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**CONDITIONS FOR DEVELOPMENT
AND CULTIVATION OF CYANOBACTERIA
FOR MULTI-PURPOSE APPLICATION
(LITERATURE REVIEW)**

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Abstract. This article contains current data on biology, ecology, and cyanobacteria taxonomi. The results of analysis of bibliographic sources on conditions for nutrition, development and reproduction of cyanobacteria, peculiarities of their life cycle, requirements for creating suitable conditions for their cultivation and methods for increasing their biomass production are discussed. An impact factor model on cyanobacteria development is considered and analyzed. Special attention is paid to analysis of information concerning optimal conditions for cyanobacteria cultivation, biomass separation and ways of biomass application for obtaining the target products.

Key words: cyanobacteria: morphology, systematics, biomass, nutrition, target product.

Introduction

The object of our studies is cyanobacteria – the most ancient group of living organisms, remnants of which were discovered in pre-cambrian stromatolites aged 2.7–3.2 billion years. Their cosmopolitism is caused by their almost unlimited adaptive capacities – wide range of environmental tolerance, high reactivity and resistance etc. Among them there are cryophiles (discovered in Antarctic ices at a temperature of -83°C) and thermophiles (live in hot springs at a temperature of $+90^{\circ}\text{C}$). The reason for such a universal tolerance is the polytropicity of cyanobacteria – the only organisms on the planet that are able to assimilate the following four

types of gas: CO_2 for photosynthesis, O_2 for breathing, H_2S for chemosynthesis, and N_2 for its fixation. Within the vegetation period (70 to 120 days), one cyanobacterium cell can produce up to 10^{20} daughter cells, i.e. one bacterium can generate 10^{20} such bacteria in this time interval. Such a high rate of reproduction causes their massive development – “bloom” of water. Cyanobacteria are the first primary producers of oxygen on Earth, that under influence of ultraviolet rays transforms into ozon; the letter allowed in due time living organism to get out of water on land. They are also the most efficient accumulative converters of solar energy, because the value of efficiency (η) of their photosynthesis energy conversion reaches 20 %; that 200 times exceeds the average value of photosynthesis efficiency (η) of terrestrial plants.

Because cyanobacteria are photosynthetic and aquatic (mainly plankton) microorganisms, they are also often called “blue-green algae” (BGA). Cyanobacteria can produce great amount of biologically active compounds with bactericidal, oncostatic, ultraviolet- and radioprotective and other qualities. For rapid increase of biomass of phototrophic organisms, the most prospective way is the using of CO_2 – product of man-made activity – in order to minimize its negative influence on the environment in general and on atmospheric and climatic processes in particular. It is reasonable to use selected biomass during «bloom» of artificial water bodies for production of target products, in particular, as feedstock for production of

energy carriers (biogas, bioethanol, biodiesel), organic mineral fertilizers, etc.

The purpose of our work is to provide critical analysis of literature sources of information on conditions for development and cultivation of cyanobacteria for using their biomass as feedstock for obtaining target products for different application (energy, fuel, chemical substances, etc).

1. Systematics of cyanobacteria

First attempts create a system of BGA were made in XIX century. (Agardh – 1824, Khtzing – 1843, 1849, Thuret – 1875). Further construction of system was continued by Kirchner (1900), and since 1914 considerable alteration of system begun, and whole range of new systems *Cyanophyta* was published (Elenkin – 1916, 1923, 1936, Bortsi – 1914, 1916, 1917, Heitler – 1925, 1932). Among them the most successful in that period of time was considered a system of A. A. Elenkin, published in 1936. New phase of development started since the 70s of 20th century, when wide range of alhologist admitted that the cell of BGA has no nucleus, and according to system of organic world by Takhtajan (1972), they refered it to subkingdom *Oxyphotobacteriobionta* of kingdom *Bacteriobiota* superkingdom *Procaryota*. In the suggested by Parker (1982) system of algae, blue-green algae are refered to kingdom *Procaryota*, division *Cyanophycota*, class *Cyanophyceae*.

In modern classification of microorganisms, the following hierarchy of taxonomic categories is adopted: domain, phylum, class, order, family, genus, species. The category of domain was suggested as superior to kingdom in order to emphasize significance of division of living organisms into three groups – *Archaea*, *Bacteria*, and *Eukarya*. According to such hierarchy, cyanobacteria are refered to domain *Bacteria*, phylum B10 *Cyanobacteria*, which is devided into five subgroups (according to taxonomic scheme of Bergey's Manual of Determinative Bacteriology). I and II subgroups include unicell ular (cocoid) forms or non-trichal colonies (palmelloid) cells, united by layers of gel-like capsids. Bacteria of each of the two subgroups differ in ways of their reproduction. III, IV and V subgroups include filamentous (trichal) organisms. Bacteria of each of these subgroups differ from each other in ways of their cellular division and, as they differ in forms of their trichomes (branched or unbranched, uniseriate or multiseriate). Hence, there are 42 genera distinguished among cyanobacteria, including the division into the subgroups: I – 9, II – 6, III – 9, IV – 7, V – 11 [1].

Table 1

Modern taxonomy of cyanobacteria
(Madigan, Michael T., Martinko, John M. (2006)
Brock Biology of Microorganisms. 11 ed. Pearson
Prentice Hall. New Jersey, USA. p. 396)

subgroup	genera
I	<i>Chamaesiphon, Cyanothece, Gloeobacter, Microcystis, Gloeocapsa, Gloeotheca, Myxobaktron, Synechococcus, Synechocystis</i>
II	<i>Chroococciopsis, Dermocarpa, Dermocarpella, Myxosarcina, Pleurocapsa, Xenococcus</i>
III	<i>Arthrospira, Crinalium, Lyngbya, Microcoleus, Oscillatoria, Pseudanabaena, Spirulina, Starria, Trichodesmium</i>
IV	<i>Anabaena, Aphanizomenon, Cyndrospermum, Nodularia, Nostoc, Scytonema, Calothrix</i>
V	<i>Chlorogloeopsis, Fisherella, Geitleria, Stigonema, Cyanobotrys, Loriella, Nostochopsis, Mastigocladopsis, Mastigocoleus, Westiella, Halposiphon</i>

2. Biology and ecology of cyanobacteria

Cyanobacteria are oxygenic phototropic prokaryotes that include chlorophylls and phycobilins. Some species of these organisms can fixate nitrogen under their free-living condition or in symbiosis with aquatic plants, for instance *Azolla* (Becking, 1978). Cyanobacteria are resistant to extreme conditions of different ecotopes. Cyanobacteria form a large, morphologic heterogeneous group of hydrophilic bacteria. Several morphologic levels of cyanobacteria organization are distinguished – cocoid, palmelloid, trichal, heterotrival (uniseriate or multiseriate). Cyanobacteria play significant role for balanced development of hydro-ecosystems, since they are the main, and sometimes the only, producers of primary organic substance in them. Cyanobacteria have adapted to all types of ecotopes of salt water, freshwater, soil, air, etc. During period of time between 2 and 4 billion years ago, cyanobacteria gained ability to photosynthesis, owing to which they secret oxygen till now as product of their vital activity. Thanks to wide and massive spread of cyanobacteria, ancient atmosphere, that at that time had been saturated with carbon dioxide, started to change significantly by oxygen saturation. It is estimated today that from 20 to 30 % of oxygen, obtained from photosynthesis in our planet, is owed to cyanobacteria. This is exactly why they played central role in alteration of air content and atmosphere structure. Cyanobacteria perform also important functions in edaphotops, providing fertility of soils via nitrogen fixation. Some plants evolved thanks

to mutualism between colonies of cyanobacteria, that develop in rhizosphere of plants. Other species of cyanobacteria create mycorrhiza with fungi hyphae. Cyanobacteria fix oxygen not only in soils, but in coral reefs as well as in other marine ecotopes, making nitrogen available to other organisms under conditions of different ecosystems [2].

3. Cytology, morphology, and biochemistry of cyanobacteria

Cyanobacteria cells are bigger in sizes and more complex as to their structure than other bacteria. Structural and functional organization of cyanobacterial cell (Fig. 1) has typical of procaryots organelles: mucous capsid of murein, that wraps cellular wall from the outside from four layers of peptidoglycan, bare ring DNA –nucleoid, submerged in sol-gel hyaloplasm, tiny compared to eukaryotic ribosomes without endoplasmic reticulum, plasmalemma, that separates cellular wall and cytoplasm, mesosomes – mono-membrane formations, that perform functions of mitochondria in prokaryotes and also simplified in structure golgiosomes. Ectoplasm contains photosynthetic thylakoids, that carry title of chromatophores, that migrate in parietal litine space alongside with movement of cytoplasm.

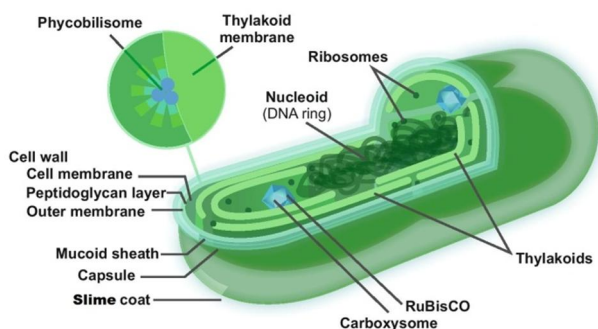


Fig. 1. Structural and functional organization of cyanobacteria cell (<http://lakes.chebucto.org/>)

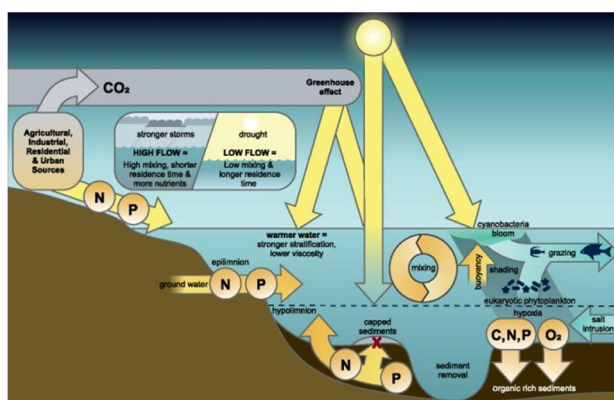


Fig. 2. Conceptual model of impact factors' influence on development of cyanobacteria (after Paerl et al. 2011)

Blue-green algae are coloured mainly in blue-green colour, under extreme conditions they have often colour with different shades of red. Green shade of cells is given by bacteriochlorophyll “a”. Red or blue colour is caused by presence of phycobilin pigments – phycocyanin and allophycocyanin (blue) and phycoerythrin (red). Carotenoids are represented only by β -carotenes and xanthophyll (lutein, zeaxanthin, oscilloxanthin, myxoxanthin, aphanin, and aphanizophyll, etc). Differentiated functioning of phycobilins provides photosynthetic apparatus of cyanobacteria with ability to absorb maximum quantity of sunlight – assimilation of energy of almost full spectrum of photosynthetic active radiation, this causes maximum value of η . [3].

Almost in all cyanobacteria the main reserve product of assimilation is glycogen-like polysaccharide – bacterio-starch. Besides carbohydrates, they also accumulate cyanophycin and volutin. Size of cyanobacteria cell can vary from 0.5 to 40 μm in diameter. Structure of wall is similar to gram-negative bacteria (Gerba, Maier and Pepper, 2000). Some cyanobacteria form complex or multilayer photosynthetic membrane system, that consists of slime coats that combine cells in the trichomes or colonies. Some filamentous cyanobacteria form heterocysts – round, empty looking cells, that specialize in nitrogen fixation, that are spread usually along or at the end of trichomes [4]. Some species are toxic (the most studied toxin is microcystin, that is produced by species *Microcystis aeruginosa* particularly) or conditionally pathogenic (species of genus *Anabaena*). Main agents of water “blooming” causing massive fish exhaustion and toxication of animals and humans, appear for instance during “blooming” of reservoirs of Ukraine.

4. Physiology and ecology of cyanobacteria

The life cycle of cyanobacteria consists of alternation of the following stages: bacterial mitosis (division), vegetative growth, and dormant state (spores). Before cellular division, the amount of DNA is doubled and then divided in two. Mitosis in cyanobacteria appears in such a way that on the side wall of cell there appears a ring plica, created by cytoplasmic membrane and inner layers of cellular wall. Growing in centripetal direction, this plica locks like diaphragm of microscope, forming cross web - septum that cuts thylakoids and protoplast in two daughter cells that during vegetation phase are increasing due to assimilation of substances and creation of new organelles, hence preparing to the next stage – mitosis or creation of spores. Under unfavorable conditions, creation of spores takes place. As in case of heterocysts, vegetation cells that transform into spores lose their gas vacuoles. This process is stimulated by different

environmental factors, but mainly by phosphorus. Contents of DNA in spores noticeably increases, sometimes in 20–30 times comparing to vegetation stage. Spores can bear desiccation and other extreme conditions. Appearing under favourable conditions, they can start growing immediately after their emergence, without any dormant state. Under absence of such favourable conditions, spores keep vital capacity for lasting period of time (several decades). During growing of spores, one sprout is created that is released through wrack of coat. Most unicellular and colonial cyanobacteria reproduce with the help of division of cells in two, in some cases it is with help of tiny cells – gonidia, that are created inside maternal cell or ribbed from the top of maternal cell. Majority of filamentous forms reproduce with the help of hormogonia – spaces where filaments are disintegrated.

Cyanobacteria do not need vitamins for existence and development. They can use nitrates or ammonia as source of nitrogen and also phosphorus compounds and microadditives of such elements as ferrum, sulphur, zinc, copper, manganum, cobaltum, molybdenum, etc. Most of their species are phototrophs, but some filamentous types can grow in darkness, using some carbohydrates (glucose or saccharose) as source of energy. Optimum conditions for cyanobacteria growth lay in complex of interrelated, mostly abiotic factors. Problem of cyanobacteria growth influence factors of *Anabaena*, *Aphanizomenon*, *Cylindrospermopsis*, *Nodularia*, *Lyngbya*, *Oscillatoria*, *Microcystis*, *Planktothrix* was researched by variety of scientists (Chorus and Bartram 1999, Carmichael 2008, Paerl and Huisman 2008, Hudnell 2010, O'Neill *et al.* 2012, Paerl and Paul 2012). Among other factors that form conditions of cyanobacteria growth, they concentrated their studies on salinity, temperature, pH, trophism, radiation, hydrodynamics of the environment. In Fig. 2, a conceptual model of factors influencing a life cycle of cyanobacteria created by Paerl *et al.* in 2011 is shown [5]. This model involves temperature, laminar conditions in growth environment, exposition of residence of cyanobacteria in the environment, supply of carbon (C), nitrogen (N) and phosphorus (P) from sources of man-made and arable contamination.

4.1. Salinity (mineralization)

Marine cyanobacteria *Prochlorococcus*, *Synechococcus* and *Trichodesmium* have shown high salinity tolerance as a result of laboratory experiments. This is why they are universally tolerant species. For instance, stenohaline tolerant species of genus *Cylindrospermopsis* vegetate in water with mineralization up to 2.5 ppt, and universally tolerant species of genera *Anabaenopsis* and *Nodularia* vegetate under salinity of 5–20 ppt

(Moisander *et al.* 2002). Species *Microcystis aeruginosa* tolerate the level of salinity up to 10 ppt at which no change in growth can be found in comparison to freshwater (Tonk *et al.* 2007). Based on results of these experiments, one may claim that under optimum growth conditions these species can vegetate in regions where the water is more salty. Over the last decades, there is a tendency of extension of area of these cyanobacteria species in littoral ecosystems under conditions of middle salinity (5–15 ppt) (Paerl and Paul 2012). For instance, «blooming» caused by *Microcystis aeruginosa* appears in Baltic Sea (Maestrini *et al.* 1999) and the San Francisco Estuary (Lehman *et al.* 2013). These scientists prove that special extension of microcystis is affected not by salinity, but by other environmental factors.

4.2. Level of concentration of biogenic elements

Like in other phytoplanktons, under optimum conditions of temperature and irradiance (so called photothermal pair of ecofactors), production of biomass in cyanobacteria proceeds in direct proportion to the quantity of biogenic elements, mainly nitrogen and phosphorus, that are available in the environment. Results of many scientists' research have shown that the growth of cyanobacteria in freshwater natural (rivers and lakes) and artificial (channels, reservoirs, ponds) ecosystems is mainly caused by excessive concentration of phosphorus (Likens 1972, Schindler 1977, Edmondson and Lehman 1981, Elmgren and Larsson 2001, Paerl 2008, Schindler *et al.* 2008). Unlike freshwater biohydrocencosis, estuarial and marine ecosystems are more sensitive to concentration of nitrogen, and eutrophication caused by cyanobacteria growth also is often related to excessive concentrations of nitrogen. (Ryther and Dunstan 1971, Nixon 1986, Suikkanen *et al.* 2007, Paerl 2008, Conley *et al.* 2009, Ahn *et al.* 2011).

The supply of nutrients from stationary and non-stationary sources (man-made and arable unpurified wastewaters) causes simultaneous increase of phosphorus and nitrogen concentrations (Paerl and Paul 2012, Paerl *et al.* 2014b). Results of research done in summer have shown that under conditions of achievement of maximum biomass of cyanobacteria under minimum concentration of nutrients, nitrogen and phosphorus both equally affect biomass accumulation in ecosystem (Paerl *et al.* 2014a). Overall, domination of both nitrogen fixating and non-fixating species *Aphanizomenon flos aquae*, *Nodularia spumigena*, *Microcystis aeruginosa* and *Cylindrospermopsis raciborskii* in phytoplankton's structure is caused by increase of both nitrogen and phosphorus concentrations (Chapman and Schelske 1997, Jacoby *et al.* 2000, Gobler *et al.* 2007, Burford *et al.* 2006, Burford and

O'Donahue 2006, Hong *et al.* 2006, Suikkanen *et al.* 2007, O'Neill *et al.* 2012). For the decrease of phytoplankton bioproductivity, concentrations of biogenic elements must be several times lower than those of phytomass. Herewith, the need in nitrogen and phosphorus compounds in cyanobacteria is higher than in eukaryotic phytoplanktons because of high demand in proteins.

4.3. Irradiance and water clarity

Due to carotenoid pigments, cyanobacteria cells dissipate excessive light energy, which, in its turn, provides access for irradiance to their photosynthetic apparatus without photoinhibition (Paerl *et al.* 1983, 1985). Due to buoyancy, such cyanobacteria as *Microcystis* vegetate very close to water surface, having tolerance to levels of irradiance that are limitation for other representatives of phytoplankton. As a result, cyanobacteria can increase density of their cells, while under typical conditions they would limit the access to light with their shadow. Due to growing almost in neuston zone, cyanobacteria are insensitive to irradiance limitation, even if there exists a high concentration of suspended pollutants in water.

4.4. Temperature and pH level

One may talk about temperature as of one of the most limiting abiotic factors that affect growth of cyanobacteria (Robarts and Zohary 1987, Butterwick *et al.* 2005, Reynolds 2006, Paerl and Huisman 2008). The range of thermotolerance for majority of cyanobacteria species in all climate types with exception of polar zones, is from 25 to 35 °C (Reynolds 2006, Lüring *et al.* 2013). During researches on eight species of cyanobacteria, it was discovered that optimal temperature for vegetation of *Microcystis aeruginosa* is 30–32.5 °C, for *Aphanizomenon gracile* optimal temperature is 32.5 °C, for species *Cynlindrospermopsis raciborskii* and *Planktothrix agardhii* 27.5 °C, and optimal temperature for «bloom» of species *Anabaena sp.* is 25 °C (Lurling *et al.* 2013). Overall, vegetation can take place under conditions from cryophilic (+4 °C) to thermophilic (+75 °C), for example in the case of *Synechococcus lividus* [6, 7]. Photosynthetic activity without visible changes takes place even at a temperature of +30 °C [6, 8]. Miyake [9] and Nishioka [10] reported on synthesis of polyhydroxyalkanoates in *Synechococcus* MA19 at a temperature of +50 °C, when almost all researchers conducted experiments in the temperature range from +20 to +30 °C. Thermophilic conditions are favourable for photosynthesis because of speeding up of biochemical processes of metabolism and due to considerably lower risk of autointoxication. Nevertheless,

cyanobacteria can produce polyhydroxyalkanoates very seldom and thermophilic synthesis in large bioreactor causes high costs of thermal isolation [6].

According to Brock, cyanobacteria are unable to grow under a level of pH lower than 4–5. For representatives of alkaliphiles, optimal pH range for growth is between 7.5 and 10. Though pH level with alkalinity and temperature affect modification of dissolved organic carbon, influence of pH on cyanobacteria growth is independent. Of course, it is impossible to generalize requirements for optimal level of pH for normal vegetation of cyanobacteria, since it depends on strain (culture) or wild race of particular species and on the pH of its natural environment [7].

5. Factors for optimum cultivation of cyanobacteria

5.1/ Application of man-made carbon dioxide

In order to provide balanced environmental management and minimize negative impact from anthropogenic activity, it is reasonable, in our opinion, to have such an approach that is based on using carbon dioxide as second photosynthesis reagent for increase of bioproductivity of cyanobacteria, hence as the only source of carbon for all biomolecules of the cell. For intensification of mitosis, that provides increase of biomass in natural or artificial, opened and closed systems, the use of industrial gas that contains CO₂ is widespread [11]. For modern cultivation systems which allow us to use obtained cyanobacteria biomass for production of high quality products (food products and nutritional supplements), the price for CO₂ is not critical. If cultivation aimed at production of polyhydroxyalkanoates, that have lower economic value then serious question emerges of the search for cheap sources of carbon dioxide. There is great number of researches who suggest using different formations of CO₂ (flue, production and other industrial gases) (Tabl. 2) [11].

Table 2

Application of carbon dioxide of different genesis for cyanobacteria cultivation

Gas type	Cyanobacteria species	Source of CO ₂
Flue gases	<i>Phormidium valderianum</i>	Coal combustion flue gases
	<i>Atrhrospira platensis</i>	
	<i>Arthrospira sp.</i>	Synthetic flue gas
	<i>Synechocystis sp.</i>	Flue gas from natural gas combustion
Biotechnological gases	<i>Arthrospira platensis</i>	CO ₂ -offgas from ethanol fermentation
		Biogas

5.2. Alternative nutrition environment for cyanobacteria

Among modern researches of dynamics of cyanobacteria biomass development under cultural conditions, high attention is being paid to application of synthetic sources of nutrition [11]. It is proved that by using alternative sources of biogenic macroelements (agricultural and industrial wastewater, degistate after biomethanogenesis, exhausted activated sludge etc) it is possible to ensure stable increase of cyanobacteria biomass [11]. The biomass weight gained in opened and closed cultivation systems reaches 0.5–1 and 2–9 g/l, respectively [12]. The necessary condition is a need in large amount of water. Purification of industrial effluents is the next important condition for providing optimum growth of microalgae, that supplies both production of valuable biomass and microalgae purification [13]. On the other hand, new requirements appear concerning contamination of cultural liquid with microbes, heavy metals, antibiotics and other growth inhibitors that are contained in wastewater. Seasonal fluctuation of concentrations is typical of all these components [14].

