
	Syrovatka	18.05-15.09	120	48	0,9	1,8	0,11	0,033	
	Bezdryk	30.04-01.10	155	25,5	1	0,23	0,01	0,004	
	Hrun	18.05-15.09	120	27,9	1	1,67	0,10	0,033	
	Rybytsa	18.05-15.09	120	30,5	0,9	2,9	0,05	0,013	
Vorskla	Vorskla	20.05-23.09	126	34,7	0,9	19	1,13	0,351	0,144
	Vorsklytsia	25.05-20.09	118	30,5	0,9	2,9	0,17	0,049	
	Boromlia	18.05-23.09	128	49	0,9	1,7	0,10	0,032	

Assessment of the quality of water resources by WPI. According to the results of the calculation of WPI for the period (1999-2015) [7], the areas of water pollution around large settlements were obtained: Sumy, Okhtyrka, Konotop, and Seredyna-Buda. These areas are characterized by the most polluted river water and belong to the IV class of water quality [2]. The rivers of the Psel basin (mainly), as well as the rivers Boromlia, Vyr, Chasha, Shostka, Ivotka, Znobivka are characterized by moderately polluted waters of the III class quality. The river waters of the Seim, Kleven, Ret and the Sula and Khorol basins within the region belong to the II class of water quality, which is characterized as "clean". In 2018, the Regional Office of Water Resources in Sumy Region calculated the surface water resources of the region. According to it, the maximum indicators of WPI – 4.29 and 3.24 were recorded for the river Bobryk (basin of the river Desna), the waters of which belong to the V class of water quality and are characterized as "dirty" (Table 4). The waters of the Psel river (the village Stare Selo, below the city of Sumy) with an WPI of 2.73 belong to the IV class – "polluted". All other river waters of Sumy region belong to the III class of water quality – "moderately polluted". Comparing the data of the river water quality assessment of the region on the basis of WPI in 2018 and for the period 1999-2015, we can conclude that in general the situation in the region has deteriorated. Thus, the waters of the Sula and Khorol rivers from the II class "clean", passed to the III "moderately polluted", the waters of the Bobryk river from the III class "moderately polluted", passed to the IV "polluted" and V "dirty". Relative improvement of water quality is observed only on the river Yezuch, which from the IV class ("polluted"), passed to the III class ("moderately polluted") [3]. In terms of the basins of the main rivers of the region, the maximum average values of WPI are typical for the basins of the Desna river – 2.4 and the Psel river – 2.2 (in the first case the impact of non-functioning sewage treatment plants in Seredyna-Buda, in the second – Communal Enterprise "Miskvodokanal" Sumy), and the minimum – in the basin of the Vorskla river – 1.55.

Table 4. Assessment of water quality of surface water bodies of Sumy region by WPI

Basins of the main rivers	River	Range	WPI	Water quality class	Average value
Desna (without Seim)	Ivotka	above the v. Yampil	1,86	3	2,4
	Ivotka	below the v. Yampil	1,74	3	
	Shostka	v. Hamaliivka	1,68	3	
	Bobryk	above the v. Seredyna-Buda	4,29	5	
	Bobryk	below the v. Seredyna-Buda	3,24	4	
	Znobivka	v. Znob-Trubchevska	1,96	3	
	Znobivka	v. Novovasylivka	2,22	3	
Seim	Seim	v. Pisky	1,48	3	1,85
	Seim	v. Chumakovo	1,5	3	
	Seim	v. Melnia	2,20	3	
	Kleven	v. Zrutsne	1,70	3	
	Yezuch	v. Viazove	2,12	3	
	Yezuch	v. Sarnavshchyna	2,13	3	
Sula	Sula	t. Romny	2,02	3	1,96
	Sula	v. Cheberiaky	1,90	3	
Psel	Psel	v. Myropillia	1,95	3	2,2
	Psel	v. Velyka Chernechchyna	1,94	3	
	Psel	v. Stare Selo	2,73	4	
	Psel	v. Byshkin	2,14	3	
	Psel	v. Kamiane	2,04	3	
	Khorol	v. Panasivka	2,36	3	
	Khorol	v. Luchky	1,91	3	
Vorskla	Vorskla	v. Velyka Pysarivka	1,45	3	1,55
	Vorskla	v. Klymentove	1,67	3	
	Vorsklytsia	v. Pozhnia	1,53	3	

Assessment of anthropogenic pressure on the basins of main rivers of the region. According to our previous study, to assess the anthropogenic pressure on the basins of small rivers of the region [2], it was found that moderate anthropogenic pressure was experienced by 8 river basins, Kan is from 1.19 to 1.99, so their condition can be defined as relatively natural, it is 16.7 % of the area of the region within the Znob-Shostka-Ivotka landscape-hydrological district of Novhorod-Siverske Polissia [10]. Almost 3/4 of territory of the region (72.5 %) is under medium (Kan 2.17-2.99) (27 basins) and high (Kan 3.06-3.96) (26 basins) anthropogenic pressure and form the area with anthropogenic and anthropogenic-altered state of the basins. 5 basins (10.8 %) are characterized by a very high level of anthropogenic pressure (Kan 4.18-4.5), which corresponds to the crisis-anthropogenic state of the basins.

The Desna river basin within the region is characterized mainly by low indicators of the Kan of small river basins – from 1.19 (Znobivka river) to 1.99 (Svyha river). Only the Shostka river basin is under a high level of anthropogenic pressure, which is 3.67 due to high rates of settlement coefficients, plowing of the coastal protection zone and low forest cover of the basin. For the Seim river basin, ambiguous Kan values from 1.53 (Seim river) to 4.5 (Kukolka river) have been recorded, but the vast majority of small river basins are subject to moderate and medium anthropogenic pressure. In the Psel river basin, most small river basins are under medium anthropogenic pressure (Kan ranges from 2.17 to 2.99), and the basins of right-bank tributaries such as Oleshnia, Hrun, Khorol (within the region) are under high anthropogenic pressure (Kan – 3.14-4.27), and the basin of the Sumka river – very high (Kan – 4.27) due to the high level of almost all studied indicators. The basins of the Sula and Vorskla rivers do not differ in contrast to the Kan of the basins of small rivers within them. Most of them are subject to high anthropogenic pressure due to high rates of plowing of the basins, soil erosion, plowing of the coastal protection zone and low rates of forest cover of the basin. When generalizing the results obtained in terms of basins of the main rivers of the region, it was found that the basins of the Vorskla and Sula rivers were characterized by a high level of anthropogenic pressure with Kan 3.29 and 3.26, respectively, basins of the Desna, Seim and Psel rivers – by an average level with Kan 2.8, 3.01, 3.05, respectively.

Integrated assessment of water resources in terms of the basins of the main rivers of the region. As it has been already mentioned, the integrated assessment of water resources in the region is calculated by formula (6) as the sum of normalized values of quantitative indicators of water resources and indicators that determine their quality. The obtained indicator $O_{w.r.}$ ranges from 1.27 to 4.17 (Table 5).

Table 5. Assessment of water resources of Sumy region in terms of basins of the main rivers

Basins of the main rivers of Sumy region	W	y_1	Total water supply runoff, thousand m^3/person per year	y_2	Local water supply runoff, thousand m^3/person per year	y_3	Groundwater supply thousand m^3/ person per year	y_4	Drainage in the surface water bodies, thousand m^3	y_5	Drainage of polluted return waters, thousand m^3	y_6	WPI	y_7	Kan	y_8	$O_{w.r.}$
Desna (without Seim)	0,867	1	3,1	0,07	3,1	1	1,6	0,6	6736	0,2	4167	0,3	2,4	0	2,08	1	4,17
Seim	0,450	0,46	12,87	1	2,4	0,7	0,85	0,3	8664	0,3	2386	0,1	1,85	0,4	3,01	0,23	3,49
Sula	0,097	0,007	2,66	0,02	2,66	0,8	2,55	1	5806	0,1	955	0,05	1,96	0,5	3,26	0,03	2,57
Psel	0,091	0	2,4	0	0,85	0	0,78	0,27	26330	0	15290	0	2,2	0,8	3,05	0,2	1,27
Vorskla	0,144	0,068	5,1	0,3	2,2	0,6	0,12	0	2788	1	234	1	1,55	1	3,29	0	3,99

The maximum indicator of integrated assessment of water resources 4.17 (above average) is typical for the Desna river basin, which is primarily due to their high quantitative indicators within the region. This basin is characterized by high indicators of total water supply and local runoff and ranks second in the provision of predicted groundwater resources in the region. Regarding water quality, the resources of the Desna basin are characterized as one of the most polluted (Bobryk, Seredyna-Buda), which is due to non-functioning sewage treatment facilities and unsatisfactory work on water treatment of industrial and municipal enterprises within the basin (Shostka). Even the maximum value of the surface water stability coefficient in the region does not improve the situation.