This is why modern researches are aimed at cultivation of cyanobacteria with using for their nutrition exhausted biomass of anaerobic digestion, so called degistate and also wastes and effluents from agricultural complex [4, 11, 15–18], aiming also to purify the latter. After primary purification of wastewater, the water can be transferred to the next level of purification or used as reclaimed, and lipids obtained through extraction of received cyanobacteria biomass can be used for production of biodiesel. [12].

5.3. Two-stage cultivation

In the case of cultivation of cyanobacteria biomass for production of polyhydroxyalkanoates, two stages of technology were studied [6]. At first, cyanobacteria grew in medium, saturated with nutrients then the obtained at first stage biomass was carried into a medium with impoverished concentrations of biogenic elements for initiation of polyhydroxyalkanoates and other products synthesis. However, under conditions of large-scale production there appear difficulties with separation of large amount of biomass from primary medium and with transportation to another stage. Moreover, it leads to emergence of stressed state in cells, and with application of transversal forces in the process of transportation of biomass and oxygen deficiency causes lagging in biomass accumulation [6]. The method of two-stage cultivation was used in researches by Gruber *et al.*, 2016 [19]. Researches were conducted with using species of green microalgae

Acutodesmus obliquus for obtaining a biomass in nutrient environment with excess and deficiency of nitrogen compounds. In this case the method of dehydration was used before carrying to anaerobic digestion (Fig. 3).

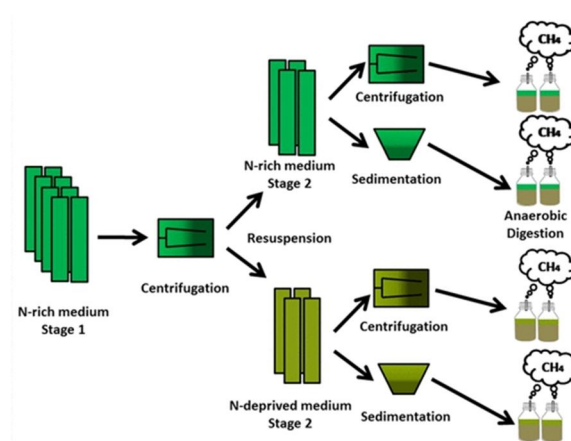


Fig. 3. Two-stage cultivation scheme by Gruber *et al.*

According to experimental construction of two-stage cultivation, microalgae were cultivated and harvested in stationary stage. After that, biomass was separated from nutrition medium by centrifugation and resuspended (inserted) at first in a nitrogen enriched medium and then in nitrogen impoverished medium. After that, biomass of microalgae was subjected to dehydration: centrifugation and sedimentation. During bioproduction processes on dynamics of methane creation under conditions of anaerobic digestion was studied [19].

5.4. Peculiarities of biomass separation

After accumulation of enough amount of biomass resulted from cyanobacteria cultivation, its excessive fraction is periodically harvested. Technical water that contains residual nutrients after biomass harvesting can be transferred to the next purification stage. Biomass can be processed in anaerobic way, or after dissolving in hydrothermal way it can be mineralized. Purification of technical water can contain cleaning from sediments of dissolved organic compounds [11–13]. It is necessary to note that cyanobacteria cultivation is accompanied by processes of autoselection. Autoselection – combination of cultivation conditions, favourable for application of strain, and non-favourable for contaminants substance – are important goals for any biotechnological process. For cyanobacteria, the selection process can be achieved by conditions of maintenance of some parameters simultaneously: the need in dissolved organic compounds of carbon, limitation of nitrogen and phosphorus compounds, value of pH not lower than 8.5 etc. Researches [6] have shown secondary growth of

green algae *Chlorella sp.* When the culture reaches its stationary phase, cells die and release in the environment secondary metabolites that can be nutrition for growth of new cells. When conducting cyanobacteria cultivation, it is important to remember that under non-sterile conditions, microbic, in particularly fungi, contamination is inevitable. Hence, purification turns out to be one of necessary requirements for final stages of cyanobacteria biomass separation for further processing [11].

5.5. Ways of utilization of cyanobacteria biomass

Cyanobacteria biomass contains many target products that are valuable for different fields of modern bioeconomics: food, pharmaceutical and perfumery industry. Under natural conditions, these bacteria massively grow for centuries as primary source of organic compounds [20]. In our time, much effort has been put in field of genetic engineering for modification of phototrophic microorganisms, especially cyanobacteria, – producers of new useful compounds (target products) that are not synthesized in natural way [21, 22]. Topical direction of modern studies is also environmental biotechnology and bioenergetics that anticipate direct application of cyanobacteria large-tonnage biomass and other massive forms of hydrobionts as raw material for biofuel production (biomethane, bioethanol, and biodiesel) and mineralorganic fertilizer [23, 24].

Task concerning management of processes of cyanobacteria biomass production depends on the choice of target product, that in its turn defines methods of its production cultivation. For bioethanol production, a method of yeast fermentation is used. In this case, the target for biotechnology is to create strains of cyanobacteria that synthesize large amount of bacteria starch or bacteria glycogen that are substrate for alcohol fermentation. In this strategic case of biomass utilization, cyanobacteria have some benefits over eukaryotes, since their cellular walls contain peptidoglycan layers [25], it can perform lysis, unlike majority of algae, walls of which consist of polysaccharides and proteoglycan [26]. Moreover, the way of residence of carbohydrates is very important, if biomass was used as substrate for fungi, in particular, for alcohol fermentation.

Different ways [20] (fermentative, chemical, physical, including desiccation, heating, acid and alkali hydrolysis) of preliminary procession of biomass *Synechococcus* aiming to release monomeric hexose were also studied. It is also familiar that species of *Synechococcus* accumulate reserve carbohydrates glycogen and cyanophycin and do not synthesize

polyhydroxybutyrate, as is seen in other cyanobacteria [27–29]. Accumulation of nitrogen compounds in biomass during process of growth of *Synechococcus* causes coordinative complex physiologic adaptations, that allow photosynthesis and growth to continue to certain limit [30–33]. It manifests itself in increase of productivity of process of polysaccharides assimilation (mainly glycogen) and dissimilation of nitrogen compounds, including light-absorbing pigments – phycobilisome proteids [27, 33]. Biomass of *Synechococcus* can be significantly degraded under impact of fermentation processes and serve simultaneously both as substrate and as source of nutrition elements for fungi fermentation. This in its turn manifests itself in greater productivity with respect to ethanol than in previous studies, where cyanobacteria cellular biomass was used [24]. During the studies it was also established that fermentative hydrolysis of biomass of cyanobacteria can be also used as a source of nutrients for increase of alcohol fermentation completeness. [34–37].

Production of another fuel type – biogas (biomethane) – using method of anaerobic fermentation of cyanobacteria (biomethanogenesis) that uncontrollably grew during summer period in reservoir water area of Dnieper watercascades (species of *Microcystis*, *Phormidium*, *Merismopedia*, *Aphanizomenon*, *Anabeana* and *Oscillatoria*) was studied by other scientists [38–54]. It was shown that an effective method of reducing of environmental risk level from uncontrolled development of cyanobacteria growth in artificial reservoirs of Dnieper watercascades can be the method of harvesting of cyanobacteria and using them as raw material for standardised biogas. There was also established an effectiveness of preliminary cyanobacteria biomass processing in field of hydrodynamic cavitation for the increase of completeness of biomass decay (amount of extracted lipids increases in 3.2 times, amount of synthesized biogas in 1.4 times) [45–54].

In many publications, advantages of using of microalgae for biodiesel fuel production in comparison to another accessible feedstock [55–64] is described. All these researchers focused their studies on artificial cultivation of microalgae. The advantage consists in the ability to use for aquatic algae plantation, which are unconsumable for the human, in life support of the microalgae by solar energy, the latter during photosynthesis converts into chemical energy of primary organic compounds, mainly carbohydrates; and another advantage is that one generation of cyanobacteria life cycle lasts several days [57]. Biodiesel production technology from microalgae includes biomass growth stage, extraction of lipids from biomass, and production of biodiesel from them with application of existing processes and technologies that were used for other

types of feedstock. For effective utilization of biomass, important is an operation of harvesting and concentration of microalgae. The price for this operation is of 20–30 % of the general price of biodiesel production [63]. Technology of microalgae concentration can include several processes (physical, chemical or biological), with the help of which a necessary level of solid and liquid phases separation is achieved.

Experiments have shown that although no universal method for harvesting and concentration of microalgae exists (it is still productive field for studies), for each particular algae species optimal economical ways and methods can be made [65, 66]. After concentration, in majority of cases, biomass dehydration is applied, this leads to the increase in its maximum term of storage. For microalgae, The following ways of dehydration are used: drum, pulverizer, sublimation or solar desiccation [67]. Extraction of lipids and pendent fatty acids from biomass is conducted directly from lyophilized biomass. For extraction, there can be used such solvents as

hexane, ethanol, or mixture of both hexane, and ethanol which allows us to extract up to 98 % of purified lipids, and fatty acids [68]. Studies [69] have shown that in case of damage of cellular wall of algae with help of ultrasound procession, extraction of target product increases from 4.8 % to 25.9 %. From the obtained feedstock, biodiesel can be produced using traditional technology– repeated esterification of plant oils. Lipid feedstock consists of 90–98 % (weight) of triglyceride and of small amount of mono- and diglyceride, it contains free fatty acids (1–5 %) and small amounts of phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds, and remnants of water [70].

Alassali *et al.* (2016) dedicated their studied to establishment of possible spectrum of small-tonnage target products, that can be obtained by means of extracting them from microalgae and to potential abilities of their application. In Fig. 4, alternatives of application of secondary metabolite from micro and macroalgae is shown [71].

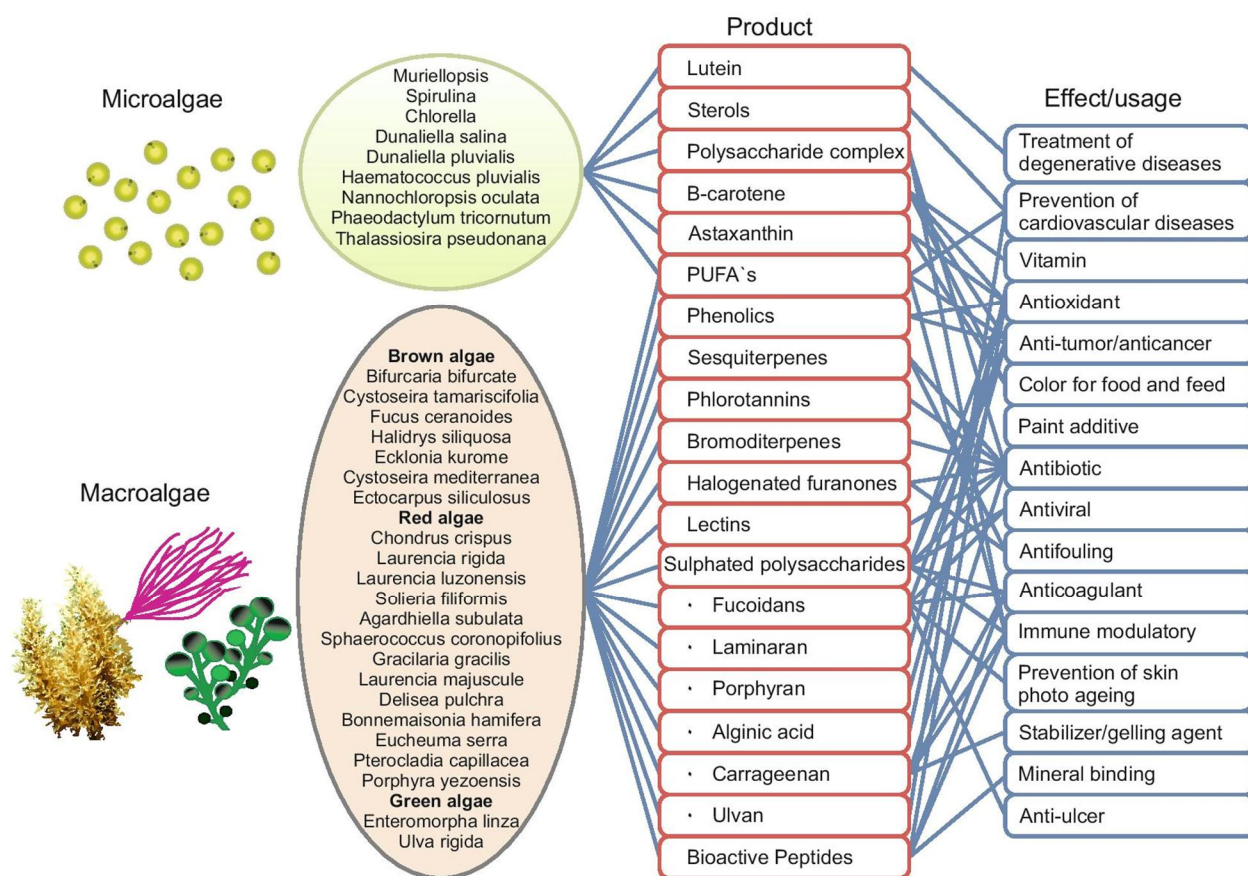


Fig. 4. Possible applications of target products from algae

Conclusions and recommendations

Cyanobacteria, that caused “oxygen revolution” at the beginning of emergence of live on the Earth, even till now play significant role in enrichment of

atmosphere with oxygen (about 30 % of all planetary photosynthetic oxygen received yearly), and in nitrogen fixation. Conditions for cyanobacteria development include a complex of interrelated environmental factors: salinity, temperature, pH, nutrients concentration,

irradiance, hydrodynamic situation, optimal parameters of which for different cyanobacteria species are in broad ranges, this determines broad extension of them in ecosystems and their ability to adapt under conditions of change of these factors. Cyanobacteria cultivation strategy, as actual direction of modern biotechnology and bioenergetics, involves the using of industrial wastes, products of fuel combustion and exhausted gases, man-made and arable wastewaters as sources of biogenic elements of nutrition (carbon-, nitrogen- and phosphorus elements). Cyanobacteria biomass released from cultural medium can be used for production of small-tonnage valuable products with unique properties. Large tonnage biomass of natural origin can be used for fuel production (biomethane, bioethanol, biodiesel).

References

- [1] Efimova M. V., Efimov A. A. Sinezelenie vodosorti li zianobakterii? Voprosy sistematiki // Sovremennyye problem nauki i obrazovaniya, 2007. – № 6–1; URL: <https://www.science-education.ru/ru/article/view?id=710> (date of last access 30.11.2017)
- [2] Scott Johnson (2017) Roles of Cyanobacteria in the Ecosystem. <https://sciencing.com/Last> accessed 30.09.2017
- [3] Manisha M. Cyanobacteria: Occurrence, Morphology and Cell Structure. 2017. <http://www.biologydiscussion.com>. Last accessed 30.09.2017
- [4] McMurdo Dry Valleys Long-Term Ecological Research Site. Cyanobacteria. <http://huey.colorado.edu.2017>. Last accessed: 30.09.2017
- [5] Berg M. and Sutula M. 2015. Factors affecting the growth of cyanobacteria with special emphasis on the Sacramento-San Joaquin Delta. Southern California Coastal Water Research Project Technical Report 869 August 2015
- [6] Drog B. et al., Photo-autotrophic Production of Poly(hydroxyalkanoates) in..., Chem. Biochem. Eng. Q., 29(2) 145–156 (2015)
- [7] Castenholz, R. W., A Handbook on Habitats, Isolation, and Identification of Bacteria, Section B, Springer, Berlin Heidelberg 1981, pp. 236–246.
- [8] De Vera, J.-P. P., Möhlmann, D., Leya, T., Photosynthesis activity of frozen cyanobacteria, snow alga and lichens as pre-tests for further on studies with simulation of Mars equatorial latitude temperatures, EPSC Abstracts 4(2009) 355.
- [9] Miyake, M., Erata, M., Asada, Y., J Ferment Bioeng 82 (1996) 516–518. doi: [http://dx.doi.org/10.1016/S0922-338X\(97\)86995-4](http://dx.doi.org/10.1016/S0922-338X(97)86995-4)
- [10] Nishioka, M., Nakai, K., Miyake, M., Asada, Y., Taya, M., Biotechn Letters 23(2001) 1095–1099. doi: <http://dx.doi.org/10.1023/A:1010551614648>
- [11] Clemens Troschl, Katharina Meixner and Bernhard Drog. Cyanobacterial PHA Production—Review of Recent Advances and a Summary of Three Years' Working Experience Running a Pilot Plant, Bioengineering 2017, 4, 26; doi:10.3390/bioengineering 4020026
- [12] Kumar, K.; Mishra, S. K.; Shrivastav, A.; Park, M. S.; Yang, J.W. Recent trends in the mass cultivation of algae in raceway ponds. Renew. Sustain. Energy Rev. 2015, 51, 875–885. [CrossRef]
- [13] Markou, G.; Vandamme, D.; Muylaert, K. Microalgal and cyanobacterial cultivation: The supply of nutrients. Water Res. 2014, 65, 186–202. [CrossRef] [PubMed]
- [14] Markou, G.; Georgakakis, D. Cultivation of filamentous cyanobacteria (blue-green algae) in agro-industrial wastes and wastewaters: A review. Appl. Energy 2011, 88, 3389–3401. [CrossRef]
- [15] Chaiklahan, R.; Chirasuwan, N.; Siangdung, W.; Paithoonrangarid, K.; Bunnag, B. Cultivation of spirulina platensis using pig wastewater in a semi-continuous process. J. Microbiol. Biotechnol. 2010, 20, 609–614. [CrossRef] [PubMed]
- [16] Cicci, A.; Bravi, M. Production of the freshwater microalgae scenedesmus dimorphus and arthrospira platensis by using cattle digestate. Chem. Eng. Trans. 2014, 38, 85–90. [CrossRef]
- [17] Fouilland, E.; Vasseur, C.; Leboulanger, C.; Le Floc'h, E.; Carré, C.; Marty, B.; Steyer, J.-P.P.; Sialve, B. Coupling algal biomass production and anaerobic digestion: Production assessment of some native temperate and tropical microalgae. Biomass Bioenergy 2014, 70, 564–569. [CrossRef]
- [18] Olguín, E.J.; Galicia, S.; Mercado, G.; Pérez, T. Annual productivity of Spirulina (Arthrospira) and nutrient removal in a pig wastewater recycling process under tropical conditions. J. Appl. Phycol. 2003, 15, 249–257. [CrossRef]
- [19] M. Gruber-Brunhumer et al. Elsevier Ltd. 2016. <http://dx.doi.org/10.1016/j.algal.2016.04.0162211-9264/>
- [20] K Benedikt Möllers et al., Biotechnology for Biofuels. 2014, vol 7, no. 1. DOI: 10.1186/1754-6834-7-64
- [21] Sauer J., Schreiber U., Schmid R., Völker U., Forchhammer K: Nitrogen starvation-induced chlorosis in Synechococcus PCC 7942. Low-level photosynthesis as a mechanism of long-term survival. Plant Physiol.
- [22] Van Baalen C: Studies on marine blue-green algae. Bot Mar. 1962, 4: 129–139.
- [23] John R. P., Anisha G., Nampoothiri K. M., Pandey A.: Micro and macroalgal biomass: a renewable source for bioethanol. Bioresour Technol. 2011, 102: 186–193. 10.1016/j.biortech.2010.06.139.
- [24] Aikawa S., Joseph A., Yamada R., Izumi Y., Yamagishi T., Matsuda F., Kawai H., Chang J.-S., Hasunuma T., Kondo A.: Direct conversion of Spirulina to ethanol without pretreatment or enzymatic hydrolysis processes. Energy Environ Sci. 2013, 6: 1844–1849. 10.1039/c3ee40305j.
- [25] Hoiczky E., Hansel A.: Cyanobacterial cell walls: news from an unusual prokaryotic envelope. J Bacteriol. 2000, 182: 1191–1199. 10.1128/JB.182.5.1191-1199.2000.
- [26] Domozych D. S.: Algal cell walls. eLS. 2011, Chichester: John Wiley and Sons
- [27] Stevens S., Balkwill D., Paone D.: The effects of nitrogen limitation on the ultrastructure of the