The water resources of the Vorskla river basin within the region are characterized by an average value with an integrated water resources assessment index of 3.99, which is explained by high water quality indicators (insignificant value of WPI and one of the highest surface water stability indicators in the region), as well as low quantitative indicators of reverse action (minimum amount of water intake to use and meet the needs of the population and, as a consequence, insignificant drainage, with a smaller share of polluted return water). However, analyzing the quantitative indicators of water resources of the basin, it should be noted that they are not high and occupy one of the last positions in water supply within the region.

Water resources of the Seim river basin within the region are also characterized by an average value with an integrated assessment of water resources of 3.49, which is primarily due to high quantitative indicators of water resources (maximum water supply, maximum total runoff and predicted resources of groundwater). At the same time, the indicators of drainage into surface water bodies occupy the second position in the region, of which 28 % are polluted. All other data taken for calculation have average values.

Water resources of the Sula river basin within the region are characterized as "average", according to the selected levels, with an integrated indicator of water resources of 2.57, but such values are close to low. All the calculated indicators are relatively insignificant, only in terms of water supply with predicted groundwater resources, the basin ranks first in the region.

The minimum integrated assessment of water resources with an index of 1.27 was obtained for the Psel river basin and is characterized as "low". These values are obtained due to the minimum indicators of surface water stability, low total water supply and local runoff, due to the dense population of the basin, low water supply values, insignificant predicted groundwater resources and, conversely, maximum drainage and high values of WPI and Kan on the river basin.

CONCLUSION

The proposed methodology is an attempt of a comprehensive (combined) assessment of water resources on water quality indicators and quantitative characteristics of water resources based on the basin principle. The methodology is based on the study of water supply (specific indicators of the population's water resources per capita) and water use in quantitative terms; stability of surface waters, water pollution and anthropogenic pressure on river basins – in terms of water quality. This method of water resources assessment has been tested on the example of the basins of the main rivers of Sumy region. It is established that water resources of the Desna river basin within the Sumy region are characterized by a level "above average", and the water resources of the Psel river basin within the region are characterized by a "low" level of integrated assessment. The obtained results are explained by the uneven distribution of water resources, different population densities within the region, as well as the uneven deterioration of the quality characteristics of natural waters, which is the result of differentiated human economic activity.

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ECOLOGICAL AND ECONOMIC DEVELOPMENT OF THE KAMIANETS-PODILSKYI MUNICIPAL MISKTEPLOVODENERGIYA ENTERPRISE

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ABSTRACT

In this section, we described the study of drinking water in the region of town Kamianets-Podilskyi. On the example of the Muksha River and the Dniester River, for example, Belanovetsky, Smotrytsky, Mukshansky underground water intakes, we presented the reader with experimental data on drinking water. We used State Sanitary Norms and Rules to determine the quality of drinking water. On the example of the municipal enterprise of the town, we enlightened readers about innovative water projects in our region. These new projects are environmentally and economically efficient. We informed about the ecological project of the thermal power plant on pellets in our town. We illustrated the environmental project Program Demo Ukraine DH installation of individual heat points. The main research methods are theoretical and experimental. Theoretical methods are the analysis, comparison, generalization, synthesis of information of the database of ecological data on water, heat, energy in the town. Experimental methods are monitoring of water quality in the Muksha River, the Dniester River in its specific runoff. These are the villages of Humentsi, Kamyanka, Pryvorottya, and Slobidka Kulchyivetska etc. In general, the section of the monograph is devoted to education on environmental and economic hydro and thermal energy projects in our region.

Keywords: Ecological, Economical, Municipal enterprise, Drinking water, innovative environmental water projects.

INTRODUCTION

The main task of a municipal Miskteplovodenergiya enterprise to provide quality services of heat supply, hot and cold water supply and drainage to the residents of the town Kamianets-Podilskyi. The staff of the company has about a thousand employees who care about the quality of heat and water in the homes of local residents.

We describe the main objectives of the enterprise.

Thus, the municipal Miskteplovodenergiya enterprise provides the residents of the town Kamianets-Podilskyi with water supply, drainage and heat supply services around the clock.

In general, the town is supply with drinking water by 27 artesian wells of Belanovetsky, Smotrytsky, Mukshansky underground water intakes, and surface water as the Dniester River. The total length of water supply networks reaches almost 300 km. Drinking water is thoroughly purifying, and its quality monitoring around the clock by employees of the enterprise laboratory. The bacteriological department of drinking water quality control monitors ready solutions for active chlorine content on a monthly basis. The quality of water supplied by the municipal Miskteplovodenergiya enterprise meets all hygienic requirements for water quality of centralized domestic drinking water supply State sanitary rules 383-96: Drinking water. Hygienic requirements for water quality of centralized domestic and drinking water supply [3].

Totally, drainage from industrial facilities and local housing providing by twelve sewage-pumping stations, which pump water to treatment plants through networks with a length of 150 km. In the future, sewage is gradually disinfected and purified.

Our town supplying with heat and hot water by powerful heat sources, 21 boiler houses, 29 central heating points and quarter blocks, 32 individual heating points, 3 heating points of budget institutions, 6 pumping stations of heating networks.

Since 2014, the utility has been looking for an alternative to gas, introducing its replacement with solid fuels. Currently, there are six boiler houses in Kamianets-Podilskyi on pellets made of straw, wood and wood chips with a total capacity of 11.47 MW.

On the wold, during the period 2011-2016, the municipal Miskteplovodenergiya enterprise managed to implement a number of important measures and carry out significant work towards the implementation of projects for the reconstruction and modernization of equipment. Reconstruction of the water supply and sewerage system has significantly reduced the energy consumption of the Kamianets-Podilskyi water supply and sewerage system, and the only automated dispatching service in the Khmelnitsky region allows to monitor the operation of water pumping and sewerage stations, artesian wells and springs.

All, the installation of cogeneration units increased the energy independence of the company, which managed to create a named Single Energy Ring in our town. It is a system of its own cable networks to supply the company's facilities with electricity of its own production. Moreover, the problem of lack of recirculation lines and installation of heat meters at the enterprise was resolved by installing individual heating points in apartment buildings.

METHODS AND EXPERIMENTAL PROCEDURES

For this section, the methods and experimental procedure consist of a theoretical analysis of electronic resources of the site of a utility Miskteplovodenergiya; a theoretical generalization of materials obtained there, a theoretical comparison of experimental data in different periods. Experimental procedure in this section implementing as the use of materials for students writing term papers and qualification.

THE RESEARCH RESULTS AND DISCUSSIONS

In general, the supply of drinking water to the population of Ukraine complicating by the unsatisfactory condition of water bodies, namely water intake sources. The water of most of them classifying as contaminated due to chemical and bacterial contamination. The most acute ecological situation observing in the basins of the Dnieper, Seversky Donets, some tributaries of the Dniester, the Western Bug rivers, where the water classifying as very dirty. The main pollutants include petroleum products, ammonium and nitrite nitrogen, heavy metals and more.

By the way, despite the threatening state of drinking water sources, the need for quality water is constant. It establishing that in towers with centralized hot water supply water use per capita averages no more than 350 l / day. In towers without hot water supply, it`s 230 l / day with water supply from a street water intake it is 50 l / day. The residents of Kamianets-Podilskyi need the same amount of water in order to prepare food, clean the apartment, do the laundry, and fulfil all the necessary household needs.

Our town, as well as the southern part of Khmelnitsky region, in which it is located, supplying with water from the Dniester River. The water of the Dniester river water supply system makes more than 2/3 of weight from the general receipt. It consuming by the main multi-storey residential areas of the town. The rest, this is up to 30% of the total amount extracted from artesian wells of considerable depth and fed mainly to private homes located in the old buildings.

All, in order to provide residents with chemically and bacteriologically safe drinking water, it subjecting to periodic testing, according to existing legislation. Before supplying consumers with water taken from the Dniester River and prepared by special methods at water treatment facilities, they monitoring every hour. Water that does not meet the requirements of the standards is additionally purified and re-examined. Town water treatment plants can remove suspended solids from the water such as water clarification, destroy microorganisms contained in the water, it is water disinfection, reduce the total salt content in the water, it is desalination, remove certain types of salts.

Alas, before supplying to the main water supply system, the water chlorinating, which has a rather negative effect on its quality. In the context of the economic crisis, respectively, and the lack of funds for re-equipment, the transition to safer methods of disinfection, such as ozonation or irradiation in the ultraviolet range, is currently not considered. As a result, the water has a sharp specific smell and contains chlorine-containing compounds, the amount of which increases during rains and floods, due to the entry of a significant amount of organic compounds into the surface source. There is also a regular control at the places of drinking water consumption in different points of the branches of the municipal networks.

In general, sanitary and laboratory control over the efficiency of water chlorination doing out according to the plan, namely the schedule, sanitary and epidemiological stations through the determination of the number of Escherichia coli and the total number of bacteria in the most characteristic points of water collection. These are the closest to the pumping station, the most remote, the most elevated, and water columns. In the process of planned research and epidemiological indicators, specifically it is at least once a month, the efficiency of water treatment with chlorine checking and according to the method established by the administration of the enterprise that operates municipal water supply networks.

By the way, sources of water supply from artesian wells are less studied. The town's groundwater treatment schemes for domestic and drinking purposes include only decontamination facilities. When using high-hard groundwater or iron-containing groundwater, the schemes should include facilities to soften or reduce iron in the water, but they are not available in Kamianets-Podilskyi.

Of course, a number of analyses performed for the presence of above normal of the maximum permissible concentrations of drinking water components. For research, water taken from Bilanivsky, Mukshansky and Smotrytsky water intakes. Smell and taste in all three studies are absent, this means equal to 0 points at a temperature of 200°C. The colour of the water sample was less than 5 degrees with a permissible value of 20 degrees. The turbidity on the standard scale was less than 0.58 mg / dm3, the transparency of the water was more than 30 cm, which also corresponded to the normative values.

We considered in more detail all the indicators of the investigated water from Bilanivka water intake. We found that water meets the requirements of regulatory and technical documentation for all studied indicators, which required by State Sanitary Norms and Rules 2.2.4-171-10 and Law of Ukraine 2918-III and State Sanitary Rules 383-96 [1, 2, 3]. Taking into consideration these and other sources there is an exception, namely the hardness of water, which exceeded the permissible values by 2.25 mg / dm3. Another exception, namely the alkalinity of water, the level of which was 2.55 mg / dm3 higher than the norm. The amount of nitrates in the water exceeded the norm by 2.09 mg / dm3. Residents of the suburban district of the same name, mostly one-story buildings, consume water supplied from the Bilanivka water intake.

Next, water from Smotrytsya water intake is similar in its characteristics to the previously described sample. It also has a higher level of hardness and alkalinity than the norm, but to a lesser extent. Thus, hardness increased only by 0.6 mg / dm3, and alkalinity by 1.6 mg / dm3 exceeds the sanitary and hygienic norm. The water of the Smotrych Reservoir distributed to multi-storey buildings located along the Smotrych River.

In the third study, when the water taken from the Mukshansky water intake, no negative impurities found and all indicators met the requirements of regulatory and technical documentation.

All, the obtained results are only the first series of studies necessary to establish a complete description of the sources of drinking water supply in Kamianets-Podilskyi. They need repeated and clarified. At the time of sampling, only water from the Mukshansky well was completely satisfying the needs of users and was not harmful to health. In this state of drinking water supply, monitoring programs for groundwater sources expanded in order to identify possible negative impacts and then eliminate them.

Based on research, innovative drinking water treatment projects implemented a municipal Miskteplovodenergiya enterprise.

In addition, this utility is constantly working to implement modern technologies that reduce the cost of purchasing energy resources and is one of the active participants in the implementation of the Regional Program for Energy Efficiency of Khmelnitsky region.

Moreover, given the constant growth in the cost of energy resources, it is important to reduce the consumption and replacement of natural gas and direct funds to the Ukrainian economy. The company pays considerable attention to the implementation of priority tasks of state policy in the field of energy security of Ukraine.

We will describe some innovative projects of this enterprise for educational activity of society in aspects of sustainable development.

So, some innovative projects for the sustainable development of the utility have already successfully completed. There are such projects that function in the mode of development and improvement.

In general, the responsibilities of the municipal Miskteplovodenergiya enterprise include the uninterrupted provision of heating, water supply and sewerage, maintenance and repair of internal network networks to the population, budget organizations and other consumers in accordance with the tariffs approved by the Founder. Another responsibility of the municipal Miskteplovodenergiya enterprise is to comply with norms and requirements for environmental protection, rational use and reproduction of natural resources and environmental safety [4].

So only, some directions of activity of the municipal Miskteplovodenergiya enterprise are

- Production of thermal energy at thermal power plants and installations using non-traditional or renewable energy sources;
- Heat supply; combined heat and power generation; electricity production;
- Transportation of thermal energy by main and local as for as distribution, heating networks;
- Centralized water supply and drainage; supply of steam, hot water and air conditioning;
- Fence of water purification and supply;
- Construction of pipelines; transmission of electricity; distribution of electricity;

- Electricity trade; sewerage, drainage and wastewater treatment;
- Production of radiators and boilers of central heating;
- Production of steam boilers, except for central heating boilers;
- Installation of water supply networks, heating and air conditioning systems;
- Waste collection; other waste management activities; other professional, scientific and technical activities; advertising agencies; provision of other individual services;
- Activities to ensure the working capacity of power plants, including as installation, adjustment, repair and maintenance of electrical and thermal equipment, apparatus and means of protection;
- Activities to ensure the working capacity of boilers, including as installation, adjustment, repair and maintenance of heating equipment, apparatus and means of protection of boilers;
- Carrying out other activities that are not prohibiting by law [4].

All consider the process of wastewater treatment at sewage treatment plants in Kamianets-Podilskyi municipal Miskteplovodenergiya enterprise.

Of course, in the town of Kamianets-Podilskyi, where sewage treatment plants built in 1971, the pollution of the surface water body with sewage is an acute problem. After purification, these waters discharged into the Muksha River. This is the second category of pollution in terms of sanitary characteristics and according to the rules of water protection from pollution. This water used by the inhabitants of the villages located below the treatment facilities along the river, in technological and economic needs. The existing technological process of wastewater treatment due to the moral and physical obsolescence of equipment and imperfection of wastewater treatment methods is such that does not fully ensure compliance with organoleptic, general, sanitary, and toxicological indicators. At the present stage of development of science, much attention paid to the selection of effective safe reagents, their dosages, which can provide quality wastewater treatment. Therefore, improvement, rationalization, optimization of these treatment facilities in the conditions of steady increase in volumes of industrial discharges and municipal and household drains is actual and timely.

Therefore, the Kamianets-Podilskyi municipal Miskteplovodenergiya enterprise is located on the northeast outskirts of Kamianets-Podilskyi on the right bank of the Muksha River and consists of three parts. This is 1) a complex of biological wastewater treatment; 2) biological ponds as for as additional wastewater treatment before their discharge into the reservoir; 3) a complex of facilities for sludge treatment. Discharges of treated wastewater carried out in the Muksha River, which flows towards the Dniester River and flows into it at a distance of 18-20 km from the town of Kamianets-Podilskyi [5].

Onwards, when planning sewage treatment plants Kamianets-Podilskyi municipal Miskteplovodenergiya enterprise took into account the circumstances that played a crucial role in the early 70's of the twentieth century. Thus, a mechanical treatment method with complete biological treatment on aeration tanks and mixers adopted in the project for urban wastewater treatment. Calculations on the self-cleaning capacity of the Muksha River revealed the need for additional treatment of treated wastewater, for example, after aeration tanks, mixers, and secondary settling tanks, at biological ponds before discharging them into the Muksha River. The villages of Mala Slobidka (3.25 km), Tarasivka (7.25 km), and Slobidka (11.75 km) are located downstream of the Muksha River.

After the village of Slobidka, the Muksha River flows into the Dniester River. Above the sewage, treatment plants are the following villages as Slobidka Kulchyivetska, Kamyanka, Humentsi and Pryvorottya. By its nature, the Muksha River, according to the sanitary characteristics and rules of protection of waters from pollution, belongs to the second category. This category intended for bathing, sports and recreation of the population, as well as a reservoir within the settlements. The river used by residents of coastal villages for technological and economic needs.

By the way, wastewater treatment is as follows a main gravity collector with a diameter of 1200 mm supplies the town's wastewater to the site of the treatment plant and then on the territory of the site by gravity collectors with a diameter of 1000 mm enter the lattice building. Dams in them automated and included in work in case of their support before lattices.

Next, after the gratings, the water enters the sand traps, where mineral contaminants and large suspended particles carried by wastewater deposited. Next, the water enters the collection channel, which mounted on a water tray, which used to calculate the volume of wastewater.

Go on, from the water tray, water enters the preaerator, which simultaneously supplied with activated sludge and air. These components coagulate the suspended particles. They also coagulate pollution in wastewater. From the preaerators through the pipeline, water enters the distribution bowl of the primary settling tanks. From the latter, the water evenly distributed between the settling tanks.