- cyanobacterium *Agmenellum quadruplicatum*. Arch Microbiol. 1981, 130: 204-212. 10.1007/BF00459520.
- [28] Stevens S. E., Paone D. A., Balkwill D. L.: Accumulation of cyanophycin granules as a result of phosphate limitation in *Agmenellum quadruplicatum*. Plant Physiol. 1981, 67: 716-719. 10.1104/pp.67.4.716.
- [29] Beck C., Knoop H., Axmann I. M., Steuer R.: The diversity of cyanobacterial metabolism: genome analysis of multiple phototrophic microorganisms. BMC Genomics. 2012, 13: 56-10.1186/1471-2164-13-56.
- [30] Luque I., Forchhammer K.: Nitrogen assimilation and C/N balance sensing. The cyanobacteria: molecular biology, genomics and evolution. Edited by: Herrero A., Flores E. 2008, Norfolk: Caister Academic Press, 335-382.
- [31] Schwarz R., Forchhammer K.: Acclimation of unicellular cyanobacteria to macronutrient deficiency: emergence of a complex network of cellular responses. Microbiology. 2005, 151: 2503-2514. 10.1099/mic.0.27883-0.
- [32] Sauer J., Schreiber U., Schmid R., Völker U., Forchhammer K.: Nitrogen starvation-induced chlorosis in *Synechococcus PCC 7942*. Low-level photosynthesis as a mechanism of long-term survival. Plant Physiol.
- [33] Paone D. A., Stevens S. E.: Nitrogen starvation and the regulation of glutamine synthetase in *Agmenellum quadruplicatum*. Plant Physiol. 1981, 67: 1097-1100. 10.1104/pp.67.6.1097.
- [34] Choi S. P., Nguyen M. T., Sim S. J.: Enzymatic pretreatment of *Chlamydomonas reinhardtii* biomass for ethanol production. Bioresour Technol. 2010, 101: 5330-5336. 10.1016/j.biortech.2010.02.026.
- [35] Harun R., Danquah M. K., Forde G. M.: Microalgal biomass as a fermentation feedstock for bioethanol production. J Chem Technol Biotechnol. 2010, 85: 199-203.
- [36] Harun R., Danquah M. K.: Influence of acid pretreatment on microalgal biomass for bioethanol production. Process Biochem. 2011, 46: 304-309. 10.1016/j.procbio.2010.08.027.
- [37] Harun R., Jason W., Cherrington T., Danquah M. K.: Exploring alkaline pre-treatment of microalgal biomass for bioethanol production. Appl Energy. 2011, 88: 3464-3467. 10.1016/j.apenergy.2010.10.048.
- [38] Nikiforov V. V. O metodakh podavleniya massovoho rozvitiya sinezelenykh vodorostey / Nikiforov V. V. // Visnyk problem biolohii I medytsyny. – 2002. – Vyp. 4. – S. 27-31.
- [39] Nikiforov V. V. Khimiko-toksykologichni problemy pidhotovky pytnoi vody pry dii ekstremalnikh pryrodnykh chynnykiv / V. V. Nikiforov, T. F. Kozlovska // Visnyk KDPU. – 2002. – Vyp. 5 (16). – S. 106-108.
- [40] Elizarov O. I. Pro mozhlyvist vykorystanna hidrobiontiv dlya otrymanna biohazy / O. I. Elizarov, A. V. Luhovoy, V. V. Nikiforov // Visnyk KPDU. – 2006. – Vyp. 6(41). – S. 43-44.
- [41] Nikiforov V. V. O metodakh podavleniya massovoho rozvitiya sinezelenykh vodorostey / V. V. Nikiforov // Visnyk problem biolohii i medytsyny. – 2002. – Vyp. 4. – S. 27-31.
- [42] Nikiforov V. V. Osobennosti khozyaystvennoho znacheniya sinezelenykh vodorostey v usloviyakh Kremenchuhs'koho I Dneprodzerzhinskoho vodokhranilishch / V. V. Nikiforov, T. F. Kozlovskaya / Visnyk KDPU. – 2002. – Vyp. 5(16). – S. 109-108.
- [43] Nikiforov V. V. Khimiko-biolohicheskie prichiny ukhudsheniya kachestva prirodnoy vodi / V. V. Nikiforov, T. F. Kozlovskaya // Visnyk KDPU. – 2002. – Vyp. 6(17). – S. 82-85.
- [44] Nikiforov V. V. Rezultati biotestirovaniya pitevoy vodi na raznikh stadiyakh ee podhotovki k potrebleniyu / V. V. Nikiforov, T. F. Kozlovskaya // Ekolohiya ta noosferolohiya. Naukoviy zhurnal Dnipropetrovskoho natsionalnoho universitetu. – 2001. – T. 10, No. 1-2. – S. 99-105.
- [45] Malovanyy V. S. Optimalni umovi otrymanna enerhii iz tsianobakteriy / M. S. Malovanyy, O. D. Sinelnikov, O. V. Kharlamova, A. M. Malovanyy // Khimichna promislovist Ukrainy. – 2014. – No. 5. – S. 39-43.
- [46] Malovanyy M. S. Otsinuvanna ekolohichnoi nebezpeky v akvatoriyakh Dniprovskikh vodoskhovyshch vnaslidok nekontrolovanoho rozvitku tsianobakteriy / M. S. Malovanyy, V. V. Nikiforov, O. V. Kharlamova, O. D. Sinelnikov // Naukoviy visnyk NLTU Ukrainy. – 2015. – Vyp. 25.6. – S. 159-164.
- [47] Malovanyy M. S. Vpliv hidrodynamichnoi kavitatsii na biolohichni objekty / M. S. Malovanyy, V. V. Nikiforov, O. D. Sinelnikov ta in. // Tekhnologichnyy audit ta rezervy vyrobnytstva – 2015. – No. 5/4(25). – S. 41-45.
- [48] Malovanyy M. Priropokhranye i enerheticheskie aspekty biotekhnologii utilizatsii tsianobakteriy kak ekoloho-ekonomicheskyy imperativ ustoychivoho rozvitiya / M. Malovanyy, V. Nikiforov, E. Kharlamova, A. Sinelnikov // Teoriya ustoychivoho rozvitiya, Varna. – 2015. – №1(22). – S. 4-9.
- [49] Malovanyy M. S. Vykorystanna zianobakteriy dlya otrymanna enerhonosiiv – shlyakh do unyknenna ekolohichnoi nebezpeky vid ikh nekontrolovanoho rosvytku v vodoskhovyshchakh Dniprovskoho kaskadu / M. S. Malovanyy, V. V. Nikiforov, O. V. Kharlamova, O. D. Sinelnikov // Stalyy rozvytok – XXI stolitt: upravlinna, tekhnolohii, modeli: Dyskusii 2015. – Cherkasy, 2015. – S. 352-361.
- [50] Malovanyy M. Prospects of combining in complex usage of different types of renewable energy and creation of renewable energy sources / M. Malovanyy, Y. Mahera, O. Zakhariv, O. Kharlamova O. Synelnikov // Naukovyy visnyk Natsionalnoho universitetu bioresursiv I pryrodokorystuvanna Ukrainy, Seriya "Biolohiya, biotekhnolohiya, ekolohiya". – 2015. – No. 214. – S. 155-163.
- [51] Malovanyy M. Mathematical model of the process of synthesis of biogas from blue-green algae / M. Malovanyy, V. Nykyforov, O. Kharlamova, O. Synelnikov // Ekolohichna bezpeka. – 2015. – № 1/2015(19). – S. 58-63.
- [52] Malovanyy M. S. Ratsionalna tekhnologiya utylizatsii synyo-zelenykh vodorostey / M. S. Malovanyy, V. V. Nikiforov, O. V. Kharlamova, O. D. Sinelnikov //

- Naukovyy visnyk NLTU Ukrainy. – 2015. – Vyp. 25.10. – S. 140–149.
- [53] Malovanyy Myroslav Reduction of the environmental threat from uncontrolled development of cyanobacteria in waters of Dnipro reservoirs / Myroslav Malovanyy, Volodymyr Nykyforov, Olena Kharlamova, Olexander Synelnikov, Khrystyna Dereyko // *Environmental Problems*. – 2016. – No. 1. – P. 61–64/
- [54] Malovanyy Myroslav Production of renewable energy resources via complex treatment of cyanobacteria biomass / Myroslav Malovanyy, Vladimir Nikiforov, Elena Kharlamova and Alexander Synelnikov // *Chemistry & Chemical Technology*. – Vol. 10, No. 2, 2016. – P. 252–254.
- [55] Li Y. Effects of nitrogen sources on cell growth and lipid production of *Neochloris oleoabundans* / Y. Li, B. Wang, N. Wu, C. Q. Lan // *Applied Microbiology and Biotechnology*. – 2008. – No. 81(4). – P. 629–636.
- [56] Li Y. Biofuels from microalgae / Y. Li, M. Horsman, N. Wu, C. Q. Lan, N. Dubois-Calero // *Biotechnology Progress*. – 2008. – No. 24(4). – P. 815–820.
- [57] Sheehan J. A look back at the U. S. Department of Energy's aquatic species program: biodiesel from algae / J. Sheehan, T. Dunahay, J. Benemann, P. Roessler // NREL/TP-580-24190, National Renewable Energy Laboratory, USA. – 1998. – 256 P.
- [58] Chisti Y. Biodiesel from microalgae / Y. Chisti // *Biotechnology Advances*. – 2007. – No. 25(3). – P. 294–306.
- [59] Hossain A. Biodiesel fuel production from algae as renewable energy / A. Hossain, A. Salleh, A. N. Boyce, P. Chowdhury, M. Naquiddin // *American Journal of Biochemistry and Biotechnology*. – 2008. - No. 4(3). – P. 250–254.
- [60] Hu Q. Sommerfeld Microalgal triacylglycerols as feedstocks for biofuels production: perspectives and advances / Hu Q., Sommerfeld M., Jarvis E., Ghirardi M., Posewitz M., Seibert M., et al. // *The Plant Journal*. – 2008. – No. 54. – P. 621–639.
- [61] Rodolfi L. Microalgae for oil: strain selection, induction of lipid synthesis and outdoor mass cultivation in a low-cost photobioreactor / Rodolfi L., Zittelli G. C., Bassi N., Padovani G., Biondi N., Bonini G., et al. // *Biotechnology and Bioengineering*. – 2009. – No. 102(1). – P. 100–112.
- [62] Rosenberg J. N. A green light for engineered algae: redirecting metabolism to fuel a biotechnology revolution / J. N. Rosenberg, G. A. Oyler, L. Wilkinson, M. J. Betenbaugh // *Current Opinion in Biotechnology*. – 2008. – No. 19(5). – P. 430–436.
- [63] Schenk P. M. Second generation biofuels: high-efficiency microalgae for biodiesel production / Schenk P. M., Hall SR. T., Stephens E., Marx U. C., Mussgnug J. H., Posten C., et al. // *Bioenergy Research*. – 2008. – No. 1. – P. 20–43.
- [64] Tsukahara K. Liquid fuel production using microalgae / K. Tsukahara, S. Sawayama // *Journal of the Japan Petroleum Institut*. – 2005. – No. 48(5). – P. 251–259.
- [65] Grima M. E. Recovery of microalgal biomass and metabolites: process options and economics / M. E. Grima, E. H. Belarbi, F. G. A. Fernandez, A. R. Medina, Y. Chisti // *Biotechnology Advance*. – 2003. – No. 20 (7-8). – P. 491–515.
- [66] Weissman J. C. Design and analysis of microalgal open pond systems for the purpose of producing fuels: a subcontract report / J. C. Weissman, R. P. Goebel. – US DOESERI, 1987. – 456 p.
- [67] Richmond A. Handbook of microalgal culture: biotechnology and applied phycology / A. Richmond. – Blackwell Science Ltd, 2004. – 322 p.
- [68] Mata Teresa M. Microalgae for biodiesel production and other applications: A review / Teresa M. Mata, Antonio A. Martins, Nidia. S. Caetano // *Renewable and Sustainable Energy Reviews*, Vol. 14(1), 2010. – P. 217–232.
- [69] Cravotto G. Improved extraction of vegetable oils under high-intensity ultrasound and/or microwaves. / G. Cravotto, L. Boffa, S. Mantegna, P. Perego, M. Avogadro, P. Cintas // *Ultrasonics Sonochemistry*. – 2008. – No. 15(5). – P. 898–902.
- [70] Bozbas K. Biodiesel as an alternative motor fuel: production and policies in the European Union / K. Bozbas // *Renewable and Sustainable Energy Reviews*. – 2008. – No. 12. – P. 542–552.
- [71] Alassali et al., *Adv Tech Biol Med* 2016, 4:1. <http://dx.doi.org/10.4172/2379-1764.1000163>
- [72] Abed R., Dobretsov S., Sudesh K.: Applications of cyanobacteria in biotechnology. *J Appl Microbiol*. 2009, 106: 1-12. 10.1111/j.1365-2672.2008.03918.x.
- [73] Canadian Council of Ministers of the Environment. Updated 1992. Canadian Water Quality Guidelines. Environment Canada.
- [74] Carmichael, W. W., and L. D. Schwartz. 1984. Preventing Livestock Deaths from Blue-Green Algae Poisoning. U. S. Dept. of Ag., Farmer's Bull. No. 2275. 11 pp.
- [75] Carmichael, W. W. 1991. Blue-Green Algae: An Overlooked Health Threat. In *Health & Environment Digest*, Freshwater Foundation. July, 1991. 5(6):1-4.
- [76] Carmichael, W. W. 1992. A Review, Cyanobacteria secondary metabolites- the cyanotoxins. In *J. Applied Bacteriology*. 72:445-459.
- [77] Carmichael, W.W. 1992. A Status Report on Planktonic Cyanobacteria (Blue-Green Algae) and Their Toxins. USEPA #EPA/600/R-92/079. 141 pp. (includes 867 references)
- [78] Chen, H. W.; Yang, T. S.; Chen, M. J.; Chang, Y. C.; Lin, C. Y.; Wang, E. I. C.; Ho, C. L.; Huang, K. M.; Yu, C.C.; Yang, F. L.; et al. Application of power plant flue gas in a photobioreactor to grow *Spirulina* algae, and a bioactivity analysis of the algal water-soluble polysaccharides. *Bioresour. Technol*. 2012, 120, 256–263. [CrossRef] [PubMed]
- [79] Dineshbabu, G.; Uma, V. S.; Mathimani, T.; Deviram, G.; Arul Ananth, D.; Prabakaran, D.; Uma, L. On-site concurrent carbon dioxide sequestration from flue gas and calcite formation in ossein effluent by a marine

- cyanobacterium *Phormidium valderianum* BDU 20041. *Energy Convers. Manag.* 2016, in press. [CrossRef]
- [80] Echlin, P. 1966. The Blue-Green Algae. *Scientific American*, 214(6):74–81.
- [81] Fay, P. 1983. The Blue-greens (Cyanophyta- Cyanobacteria). Edward Arnold (Pubs.), Baltimore, MD. 88 pp.
- [82] Ferreira, L. S.; Rodrigues, M. S.; Converti, A.; Sato, S.; Carvalho, J. C. M. *Arthrospira (spirulina) platensis* cultivation in tubular photobioreactor: Use of no-cost CO₂ from ethanol fermentation. *Appl. Energy* 2012, 92, 379–385. [CrossRef]
- [83] Haynes, R. C. 1988. Deptt of Env. Qual. Engg., Commonwealth of Massachusetts. An Introduction to the Blue-Green Algae (Cyanobacteria) with an Emphasis on Nuisance Species. *North Am. Lake Manage. Soc.* 19 pp.
- [84] He, L.; Subramanian, V. R.; Tang, Y. J. Experimental analysis and model-based optimization of microalgae growth in photo-bioreactors using flue gas. *Biomass Bioenergy* 2012, 41, 131–138. [CrossRef]
- [85] Kumari, A.; Kumar, A.; Pathak, A. K.; Guria, C. Carbon dioxide assisted *Spirulina platensis* cultivation using NPK-10:26:26 complex fertilizer in sintered disk chromatographic glass bubble column. *J. CO₂ Util.* 2014, 8, 49–59. [CrossRef]
- [86] Lambou, V. W., F. A. Morris, R. W. Thomas, M. K. Morris, L. R. Williams, W. D., Taylor, F. A. Hiatt, S. C. Hern, and J. W. Hilgert. 1977. Distribution of phytoplankton in West Virginia lakes. Working Paper No. 693, National Eutrophication Survey, USEPA. 23 pp.
- [87] Madigan, Michael T., Martinko, John M. (2006) *Brock Biology of Microorganisms*. 11 ed. Pearson Prentice Hall. New Jersey, USA. p. 396
- [88] Markou, G.; Chatzipavlidis, I.; Georgakakis, D. Cultivation of *Arthrospira (Spirulina) platensis* in olive-oil mill wastewater treated with sodium hypochlorite. *Bioresour. Technol.* 2012, 112, 234–241. [CrossRef] [PubMed]
- [89] Needham, J. G., and P. R. Needham. 1964. A guide to the study of Fresh-Water Biology. 5th Ed. Holden-Day, Inc., San Francisco, CA. 108 pp.
- [90] Nishiwaki-Matsushima, R., T. Ohta, S. Nishiwaki, M. Suganuma, K. Kohyama, T. Ishikawa, W. W. Carmichael, and H. Fujiki. 1992. Liver tumor promotion by the cyano- bacterial cyclic peptide toxin microcystin-LR. In *J. Cancer Res. Clin. Oncol*, Springer-Verlag. 118:420-424.
- [91] Prajapati, S. K.; Kumar, P.; Malik, A.; Vijay, V. K. Bioconversion of algae to methane and subsequent utilization of digestate for algae cultivation: A closed loop bioenergy generation process. *Bioresour. Technol.* 2014, 158, 174–180. [CrossRef] [PubMed]
- [92] Rosgaard L., de Porcellinis A. J., Jacobsen J. H., Frigaard N.-U., Sakuragi Y: Bioengineering of carbon fixation, biofuels, and biochemicals in cyanobacteria and plants. *J Biotechnol.* 2012, 162: 134–147. 10.1016/j.jbiotec.2012.05.006.
- [93] Soil & Water Conservation Society of Metro Halifax. 1992. Phytoplankton assemblages in six Halifax County lakes. 56 p.
- [94] Soil & Water Conservation Society of Metro Halifax. 1993. Phytoplankton Assemblages in 21 Halifax Metro Lakes (Phase-B3 Limnology project), November 1993. 130 p.
- [95] Soil & Water Conservation Society of Metro Halifax. 1993. Synopsis titled “Phytoplankton” (of fresh waters). 11p.
- [96] Sumardiono, S.; Syaichurrozi, I.; Budi Sasongko, S. Utilization of Biogas as Carbon Dioxide Provider for *Spirulina platensis* Culture. *Curr. Res. J. Biol. Sci.* 2014, 6, 53–59.
- [97] Wang B., Wang J., Zhang W., Meldrum D. R.: Application of synthetic biology in cyanobacteria and algae. *Front Microbiol.* 2012, 3: 344
- [98] Wedepohl, R. E., Knauer D. R, Wolbert G. B., Olem H., Garrison P. J., and Kepford K.. 1990. Monitoring Lake and Reservoir Restoration. EPA 440/4-90-007. Prep. by N. Am. Lake Manage. Soc. for U.S.E.P.A. 142 pp.

**ASSESSMENT OF ECOLOGICAL SAFETY LEVEL
OF KAMYANETS-PODILSKY CITY BY THE DENSITY
OF PETROL STATIONS PLACEMENT**

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Abstract. The article is devoted to the assessment of the environmental threats from petrol stations. During operation, petrol stations cause the inflow of pollutant substances into natural environment. Besides this, the emergencies, leaks and spills of petroleum products during repairs and service of technological equipment are probable. The aim of the article is systematization of environmental risks from petrol stations at the urban territories as well as analysis of environmental threats from their manifestation.

Key words: petrol station, environmental risk, integral indicator of environmental safety, density of petrol stations placement, urbanized territory.

Introduction. The provision of environmentally safe conditions of human life and preservation of the environment are among the priority national interests of Ukraine. For provision of environmental safety and for fulfillment of the tasks formulated in The Law of Ukraine “On the Main Principles (Strategy) of the National Environmental Policy of Ukraine for the Period until 2020” [Помилка! Джерело посилання не знайдено.], there is a need for a predictive environmental risk assessment as a measure of existing threats for adoption of preventive measures to reduce this level of risk, which is becoming more and more relevant.

At the beginning of 2016, in Ukraine, there were above 10 million vehicles owned by private owners,

state and communal enterprises [2]. Besides this, it is necessary to take into account a significant number of agricultural, construction and road vehicles [1]. For service, and provision of all these vehicles with fuel, a wide network of petrol stations (which exceeds 7000) is developed in the country. By the beginning of 2000, the majority of petrol stations had been situated, as a rule, outside the cities, at the entrances to the cities, in industrial zones, on the roads outside urban areas. In recent years, the situation has changed significantly. New petrol stations are placed in the city lane, residential neighborhoods, near large shopping and entertainment complexes [[10]].

The increasing density of petrol stations within urbanized territories causes the increase in pollution of the environment due to the inflow of fuel evaporations into the air. The analysis of petrol station operation shows that pollution of environment by fuel vapors is observed during refueling of petrol stations from refueling tanks; storage of fuel in tanks; direct refueling of cars. The main pollutant substances during petrol station exploitation (during operation with gasoline, diesel fuel and liquefied hydrocarbon gas) are saturated hydrocarbons: propane, butane, ethane and methane. The prevailing emissions sources, directly at petrol stations during technological processes, are: respiratory valve of fuel tank (organized source) – pollutant substances get into environment during tank filling from gasoline tank and during storage of fuel in reservoirs; mouth of fuel tank (non organized source) – pollutant

substances get into environment during refueling of motor vehicles tanks. The presented data give an opportunity to affirm, that such activity is potentially dangerous due to the increasing environmental risk. The issues related to environmental risks assessment are studied by domestic and foreign experts, among which special contribution to the study of this issue has been made by: S. P. Ivaniuta [7], K. V. Taraniuk [7], A. B. Kachinskyi [8], V. V. Vitlinskyi, O. O. Veklich, M. V. Golovanenko, S. M. Illiashenko, O. V. Kozmenko, S. K. Harichkov, E. V. Hlobistov, P. A. Vaganov, K. Richter, O. N. Rusak, O. V. Sadchenko and others [4]. Characteristics of soil contamination level by petrochemicals near petrol stations are presented in the work [19]. Authors conducted researches at petrol stations in Kyiv. In general, soil contamination level on the territories of petrol stations varies in wide ranges. In relation to allowable concentration, (4000 mg/kg) soil contamination level varies from 0.6 to 5.3 of particles that certainly confirms the assumption about high pollution level. According to the recommendations of V. I. Soloviov [16] the analyzed samples can be divided into:

- Uncontaminated – 12 %;
- Slightly contaminated – 21 %;
- Moderately contaminated – 47 %;
- Highly contaminated – 20 %.

Some results of the selected samples are presented in Table 1.

Table 1

Evaluation of soil contamination by petrochemicals

№	Mass fraction of petroleum products, mg/kg	Contamination level of soils in relation to allowable concentration
1	3765	0.94
2	3149	0.78
3	4223	1.05
4	3017	0.75
5	7490.5	1.87
6	7683	1.92
7	8816	2.20
8	7088	1.77
9	10014,6	2.50
10	11234	2.80
11	11166	2.79
12	11187	2.79
13	10563	2.64

Researches results of soil contamination by petrol stations are presented in the article [1]. Authors submit information on concentration of petrochemicals in the samples taken from different depths. In general, the territories of three petrol stations were researched by the scientists. A borehole for sampling was drilled at each station. The statistical information about soil contamination in the territory of one of the stations is presented in Table 2.

Table 2

Vertical distribution of petrochemical contamination of soil on the territory of petrol station

Borehole	Layer depth, m	Compound	µg/kg of wet soil median (n = 3)	Standard deviation	GROs median, µg/kg of wet soil (n = 3)	Standard deviation
1	2	3	4	5	6	7
T1	0–1	Naphtalene	3.02	0.26	14.00	1.39
	1–2	–	not detected	not detected	6.02	0.60
	2–3	Hexane	18.44	11.56	37.71	24.31
		Octane	8.88	7.26		
	3–4	Naphtalene	4.00	2.01	8.99	7.90
		Hexane	3.63	3.00		
	4–5	Naphtalene	1.81	1.59	5.79	0.96
		Hexane	2.43	0.55		
	5–6	Hexane	21.42	10.82	37.04	26.05
		Octane	5.00	2.34		
		Decane	1.73	2.58		
		Naphtalene	1.86	2.26		
	6–7	Hexane	4.80	0.51	6.33	1.17
	7–8	Hexane	9.53	5.40	13.40	8.25
		Octane	2.42	2.85		
		Hexane	2.35	0.21		
	8–9	Hexane	2.35	0.21	3.40	0.13
	9–10	Hexane	5.91	3.23	8.11	5.64
		Octane	1.28	2.12		
		Hexane	7.36	0.08		
Blank		Hexane	7.36	0.08	7.71	0.32

Continuation of table 2

1	2	3	4	5	6	7
T2	0–1	Decane	3.92	0.50	20.92	2.03
	1–2	Decane	3.41	0.52	17.40	2.17
	2–3	Decane	3.56	0.39	18.09	0.87
	3–4	Hexane	6.15	2.34	10.11	1.51
	4–5	Hexane	2.11	0.17	5.09	0.34
	5–6	Hexane	2.44	2.78	4.22	2.82
	6–7	Hexane	3.69	1.42	8.25	4.28
		Toluene	3.41	3.09		
	7–8	Hexane	1.72	0.41	2.83	0.62
	8–9	Hexane	2.15	0.71	3.24	0.82
T3	9–10	Hexane	1,30	0.34	2.18	0.47
	Blank	Hexane	2.57	0.20	3.26	0.19
	0–0.3	Hexane	5.54	3.72	3185.74	5414.42
		Ethylbenzene	3.49	2.97		
		o-Xylene	4.71	3.98		
		1,3,5-	6.52	5.53		
		Trimethylbenzene				
		1,2,4-	26.27	22.47		
		Trimethylbenzene				
		Naphtalene	19.68	17.49		
	0.3–0.6	Hexane	3.49	0.62	17.63	21.23
		1,2,4-	4.12	6.56		
		Trimethylbenzene				
		Naphtalene	5.89	9.17		
	0.6–0.95	–	not detected	not detected	6.53	1.76
0.95–1,20	–	not detected	not detected	6.49	2.56	
Blank	Hexane	2.21	0.10	2.80	0.10	

Concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) in the samples from T1, T2 and T3 boreholes (Table 2) indicate considerable variability among the three replicates of each sample. The fact that VOCs have been detected in the headspace containing only the Modifying Matrix Solution (MMS) suggests the possibility of the sample contamination by the atmosphere, in this case, by the gases from the combustion in the equipment used for drilling boreholes at the petrol station. Similarly, the high octane concentration from the 5 m depth in T1 borehole is not real because during the gas chromatography mass spectrometry (GC-MS), laboratory technicians were working with this compound very close to the GC-MS equipment where BTEX and (Gasoline Range Organic) GROs determination was being carried out. Additionally, it may be due to a laboratory contamination: a residual concentration in the atmosphere by hexane solvent used to perform other chemical determinations by a lab technician.