Then, after the settling tanks, the settled water enters the averaging unit. This averaging mixes town wastewater and industrial effluents bypassing primary settling tanks.

Therefore, the averaging unit is a chamber with partitions to which compressed air supplied. All this contributes to good mixing of purified water. After the averaging, the wastewater enters the aeration tanks and mixers for biological treatment.

In general, dispersed supply of purified water through the longitudinal channel of aeration tanks and intensive supply of compressed air allows biological treatment in aeration tanks of wastewater with a concentration of contaminants of substances reaching 1000 g / m3. After aeration tanks, the concentration of biochemical oxygen demand in the effluent reaches 15 g / m3. Activated sludge formed in aeration tanks carried to secondary settling tanks, where it deposited.

Onwards, after the secondary settling tanks, the water enters the biological ponds, where it is further biological purified with bringing the biochemical oxygen consumption to 6.27 mg / l.

Then the purified water discharged into the river at high speed in the form of a rectangular tray with artificial roughness. To repay the high speed in the rapids, the latter ends with a water well, after which the speed is 1.74 m / sec. The treated wastewater discharged into the Muksha River, which flows in the direction of the Dniester River and flows into it at a distance of 18-20 km from the town of Kamianets-Podilskyi.

Therefore, the composition of wastewater contains various pollutants such as mineral, organic, inorganic, require removal from wastewater or reduce their number in accordance with the established limits.

These limits set based on maximum permissible concentrations of substances at the inlet and outlet of sewage treatment plants in accordance with the order. This order registered with the Ministry Justice Ukraine on January 15, 2018 under number 56/31508: On approval of the Rules, the amount of the fee charged for excessive discharges of wastewater into centralized drainage systems.

According to the established limits technological lines of treatment facilities work.

The rules for the protection of surface waters from sewage pollution set the conditions for the discharge of wastewater into reservoirs. These rules set water quality standards for reservoirs.

These reservoirs used for swimming, sports and recreation. There are also other reservoirs within the settlements. This is the river Muksha.

According to these rules, the content of suspended solids in the water of cultural and domestic water bodies should not increase by more than 0.75 mg / l after the discharge of wastewater. It is not allowing discharging sewage with the content of suspended solids into reservoirs. Prohibition of action in such a condition when the rate of water loss exceeds 0.4 mm / sec for running water.

All, the content of dissolved oxygen in the water of reservoirs should not be less than 4 mg / l after mixing with it wastewater.

The total oxygen demand should not exceed 6 mg / l at 20 ° C for water from cultural and domestic water bodies. The reaction of the pH of water in reservoirs should not be below 6.5 named weakly acidic and above 8.5 named alkaline after mixing it with wastewater.

Reservoirs must not contain mineral oils and other floating substances. These oils and substances can form films and stains on the surface. For toxic and radioactive substances, the maximum permissible concentrations of them in the reservoir at the places of release have been establishing.

Onwards, the rules regulate the intensity of smells and tastes, colour, norms of mineral composition, temperature, pathogens as well.

The composition and properties of water must meet these requirements 1 km upstream from the point of water use.

Let us go, studies show that it is extremely important to pay attention to the growth rates of pollutants in the surface waters of the Muksha River below the downstream treatment plants. Some companies make a significant contribution to this overall picture. Therefore, based on this, these companies need to take measures to eliminate such high levels of pollutants in wastewater.

The parameters of wastewater quality that need to be improved, i.e., reducing the content of these pollutants and bringing the relevant ingredients to acceptable standards in order to improve the environmental quality of surface waters in the Muksha River. To implement these tasks possible, reducing to 35-50% of existing indicators ingredients in wastewater due to additional dilution of water that reduce the level of the same indicators in the surface waters of the Muksha River in the area of wastewater discharges from treatment plants and downstream.

Thereby, during the period 2011-2020 in Kamianets-Podilskyi, we managed to implement a number of important measures and carry out significant work towards the implementation of projects for the reconstruction and modernization of equipment [6].

Taking into consideration these, an important project of the National Program of Energy Efficiency and Energy Independence of Ukraine in the town of Kamianets-Podilskyi was the construction of the newest thermal power plant with a capacity of 45 MW, which commissioned in July 2018. The station works with the combined production of thermal and electric energy by gas and solid fuel boilers. The thermal power plant is equipped with a unique turbine with an ORC module called the Organic Rankine Cycle, which is the organic Rankine cycle. The module has a capacity of 1.5 MW. The town Kamianets-Podilskyi became the first town in Ukraine, the fifth in the World and the third in Europe to use this modern method of thermal energy production.

Onwards, reconstruction of the water supply and sewerage system has significantly reduced the energy consumption of water supply and sewerage. In addition, the only automated dispatching service within the Khmelnitsky region has started operating at the enterprise. This dispatch service allows you to monitor the operation of water pumping and sewage stations, artesian wells and boilers online.

Nice then consider the current innovative environmental water projects at the enterprise Miskteploenergiya for the purpose of education.

1. Program Demo Ukraine DH installation of individual heat points (fig.1)

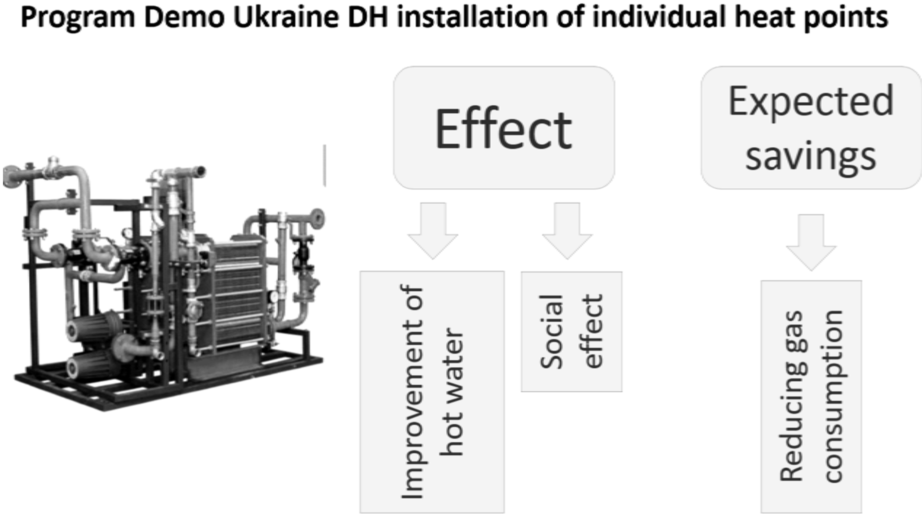

Fig 1. Individual heat points

2. Construction of a thermal power plant (fig.2)

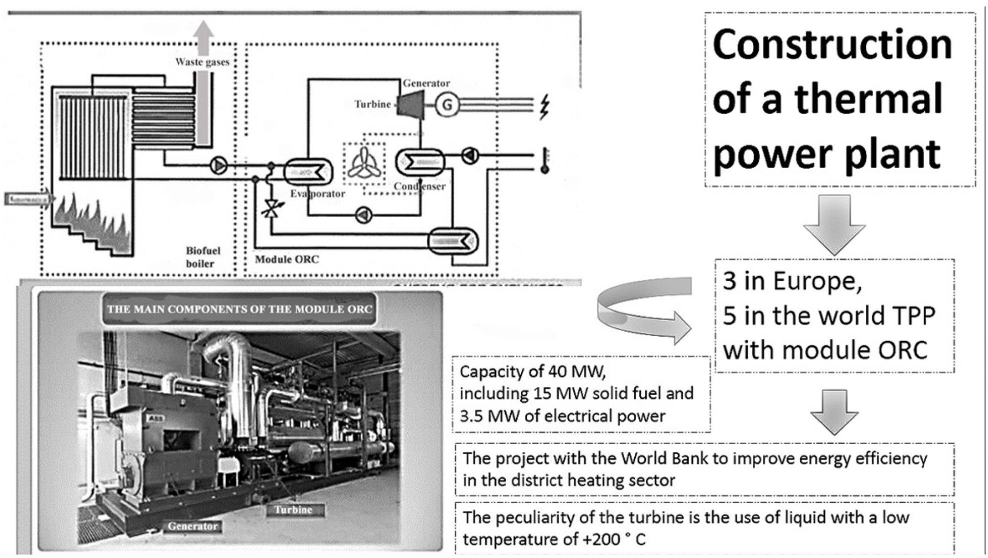

Fig 2. Construction of a thermal power plant

Taking into consideration these, of commissioning of a new thermal power plant, the production of electricity expected to be 7421 thousand KW / year with the use of solid fuel and replacement of natural gas by 8413 thousand m3 / year.