The highest recorded hexane value in the subsoil samples is 18 µg/kg of wet soil which belongs to T1 borehole at the 2–3 m depth. Individual concentrations of BTEX have been detected and quantified. Toluene has been quantified in the concentration of 3.41 µg/kg of

wet soil in T2 borehole at the 6–7 m depth. Concentrations of ethylbenzene and oxylene have been detected in the first 30 cm in T3 with the values of 3.49 and 4.71 µg/kg of wet soil respectively. Naphthalene was detected with the highest concentration (19.68 µg/kg of wet soil) in T3 borehole in the surface layer, from 0 to 0.03 m, in T3 at the 0.6 m depth (5.89 µg/kg of wet soil) and in T1 at a depth of the first meter with an average concentration of 3.02 µg/kg of wet soil. A downward trend can be seen in the concentration of GROs with increasing depth, which is obvious as GROs compounds are more volatile than Diesel Range Organic and Waste Oil Organic, and therefore, they migrate to the surface and suffer significant losses due to volatilization. The highest concentrations in these three boreholes are presented at a depth of 3 m.

Despite the deep ecological and economic crisis in Ukraine, the introduction of effective methods for regulation of nature use, namely environmental risk assessment as well as monitoring and assessment of environmental safety level) remains one of the top tasks for further sustainable development of Ukraine. But unfortunately, this problem is not paid enough attention to and it needs further development.

Materials and methods of research. Risk is a quantitative degree of danger. The application of the term “risk” allows transferring danger to the measured categories [[1]]. The main conception of risk assessment is identification of risks quantitatively or at least in a comparative form (qualitatively), relative to any other risks.

Almost all ecological processes are accompanied by uncertainty elements, which lead to ambiguity of the result. The corresponding risk is determined by quantitative and qualitative characteristics of probability for different variants of risks. The definition of risks is connected with compulsory studying of statistics and fulfillment of the following conditions: the availability of full amount of necessary information and factors concerning the uncertainty; the necessity of evaluation of all possible options and their consequences; choosing the best probabilities out of the available ones. The choice is made in the presence of alternative options by objective, subjective or subjective-objective estimates depending on the purpose of choosing a solution and its implementation.

The identification and assessment of risks should be based on the results of control of the technical condition at a petrol station, statistical data about failures, incidents, accidents and emergencies of anthropogenic nature, the data on dangerous geological and hydro-meteorological processes monitoring, the condition of urban ecosystem, statistical data on natural disasters, as well as on the results of modeling and forecasting of relevant hazardous events and situations [[5], 10].

The quantitative assessment of environmental risks creates the basis for classification of all petrol stations, and ranking of urbanized territories in the country by the degree of danger. Such assessment allows applying legal norms and state mechanisms of administrative and economic impact in proportion to the risk of danger in order to ensure an acceptable level of risk to achieve life safety for the society [[5], 10].

For Ukraine, the following basic risk indicators are defined: insignificant risk, acceptable risk, marginally tolerable and unacceptable risk [6]. Herewith, the acceptable risk is “risk, which is ensured in full compliance of the conditions and safety of work with the requirements of normative and legal acts on labor protection, but allows presence of grave and harmful working conditions, work in which is rewarded by benefits and compensations in accordance with current legislation” [[1], 10].

The generalized procedure for the assessment of risk from petrol stations can include such steps [17]:

1. Danger source identification. Given information can be used to receive the answers to the questions:

– What is the genesis of primary and secondary sources of danger of petrol stations for urban ecosystems?

– where, when and under what conditions did the urban ecosystems (or their separate components) suffer from petrol stations, or when will they suffer from them?

2. The assessment of a hazard level of petrol station sources – the analysis of spatial-temporal and volume-powerful parameters of hazard sources, detected in relation to the urban ecosystem.

3. General assessment of ecological vulnerability of the personnel, urbanized territory, and population within the urbanized territory and objects of management adjoined to the territory of the petrol station.

4. Risk assessment of the accident transformation into a complex accident or into a crisis.

5. Justification of measures to minimize risks with consideration of economic, social and environmental requirements and possibilities of the urban ecosystem (in the vicinity of the petrol station placement).

The assessment of risks from petrol station functioning can be based on relationships [6]:

$$R_{ns}(W_j) = P_s(W_j) \cdot V_{sf}(W_j) \cdot V_{nt}(W_j) \cdot V_{ns}(W_j) \cdot N_s, \quad (1)$$

where $R_{ns}(W_j)$ is collective risk of death or loss of health in an urbanized territory S from j types of impact from petrol stations W_j (pers./year); $P_s(W_j)$ is the probability of impacts manifestation from petrol stations (W_j) at the urbanized territory S (cases/year); $V_{sf}(W_j)$ is physical vulnerability of the urbanized territory S from the impacts of petrol stations W_j , that is determined as the ratio of the affected territory S_j to the general area of the territory S ; $V_{nt}(W_j)$ is time vulnerability of the population, determined as the probability of presence on the urbanized territory S during the manifestation of the impressive impacts of the petrol station; W_j ; $V_{ns}(W_j)$ is spatial vulnerability of the population, determined as the probability of getting into the affected part of the urbanized territory S ; N_s is total population within the urbanized area S [[2].

Further scientific research is to find out the mechanisms that cause the development of hazardous processes during the petrol station exploitation, identification of the main natural and man-made factors that contribute to their activation, zoning of the urbanized area by intensity, scale and nature of hazardous processes manifestation (at petrol stations), quantitative assessment of risks from the petrol station functioning.

Due to the transformation of methodology for environmental risk assessment, the following algorithm of research is proposed: First of all, the most serious threats are determined and their ranking is conducted. Then risk assessment and assessment of environmental safety level are made. It is important to take into account the components that may cause ecological threats, because they can serve as information and statistical basis in the form of specific indicators, characterizing

the quantitative parameters of risk or violation of the ecosystem functioning in the region, settlement, city district, etc. [[10]].

To determine the environmental safety of the territory by the density of petrol station placement, the application of relative indicators is proposed. The proposed indicators can be divided into three levels: the level of petrol station density in the territory, the level of petrol station density per inhabitant, and the level of petrol station density in relation to the area of recreational territory. The chosen indicators reflect the level of man-made load from the number of petrol stations at a specific territory [10].

The assessment of the level of petrol station density in the territory is carried out by the calculation of an individual indicator for a petrol station placement (by density) for the corresponding region (settlement, city district), and is determined as a correlation:

$$S_n = \frac{n}{S_{n.n.}}, \quad (2)$$

where S_n is the maximum value of an individual indicator of the petrol station placement (by density), for the corresponding region (settlement, city district), un./km²; n is the number of petrol stations placed in the territory of the district (settlements, city districts), un.; $S_{n.n.}$ is the territory of the region (settlement, city district), km².

The evaluative individual level of the petrol station density per inhabitant is calculated by the formula:

$$N_n = \frac{n}{N_{n.n.}}, \quad (3)$$

where N_n is the maximum value of an individual indicator of the level of the petrol station density per inhabitant in the corresponding region (settlement, city district), un./per; n is the number of petrol stations placed in the territory of the district (settlement, city districts), un; $N_{n.n.}$ is the number of the population in the region (settlement, city district), persons.

The evaluative individual degree of the petrol station density in relation to the area of the recreational territory of the region (settlement, city district) is calculated by the formula:

$$L_n = \frac{n}{L_{n.n.}}, \quad (4)$$

where L_n is the maximum value of the evaluative individual degree of the petrol station density in relation to the area of the recreational territory of the region (settlement, city district), un./km²; n is the number of petrol stations placed in the territory of the district (settlement, city district), un.; $L_{n.n.}$ is the area of the territory of the region (settlement, city district), km².

A separate indicator can not be the basis for ranking of the region (settlement, city district).

To compare individual time periods with further determination of the integral indicator of the ecological safety of the territory, the values of the level of the petrol station density in the territory, the level of the petrol station density per inhabitant, and the level of the petrol station density in relation to the area of the recreational territory of the corresponding region (settlement, city district) should be used.

The normalized individual indicator of the petrol station placement for the corresponding region (settlement, city district) is calculated by the formula:

$$S = \frac{S_n}{S_n^{\max}}, \quad (5)$$

where S_n^{\max} is an individual indicator for the petrol station placement (by density) among the considered regions (settlement, city district) during the analyzed period.

The normalized individual level of the petrol station density per inhabitant of the corresponding region (settlement, city district) is calculated by the formula:

$$N = \frac{N_n}{N_n^{\max}}, \quad (6)$$

where N_n^{\max} is the maximum value of the individual level of the petrol station density per inhabitant among the considered regions (settlements, city districts) during the analyzed period.

The normalized individual degree of the petrol station density in relation to the area of recreational territory of the region (settlement, city district) is calculated by the formula:

$$L = \frac{L_n}{L_n^{\max}}, \quad (7)$$

where L_n^{\max} is the maximum value of the individual degree of the petrol station density in relation to the area of the recreational territory among the considered regions (settlements, city districts), during the analyzed period.

Integral indicator of ecological safety of the territory by the density of the petrol station placement is:

$$D_{A3C} = g_k \cdot S + g_k \cdot N + g_k \cdot L, \quad (8)$$

where k is the number of hazard indicators from petrol stations of the region (settlement, city district), in the given case $k = 3$; γ_k is the weight coefficient, in the first approximation $\gamma_k = 1/k$.

It is proposed to apply the given methodology to determine the acceptable risk in the region (settlement, city district), the degree of which is determined depending on the environmental situation, the level of population morbidity and the number of emergencies at man-made objects [10].

By the results of the assessment of the integral indicator of environmental safety, special ranking of

regions (settlements, city districts), aimed at classification of the regions in terms of safety level, is carried out. It should be taken into account that the highest value of this indicator shows the lowest level of environmental safety of the region (settlement, city district).

Having determined the quantitative assessment of environmental risk, it becomes relevant to implement a qualitative interpretation of the calculated values by identifying quantitative values of risk, that is, a degree of risk. For qualitative interpretation of the calculated values, it is proposed to divide the numerical interval of ecological risk level (which has all possible values from zero to one) into five intervals, that is, to define such intervals and their qualitative interpretation [10]:

- I [0.00–0.20) – ecological risk of low level;
- II [0.20–0.40) – ecological risk of moderate level;
- III [0.40–0.60) – ecological risk of average level;
- IV [0.60–0.80) – ecological risk of high level;
- V [0.80–1.00) – ecological risk of extremely high level.

According to the proposed scale, the received values of risks can be divided into five classes of environmental hazard:

- Extremely hazard level of danger – ecological risk level above 0.80;
- High danger – ecological risk level in the range of [0.60–0.80);
- Increased danger – ecological risk level in the range of [0.40-0.60);
- Moderate danger – ecological risk level in the range of [0.20- 0.40);
- Relative danger – ecological risk level below (0.20).

The results and their discussions. The area of Kamyanets-Podilsky is 27,871 km². In January 2016, the population of the city was 101 235 people. The density of petrol stations within the city was 0.72 un./km² and 1.98·10⁻⁴ un./per. From the end of 2016 to the middle of 2017, 20 petrol stations were placed within the city.

According to the methodology used to determine environmental safety level, placement of petrol stations requires the analysis of the scheme of functional zoning of the settlement territory.

The chosen indicators, presented in the research methodology, reflect the level of man-made load from the number of petrol stations in a specific territory, so within Kamyanets-Podilsky it is necessary to select areas of the city that could be compared (ranked) with each other. By the Department of Housing and Communal Services of Kamyanets-Podilsky City Council, the territory of Kamyanets-Podilsky is divided into four districts, which are serviced by four housing and communal enterprises (Fig. 1). The given scheme was used as a basis for our research. The separate

districts of the city are marked by Latin numbers: I – Northeastern district of the city; II – Central district of the city; III – Southwestern district of the city; IV – Southern district of the city.

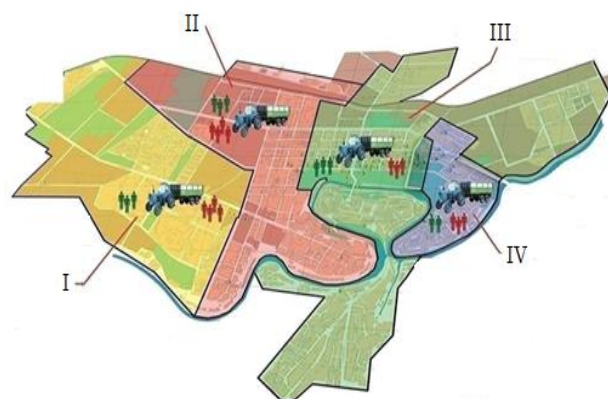


Fig. 1. Map of the territory and experimental districts of Kamyanets-Podilsky city

According to the methodology, the indicators of the city districts area, the number of the city districts, and the area landscape and recreational zone of the city are applied as the initial data to calculate integral estimation of ecological safety level of the territory by the density of petrol stations placement (Table 1).

Table 1

The numerous characteristics of Kamyanets-Podilsky city

District of the city	Area, m ²	Number of petrol stations, units	Population, pers.	The area of the landscape and recreation zone, m ²
I – Northeastern	9931587	12	43986	433100
II – Central	7400006	4	31279	301400
III – Southwestern	9379400	2	9082	48000
IV – Southern	1702982	2	16115	195100

The individual indicators of petrol station placement (by density), petrol station density per inhabitant, level of petrol station density in relation to the landscape and recreation area of the city districts, are presented in Table 2.

Table 2

The normalized individual indicators of petrol stations placement

District of the city	S _n	N _n	L _n	S	N	L
I – Northeastern	1.31	0.0002	30.2	1.00	1.0	0.604
II – Central	0.54	0.0001	13.3	0.41	0.5	0.266
III – Southwestern	0.21	0.0002	50.0	0.16	1.0	1.000
IV – Southern	1.18	0.0001	10.5	0.90	0.5	0.210

The integral indicators of ecological safety of the territory by the density of petrol stations placement, and their ranking are presented in Table 3.

Table 3

**Integral indicators of the territory
by the density of petrol stations placement**

District of the city	D	Risk level	Class of environmental hazard
I – Northeastern	0.87	extremely high	extremely high
II – Central	0.39	moderate	moderate
III – Southwestern	0.72	high	high
IV – Southern	0.54	average	increased

Qualitative interpretation of the calculated values by identification of the received quantitative risk values according to the proposed scale indicates the timeliness of the conducted evaluation. The received results allow performing integral assessment and defining districts of Kamyanyets-Podilsky, which are situated in the zone of dangerous man-made load. The further improvement of the methodology will allow conducting more detailed evaluation in the future, and applying its results for adoption of management solutions concerning planning of the settlement territory.

Conclusions

1. The development of urbanized territories and rapid growth of the number of vehicles in the vicinity of urban ecosystems led to the increase in the number of petrol stations. But the issues concerning boundary capacity of the territory and capabilities of the urban ecosystem to withstand the load caused by the increase in the density of placement of high danger objects are almost not studied.

2. Modern legislative and town-planning documentation regulate local conditions and limitations of petrol station placement, but do not provide assessment of the impact on the environmental safety level of the whole urban ecosystem, which significantly differs in the peculiarities of structural organization and technological scheme of petrol stations exploitation.

3. The ecological threats during petrol station exploitation are caused by getting pollutant substances into the air, water, soil, through emission of steam and air mixture from the reservoirs of the station, and car tanks during refueling, exhaust gases of automobile engines, oil spills during drainage from tank-vehicles into the tanks of the station and during refueling of vehicles, oil leaks and oil spills during repairs and maintenance of technological equipment, emergency situations.

4. According to monitoring results it was found that there are 20 petrol stations within the urban ecosystem

of Kamyanyets-Podilsky. It means that the density of stations concentration within the urbanized area is 0.72 n./km² and 1.98·10⁻⁴ n./per.

5. The integral indicators of ecological safety of Kamyanyets-Podilsky city by the density of fuel stations placement are: I – 0.87, II – 0.39, III – 0.72, IV – 0.54. Thus, the city districts belong to the following classes of ecological danger: I – extremely high, II – moderate, III – high, IV – increased. The further improvement of the methodology will allow conducting more detailed evaluation in the future and applying its results for the adoption of management solutions concerning planning of the settlement territory.

References

- [1] Averin H. V. Otsinka ryzyku vynyknennya avariy na ob'ektakh pidvyshchenoyi nebezpeky / H. V. Averin, V. M. Moskalets // Okhorona pratsi. – 2008. – No. 6. – S. 17–21.
- [2] Veres O. M. Doslidzhennya mnozhyny ryzykiv pryynyattya rishen' v haluzi ekolohiyi / O. M. Veres, V. M. Holysh // Visnyk Natsional'noho universytetu "L'vivs'ka politekhnika". – 2010. – No. 689. – S. 67–80.
- [3] Hadets'ka Z. M. Otsinka ekolohichnoho ryzyku na terytoriyi Ukrainy / Z. M. Hadets'ka, N. V. Kuz'mych // Elektronne naukovе fakhove vydannya "Efektyvna ekonomika". – 2015. – # 12. – S. 46-54. – Rezhym dostupu: http://www.economy.nayka.com.ua/pdf/12_2015/77.pdf
- [4] General'nyy plan m. Kam"yanets'-Podil's'koho Khmel'nyts'koyi oblasti. Osnovni polozhennya (broshura) / Ministerstvo rehional'noho rozvytku ta budivnytstva Ukrainy; Derzhavne pidpryemstvo "Naukovo-doslidnyy i proektnyy instytut mistobuduvannya". – Kyiv, 2010. – 44 s.
- [5] Zerkalov D. V. Naukovi osnovy tekhnohennо-ekolohichnoyi bezpeky [Elektronnyy resurs] : monohrafiya / D. V. Zerkalov, M. D. Katsman, M. I. Adamenko ta in. ; za red. D. V. Zerkalova. – Elektron. dani. – K. : Osnova, 2014. – 1 elektron. opt. dysk (CD-ROM) ; 12 sm. – System. vymohy : Pentium ; 512 Mb RAM ; Windows 98/2000/XP ; Acrobat Reader 7.0. – Nazva z tyt. ekrana.
- [6] Ivanyuta S. P. Ekolohichna bezpeka rehioniv Ukrainy / S. P. Ivanyuta [Elektronnyy resurs] // Stratehichni priorytety. – 2013. – No. 3 (28). – C. 157–164. – Rezhym dostupu : http://irbisnubv.gov.ua/cgi-bin/irbis_nubv/cgiirbis_64.exe?C21COM=2&I21DBN=JRN&P21DBN=UJRN&IMAGE_FILE_DOWNLOAD=1&Image_file_name=PDF/spa_2013_3_23.pdf. – Nazva z ekranu.
- [7] Kachyns'kyy A. B. Ekolohichna bezpeka Ukrainy: systemnyy analiz perspektyv pokrashchennya / A. B. Kachyns'kyy [Elektronnyy resurs]. – Rezhym dostupu : <http://old.niss.gov.ua/book/Kachin/2-7.htm#a1>.
- [8] Kozachenko T. I. Heoinformatsiyne kartohrafuvannya tekhnohennykh zahroz vid potentsiyno nebezpechnykh ob'ektiv / T. I. Kozachenko // Visnyk heodeziyi ta kartohrafiyi. – 2012. – No. 1 (76). – S. 14–25.

- [9] Mistobuduvannya. Planuvannya i zabudova mis'kykh i sil's'kykh poselen' : DBN 360-92. – K. : Derzhbud Ukrainy, 2002 – 138 s.
- [10] Movchan Ya. I. Otsinka rivnya ekolohichnoyi bezpeky terytoriy za shchil'nistyuu roztashuvannya avtozapravnykh stantsiy / Ya. I. Movchan, V. V. Sharavara // Materialy KhIII mizhnarodnoyi naukovo-tekhnichnoyi konferentsiyi Avia-2017 (m. Kyiv, 19-21 kvitnya 2017 roku). – K. : NAU, 2017. – S. 28.34–28.38.
- [11] Orel S. M. Ryzh. Osnovni ponyattya / S. M. Orel, M. S. Mal'ovanyy. – L'viv : NU “L'vivs'ka politehnika”, 2008. – 88 s.
- [12] Plan zonuvannya terytoriyi (zoninh) m. Kam'yanets'-Podil's'koho Khmel'nyts'koyi oblasti. Tom I. Poyasnyval'na zapyska / Ministerstvo rehional'noho rozvytku, budivnytstva ta zhytlovo-komunal'noho hospodarstva Ukrainy; Derzhavne pidpryyemstvo “Naukovo-doslidnyy i proektnyy instytut mistobuduvannya”. – Kyiv, 2015. – 145 s.
- [13] Pro osnovni zasady (stratehiyu) derzhavnoyi ekolohichnoyi polityky na period do 2020 roku [Elektronnyy resurs] : Zakon Ukrainy vid 21.12.2010 r. No. 2818-VI. / Verkhovna Rada Ukrainy. – Rezhym dostupu : <http://zakon5.rada.gov.ua/laws/show/2818-17>. – Nazva z ekrana.
- [14] Pro zatverdzhennya Derzhavnykh sanitarnykh pravyl planuvannya ta zabudovy naselenykh punktiv [Elektronnyy resurs] : Nakaz Ministerstva okhorony zdorov'ya Ukrainy vid 19.06.1996 r. No. 173 / Ministerstvo okhorony zdorov'ya Ukrainy. – Rezhym dostupu : <http://zakon2.rada.gov.ua/laws/show/z0379-96/page>. – Nazva z ekrana.
- [15] Taranyuk K. V. Metodychni osnovy upravlinnya ekolohichnymy ryzykamy na rehional'nomu rivni / K. V. Taranyuk // Mekhanizm rehulyuvannya ekonomiky. – 2012. – # 4. – S. 132–138.
- [16] Ustinova E. I. Mis'ke komunal'ne hospodarstvo : navch.-metod. posib. / E. I. Ustinova, A. Ye. Hay, O. O. Marits [ta in.]. – K. : NAU, 2008. – 116 s.