The expected economic effect of the new thermal power plant will be 37.5 million UAH.

Onwards, at the same time, it planned to reach the general level of natural gas substitution at the enterprise of 65%, and the substitution of natural gas for hot water supply in the summer will reach 100%.

The first step on the way to energy independence at the enterprise was the introduction of cogeneration units. These plants work with the combined production of heat and electricity from one type of fuel. In 2011-2012, four installations putting into operation at three boiler houses of the enterprise. For three years of their work 28192.6 thousand kW were supplied to the network electricity [6].

Let us go, installation of cogeneration units increased the energy independence of the enterprise and allowed to create a single energy ring in the town. It is a system of its own cable networks to supply the company's facilities with electricity of its own production. In addition, the reconstruction of energy-intensive equipment of the water supply and sewerage system allowed the company to replace the main equipment and reduce electricity costs.

Thereby, the problem of lack of recirculation lines and heat meters at the enterprise solved by installing individual heating points in apartment buildings. We managed to implement the project by obtaining grant funds under the Demo Ukraine DH program [6].

Today, the municipal Miskteplovodenergiya enterprise focused its maximum attention and efforts on the commissioning and operation of the newest thermal power plant. This TPP works with combined heat and power generation with gas and solid fuel boilers.

Two modern fuel boilers with a total capacity of 15 MW are located in the modern building of the TPP and two gas boilers of 12 MW each [6].

Onwards, the project, which the company implemented with a loan from the World Bank, deserves the title of exclusive. A turbine with an ORC Module called the Organic Rankine Cycle installed here. This is Rankin's organic cycle. The uniqueness of the module is the use of liquid with a temperature of 200 ° C. The town Kamianets-Podilskyi has become the fifth town in the World and the third in Europe to use this modern method of thermal energy production. Thus, the latest TPP significantly has been reduced gas consumption and will be replace it by 8413 thousand m3 per year [6].

Thereby, a special part of the work of the municipal Miskteplovodenergiya enterprise is the water supply of the town. Water supply provided by the Dniester River Water Supply System. In addition, there are nineteen artesian wells in the town and district. They are equipped with pumping stations and a complex of treatment facilities.

Let us go, the history of this direction of the enterprise's work dates back to 1912, when the construction of the Town Water Supply System began in Kamianets-Podilskyi. The Water Supply System was to provide drinking water to both the Old Town and the New Plan. Due to the beginning of the First World War, the work on laying networks stopped, but soon resumed with new plans.

Therefore, in 1930-1931, a highway built in the town, which crossed the Polish farms. In addition, the plans for 1932 include water supply of the central part of Kamianets-Podilskyi and construction of another artesian slit.

By the end of 1935, the people of Kamianets had the opportunity to receive water from the Town Water Supply.

Thus, on May 15, 1936, pumping station number 2 put into operation. In the same year, 1936, a sewerage project was prepared for the town. This project planned for the construction of two sections of silt sites, 3 km of the main collector and sewerage network.

Then, during the war of 1941-1944, the Kamianets-Podilskyi Town Water Supply System temporarily ceased its activities and resumed operation on March 26, 1944.

Then, on November 1, 1951, the Water Supply System renamed the Kamianets-Podilskyi Town Water Canal. Next, in 1954 the Smotrytsya water intake with a pumping station of the second rise built. Then, in 1957, the Bilanivsky wells launched.

Water soon found on the outskirts of the village of Muksha Kitaygorodskaya, near the Muksha River. There they began to build a water complex as well. The work lasted 2 years. In 1971, the complex began to operate.

The construction of a cement plant was a significant event for the development of water supply in the town Kamianets-Podilskyi. To provide the enterprise with technical water and the town with clean drinking water, in 1966 the development of the project for the construction of the Dniester Water Supply System began. Construction began in 1969 and in October 1973, technical water began supplied to the town's enterprises.

Taking into consideration these, in 2001, the Kamianets-Podilskyi production department of the Water Supply and Sewerage System reorganized into the Vodokanal Utility Company. Today it exists as a structural unit of the municipal Miskteplovodenergiya enterprise, and the town receives quality drinking water around the clock and almost without interruption.

Let us go, the history of the heat supply company, which eventually became a structural subdivision of the municipal Miskteploenergiya enterprise, began in 1970. By the decision of the executive committee of the town council, the Enterprise of United Boilers of the town organized then. During the first three months of operation, the company accepted 39 boiler houses.

Onwards, the municipal Miskteplovodenergiya enterprise has been repeatedly recognizing as the best enterprise of communal heat energy of Ukraine. According to various indicators of its activity, the company annually occupies a worthy place in the ranking of enterprises not only in Khmelnitsky region, but also in the state [6].

Since the coronavirus epidemic came to Ukraine, the municipal Miskteplovodenergiya enterprise has not hidden behind a fence of indifference. In addition, the municipal Miskteplovodenergiya enterprise was the first to offer its help to medical and social institutions of the town and region in disinfectants. The company has established the production of much larger amounts of sodium hypochlorite than it has needs for technology and helps with it hospitals, perinatal centres, nursing homes, utilities, military units [6].

As the European Centre for Disease Prevention and Control recommends using a solution of 0.1% sodium hypochlorite to disinfect surfaces, medical institutions use it to disinfect water and to prepare a disinfectant solution. Hypochlorite provides a high quality and powerful disinfecting effect. Due to a certain concentration of active chlorine, which destroys all pathogenic microorganisms and viruses. In this case, unlike liquid chlorine, sodium hypochlorite does not affect the organoleptic characteristics of water.

Sodium hypochlorite the municipal Miskteplovodenergiya enterprise produces by electrolysis of common salt at the production facilities of the Dniester Water Supply.

Since the beginning of the 2020 pandemic, the company has produced and sold at cost more than 30 thousand litres of sodium hypochlorite. In addition, a barrel of disinfectant solution is constantly standing at the checkpoint so that people can pick it up at home [6].

In general, the municipal Miskteplovodenergiya enterprise will continue to do everything possible for the epidemic safety of the population of our town.

CONCLUSION

Water in human life is the main need for its existence. We are aquatic creatures that live on land and cannot live without water. This is the paradox of our imperfect existence on planet Earth. It is for such urgent reasons that we should take maximum care of the purity of the water.

In our region, in particular in the town of Kamianets-Podilskyi, the municipal Miskteploenergiya enterprise engaged in such a responsible process. In the modern period, this company is developing ecologically and economically in the direction of European landmarks. In this section of the monograph, we have described the analysis of drinking water quality in our region and town from the Muksha River and the Dniester River. The utility company implements modern European projects for environmental friendliness, in particular water resources.

Today in Ukraine, the quality of drinking water and providing the population of the whole country with water remains a global problem. Standardization of drinking water quality in Ukraine is very different from the standardization of drinking water quality in EU countries. In Ukraine, many additional criteria for water rationing taken into account. Among which are the content of heavy metals, toxic substances, radiation substances. In the EU, such criteria for water quality not provided. It is for such reasons that we cannot fully assess the quality of water in Ukraine according to EU standards. The solution of the described problem realized through introduction of uniform standardization of quality of drinking water in Ukraine and the EU countries. Nevertheless, outdated water pipes do not allow selling high-quality clean water to the population of Ukraine. Therefore, the problem of drinking water quality in Ukraine is threefold, namely environmental, economic and social. Thus, the continuous sustainable development of Ukraine with an emphasis on innovative water resources projects will help solve the global problem of the state, our region in particular.

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I want to thank Kamianets-Podilskyi municipal Miskteploenergiya enterprise for using it as an example ecological and economic development within the water and energy resources.

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WATER SAFETY ON THE BASIS AGAINST-EROSION ORGANIZATION OF MELIORATIONED LAND

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ABSTRACT

The article analyzes the scientific principles of water safety in the organization of anti-erosion measures and erosion control of agricultural lands. It is noted that in Ukraine the problem of erosion danger is quite relevant given that 2/3 of arable land suffers from the development of erosion-hazardous processes. It is determined that the solution of this issue lies in the plane of the consolidated approach of water and land resources management on the positions of water safety, strategic planning of anti-erosion organization of the territory with the use of organizational, agrotechnical, phytomeliorative, hydrotechnical and other measures. Attention is focused on the sequence of implementation of a set of anti-erosion measures: field survey of the territory by route survey of the territory and remote sensing, processing of results and selection of contours of washed soils, soil erosion mapping, implementation in nature (on the ground). It is indicated that special attention is paid to the formation of ecological and technological groups of lands for placement and ordering of crop rotations, design of a set of anti-erosion measures, identification of areas that require continuous afforestation and laying and backfilling of ravines. It is noted that anti-erosion reclamation is focused on measures performed within the ravine-beam system to obtain the maximum economic effect. It is emphasized that zonal complexes of complementary agrotechnical, forest reclamation, hydrotechnical and organizational-mass measures are being developed to combat soil erosion.