ENVIRONMENT CONTAMINATION WITH HEAVY METALS CONTAINED IN WASTE

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Abstract. The paper analyzes the sources of the most widespread heavy metals contained in waste. Different directions of human activity are considered with emphasis on the waste containing heavy metals. It is established that the largest suppliers of heavy metals include waste of metallurgy, chemical industry, production of electrical appliances, batteries and accumulators, sewage sludge, ash and slag of coal-fired power stations and waste incineration plants, and the recent one is household waste. In agricultural regions these sources include waste of pesticides and fertilizers production and application. The sources are described for each heavy metal, and for household waste they are analyzed concerning to certain types of waste.

Key words: heavy metals, waste, contamination, environment.

1. Introduction

It is known that waste that is constantly produced in large volumes contains hazardous substances including heavy metals. From an environmental point of view, heavy metals of most concern are the most dangerous to living organisms and the environment. They include lead, cadmium, nickel, mercury, chromium, zinc, copper and arsenic. It should be noted that waste management practice is mostly inappropriate in many countries. As a rule, waste is not processed and it gets into the environment easily, contaminating it. The authors [1] indicate that most heavy metals compounds are not decomposed by microorganisms and chemicals. Therefore, their total concentration in the environment remains stable for a long time. Regarding potential environment pollution with heavy metals, particular danger is caused by waste of galvanic manufacturing and metallurgy, as well as by hazardous components of household waste investigated by the authors [2–4].

One should note heavy metals predisposition to accumulation in the environment, but not decomposition

unlike many other pollutants [5]. It is known [1] that the form of environment contamination by heavy metal depends primarily on the type of process of its formation. The content of every heavy metal and its physical and chemical properties are also influenced by the way of waste treatment (recycling). Besides, subsequent heavy metal influence and its dissemination depend on the soil condition, the chemical composition of groundwater and the existing migration mechanisms in the environment.

The total heavy metal content in the environment does not fully reflect its danger to the environment. The more important is the available (mobile) content, i.e., the part of the total heavy metal amount, which can migrate to the environment or be absorbed by living organisms [6].

There are many papers dedicated to sources of environment pollution with heavy metals. However, most of them cover general emissions into the environment. The purpose of this study is to separate and analyze the potential sources for heavy metals contained in the waste.

2. Analysis of sources of environment pollution with heavy metals as part of waste stream

One of the main sources of heavy metals is industrial waste. Among the most influential industries are chemical industry (As, Cu, Pb, Ni, Zn, Cr, Co, Cd), production of ceramic products (Cd, Cr, Cu, Pb, Hg, Ni, Zn), electronics manufacturing (Cu, Zn, Pb, Cr, Co, Hg), metallurgy (As, Cr, Pb, Mn, Ni, Zn, Cd, Cu, Hg), production of batteries and accumulators (Pb, Zn, Cd, Ni, Hg), printing industry (Pb, Cd, Zn, Cr), production of catalysts (Co, Ni, Zn), pigments and paints (Pb, Cr, As, Hg, Cd, Zn, Co), and stabilizers for polymers (Pb, Cd, Zn) [6].

Heavy metals are also accumulated in ash and slag of coal-fired power plants and waste incineration plants. The content of Zn, Pb, Cd, and Cu is the highest in such ash [7]. Their concentration is even higher in a volatile ash: As – up to 230 mg/kg, Cu – up to 1300 mg/kg, Pb – up to 8300 mg/kg, Zn – up to 27000 mg/kg [6].

Besides, high content of heavy metals (primarily Pb, Ni, Cd, Cr, Cu, Zn) is found in sewage sludge, including those from household dwellings. According to [1] more than 30% of that sludge is often used then as fertilizers for agricultural land, which leads to further heavy metals migration to the environment.

The significant source of heavy metals, especially in agriculture regions, is waste of pesticides production and use. It contains, for example, lead arsenate (AsHO_4Pb), “paris

green” copper acetoarsenite ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$), bordeaux mixture ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$), copper oxychloride $3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2$ and phenyl mercuric chloride ($\text{C}_6\text{H}_5\text{ClHg}$) [6].

Based on the analysis and taking into account other numerous studies [5, 6, 8–13], Table 1 was compiled summarizing the sources of emission of the most widespread heavy metals into the environment as a part of waste.

Table 1

Sources of some heavy metals in waste

Metal	Metal-containing waste
Pb	cement, pesticides, paints and pigments, enamels, varnishes, dyes, catalysts, batteries and accumulators, printing products, TVs and other electrical devices, fluorescent lamps, coloured glass, ammunition, construction waste, waste of leather industry, waste of mining industry, waste of vehicles (tires, engines), metal products (lead-asbestos plates, anticorrosive containers, anti-radiation screens), technical oils, sewage sludge, waste of machine industry, ash of coal and waste incineration, waste of plastic production, metallurgical slag, waste of polymer stabilizers manufacturing, soldering waste, waste of ceramic coatings production
Cd	batteries and accumulators, electrical cables, car radiators, cement, waste of pesticides and fertilizers manufacturing and use, PVC-plastics, coloured glass, paints, glues, waste of solar panels manufacturing, sewage sludge, ash of coal and waste incineration, waste of ceramic coatings production, metallurgical slag, waste of printing industry, waste of polymer stabilizers production, waste of machine industry, galvanic waste
Ni	batteries and accumulators, cement, pesticides, slag of mining industry, waste of nonferrous metallurgy, waste of chemical, machine, and metal-processing industries, old vehicles, sewage sludge, waste of ceramic products production, catalysts
Hg	thermometers, fluorescent lamps, batteries, dyes, PVC-plastics, pesticides, paints, printing products, TVs and other electrical devices, accumulators, barometers, manometers, waste of synthetic polymers production, metallurgical slag, waste of cement industry, ash of coal and waste incineration
Cr	cement, varnishes, paints and pigments, dyes, batteries, printing products, waste of refractory brick production, waste of leather industry, waste of chemical industry, metallurgical slag, sewage sludge, waste of ceramic products production, waste of electronic devices production, metal products made from stainless steel, galvanic waste
Zn	cement, pesticides, paints, waste of medicines, batteries and accumulators, fluorescent lamps, waste of office supplies, construction waste, metallurgical slag, galvanic waste, sewage sludge, ash of waste incineration
Cu	electrical cables, cement, car radiators, pesticides, coloured glass, paints, varnishes, dyes, printing products, sewage sludge, ash of waste incineration, agriculture waste (livestock)
As	paints and dyes, waste of medicines, pesticides, printing products, ash of waste incineration, metallurgical slag

Lead is used for manufacturing water pipes, ammunition, paints, printing alloys, solder, accumulators, various metal products, chemicals and dyes, as building material and for casting [11]. It is also widely used for the soundproofing materials production. High corrosion resistance causes its application in the construction industry. Anti-vibrating lead-asbestos gaskets are used in construction of the buildings located in the intensive traffic zone, in installation of laundry equipment and ventilation systems, and in heavy industry. Besides, lead is used in the production of cable shells, collapsible pipes, coating materials, anticorrosive containers. The use of lead in decorative paints production (lead white and coloured paints) is noticeably reduced, but the production of lead sulfur and lead chromate remains intensive due to their low cost and good anti-corrosion properties. Lead is also used in automobile wheels production, as ship ballast, for the production of various alloys and lead ferrite, which is used as a permanent magnet in small electric engines. The use of lead-porcelain enamels for aluminum coating and radiation-protection screens constantly increase. Organometallic compounds of lead are used in the

production of paints for covering ship bottom, as additives to technical oils, in the production of polyurethan catalysts, antibacterial agents and various pesticides. An important source of lead emission into the environment is mining industry. In some cases, lead content in the solid waste of mines can reach 20000 mg/kg. All of the above-mentioned productions are potential sources of lead in waste.

Cadmium-containing waste is produced by many industries. Cadmium is applied to products to provide gloss and corrosion resistance. These products include, for example, details in car and aviation industries, metal parts of marine crafts, radio and television equipment, household appliances and other metal products. One of the main cadmium sources in the soil is the waste of fertilizers production and use [9]. First of all, these are phosphate fertilizers, where its concentration can reach more than 100 mg/kg according to [6]. Cadmium is also used for the packaging materials production (except food industry). Cadmium sulfides (orange-yellow colour) and cadmium sulphoselenides (pinkish-red and chestnut colours) are used as dyes in the production of plastics, ceramics, paints and coating materials. Cadmium pigments are used for

colouring vehicles, and during processing high-quality industrial products. Cadmium stearates are used as stabilizers in the production of polyvinyl chloride plastics (PVC-plastics). However, cadmium-based stabilizers are not used in the production of flexible PVC-based plastics for food products packaging because of the potential danger of contamination. Cadmium is also widely used in accumulators due to a high degree of electrochemical reactions reversibility in a wide range of temperatures, low discharge velocity and the simplicity of battery recharge. These batteries are used in different appliances: in electric toothbrushes and razors, other electric tools (drills, scissors, etc.), medical devices, mobile phones, emergency light sources, airplanes, satellites and rockets. Other areas of cadmium use are cadmium coatings of fluorescent lamps, X-ray screens, phosphorescent labels; cadmium alloys in cadmium-silver solder, in automatic fire suppression systems, valve gaskets of high pressure gas cylinders, in transport and telephone wires, car radiator grates; electrical and electronic devices: relays, switches, car interrupter contacts, solar panels [10, 11]. An important source of cadmium-containing waste is also mining industry (in particular, residual rock waste) and metallurgical slag.

The majority of nickel is emitted into the waste as inert form of alloys (first of all, stainless steel and steel alloys) and with used products having galvanic coating. Among the industrial waste containing stainless steel with nickel there is scrap metal and equipment (parts of cars, food industry equipment, electrical equipment, construction waste, tools, etc.), used rails and solar panel elements. Nickel is also found in solid and liquid waste of chemical industry (fertilizer production) and oil industry (in oil refining). Waste of nickel alloys with chromium, molybdenum, titanium, niobium is produced in chemical, electronic, nuclear and aviation industries. Besides, nickel-chrome alloys are used in some industrial furnaces. Pure nickel can be emitted to the environment with used household appliances and as waste of catalyst for edible fats production. One of the major sources of active (available) nickel compounds is production of nickel-cadmium batteries for various power sources and zinc-nickel acid accumulators, as well as power sources themselves after use [11].

Most of all mercury is accumulated in water bodies with about 0.1 % remaining in dissolved form. Moreover, the author [14] points out that the highest mercury emission into the environment takes place in economically less developed areas. Despite the fact that mercury discharges into the water according to forecasts [11] will decrease in the next 50 years, contaminated bottom sediments will remain a source of secondary pollution. The use and further recycling of mercury-containing devices is the main human source of mercury. Significant mercury amounts also are emitted into the environment with waste of industrial companies using liquid mercury as an electrode in salt solutions electrolysis for chlorine and caustic soda production, in the production of thermometers and research equipment,

in fluorescent lamps production and with metallic mercury waste used for gold and silver mining and processing, and amalgam waste in dentistry [10].

The main source of chromium in waste is metals processing (galvanic coatings, etching, polishing). Chrome is used in ferroalloys production (high- and low-carbon ferrochrome and silicon-containing ferrochrome). Ferrochromium alloys are widely used in the production of stainless and heat-resistant steel, which is used in aggressive environments, petrochemical industry, turbines and metallurgical furnaces, cutting tools manufacturing, decorative finishing, machine tools, jet engines, etc. Besides, chromium-containing waste is produced in textile industry (production of pigments, dyes and fasteners), leather industry (tannins production), as well as in many other manufacturing processes: chrome plating, anodizing, metal etching, saccharin production (chrome is used as oxidant and catalyst), oils and fats bleaching and refining, adhesives and inks production (chromium compounds are used to improve moisture resistance of products) and others [11].

Zinc is mostly emitted into the environment as waste of machine and construction industries (production of materials for roof, external coatings and overlaps, door and windows handles, carburetors, pumps, door locks for car and coating of car bottom (zinc is used as coating of iron and steel to enhance corrosion stability of details). There is although a tendency to reduce zinc use and accordingly zinc-containing waste production in these industries. Also, zinc-containing waste is produced in natural and synthetic rubber production (zinc oxide is used as a catalyst for vulcanization), dry batteries, lithographic plates, roofs, paints, paper, cosmetics, medicines, as well as in photography and agriculture [11]. The new powerful source of zinc is old nickel-zinc batteries used in electric vehicles. Besides, polymer waste contains zinc salts providing polymer protection from chlorine or chlorides excess formation.

Copper-containing waste is produced primarily in metallurgical, electrical, construction and car industries, as well as in the production of water supply equipment. The main source of copper in the environment is the production of non-ferrous metals, electronic and electrical equipment, and power supply equipment. Other sources include the production of heat exchangers, wiring and winding in engines, transformers and generators [11]. Copper-containing pesticides were previously widely used, but now their use has decreased significantly and this source of copper in waste also reduces.

The main sources of arsenic compounds in the waste are as follows [11]: metallurgical waste, production of cement, medicines, bullets (in lead alloys), pyrotechnics, hair removal means, enamels, pesticides (insecticides, herbicides, desiccants in the form of calcium arsenate or sodium arsenate, fungicides for wood impregnation), food additives, cleaning chemicals, waste of tissue dyeing and glass discoloration. Relatively new strong source of arsenic in waste is electronic industry.

Household waste of heavy metals emission into the environment, which is investigated by the author, is worth mentioning [15] (Table 2). There is a large amount of cadmium, nickel, mercury and zinc in batteries and accumulators. After the completion of their life cycle, they become waste. For example, batteries contain cadmium as electrolyte salt CdSO_4 . Cadmium is also emitted into household waste in the form of cadmium sulfide and sulfoselenide, which are used in paints for providing red colour.

Table 2

Heavy metals in household waste

Type of waste	Metals contained in waste
Construction waste	Zn, Pb, Cu, Ni, Cr, Cd, As
Expired medicines	Zn, As
PVC-plastics	Hg, Cd
Pesticides / fertilizers	Hg, Cu, Pb, As, Zn, Cd, Ni, Mn
Paints, varnishes	Pb, Cr, As, Hg, Cu, Zn
Batteries	Pb (PbSO_4), Cr (Cr_2O_7), Zn, Cd, Ni, Hg, Cr, Hg
Printing products	Pb, Cr, As, Hg, Cu
TVs	Pb, Hg
Accumulators	Ni, Cd, Pb, Zn
Electronic devices	Pb, Cg, Hg
Fluorescent lamps	Hg, Cu, Ni, Zn, Pb
Coloured glass	Cu (CuO), Pb (PbO), Cd (CdS , CdSe)

Copper gets into household waste in the form of copper (II) oxide in sodium-calcium glass (provides blue colour) and in potassium-zinc glass (provides green colour). Lead gets to landfills in the form of dyes for glass (lead (II) oxide strengthens the colour of glass and gives bright hues). Stibium-lead batteries (in the form of PbSb_2O_6) are also the source of Pb. Nickel along with lithium-ion batteries gets to the environment most often in the form of LiNiO_2 . Besides, nickel-chrome alloys have been used in household heating appliances for a long time. A significant amount of mercury compounds is present in mercury-containing household waste at landfills (used fluorescent lamps and thermometers). Chromium is mostly found in household waste inside used power supplies and residues of paint and varnish materials. Zinc compounds are a part of various office equipment. Zinc and arsenic are also widely used in cosmetics and medicines.

3. Conclusion

The analysis of the sources of heavy metals emitted into the environment together with waste shows a large scale of predictable pollution. A lot of different fields of human activity supply heavy metals to the environment. First of all, these are waste of metallurgy, chemical industry, electrical appliances production, batteries and accumulators, sewage sludge, ash and slag of coal-fired power plants and waste incineration plants, and waste of pesticides and fertilizers production and use for agricultural regions. Besides, household waste and

landfills, where they are accumulated, have become a powerful source of heavy metals in recent years. Not only inert compounds, but also a large amount of mobile (available) forms of metals get into soils and water bodies. Under certain conditions they are able to change the environment significantly.

References

- [1] Wuana R. A., Okieimen F. E.: Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation, *ISRN Ecology*, 2011, 11, 1–19.
- [2] Ishchenko V.: Soil contamination by heavy metal mobile forms near landfill, *International Journal of Environment and Waste Management*, 2017, 20(1), 66–74, DOI: 10.1504/IJEW.2017.10006953
- [3] Ishchenko V., Pohrebennyk V., Kozak Y., Kochanek A., Politylo R.: Assessment of batteries influence on living organisms by bioindication method, 16th International Multidisciplinary Geoconference SGEM 2016, Book 5. Ecology, Economics, Education and Legislation, SGEM2016 Conference Proceedings, June 28 - July 6, 2016, vol. II, 85-92, DOI: 10.5593/SGEM2016/B52/S20.012
- [4] Ishchenko V., Petruk R., Kozak Y.: Hazardous household waste management in Vinnytsia region, *Environmental Problems*, 2016, 1(1), 27–30.
- [5] Wang L. K., Chen J. P., Hung Y. T., Shamma N. K.: Heavy metals in the environment. CRC Press, New York 2009.
- [6] Alloway B.J.: Sources of Heavy Metals and Metalloids in Soils. In: Alloway B. (eds) *Heavy Metals in Soils. Environmental Pollution*, vol 22. Springer, Dordrecht 2013.
- [7] Flyhammar P.: Estimation of heavy metal transformations in municipal solid waste. *Science of the total environment*, 1997, 198(2), 123–133.
- [8] Recknagel S., Radant H., Kohlmeyer R.: Survey of mercury, cadmium and lead content of household batteries. *Waste management*, 2014, 34(1), 156–161.
- [9] Six L., Smolders E.: Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils. *Science of the Total Environment*, 2014, 485, 319–328.
- [10] Sarkar B.: *Heavy Metals in the Environment*, CRC Press, New York 2002.
- [11] Moore J. W., Ramamoorthy S.: *Heavy metals in natural water*. Springer, 1984.
- [12] Korbiak T., Tretiakov P.: Zabrudnennya gruntiv Zolochivskogo rajonu Lvivskoji oblasti Mn, Cr, Ti, Zr, Ni, Ba ta Cu. *Visnyk Lvivskogo Universytetu. Seria geografichna*, 2009, 36, 183–193.
- [13] European Commission DG ENV. E3: *Heavy Metals in Waste- Final Report*. Project ENV.E.3/ETU/2000/0058, COWI A/S, Denmark 2002.
- [14] Watson W. D., Jr.: Economic considerations in controlling mercury pollution. In: Nriagu J. O. (Ed.): *The biogeochemistry of mercury in the environment*. Elsevier-North-Holland Biomedical Press, Amsterdam 1979, 41–77.
- [15] Ishchenko V.: Vplyv poligoniv pobutovyh vidhodiv na riven zabrudnennia gruntiv vazhkymy metalamy. V-j Vseukrajinskyj zjazd ekologiv z mizhnarodnoju uchastiu, 23–26.09, 2015, Vinnytsia, 51.

SORPTION PURIFICATION OF NATURAL WATER FROM MICRO-MIXTURES OF HARD METALS

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Abstract. The purpose of the research is to determine the effectiveness of using different types of activated carbon in the process of water purification from heavy-metal ions for technological purposes in the food industry. Different types of activated carbon are used as sorbents. The study determines the factors that influence the efficiency of drinking water purification from heavy metal ions through activated carbon. It also proves the highest efficiency of oxidized form of activated carbon.

Key words: water purification, activated carbon, sorbent, heavy metals, purification efficiency.

The food industry is one of the most developed branches of material production in Ukraine. It is also one of the largest consumers of freshwater, with its annual requirement of more than 2 billion m³. The deterioration of the quality of natural water in industrially developed regions under the influence of man-made factors, in particular heavy metal ions, makes it problematic for its further use in the technological processes of food production [1].

Much of the water in the food industry is used as raw material and solvent as well as for washing raw materials and equipment, which results in high water quality requirements [2]. In this regard, the crucial

task is to determine the possibilities of ensuring the quality of technological water in food industry based on the use of advanced water treatment technologies. Sources of drinking water supply, i.e. natural water, are characterized (especially in the industrial regions of Ukraine) by high amount of heavy-metal ions, which can be 1-5 times higher than maximum allowable concentration. Such an increased concentration of heavy-metal ions in water can be caused both by natural factors (geochemical characteristics of water supply sources) and by man-made factors [3].

The risk from heavy metals is caused by the stability of their ions in the external environment, solubility in the water, sorption by soil and later by plants. This leads to accumulation of heavy metals in hazardous concentrations in food products and the emergence of a number of so-called ecologically dependent diseases (toxicodermia, allergies, cancer, and etc.) [4].

The purpose of the research is to determine the effectiveness of using different types of activated carbon in the process of water purification from heavy-metal ions for technological purposes in the food industry. Table 1 presents physical and chemical indicators of four categories of natural water used in the studies.

Table 1

Physical and chemical indicators of natural water

№	Indicators and unit of measure	River-water	Artesian Water	Tap water	Pond Water
1	Hydrogen index (pH)	5,86	7,49	7,41	6,5
2	General stiffness, mmol/dm ³	7,0	10,2	8,2	7,5
3	Permanganate oxidation, mgO/dm ³	8,3	1,84	4,38	9,8

Table 2 indicates the concentration of micro-impurities in the studied natural water of the four categories.

The following types of activated carbon were used in the capacity of sorbents: bituminous coal Filtrasorb-300 (produced in Belgium), activated anthracite CWZ-3 (produced in Poland), activated fruit-stone carbon and its

oxidized form, obtained from the experimental production at the Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine. The fractional composition of various types of coal was practically the same and amounted to 0.5–2.5 mm. Table 3 presents physical and chemical and structural-porous characteristics of the studied types of coal.

Table 2

Concentration of micro-impurities in investigated natural water

№	Concentration of micro-impurities, mg/l	River-water	Artesian Water	Tap water	Pond Water	MAC of Micro-impurities, mg/l
1	zinc	1.84	3.38	5.62	2.03	5
2	copper	0.52	0.63	0.46	0.7	1
3	aluminum	0.32	0.46	0.35	0.5	0.5
4	iron	0.29	0.24	0.2	0.25	0.3
5	nickel	0.07	0.09	0.09	0.07	0.1
6	manganese	0.08	0.08	0.09	0.06	0.1
7	lead	0.01	0.01	0.01	0.01	0.03
8	cadmium	0.003	0.003	0.004	0.002	0.005

Table 3

Characteristics of activated carbon used in experiments

№	Indicator and unit of measurement	Activated carbon			
		F-300	CWZ-3	activated fruit-stone carbon	oxidized form of activated fruit-stone carbon
1	Bulk density, g/cm ³	0.56	0.47	0.45	0.46
2	Adsorption activity on methylene blue, mg/g	230	200	220	210
3	Adsorption activity on iodine, mg/g	95	80	75	70
4	Total volume of sorption pores ($V_{mi}+V_{me}$), cm ³ /g	0.40	0.56	0.52	0.48
5	Specific surface area (in BET), m ² /g	1000	1080	960	920
6	Static exchange capacity in Na ⁺ -cation, mg-eq/g	0.2	0.15	0.2	0.9

The experimental procedure was as follows: the model solutions containing micro-impurities of heavy metal salts (concentration 5 MAC) were prepared from natural and tap water. Sorption experiments were conducted within dynamic conditions (column tests). After a certain amount of water passed through the water column (column volume CV), samples were taken for analysis on the content of ions of the investigated metals by atomic absorption spectroscopy [5] and pH.