Keywords: water safety, anti-erosion organization of agricultural lands, hydrotechnical reclamation, water and land resources management, ecological and technological groups of lands

INTRODUCTION

Water supply of the regions is an urgent problem of Ukraine. According to the National Academy of Agrarian Sciences more than 80% (about 30 million hectares) of arable land is deficient in moisture and suffers from significant water problems and requires reclamation measures. Insufficient level of soil moisture poses huge risks to agricultural production, because

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the lack of soil moisture automatically means a lack of harvest. The last five years have been marked by low water content, which has led to the shallowing of most watercourses in Ukraine.

According to research institutions, more than 10,000 small rivers have disappeared from the map of Ukraine over the past 20 years. It is established that "water threats" arise due to deteriorating conditions of formation or limited water resources. Urgent questions: How to save water resources? What changes in water and land management are needed for this?

It is clear that the solution to this problem is possible in the positions of water security, taking into account the consolidated approach to the formation of strategic planning at the junction of water and land resources management, the agricultural sector of the economy. The complexity of solving this problem is burdened by climatic factors and changes in the amount of water resources in modern conditions. Over the past ten years, temperatures in Ukraine have risen much faster in the face of intense climate change. What are the consequences of climate change? In addition, the amount of precipitation either remains unchanged or decreases, and the level of evaporation increases. Today, more than 80% of arable land (about 30 million ha) have a shortage of moisture and automatically determine a high risk for agricultural production, as lack of moisture means a lack of harvest. In 2020, droughts were observed throughout Ukraine, even in areas belonging to wetlands, and this poses a threat to agribusiness.

Due to the presence of a granite crystal shield on the territory of Ukraine there is no groundwater, there are no underground aquifers in several regions from northwest to southeast. The specifics of water use show that the country's surface water resources are used for 70% of total water use, and groundwater - for 30%. We have three large explored underground basins - Volyn-Podilsky, Dnieper-Donetsk (Chernihiv, part of Kyiv, Poltava, Sumy, Kharkiv regions), Black Sea (northern Crimea and the whole south of Ukraine).

The specifics of water resources distribution require a planned strategy of water consumption and water use, based on the components of the water balance, which is formed from the amount of precipitation in the catchment and resource, concentrated in storage sources (reservoirs and lakes), groundwater and groundwater. This is a resource that we can use, given the cost part of the balance sheet, which consists of water intake, filtration and evaporation losses.

Water safety of reclaimed lands is focused on optimizing a set of hydro-technical measures aimed at improving lands with unfavorable water regime (wet, over-drained, etc.), regulating water regime by creating special hydro-technical structures on sloping and other lands, improving water and air regime, protection them from the harmful effects of water (flooding, inundation, erosion, etc.).

METHODS AND EXPERIMENTAL PROCEDURES

The theoretical and methodological basis of the study were the works of leading scientists on the anti-erosion organization of agricultural land, the use of land resources on a sustainable basis. Research methods are used such as analysis and synthesis - for the theoretical generalization of modern research on the topic of substantiation of the components of the mechanism of agricultural land management on the basis of water safety of reclaimed lands; project management method - for the analysis of empirical data and identification of trends in the formation of strategies for soil erosion protection in the context of sustainable development; graphic - for visual results of scientific research; abstract-logical - for theoretical generalization and formation of conclusions.

THE RESEARCH RESULTS AND DISCUSSIONS

Ukraine, as an industrial and agricultural country, is a leading exporter of agricultural products and food, "the breadbasket of Europe." Achieving an appropriate level of water security is the ultimate goal of water policy based on sustainable development. The relevance of erosion processes of agricultural soils stays without a doubt, given that the state of water and land resources, water supply of the population and sectors of the economy remain a priority issues of national security.

Soil erosion has led to a significant economic loss of fertility (full or partial) on more than half of the planet's land (1.6-2.0 million km^2 with modern use of 1.4-1.6 million km^2) during the development of terrestrial civilization. About 50 to 70 thousand km^2 of land (more than 3% of the agriculture land used) are withdrawn from agricultural circulation due to the intensive development of erosion processes annually [1].

Eroded soils are distributed almost throughout Ukraine. Flushing of fertile upper horizons leads to soil depletion due to: reduction of humus and available minerals; deterioration of physical properties and quality of soils; violation of the water regime of soils. The accumulation of erosion products in the lower parts of the slopes, on the bottoms of the beams, in the take-out cone to the formation of strips of land rich in nutrients.

Water erosion is a process of destruction of soils, geological rocks by meltwater and rainwater. It is divided into lateral, deep, irrigation, drip, planar, underground and is accompanied by the development of ravines.

Modern erosion processes cover large areas within the elements of the hydrographic network [2]:

- basins is used for plowing and are characterized by the following indicators: depth of depressions 0.3-2 m; terrain slope 5-6°, width up to 4 m, area up to 50 ha;

- ravines - deeper formation, characterized by: depth of descent to 8-10 m; the slope of the terrain is 10-20°, the width of the contour interval at the top is 30-70 m, the width of the contour interval at the bottom is 10-20 m, the area is up to 500 ha;

- land (continental surface), which are defined within the following features: shores, as asymmetric formations with a depth of depressions to 15-20 m; the slope of the terrain is 20-25°, the width of the contour interval at the top is 200-700 m, the width of the contour interval at the bottom is 20-25 m, the area is up to 5000 ha;

- river valleys with an area of over 5,000 ha.

The nature of the terrain affects the intensity of erosion, namely the shape, steepness and length of slopes, the size and shape of watersheds. Erosion is intensified on convex, steep and long slopes. Narrow watersheds contribute to the formation of ravines, if they narrow and have an elongated shape in length.

Manifestation of water erosion is promoted by lack of a vegetative cover on arable soils in the spring at snow melting and in the period of autumn rains. In arable soils the structure is destroyed, the soil surface is compacted, the amount of organic matter is reduced due to the influence of agricultural machinery. The particle size distribution of soils and their structural state also affect the intensity of water erosion. Erosion is less active in structural soil enriched with organic matter. This is due to the fact that the surface runoff is converted into intrasoil. On the contrary, loams are especially easily washed away by water As a result of water erosion, there are changes not only in physical properties (deterioration of the structure, compaction of the arable layer), but also the humus horizon is reduced or destroyed. As a result, the reserves of humus, nitrogen, phosphorus, potassium and other nutrients are significantly reduced. The soil loses its fertility.

Wind erosion (deflation) occurs as a result of wind blowing of mineral particles from the soil, as well as the transfer, redeposition of fine weathering products.

The soil (and sometimes the whole arable layer) is depleted of humus and the main elements of plant nutrition.Its fertility is reduced as a result of blowing soil aggregates. Undesirable consequences of wind erosion are blowing out the soil from under the plants and exposing the roots, which leads to plant death.

The position of preservation and reproduction of soil fertility, rational use and protection of lands and water resources are defined at the legislative level. Table 1 presents and analyzes the regulations that determine the principles of legal regulation of public relations in the process of land reclamation.

Table 1. Normative legislation in the field of anti-erosion organization of reclaimed lands

Legal act	Substantive provisions
Law of Ukraine "On Land Protection"of June 19, 2003 № 962-IV [3]	The law defines the legal, economic and social bases of land protection in order to ensure their rational use, reproduction and increase soil fertility, other useful properties of land, preservation of ecological functions of soil cover and environmental protection.
Law of Ukraine "On Land Reclamation" of October 16, 2020, № 1389-XIV [4]	The law defines the principles of legal regulation of public relations arising in the process of land reclamation, use of reclaimed land and reclamation systems, and the powers of executive authorities and local governments in the field of land reclamation and aims to ensure environmental safety of reclamation systems and protect public interests.
Order No. 206/638 "On the Procedure for the Use of Reclaimed Land and Reclamation Funds" of November 2, 2006 [5]	The procedure establishes the basic requirements for physical and legal entities that use in their activities reclaimed land and reclamation funds, and regulates the relationship of local executive bodies of local governments, business entities, as well as organizations that exercise state control over the use of reclaimed lands and reclamation funds.

At the state level, the procedure for developing and approving state targeted and local land reclamation programs is determined by the Cabinet of Ministers of Ukraine. Development and approval of state targeted, interstate and local land reclamation programs is based on the need to preserve natural ecosystems, especially those of international importance, and on the basis of analysis of ecological and economic efficiency of land reclamation by individual species or complexes, and in the case of design creation of reclamation systems - forecasting the environmental consequences of their construction and operation.