Column parameters: diameter – 2.8 cm; overall height – 40.3 cm; height of the sorbent layer – 16.8 cm; the volume of sorbent – 103.4 cm³. Speed of water passing: volume velocity – 1l/hour; linear velocity 1.62 m / hour.

The influence of contact of water with activated carbon on its hydrogen index is of great importance in purification. It is known that water contains many dissolved electrolytes, which can significantly affect its pH [6]. Fig. 1 shows the results of measurements of pH

of artesian water after contact with activated carbon of various types.

It is evident that at the initial stages of contact of water with coal there is a certain change in the pH of water in such a way that F-300 and CWZ-3 coal somewhat alkalifies water, activated fruit-stone carbon practically does not change the pH, and oxidized form of activated fruit-stone carbon acidifies it. These phenomena are observed when pumping through the sorbent of the first 200–300 column volumes. During further pumping of water through coal, its pH remains virtually unchanged and cannot affect the sorption of metal ions.

Table 4 shows the results of sorption extraction of ions of some heavy and transition metals by carbon sorbents of various types, in percentage of the micro-impurities from its initial concentration, after pumping a volume equal to 200 column volumes.

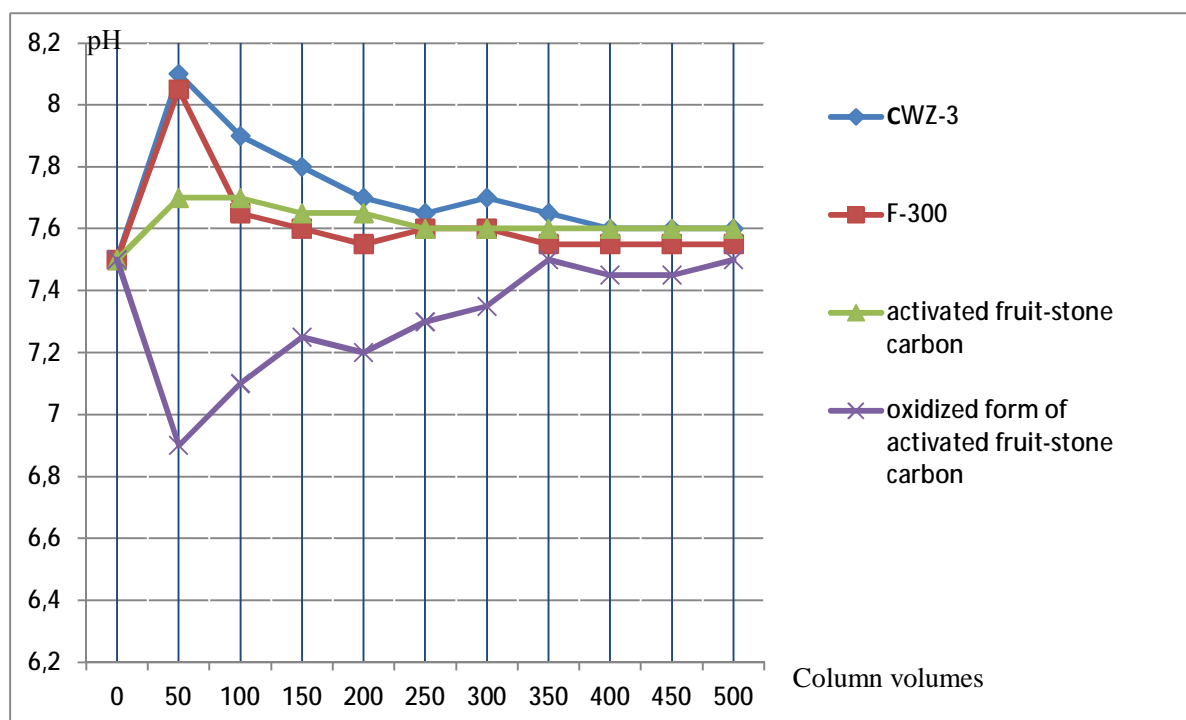


Fig. 1. Dynamics of pH changes of artesian water due to interaction with different types of activated carbon

Table 4

Efficiency of sorption extraction of heavy metals and aluminum ions by carbon sorbents of various types

№	Metal ion	Water type	Type of coal			
			F-300	CWZ-3	activated fruit-stone carbon	oxidized form of activated fruit-stone carbon
1	2	3	4	5	6	7
1	Zn	artesian	26	29	20	29
		river	97	97	97	98
		tap	31	37	28	47
		pond	74	56	82	80
2	Cu	artesian	7	23	64	91
		river	82	98	86	93
		tap	45	56	78	86
		pond	96	96	96	98
3	Al	artesian	81	83	86	85
		river	90	84	86	93
		tap	80	55	81	80
		pond	99	98	98	100
4	Fe	artesian	67	73	78	87
		river	81	84	83	90
		tap	36	64	38	53
		pond	100	100	100	100
5	Ni	artesian	37	42	42	56
		river	100	100	100	100
		tap	78	78	69	100
		pond	82	75	63	85
6	Mn	artesian	45	46	35	35
		river	57	48	48	57
		tap	22	22	18	24
		pond	36	30	46	54

1	2	3	4	5	6	7
7	Pb	artesian	100	100	100	100
		river	100	100	100	100
		tap	100	100	100	100
		pond	100	100	100	100
8	Cd	artesian	0	2	10	10
		river	90	90	90	90
		tap	61	43	5	5
		pond	90	90	90	90

Many factors influence the efficiency of potable water purification by activated carbon. In particular, the content of humic substances and chemistry of the surface of carbon material in the water play a critical role. The selectivity of the adsorption of various metal ions is proportional to the surface of the carbon material and the concentration of active functional groups on its surface [6]. Ions can be divided into 3 groups, according to the efficiency of their extraction:

– ions, the extraction of which depends on the content of organic impurities in the water (zinc, copper, nickel and cadmium). During adsorptive copper removal, F-300 and CWZ-3 coal successfully operate only for river and pond water. At the same time, activated fruit-stone carbon can essentially bind copper in all the investigated types of water (up to a level below 0.3 MAC, and activated fruit-stone carbon – up to 2 MAC). Apparently, chemistry of the coal surface plays a decisive role when using the oxidized form of activated fruit-stone carbon to bind copper ions;

– ions that are badly removed from different types of water and are little dependent on the content of organic impurities (manganese);

– ions, which are almost completely removed from water, regardless of impurities of organic impurities in the water (lead, aluminum, iron).

Thus, the most expedient way to clean water is to use oxidized coal. The known types of coal, namely, F300, CWZ and activated fruit-stone carbon have similar values of the efficiency of water purification from metal ions, while the oxidized form of activated fruit-stone carbon has considerably higher rates. It is likely that the complex formation on the surface of

oxidized coal greatly contributes to the removal of ions from their aqueous solutions.

Therefore, the comparative characteristic of the effectiveness of various types of carbon sorbents in relation to heavy metal ions during their sorption from water of various categories indicates the benefits of oxidized form of activated fruit-stone carbon in achieving maximum removal of heavy metal ions. The use of other types of activated coal can be justified for the purpose of extracting one or another ion taking into account the degree of purity of the source water and the requirements for the quality of technological water during the processes of food enterprises.

References

- [1] Shevchenko O., Sokolenko A, Poddubnyj V. Produkty pitaniia. Kiev: PP Ljuksar, 2011, 390. (in Russian)
- [2] Domaretskyi V, Shyian P.: Zahalna tekhnolohiia kharchovykh vyrobnytstv. Kyiv: Un-t "Ukraina", 2011, 814. (in Ukrainian)
- [3] Arkhipova H., Mudrak T, Zavertana D. Visnyk Natsionalnoho aviatsiinoho universytetu, 2010, 1, 232. (in Ukrainian): <http://dspace.nuft.edu.ua/jspui/bitstream/123456789/2004/7/Arhipova.pdf>
- [4] Dubinina A. Toksychni rehovyny i metody yikh vyznachennia. Kharkiv : KhDUKhT, 2016,106. (in Ukrainian)
- [5] GOST 30178-96:1996. Syr'e i produkty pishhevye. Atomno-absorbciionnyj metod opredelenija toksichnyh jelementov. (in Russian)
- [6] Zapolskyi A. Vodopostachannia, vodovidvedennia ta yakist vody. Kyiv: Vyshcha shkola, 2005, 671. (in Ukrainian)

MODIFIED REDFIELD RATIO COMBINED WITH ARTIFICIAL NEURAL NETWORK SIMULATION TO ESTIMATE THE ALGAL BLOOM PATTERN

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Abstract. In previous work (Hushchyna and Nguyen-Quang, 2017), we have introduced the Modified Redfield Ratio (MRR) to estimate algal blooms occurring in Mattatall Lake, Nova Scotia (Canada). The goals of this paper are to test this modified index based on nutrient level to estimate bloom patterns via field experimental data and by the mathematical simulation with a supervised learning model Artificial Neural Network. Although the original Redfield ratio, a molar index applied in marine water based on the C:N:P ratio, is still discussed, the MRR based on Nitrates/Phosphates ratio we suggested herein seems to have many practical aspects for fresh water to evaluate the onset of bloom patterns.

Key-words: Cyanobacteria, Harmful Algal Blooms (HAB), Modified Redfield Ratio (MRR), Artificial Neural Network (ANN)

1. Introduction

Mattatall Lake (ML) in Nova Scotia (Fig. 1) started to experience severe algal blooms in 2013. During the fall of 2014, massive algal blooms appeared in ML, and persisted until late December. This phenomenon was observed and recorded by our team in the fall-winter of 2014 (Nguyen-Quang, 2015). The duration of this phenomenon was extremely unusual as algal blooms have not been known to last until the winter season or coexist with icy conditions. The dominant species in this bloom was identified to be *Anabaena planctonica* (*Dolicospermum planctonicum*) with a cell count around 250 000 cells/ml, which may produce the neurotoxin *Anatoxin-a*. This cell count is approximately two and a half times higher than the alert level 2 guideline from World Health Organization's drinking water standards (Chorus and Bartram, 1999).

There are certain combinations of multiple factors that trigger HAB specific to each waterbody. However, their coupling effects are not yet understood. No research or data related to ML has been done. Moreover, in Nova Scotia, no systematic investigation has been sketched for cyanobacterial bloom patterns.

Hushchyna and Nguyen-Quang (2017) have presented the Modified Redfield Ratio (hereafter denoted MRR) to estimate the HAB occurrence in Mattatall lake (Nova Scotia, Canada), served as a pilot site for our pioneering systematic study in order to evaluate the recent bloom phenomena in the entire province and in Atlantic Canada.

In this paper, we try to:

- Evaluate the coupling effects of different governing parameters on the recent bloom phenomenon occurring over the last two years. For the first step, we deal with 3 parameters involving in algal growth including Nitrates, Phosphates and Dissolved Oxygen (DO). We consider 2 biological pigments Chlorophyll-a (Chl-a) and Phycocyanin (PC) released by cyanobacterial species as the effects from these causes.

- Sketching again the Modified Redfield Ratio to estimate the onset of algal bloom, i.e the state of instability where there appear some scums of algae.

- Using a mathematical model (Artificial Neural Network – ANN) in simulating coupling cause-effect relationships of five factors (Nitrates, Phosphates, DO, Chl-a, PC). From that, the validation for MRR and prediction for HAB risks in function of environmental factors could be estimated.

2. Experimental processes and methodology

2.1. Experimental processes

Different equipment for field sampling and Lab analysis were used, such as a YSI probe (Professional

Plus, Hoskin scientific LTD, USA) for pH, Dissolved Oxygen (DO), conductivity, and temperature in the water; a Fluorometer for Chlorophyll-a and Phycocyanin measurements; and Photometer for evaluating nutrient components. Samples were taken tri-weekly or every month, depending on the weather conditions, starting from May to November yearly, at the surface and bottom levels. It is also noted that the lake is quite shallow with the maximum depth around 8m. Predetermined sampling locations are represented in Fig. 1 with equivalent coordinates in Table 1. If there were some other places that are not included in the predetermined points that had an algae bloom present, samples were taken at these points as well. A HOBO weather station was installed in one fixed location of the lake. As soon as sampling was finished, they were taken to the lab for micronutrient analyses.

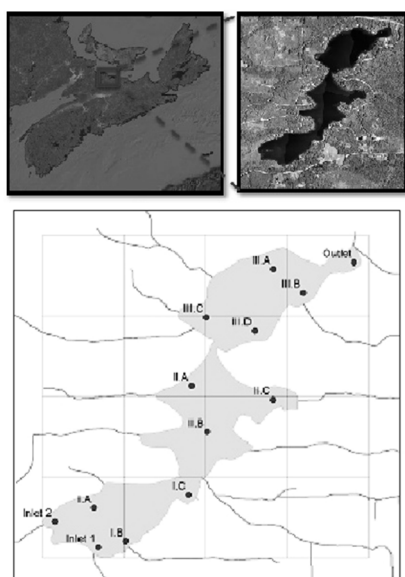


Fig. 1. Above: Google Earth view of Nova Scotia highlighting ML area (left) and Government of Nova Scotia aerial photograph of ML (right). Coordinates of ML are $45^{\circ} 42' 17''$ N, $63^{\circ} 19' 39''$ W

Below: Sample stations (locations) predetermined and monitored.

Chlorophyll-a is usually used as a parameter to determine the quantity of primary photosynthetic pigment in cells of aquatic micro plants. Measurement and determination of this parameter are the basic analysis to evaluate the characteristics of algal blooms in many research works in the world. Unfortunately, Chl-a represents just the whole quantity of photosynthesis pigment released from all algae and micro-plants present in water, hence it cannot help to distinguish cyanobacteria existence among all living micro-plants and algae in the waterbody. To be able to define and confirm the presence of Cyanobacteria species in the composition of aquatic microalgae in the waterbody,

another pigment form, Phycocyanin (PC), is used. This pigment can determine different cyanobacteria species from another planktonic species.

Table 1

Coordinates of sampling points in Mattatall Lake

Point	X (Longitude/Latitude)	Y (Longitude/Latitude)
IA	-63.483759 W	45.683914 N
IA1	-63.482013 W	45.681338 N
IB	-63.480922 W	45.681845 N
IC	-63.475384 W	45.684767 N
IIA	-63.475148 W	45.691568 N
IIB	-63.47378 W	45.688689 N
IIC	-63.467932 W	45.690711 N
IIIA	-63.467907 W	45.698875 N
IIIB	-63.46526 W	45.697408 N
IIIC	-63.473843 W	45.695859 N
IIID	-63.469584 W	45.695011 N
Inlet 1	-63.483369 W	45.681467 N
Inlet 2	-63.487229 W	45.683072 N
Outlet	-63.460799 W	45.699303 N

2.2. Redfield ratio (RR) and Modified Redfield ratio (MRR)

Redfield (Redfield, 1958) suggested an optimal ratio between Nitrogen and Phosphorus which were contained in living organisms. This ratio, known under the name of 'Redfield ratio', can be used to estimate the algal status in a water body. With a mass conversion, Bulgakov and Levich (1999) defined ranges of this ratio (N/P): 1) from 5 to 10: *Cyanophyta* species domination would be considered; 2) from 20 to 50: green algae growth would be favored.

Inspired from this idea, our suggestion however did use Nitrates and Phosphates (not TP and TN) as we believe that mineral form of these nutrient components triggered the bloom in ML and could be the main cause of it. The mass conversion is based on the ratio of *Nitrates to Phosphates* to define the blooming possibilities as well as their limits for the development of two main potential groups leading to bloom patterns: *green algae* and *blue-green algae*. For a detail of our Modified Redfield Ratio calculation, we refer to Hushchyna and Nguyen-Quang (2017).

2.3. Mathematical model

An Artificial Neural Network (McCulloch and Pitts, 1943) was used as the mathematical model in this research. The model has simple processing elements called neurons or nodes. Direct communication links are what connect the nodes to one another, and each node

has a weight function. The weights represent information being used the net to solve the problem. We suggest the back-propagation multi-layer neural network in which, nodes are arranged into layers: input layer (Data observations), hidden layer(s) (intermediate nodes) and output layer (conclusions) (Fig. 2).

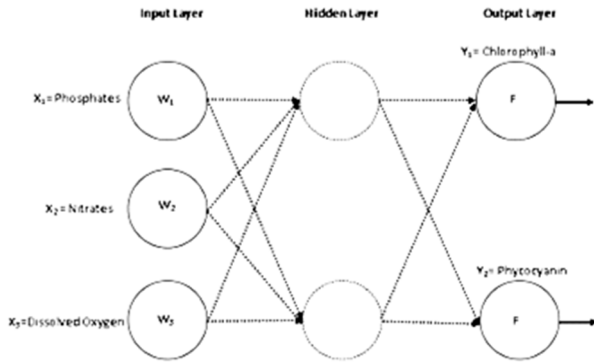


Fig. 2. Multilayer ANN model for Chlorophyll-a and Phycocyanin development

Our study herein is limited on a set of three main parameters for the input sets represented by 3 variables, X_1 , X_2 and X_3 equivalent to: 1) Phosphates; 2) Nitrates; 3) Dissolved Oxygen (DO). Two outputs in this model are the quantity of Chlorophyll-a and Phycocyanin (Y_1 and Y_2), representing the growth of cyanobacteria or output layer (Fig. 2). The input layer data was collected over the summer months, and over 150 data points was used to train and validate the model.

The weight layer signals form a weight matrix: W_{ij} . The weights undergo a “training step” where they are fed data and adjusted until they can produce results that are similar to the actual outputs. Mathematically, the input can be expressed in a vector form as $\{X\} = \{X_1 \dots X_n\}$. The i^{th} component of the vector X_i that comes out from the input node i is transferred to a node j on a hidden layer ($j=1, 2, \dots, m$) through the weight matrix W_{ij} .

Each hidden node has a summation function operating on the input values, the total input u_j received by the hidden node is:

$$u_j = \sum_{i=1}^k W_{ij} X_i. \quad (1)$$

The hidden node j has a transfer function that performs a nonlinear transformation on the total input u_j , and produces an output which becomes the next input fed into a node p of the output layer j ($j=1, 2, \dots, n$), which also has a summation function, through another weight V_{jp} .

The total input received by the output node p becomes its output, y_p , expressed as:

$$y_p = \sum_{j=1}^n V_{jp} f(u_j). \quad (2)$$

The outputs can be given in a vector form as $\{Y\} = \{y_1 \dots y_n\}$. This neural network performs a nonlinear

transformation on $\{X\}$ as expressed in the following equation.

$$\{Y\} = f(\{X\}). \quad (3)$$

The network is ready to be trained once it has been structured properly. The standard back-propagation algorithm was used for training the network. To train the network, random initial weights are assigned to each node and then known input values and target values are added to the network. Output values are estimated from the input values and then compared to the target values. This is done continuously by the model until the mean squared error R^2 is as low as possible (between the output and target values). Once the model was trained, it was tested with a set of data that was independent from the training data.

3. Results and Discussion

3.1. Risk estimation from field data

The attempt to predict the HAB occurrence and proliferation under complex context of environmental conditions (nutrient, light, meteorological factors, etc.) led to many indexes for the estimation of HAB risks based on chemical components such as micronutrient factors of the waterbody that contribute significantly to algal growth. The simplest index is based only on one factor such as the TP level, Chlorophylla or cell counts.

In the context of this paper, we suggest to use our modified Redfield ratio (MRR) mentioned above (Hushchyna and Nguyen-Quang, 2017) to estimate the HAB risk in a ‘simple’ way which combine Chlorophyll-a and PC indexes, shown in Table 2. For Chl-a and PC criteria, we refer to Novotny and Olem (1994), Bulgakov and Levich (1999), Brient et al. (2008) and Brylinsky (2009).

Based on the field data obtained during 2015–2016 with our field observations (174 points), we established a table of Index equivalent to PC and Chl-a measured and illustrated by the graph in Fig. 3.

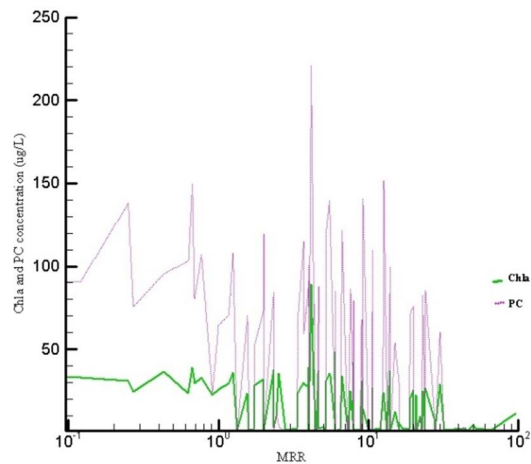


Fig. 3. Chlorophyll-a and Phycocyanin versus MRR (field data 2015 and 2016)

When MRR value of 0-10, the graph contains the most Chl-a values, as well as the highest (120 points, 68.96 %).

From Fig. 3 (with the log scale for MRR), we can see that when MRR between 3.25 and 6.5, all Chl-a greater than 20 $\mu\text{g/L}$ and PC greater than 100 $\mu\text{g/L}$. In this range, we also have the highest values of Chla (>90 $\mu\text{g/L}$) and PC (>220 $\mu\text{g/L}$) at MRR=3.5. In combining Table 2, this show a high risk of HAB. There were in total 27 points that fell into this category of a ratio between 3.25 and 6.5.

With points with MRR less than 3.25, we can observe that Chl-a values vary between 5 and 30 $\mu\text{g/L}$ while PC varies from 20 to 150 $\mu\text{g/L}$. There were 69 points (39.6 %) with a ratio MRR less than 3.25, and of those points, there was only one point that had the low Chl-a value: 9.91 $\mu\text{g/L}$. In referring to Table 2, it could be said that there was a medium to medium high risk of HAB.

Table 2

Risk indexes, adapted from Novotny and Olem (1994), Bulgakov and Levich (1999), Brient et al. (2008), Brylinsky M. (2009), Hushchyna and Nguyen-Quang (2017)

Risk	Chl-a index	PC index	Our Modified Redfield Ratio (MRR)
Low risk of HAB	0–5 $\mu\text{g/L}$	$\leq 30 \pm 2$ $\mu\text{g/L}$	≥ 6.6
Medium risk of HAB	5–10 $\mu\text{g/L}$	Between 30 and 90 $\mu\text{g/L}$	≤ 3.25
High risk of HAB	$\geq 10 \mu\text{g/L}$	$\geq 90 \pm 2$ $\mu\text{g/L}$	3.26–6.5

When MRR value of 10-30: This section of the graph has the second highest number of points in the

total data distribution (45 points, 25.86 %). Among them, there are 29 points having the Chl-a values between 0 and 5 $\mu\text{g/L}$, and the rest varied from 5 to 30 $\mu\text{g/L}$. Regarding PC, the distribution was not homogenous: some points having high values (over 70 $\mu\text{g/L}$) and some points have less than 30 $\mu\text{g/L}$. If we consider both PC and Chl-a criteria in the same time as indicated in Table 2, this MRR range should be potentially at low to medium risk.

When MRR value > 30: All points have a very low risk of HAB (9 points, 5.17 %). All of the points have chlorophyll-a values below 5 $\mu\text{g/L}$. The PC values vary: between 10 and 40 $\mu\text{g/L}$, except for some outliers with high values (over 80 $\mu\text{g/L}$). This showed a low risk of HAB.

Actually, our field observations recorded during two summer seasons 2015-2016 showed different bloom scenarios fitting quite well with the above estimation, as illustrated in Figure 4 and Table 3.



Fig. 4. Presence of algal blooms in Mattatall Lake in August 2015

Table 3

Cases of potential blooms based on the modified ratio *nitrate/phosphate*

	2015						2016				
	11-Jun	30-Jul	17-Aug	10-Sep	04-Oct	27-Oct	14-Apr	10-May	17-Jun	16-Aug	04-Oct
Cyanobacteria domination	6	4	5	1	6	8	0	4	4	0	0
Green Algae domination	8	9	10	4	1	5	3	0	3	0	0
Potential Cases	12	10	18	26	18	13	0	0	4	22	25

3.2. Simulated results from ANN model versus the risk criteria

The mathematical simulation is highlighted via the relationship curve MRR vs PC and MRR versus Chl-a in Figs. 5 a, b (discontinuous lines) which show the regression tendencies generated for both field and simulated data. The discrepancy was due to the fact that the field data was

individually measured for each parameter, and the simulated data were combined from mathematical model with coupling parameters (herein with nitrates, phosphates, and DO). These regression curves for both field and simulated data have been chosen so that they are as similar as possible in shape (MRR vs PC or Chl-a). They are both high order polynomial functions.

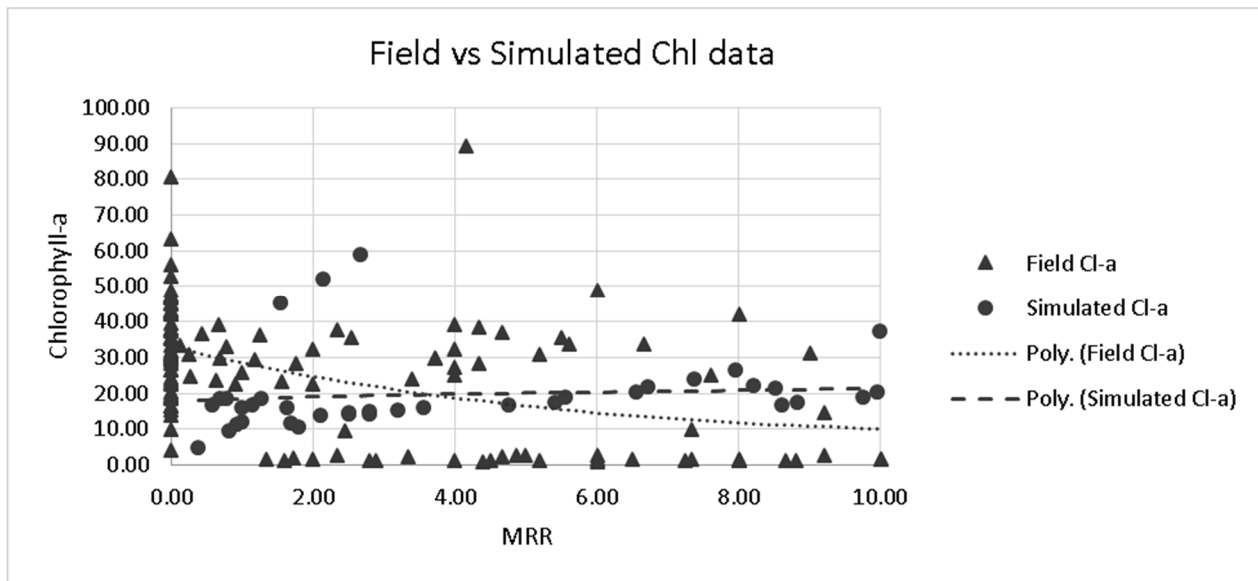


Fig. 5a. Chlorophyll-a versus MRR: Comparison for field data and simulated results

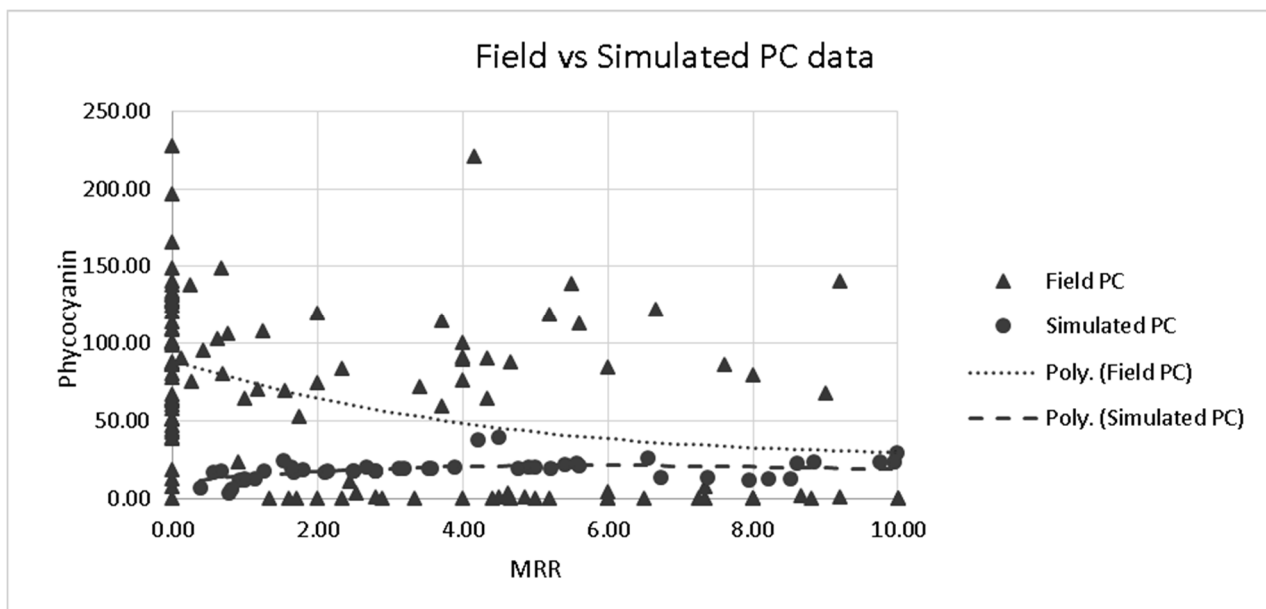


Fig. 5b. Phycocyanin versus MRR: Comparison for field data and simulated results

For Chl-a, the field data curve had higher values than the simulated curve for a short range (MRR approximately 0 to 3.5) (Fig. 5a), the curves have a similar shape, but there is a difference in the concentration between them and simulated data are higher. Two curves cross each other at MRR of 3.5, where the separation two field and simulated curves is easily noticeable. In comparing with Table 2, this value is quite close to the suggested MRR= 3.25.

For PC (Fig. 5b), if considering the MRR range from 0 to 10, we can notice the field data is higher than the simulated data. It appears that the simulated data

would cross the field data curve and predict higher numbers shortly after the MRR value of 10.

These regression curves do not fit the data very well due to 1) the high nonlinearity of data and 2) the complexity of the coupling effects between parameters.

To consider the combined effects of MRR and DO, for a linear regression, we can see that as the DO increases, so does the concentration of Chl-a (Fig. 6a). As the MRR increases, the Chl-a concentration decreases. From Fig. 6a, DO increases and MRR remains less than 27.5, the concentration of Chl-a will increase. Beyond this value MRR = 27.5, Chl-a decreases and even disappears.

In eliminating some outliers, we built the nonlinear regression surface for the Chl-a pattern and recognized that the range MRR 0-3 is an interesting range (Fig. 6b). This range actually shows a ‘chaotic’ situation where the Chl-a has, at the same time, increasing and decreasing tendencies. When compared with Table 2, it is noticed that when MRR

is < 3.25 , we have a medium risk for HAB. The medium risk can be understood in the sense that the ‘transition’ situation could lead to bloom or be diminished, depending on other intervening factor(s). This intervening factor herein is DO: obviously in Fig. 6b, when DO is in between a certain range (0 to 10 mg/L), the risk is higher as Chl-a will increase.

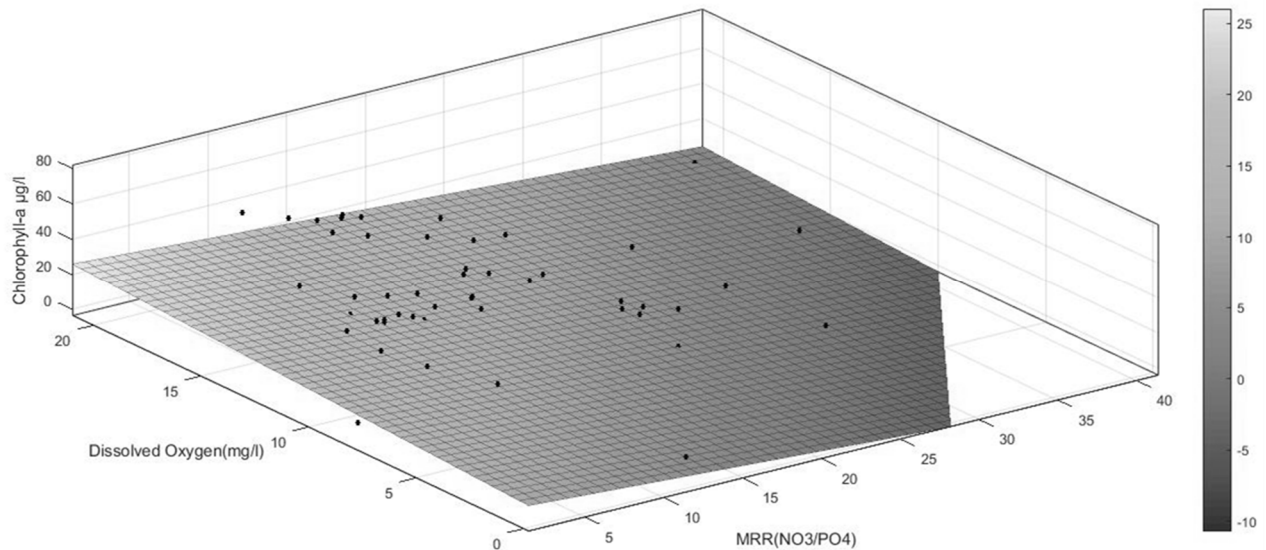


Fig. 6a. Chlorophyll-a vs MRR and DO (Polynomial degree = 1, $R^2 = 0.9199$)

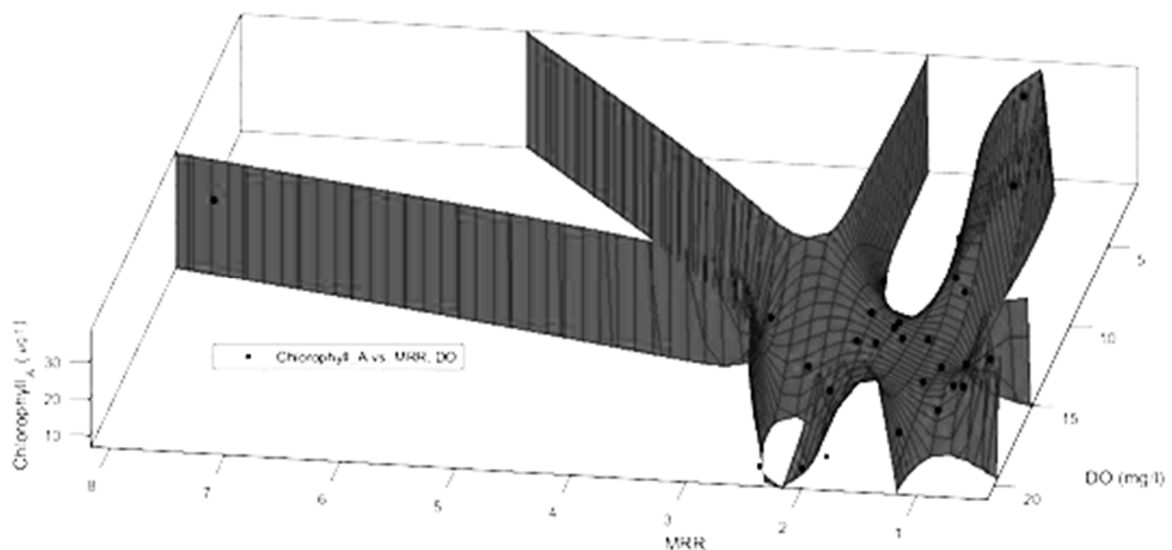


Fig. 6b. Chlorophyll-a vs MRR and DO (Polynomial degree = 5, $R^2 = 0.6407$)

Also from Fig. 6b when MRR went from 3 to 5.5, the combining effects of MRR and DO showed a high value of Chl-a, almost as indicated in Table 2 for the high risk area (MRR 3.25–6.5). Beyond this range, depending on the DO value, the Chl-a value can be diminished.

A low order of regression showed the effect of DO on the PC values in the function of MRR (Fig. 7a). The simulated graph reflected some PC patterns obtained from the field trips when Nitrates = 0 (MRR = 0). We also noticed that when DO is in the 0 to 10 mg/l range, PC decreases and then increases at the value of MRR

around 5.5. Again, comparing to Table 2, the MRR range belonging to 0 to 6.5 advised a medium to high risk of HAB. As the value of MRR increases beyond than 5.5 as indicated in the graph, the PC increases, depending on DO.

A close look on the nonlinear regression surface as shown in Fig. 7b explained the combining effects

of DO and MRR. We can see that from the MRR range 0 to near 3.5 a 'chaotic/transitive' situation of PC depends on DO. Beyond 3.5, only with the range of DO from 10 to 13 mg/l PC would continue to increase. All other DO values lead to a PC-free situation no matter what the MRR is (as long as it is greater than 3.5).

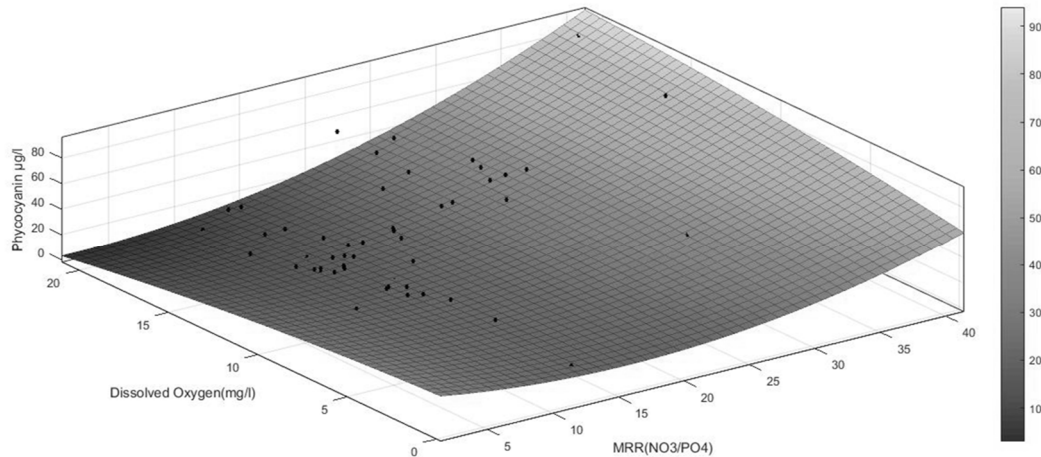


Fig. 7a. Phycocyanin vs MRR and DO (Polynomial degree = 2, $R^2 = 0.8136$)

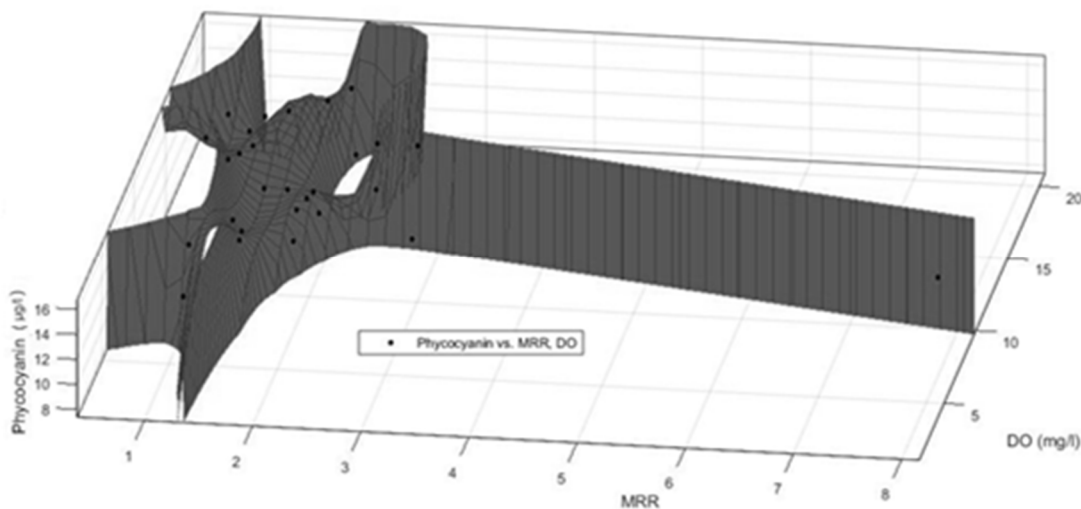


Fig. 7b. Phycocyanin vs MRR and DO (Polynomial degree 5, $R^2 = 0.9453$)

This finding is interesting as by our field records, the 'optimal' values of DO can be observed when algae growing are around 9 to 14 mg/l. However, DO is a complex factor to be counted in the model and needs to be more studied as it shows in the same time cause and effect, i.e. DO contributes to the environmental conditions for algal development, and once algae grow and bloom, they also increase DO by their photosynthesis process. The change DO values shows us how algae consume or produce oxygen.

4. Conclusions

With the data from two years (2015–2016), ML showed a moderately eutrophic level and contained potential toxic algal species. The formation of blooms can occur only when an optimal combination of favorable conditions including micronutrients, water temperature, etc. Two main categories of blooms were observed in ML seasonally – one normal category of algal bloom from July to September, formed with non-toxic species *Mougeotia sp.* and another one with

Anabaena sp., specifically *A. planctonica* (*Dolicospermum planctonicum*), which started in September and lasted until December, and this species generated blooms in the fall term.

Difference between field data regression and simulated regression are due to:

- High nonlinearity of the problem and hence of data.
- The coupling effects between involving parameters are very visible via the simulated data. We used here the combination of only 3 factors and noticed the discrepancy between the single effect and combined effects between parameters.

The research throughout this paper showed an important insight: bloom patterns can only be explained and predicted by coupling effects of all involved parameters. To combine all effects of all possible parameters, only a mathematical model can help us to deal with this complex issue. The mathematical approach can be a powerful tool to deal with the coupling effects of governing parameters in the bloom occurrence issue. Therefore, the more numerous factors that are combined, the better simulation and hence prediction are. Our main target is to define the declining coupling factor(s) for the pattern HAB which cannot be based on just one or two parameters, but a combination of many involving ones. The threshold of pattern will be hence elucidated only with a mathematical model that we will present in the future.

Although our simulated results herein are not very sophisticated yet, they can show the feasibility and robustness of the mathematical model for the difficult task to predict blooms under coupling effects of all involved physical, chemical and biological factors. And we need more data to process and improve a precise simulation/prediction in the future. The ANN model can be applied to other parameters involving in the HAB pattern, and the simulation and hence prediction will be much more precise and reliable (with the same above structure, there will be more inputs representing involving factors and more outputs standing for effects/consequences). However, more data also would contribute to the precision of the model.

Finally, the value MRR between 3.25–3.5 can be considered as the threshold for the HAB pattern and Modified Redfield Ratio showed a reasonable reliability to be used for estimating quickly the HAB risks.

Although the original Redfield ratio, the molar index applied in marine water is still discussed, the MRR based on Nitrates/Phosphates ratio we suggested herein seems to have many practical aspects for fresh water to evaluate the algal instability state leading to the onset of bloom patterns. It needs to be more studied and validated by different data sources.

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References

- [1] Brient, L., Lengronne, M., Bertrand, E., Rolland, D., Sipel, A., Steinmann, D., Baudin, I., Legeas, M. le., Rouzic, B. Le. and Bormans, M. (2008), "A phycocyanin probe as a tool for monitoring cyanobacteria in freshwater bodies", *Journal of Environmental Monitoring*, Vol. 10, pp. 248–255.
- [2] Brylinsky, M. (2012), An Assessment of the Sources and Magnitudes of Nutrient Inputs Responsible for Degradation of Water Quality in Seven Lakes Located Within the Carleton River Watershed Area of Digby and Yarmouth Counties. *Nova Scotia Environment, Wolfville Nova Scotia*.
- [3] Brylinsky, M. (2009), Lake Utopia Water Quality Assessment. *Commissioned by the New Brunswick Department of the Environment*.
- [4] Brylinsky, M. and Sollows, J. (2014), Results of the 2013 Water Quality Survey of Eleven Lakes Located in the Carleton River Watershed Area of Digby and Yarmouth Counties, Nova Scotia.
- [5] Bulgakov, N. G. and Levich, A. P. (1999), "The Nitrogen/Phosphorus ratio as a factor regulating phytoplankton community structure". *Archiv für Hydrobiologie*, Vol. 146 No.1, pp. 3–22.
- [6] Chorus, I. and Bartram, J. (1999), Toxic Cyanobacteria: A guide to their public health consequences, monitoring and management. *WHO (World Health Organization)*, E & FN Spon. London.
- [7] Hushchyna, K. and Nguyen-Quang T. (2017), Using the Modified Redfield Ratio to estimate Harmful Algal Blooms. *Environmental Problems*, 2 (2), pp. 101–108.
- [8] McCulloch, W. S. and Pitts, W. (1943), "A logical calculus of the ideas immanent in nervous activity", *The bulletin of mathematical biophysics*, Vol. 5, No. 4, pp. 115–133.
- [9] Nguyen-Quang, T. (2015), "The Mattatall Lake Algal Bloom Study", scientific report. BBML (Biofluids and Biosystems Modeling Lab), Department of Engineering-Dalhousie University Faculty of Agriculture.
- [10] Novotny, V. and Olem, H. (1994), "Water Quality: Prevention, Identification, and Management of Diffuse Pollution". Wiley, 13 Jan – Technology & Engineering
- [11] Redfield, A. (1958), "The biological control of chemical factors in the environment", *Am. Sci.* Vol. 46, pp. 205–220.
- [12] WHO. (2003), Guidelines for safe recreational water environments. *World Health Organization*. Vol. 1: Coastal and fresh waters, 253 p.