The definition of priority areas in the selection and implementation of a certain type of land reclamation is carried out depending on the natural and climatic features, the ecological situation of the region and the subsequent agricultural use of reclaimed land.

Anti-erosion organization of the territory is considered as a set of scientifically substantiated and tested in practice reclamation measures (organizational, agrotechnical, phytomeliorative, hydrotechnical and other measures) carried out on the territory for the purpose of ecologically justified use of lands and prevention of soil erosion.

Anti-erosion organization of agricultural lands provides for [6]: allocation of land; development and implementation of technical reclamation to prevent water erosion; design and creation of an effective system of phytomeliorative plantings. Particular attention is paid to the formation of ecological and technological groups of lands for placement and management of crop rotations, designing a set of anti-erosion measures, identifying areas that require continuous afforestation and work on laying and backfilling ravines.

The basis of reclamation is anti-erosion measures, which are carried out within the ravine-beam system comprehensively in close connection with anti-erosion measures carried out in the catchment area. The reclamation complex includes afforestation, hydraulic structures and phytomelioration with the provision of conditions for obtaining the maximum anti-erosion, economic and recreational effect. The degree of damage to lands by ravines is determined depending on the indicators of dismemberment, ravines, density of ravines and intensity of ravines (Table 2).

Table 2. Grouping of beams and their systems by the degree of damage to ravines [7]

Degree lesions beam of ravines	Показники			
	Dissection, km/km^2	Distribution of ravines, ha/km^2	Density of ravines, pcs/km^2	The rate of ravines formation, km/km
Very weak	<0,15	<0,2	<1	<0,005
Weak	0,15-0,6	0,2-0,9	1-4	0,005-0,15
Average	0,6-2,2	0,9-3,5	4-17	0,15-0,55
Strong	2,2-9,0	3,5-14,0	17-67	0,55-1,25
Very strong	>9,0	>14,0	>67,0	>1,25

Surface runoff of melt and rainwater is determined on the basis of available data from each area of a particular type of agricultural use. Taking into account the erosion winds and the volume of runoff in these areas, a set of agrotechnical anti-erosion measures is performed. The delayed and final runoff is determined further, depending on the magnitude of which design water-regulating forest belts. If the drain does not stop after that, the excess runoff must be completely stopped or safely discharged by hydraulic anti-erosion measures.

The development of a set of anti-erosion measures begins with a field survey of the territory, processing of its results and soil erosion mapping.

The following works are carried out during soil erosion mapping [8]:

- collection of information on land use and agricultural properties of soils;

- survey of the territory along the general route;

- selection of contours of washed soils and their complexes on the materials of remote sensing in the period before field work;

- preliminary determination of the degree of soil erosion based on the results of laying sections (excavations) in the field;

- sampling of soil for further determination of quantitative indicators;

- final in-house clarification of the contours of washed soils and their complexes on the basis of laboratory tests;

- creation of soil-erosion map;

- performance of field and cartographic works.

In Ukraine, the hydrographic fund includes a reclamation strip, which varies with a width of 12.5-21 m in order to accommodate beam forest belts, runoff sprays, drainage and water retention shafts. The reclamation strip of this size occupies from 2.4 to 4% depending on the degree of damage to the ravines, on average 3.3% of the catchment area.

Reclamation and economic measures on ravine-beam systems include the following works [9]:

- leveling the surface in areas with beams and ravines, leveling hilly landslides, small ravines with slopes up to 1.5–2 m deep and their siltation;
- leveling of ravines with construction of hydraulic structures that prevent new erosion (trays, high-speed currents, mine spills, falls, etc.);
- devices of runoff sprays and anti-erosion hydratechnical structures (water retention and drainage shafts, ditches, dams-jumpers, bottom dams and semi-dams, etc.);
- backfilling of slopes in ravines and their preparation for afforestation;
- creation of beam (coastal) forest belts and plantings on the dumped slopes of ravines;
- cultivation of coastal and bottom plantings on the hydrographic network, siltation of flat shores and bottom areas of beams;
- construction of reservoirs, road network and organization of recreational zones.

The sequence of work on the ravine-beam system roughly corresponds to the order of this list. Anti-erosion reclamation begins in the spring with the leveling of pits and small ravines (up to 2–3 m deep) set aside for forest belts, as well as the banks of beams with a steepness of up to 12°.

The next stage is the alignment of the slopes of ravines to a depth of 5 m, the construction of drainage and retaining shafts, dams and other hydraulic structures. At the beginning of summer, meadow reclamation works are carried out on the shores and wide bottom areas of the beams before heavy rains, and forest reclamation works are carried out in the summer-autumn period.

Strait-beam systems are distinguished depending on the intensity of modern erosion processes, the degree of erosion and development of soils, as well as the steepness of banks and slopes. They were divided into ten categories with adaptation to complex reclamation development [10]:

- ravine and girder land plots with a slope of up to 8º;

- slopes up to 12^0, pits and small ravines up to 2 m deep are found. In some parts of the slopes landslide processes develop;

- slopes up to 20º, there are ravines and small ravines;

- slopes of beams with a steepness of 20-35 про with ravines and small ravines up to 2 m;

- short sections of slopes of beams with a slope up to 25 до, inter-tier parts of slopes adjacent to the edge of the hydrological network with an area of up to 0.5 ha, which are not used in agriculture;

- wide bottom sections of beams with a stable or weakly pronounced watercourse;

- bottom sections of beams with a wandering channel of a watercourse and the expressed relief;

- slopes of ravines in the stage of stable equilibrium with a steepness of 35-40º;

- operating ravines with an undeveloped equilibrium profile;

- bottom sections of ravines with undeveloped equilibrium profile, as well cone of the take-out ravine.

After reclamation, ravine-beam lands are used under industrial forests, orchards and vineyards, fodder lands for domestic and wild animals, under plantations for cultivation of technical and medicinal crops, under ponds and reservoirs, as well as as recreational zones.

Various anti-erosion measures are used to stop the formation of ravines, erosion and landslides on the banks of rivers, reservoirs, artificial canals and hydraulic structures. ***Forest anti-erosion reclamation.*** The location of forest anti-erosion plantations is due to relief and erosion formations. Forest belts that regulate water or absorb wastewater, intercept sloping water from above, transfer surface runoff into the underground and protect the steep slope from being washed away. Located on arable slopes, such strips also protect the field.

Water-regulating forest belts up to 15 m wide are designed mainly on convex or straight slopes. They are placed strictly across the slope at the transition from a gentle slope to a steeper one. It is necessary that the flowing scattered streams of water enter the forest belt at right angles, otherwise in the presence of plowing water accumulation is inevitable, which can lead to the formation of ravines. To strengthen the ability of the strips to collect water, harrowing is carried out between rows and a shaft is built along the lower edge of the forest belt by double-passing the plow and forming ditches with a heel height of 0.5–0.6 m).

Shafts are arranged to retain water at the intersection of forest belts with beams. The distance between the water control strips on the slopes up to 4° should not exceed [11]:

- on gray forest soils and podzolic chernozems - 350 m,

- on leached, typical, ordinary and southern chernozems - 400 m,

- on dark chestnut soils - 300 m.

The design of water-regulating strips is openwork. The 12.5–21 m wide riparian and coastal forest belts are in the form of rectilinear segments for ease of tillage. They are built along beams and ravines. The construction of such strips is dense, the type of planting is woody-shrubby. The distance between the rows is 2.5-3.0 m, in a row - 0.5 m.

In the steppe and forest-steppe zones of Ukraine, pedunculate oak (lat. *Quércus róbur*) is planted in the beams of forest belts, and in the forest zone - scots pine (lat. *Pínus sylvéstris*) and siberian larch (*Larix sibirica* Ledeb.). Maple and field maples should not be planted because they do not grow well on washed soils. Group plantings of willows are created at the rate of about 20 plants per site, arrays are formed with a landmark of 400-500 pieces/1 ha.

Continuous and solitary plantings on ravine slopes, steep slopes, as well as on the bottom and cones of ravines are used to prevent soil erosion and improve the landscape. Root shrubs and small trees (cherry and steppe, thorns, sea buckthorn, white acacia) should be planted near the beams, forming strip plantings. Birch, poplar, aspen gives abundant roots. Thus, water safety on the basis of phytomelioration of eroded lands must be ensured on the basis of optimizing the impact of phytomeliorant on the area occupied by it and the environment.

Meadow-reclamation measures. The least eroded ravine-beam lands are allocated for meadow-reclamation measures, including slope and bottom areas. Good grass cover on some slopes can be restored naturally after the cessation of cattle grazing. Eroded areas are subjected to radical alkalinization, depending on the quality of the grass, taking into account local conditions.

Perennial grasses are the main ameliorant for the accelerated structuring of heavily washed slopes, under their influence erosion processes stop and solid sediments brought by water are deposited. Grasses grown in beams and large ravines increase roughness, reduce the speed of water flow, strengthen the soil by roots and prevent erosion. Grasses prevent erosion of shores, strengthen slopes on a hydrographic network. Turfing of the territory is carried out to increase the stability of hydraulic structures. Shores and slopes of beams, the small hilly shifts which are weakly exposed to washing away, sow

perennial herbs. Cultural pastures with normalized cattle grazing are sometimes placed here. Continuous soil preparation on the banks up to 30 m wide or strips 10-20 m wide is carried out for sowing grass.

Seeds are sown with grain and grass drills with fertilizers. Then they are rolled, milled to improve natural grasslands. The range of grasses and technology of their application is chosen at phytomelioration of spring-beam lands.

Grass mixtures with the content of field fire, goose foxglove and other grasses are used at the foot of steep eroded shores and slopes of ravines for fastening loose talus. The grasses are resistant to siltation and overwetting, which are sown in the cones of removal: kostrytsay luchna (lat. *Festuca pratensis* L.), vivsyanytsya luchna (lat. *Lolium pratense*, Huds.), rayhras pasovyshchnyy (lat. *Lolium perenne* L.), lyadvenets′ rohatyy (lat. *Lótus corniculátus*), konyushyna povzucha (lat.*Trifolium repens*).

The method of accelerated sowing of grasses is recommended for the northern forest-steppe areas, which involves sowing perennial lupine. It is grown in pure crops and in combination with other herbs. Lupines are sown simultaneously with the consolidation of ravines by hydraulic structures. In the spring it is sown on the upper slope of the ravine, the sowing rate is 35-40 kg / ha. It is also used to prepare the land for the next planting.

Lupine is used as a preliminary crop with planting for 3-4 years in the process of preventing the growth of eroded areas on the slopes and banks of the beams. Lupine-grass grass mixes with root-rod and root plants apply to fixing of tops of ravines on hills and steep slopes.

Soil structure plays an important role in increasing erosion resistance. Recently, along with soil protection measures (timely tillage, sowing of perennial grasses, etc.), structuring polymers are used for soil structuring. They are especially effective on light soils.

On lands subject to water erosion, plowing is carried out with one elongated shelf, which forms rollers 16–20 cm high on the plowed field, on sloping lands plowing is also carried out with a 4-body plow, in which the first and third shelves are shortened. As a result of the passage of such a plow, two furrows and two rollers are formed, which increases the accumulation of moisture and reduces soil erosion. Step and combined step plowing can also be used. The essence of the step plowing is that the second and fourth buildings are plowed to the usual depth, and the first and third - 12-15 cm deeper. Shelves are removed for combined-step plowing from the first and third buildings. This tillage reduces the flow of stagnant water by 50-60 mm and reduces soil washing by 2-3 times.

Terracing of slopes is actively used among water safety measures in the anti-erosion organization of territories. This measure is an artificial transformation of the surface of the slopes into horizontally leveled or sloping stairs, which are similar to anti-erosion sites to stop soil erosion and use the slopes for crops and forest crops (fig. 1)

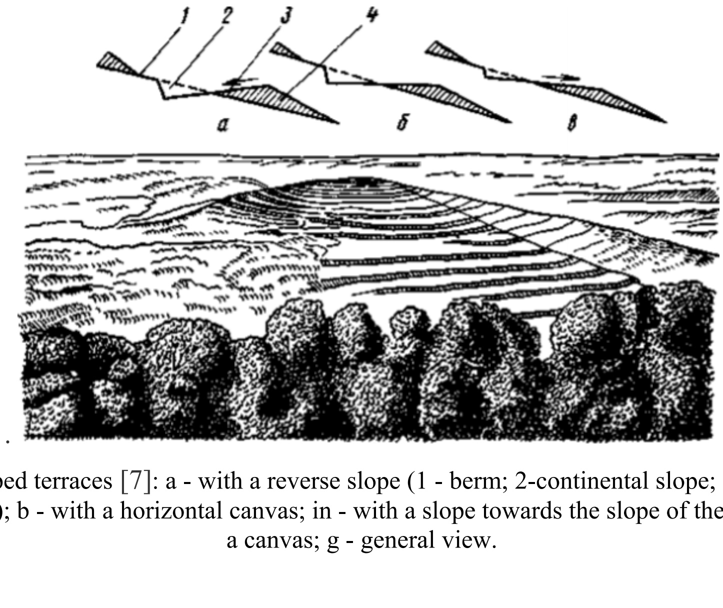

Fig. 1. Stepped terraces [7]: a - with a reverse slope (1 - berm; 2-continental slope; 3 - canvas; 4 - bulk slope); b - with a horizontal canvas; in - with a slope towards the slope of the terrain with a canvas; g - general view.

Hydraulic structures are built to prevent the formation and growth of ravines, which can be divided into simpler and more complex. Simple hydraulic structures include those made of local soils, namely sewage sprayers, drainage shafts, canals, and complex - highways, drops, cantilever dumps.

Fight against erosion and mudslides in the mountains. Soil erosion is more pronounced in the mountains than on low slopes. This phenomenon causes great damage to the national economy not only in the eroded territory, but also in the valleys. In mountainous conditions, an increased concentration of surface runoff is formed due to the strongly pronounced relief, possible steep landslides and mudflows.

Landslides occur due to waterlogging of soils on steep slopes, which are composed of successive layers of clay water-resistant and aquifers. Creep is enhanced if the layers are inclined towards the slope. Landslides cause great damage to the economy, because they can destroy large areas of rivers and seas. They often affect agricultural lands, industrial enterprises, roads and settlements.

Landslides are observed in the spring most often after thawing of the soil. In Ukraine, they are widespread on the right bank of the Dnieper, on the Black Sea coast, on the southern coast of Crimea, in the Carpathians. Upland and hunting drainage channels are arranged in order to avoid landslides. These hydraulic structures drain the landslide. Retaining walls (buttresses) are also built to prevent landslides; strengthening the slope by planting shrubs, grasses. If irrigation is carried out on a landslide, all measures are taken against the filtration of irrigation water into the subsoil layer, namely, anti-filtration channels are arranged, and minimum irrigation norms are set.

Mudflows occur in the mountains and foothills due to downpours, prolonged rains, melting glaciers and other causes. They are short mud-stone streams. The flow of mudflows reaches 2000 m3 s and more. Mudflows move at high speed, often dry channels, causing enormous destruction. The damage from mudslides reaches tens of millions of dollars. The fight against villages is a very difficult problem. It includes administrative, hydro-technical and reclamation measures.

Hydro-technical measures are built on the path of the mudflow and are a system of massive bulk gravity dams, as well as mudflows and reservoirs. The main of these measures is the construction of hydro-technical structures. Afforestation and preservation of all kinds of vegetation in the watershed is an effective and long-lasting anti-mud factor. However, afforestation in hazardous areas is very difficult due to the dry climate.

CONCLUSION

Water and environmental problems of regions in Ukraine and threats to the use of agricultural land are focused on the design of fields and work areas in difficult terrain. Eroded soils are distributed almost throughout Ukraine. Flushing of fertile upper horizons leads to soil impoverishment due to a decrease in the supply of humus and available minerals, deterioration of physical properties and water regime of soils, the formation of poorer and drier landscapes compared to non-eroded lands. Water safety of reclaimed lands is aimed at achieving the most rational ecological balance. Long-term prospects for agricultural development combine anti-erosion components and areas with varying degrees of human transformation. The integrity of the use of agricultural land is based on the basic principles and methods of soil protection from erosion, the scientific basis of land management in conditions of advanced soil erosion, complex plans of agricultural soil groups and relief, erosion of technological groups of lands, design of protective, water-regulating and anti-erosion.

Spatial organization of reclaimed lands is implemented on the basis of water safety, taking into account the prevention of deterioration of ecological and reclamation conditions of lands and technical condition of reclamation systems on the conditions of restoration or improvement of ecological situation and soil fertility. The set of anti-erosion measures is determined by a number of indicators: the presence, composition, location and diet of water sources, the balance of water supply and consumption, its physical properties and chemical composition, suitability for drinking and household needs.

The design of a set of anti-erosion measures and monitoring of their effectiveness is based on accurate information on soil erosion, soil erosion resistance and the current intensity of erosion or runoff processes. Based on this information, the composition and characteristics of anti-erosion measures determine which should be implemented within a particular farm, as well as adjust the already implemented measures. Further development of effective implementation of the state water policy in the field of land use is based on the improvement of the ecological substantiation of the agro-landscape anti-erosion organization of the territory.

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