HAZARD MONITORING AND APPLICATION OF COMPLEX TERRITORIAL ANALYSIS TO ASSESS THE DEGREE OF PROTECTION FOR A CERTAIN REGION

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Abstract. The analysis of typical natural and man-made hazards for the Lviv region is carried out. The statistics of official documents are processed. The coefficient of protection of the region against dangers is calculated and the degree of its protection is determined.

Keywords: monitoring, risk of nature use, protection coefficient from the dangers.

Introduction

The environment, comfortable climate, landscapes convenient and well-organized management generally determines the region attractiveness and the population living quality. The infrastructure level significantly effects on the ecological stability, associated with the impact on the environment and activities to preserve and restore territories. Changing landscapes, terrestrial and aquatic ecosystems under the influence of human activity requires a rational approach to assessing the risk of nature use, developing monitoring and response programs for a particular region and the state as a whole.

Analysis of natural and man-made threats, development of reasonable preventive measures aimed at the prevention of hazards is an essential part of ensuring the safety of human life at the present stage of development. Ecological, economic and socio-political problems contribute to the growth of man-made or natural processes that bring material damage and adversely affect the health and psycho-emotional state of society [1].

Ukraine, integrating into the European community, needs urgent solution to the issue of the natural environment safety, namely, strategies, tactics and technology of environmental protection measures. To do this, it is necessary to conduct socio-ecological zoning of the country and regions and to classify the selected

areas by the degree of nature use balance, the level of pollution and the suitability of the natural environment for human life.

Risk assessment of nature use and systematic analysis of the dynamics changes in load on the ecosystem can be used to substantiate the choice of priorities of both state and regional environmental policy in order to prevent large-scale losses, guarantee public safety and stability of development. Taking into account the change in the distribution of powers between central and local authorities in Ukraine, the regional level of prioritization has the advantage of taking environmental protection decisions.

The purpose of the article is an analysis of the man-made and natural safety, conditions of the threats and risks spread of Lviv region environmental and directions definition of regional ecological policy implementation. It is risk assessment of natural use for the region on the basis of its current socio-economic and environment conditions.

The main tasks and goals of the risk assessment are:

- collecting information on major hazards and risks in the territory;
- determination of the emergencies risk degrees;
- assessment of the dangerous events consequences, the impact of the injurious factors on the population.

Analysis of recent researches and publications

Until recently, the primary attention in resolving the problems of protecting the population and territory from emergency situations was given to the elimination of the consequences of accidents, catastrophes, natural disasters. However, these efforts are becoming less

effective and more expensive. The limited available resources should be primarily aimed at reducing the risk, developing reasonable preventive measures and ensuring human security, not to eliminate the consequences and compensation for the damage.

According to the international experts' calculations, the cost of measures to prevent natural disasters is much smaller compared to the costs required to eliminate damage [2, 3].

The tendency of yearly growth in the quantity and level of the consequences of accidents, catastrophes and natural disasters makes it necessary to seek new solutions to the problems of protecting people and territories from emergencies, to predict future threats, risks and dangers, to develop methods for their prediction and prevention.

In the bases of population and territory safety regulation system and overcoming the number growth negative tendency of natural and man-made emergencies can be used the science of the risks – cindynique [4]. For example, in Western Europe, where measures of state regulation are implemented to reduce the emergency risks, the accident and disaster numbers have decreased by 7–10 times in the last ten years [5]. These measures are the least costly and economically.

Scientific researches on dangers and risks emergencies cover various aspects and relate to the names of many well-known scientists. Particularly, the general issues of ecological safety of Ukraine are highlighted in the works of L. G. Rudenko, A. B. Kaczynski, G. V. Lisyhenko, B. M. Danylyshin, A. V. Stepanenko, N. M. Kussul, S. V. Skakun, A. Yu. Shelestov, P. V. Zhuk and others.

The risk analysis methodology of the dangerous environmental factors impact on the population safety is a new and relatively young, interdisciplinary scientific trend that is developing rapidly throughout the world. The main provisions of this methodology, formulated in the United States in the early 80's and in the new conditions are not always sufficient [6]. This necessitates the creation of modernized strategies for preventing and eliminating the consequences of natural disasters and catastrophes.

Since the risk factors of a territory or its protection from them are often closely related to the lives of people in a particular society, safety researches usually refers to well-defined territories [7]. Comparison between different territories and societies is not so common. The absence of comparative elements indicates the complexity of positioning the natural disasters on a certain scale.

An overview of the various definitions proposed for safety assessment shows that two approaches are important: firstly, an approach aimed at assessing the protection from the point of view of financial losses that will be incurred as a result of a natural disaster, and secondly, an approach that combines a wide range of social, demographic, cultural and historical factors.

In his work, Gilles Andre, in a comparative study of the protection degree to natural hazards for each country, combined social and economic probabilistic approaches. In this paper [8], the author highlights the fact that, using a social approach to assessing the safety of countries in the world, there is a large inequality between “rich” and “poor” countries, where the latter present higher levels of exposure to risk, while using the economic approach to assessing the safety, “rich” countries present the highest levels of exposure to risk. In terms of a social approach, the level of risk for Ukraine is the lowest in this comparison, concerning the economic approach, such an assessment for our country is absent.

The article [9] presents the results of assessments of natural hazards, protection from natural disasters and risk of nature use for all countries of the world according to the original author's method. The approach proposed by Kuzmin S. B for assessing the risk of nature use is based on the current (actual) socio-economic and natural state of the countries with the use of integrated territorial analysis and planning. In the statistical analysis, the author included all countries of the world with an area of over 50 km² and a population of more than 25 thousand people, for which the necessary statistics are known in open databases and in periodicals over the past 10 years. According to the analysis [9] at low values of natural hazards coefficients (1–1.4 maximum value 4) and the risk factor of nature use coefficient (0.3–0.6 maximum value 4) Ukraine refers to countries with a low degree of protection from natural disasters (1.9–2.9 with a maximum value of 17).

Risk analysis is used to study and understand not only the physical manifestation of natural hazards, but the factors that affect the protection of property, territories and population, as well as to develop preventive measures for their protection.

Research results

The risk assessment methodology includes identifying, analyzing and forecasting the negative impact of hazardous factors on the environment and population. According to the definition of the United States National Academy of Sciences [10], risk assessment is the use of available scientific information and scientifically based predictions to assess the hazard of exposure to harmful environmental factors and conditions on human health.

The main stages of analysis and predicting of risk emergencies are:

- detection and identification of possible sources of natural and man-made disasters;
- assessment of the frequency of natural disasters, accidents, natural and man-made disasters;
- forecasting of the possible consequences of the emergency injured factors influence on the population and territory;

– provision of rescue forces and means for the elimination of predicted emergencies [11].

In our study, we monitored the natural and man-made hazards and attempted to identify a number of indicators that would allow assessing the vulnerability of the territory to emergencies. For this, we were looking across a variety of databases, public institutions, public organizations and publications. Since compilation was conducted from different sources and the level of reliability and exhaustiveness of the information varies from one period to another, so we decided to focus exclusively on the last 10 years, because we believed that this information was more reliable and more complete.

The territory of Lviv region is characterized by the presence of some man-made and natural dangerous processes that can lead to technogenic and ecological disasters and accidents.

Among the most dangerous natural processes and phenomenon in Ukraine most often occur: geological, meteorological, hydrological, natural fires, and medico-biological. According to the data on natural disasters, we grouped the events in the main classes and did not consider natural phenomena, which make up a small part (Fig. 1). Natural threats in the territory of the Lviv region are represented by dangerous exogenous geological processes, hydrometeorological phenomena, natural fires and medico-biological emergency situations.

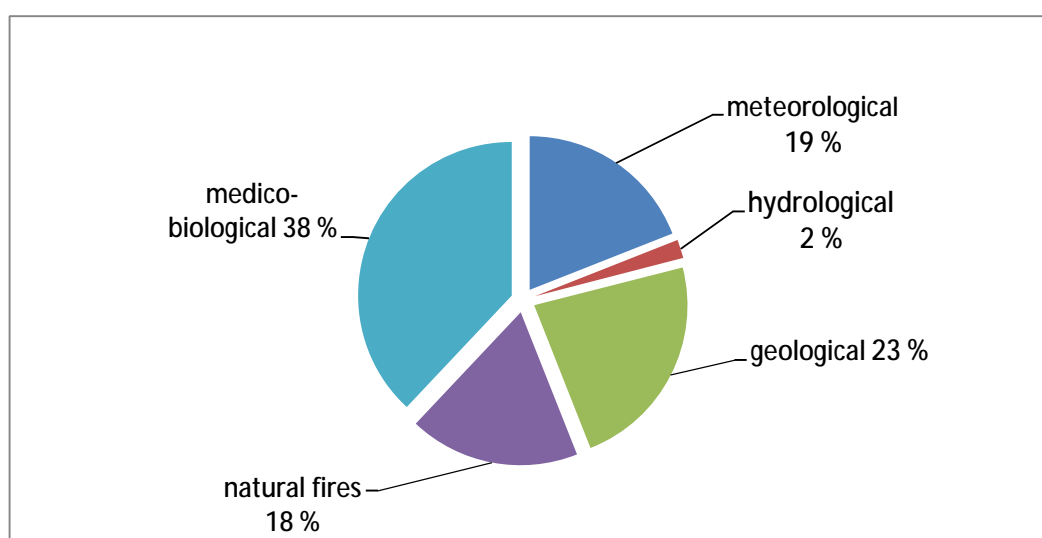


Fig. 1. Ratio of natural emergencies on the territory of Lviv region during 2006–2016 [12]

The specificity of the geological and geomorphological structure of the region determines the basic conditions for the formation and development of exogenous processes: landslides, karsts and mudflows. In Lviv region, the total number of landslides are 1347 units, of which 19, with an area of 0,42 km², are active. In the framework of development, 162 landslides were recorded, of which 8 – active, 29 – located near economic objects [12].

The activity of the karst process takes place through economic activity, which leads to an anthropogenic change in the hydrogeological conditions. The development of karst in the region is also associated with the earth subsidence over mining. The created cavities constitute a danger to the sanitary-protection zone of Truskavets resort, Drohobych, Stebnyk, Boryslav cities, for power lines, Drohobych-Truskavets road, water supply and other communications [12]. Natural hazards of a geological nature make up 23 %.

Hydrometeorological dangers of the region, which account for 21 %, are most often manifested in the form of strong precipitation, storms and in

recent years the continued containment of hot weather in the summer. Due to significant rainfall, winter thaw and rapid melting of snow, flooding of large areas with the infrastructure, industrial facilities and residential buildings damage in the region is possible.

The largest share among the natural hazards of the area is medico-biological – 38 %. The most common of these are mass poisoning of the population with low-quality products.

The fires in natural ecosystems are 18 %. The reasons for these are anomalous manifestations of atmospheric processes that are associated with global climate change and ignoring the fire safety requirements.

With technical progress the impact of human economic activity on the environment is becoming more and more devastating. The main causes of man-made accidents remain:

– constant growth of anthropogenic impact on the environment;

- potentially dangerous and obsolete production technology;
- high depreciation rates of fixed assets and low rates of production modernizations;
- poor compliance with safety and low technological discipline in the factories;

- ignoring the requirements of fire safety and other norms and standards in industry, construction, public utilities, transport and other economy sectors.

For example, in the Lviv region from 2006 to 2016 the largest number of emergency man-caused accidents were recorded in 2006 (Fig. 2).

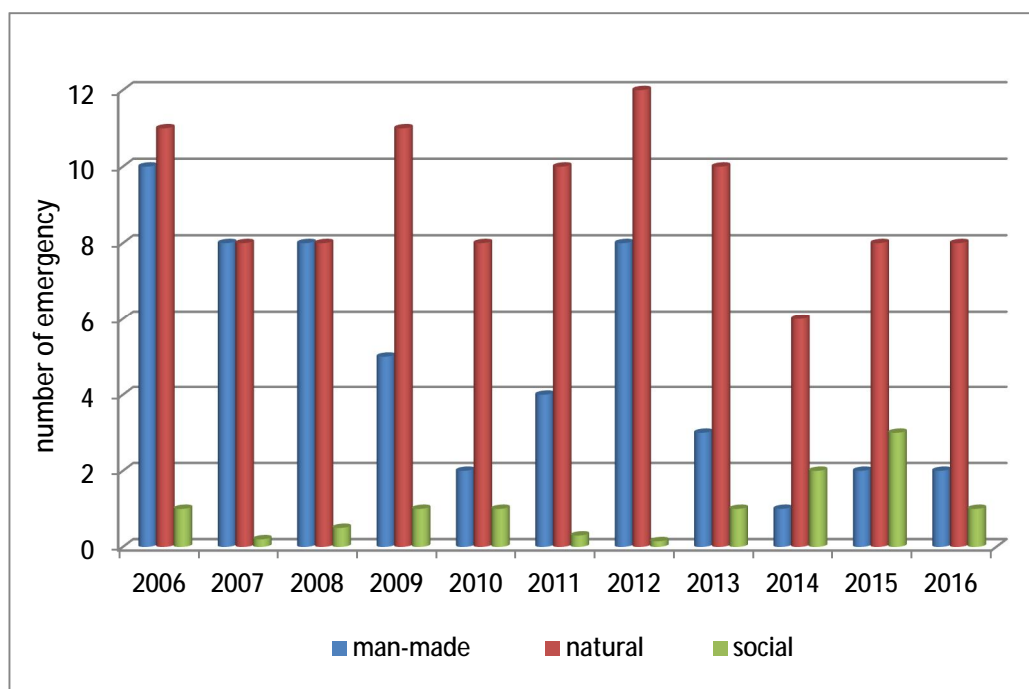


Fig. 2. Emergencies in the Lviv region for the period of 2006 – 2016 [12]

Two types of atmospheric pollution are characteristic to Lviv region: areal (emissions from industrial enterprises and transboundary transport of polluting substances by air) and linear (pollution of the atmosphere along roads by transport).

A significant proportion of the volume of air pollution accounted for road transport, through increased car traffic in urban area and on the main highways. Among pollutants from stationary sources that enter the air, gaseous substances predominate: carbon and nitrogen oxides, sulfur compounds, formaldehyde, dust and ammonium nitrogen. The main pollutants of the air remain Dobrotvyr TPP (within the sanitary protection zones for sulfur dioxide exceeded the limit-permissible concentration) and JSC “Mykolaivcement”, as well as losses in gas transportation by the division of UMG “Lvivtransgaz” and State Enterprise “Lvivgazvydobuvannya”. At present, 1164 potentially dangerous objects have been registered in the territory of the region, including 370 – increased danger, which are registered in the State Labor Inspectorate in the Lviv region [13].

The chemical safety of the region is conditioned by the operation of 35 chemically hazardous objects classified by the degree of chemical danger: 7 objects of the third degree of chemical danger and 28 objects of the

fourth degree of chemical danger. Mainly enterprises of the region use the following hazardous chemicals: ammonia – 16 objects; chlorine – 16 objects, acid (hydrochloric) – 3 objects. Experts estimate that over 60,000 people live in the zone of possible chemical pollution. The maximum amount of chemically dangerous substances transported by rail over the region territory for a day is more than 1,200 tons [13].

The developed network of transit and domestic oil product pipelines, storage and transfer of oil and petroleum products is a problem of petrochemical pollution, as a result of violations during repair and maintenance works, corrosive damage or deliberate damage for the purpose of theft. The developed network of transit and domestic oil product pipelines, storage and transfer of oil and petroleum products is a problem of petrochemical pollution, as a result of violations during repair and maintenance works, corrosive damage or deliberate damage for the purpose of theft. The regions territory includes: the oil pipeline of the branch of MN “Druzhba”, JSC “Ukrtransnafta”, the Urengoy-Uzhgorod gas pipeline, the product pipelines “Prykarpatransnaftoprodukt” and the interregional gas pipelines, in the case of possible accidents where the threat of environmental pollution is likely. The main pipelines in the cities of Brody and Skole, which have

oil storage tanks, with a total capacity of about 200000 m³ are dangerous.

A surface water of the Lviv region controlled by several government agencies, but the analysis results in recent years has shown their imperfections and subjectivity. In general, monitoring studies indicate excessive pollution caused by emissions of insufficiently-treated municipal and industrial wastewater. Despite the decline in production and the stop of many enterprises, there is no significant improvement in the quality of waste water and the reduction of discharges of crude and insufficiently treated sewage. The largest number of excessive limit-permissible concentration in the studied water samples was recorded in the basins of the Western Bug and Dniester rivers.

The environmental safety problem has become particularly acute in the Lviv region through the formation of large amounts of hazardous waste. The accumulation of waste in landfills is an important issue that should be solved by reducing the volume of waste

production as well as the recovery of secondary raw materials and energy from waste. The largest amount of industrial waste from the Lviv region is concentrated on the waste heaps near coal mines (about 108 million tons). Industrial and communal facilities yearly produce approximately 5.0 million m³ of solid waste, of which only 1.8 million m³ (37 %) covered by organized collection. For today, there are 51 organized dumpsites of household waste and about 521 objects of illegal waste storage in the region [14].

Statistical data on the total number of emergencies in the Lviv region during 2006–2016 show a small number of a socio-political emergencies and a tendency to reduce the number of man-made emergencies, especially during the last four years.

Environmental pollution also negatively affects the physical potential of society. Unsatisfactory ecological condition leads to higher rates of mortality and fertility reduction. These negative trends lead to a significant deterioration of natural population increase indicators (Fig. 3).

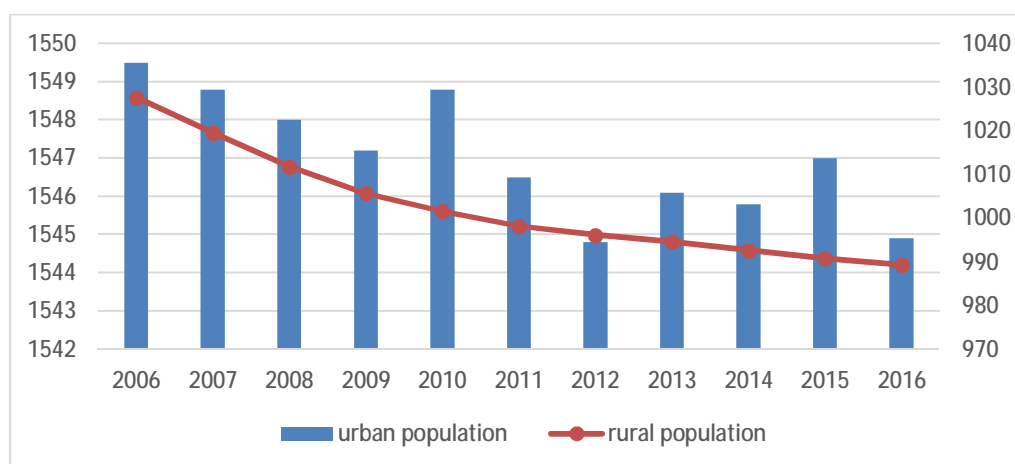


Fig. 3. Dynamics of changes in the region population for the period 2006-2016 [15]

In recent decades, there have also been significant changes in the structure of the diseases, which indicates the growing cases of diseases caused by the use of low-quality drinking water and food, polluted air, in particular, hepatitis, pulmonary diseases and cancer.

Taking into account the assessment of the natural hazards level impact on each country in the world and the protection degree, using various approaches presented in the literature [8, 9], Ukraine refers to the countries with low levels of natural hazards. At the same time, the level of the preparedness of our country to resist natural disasters is low (1.9–2.9 with a maximum value of 17).

Since the readiness of a particular territory or a society to withstand emergency situations depends on the type of construction, prevention and protection policies, as well as the density and level of urbanization of the population, then the degree of the territory protection is better to assess at the local level. It is

expedient to assess the territory safety and the society readiness to withstand the dangers at the scale of one administrative unit (city, area or region). In order to determine the protection degree and assessment of Lviv region dangers, the information needed for the calculations was collected [12-16].

The protection coefficient against natural disasters and catastrophes is calculated by the formula (1):

$$V_o = \frac{(GDP + P_j + T + C + W + L + K)}{(P_p + CHD + E)}, \quad (1)$$

where GDP (Gross Domestic Product) – GDP ratio in the region per capita; P_j – the proportion of the working population; T – telecommunication coefficient; C – transport coefficient; W – military resources coefficient; L – life expectancy coefficient; K – literacy rate; P_p – proportion of the population below the poverty line; CHD – infant mortality rate; E – coefficient of intensity of environmental problems.

All the coefficients are given to the unit which is defined as the maximum value of any indicator.

The telecommunication coefficient T , which reflects the reliability of information transfer, the timeliness and the mass notification of the population about dangers and rescue measures, was calculated according to the formula (2):

$$T = \frac{(Tph + Tmph + Trd + Tv + Tint)}{P}, \quad (2)$$

where Tph – number of phones; $Tmph$ – number of mobile phones; Trd – number of radios; Tv – number of TVs; $Tint$ – number of Internet users; P – region population.

The transport coefficient C , which is an indicator of the country's transport infrastructure development, the possibilities of its use for evacuation of the population from the centers of natural disasters, the placement of refugees, the transportation of food, medicines, and other humanitarian aid, was calculated according to the formula (3):

$$C = \frac{(CR + CA + CL)}{(P + S)}, \quad (3)$$

where CR – length of railway tracks, km; CA – length of highways, km; CL – airlines coefficient (number of airports per 100 km – the minimum radius of the airway); S – area of the region, km².

The coefficient of military resources W was calculated by the formula (4):

$$W = \frac{PW}{P}, \quad (4)$$

where PW – number of human military resources, people.

Having carried out the calculation, we obtained the coefficient of protection against dangers for the Lviv region, the value of which is 2.4 and is within the values calculated for Ukraine (1.9-2.9). The scale of the danger protection coefficient in [9] is in the range of 0.5 to 17. Given the fact that the greater is value of the coefficient, the greater is willingness of a particular territory and society to withstand emergency situations and recover more quickly after the disaster, the Lviv region as well as Ukraine relates to territories with a low degree of protection.

In order to increase the level of protection of the Lviv region from dangers and the necessary regional reserve of material and technical resources creation for carrying out preventive measures in the event of a threat of anthropogenic and nature emergencies, eliminate their consequences, from since March 2016 the “Integrated Program of Civil Protection of Population and Territories of Lviv region from man-made and nature emergencies” is processed.

Conclusions

At the present, the issue of creating and operating of monitoring and forecasting system of emergency situations, which will allow us to analyze and systematize the risks, as well as to collect information in

order to increase the level of society readiness to withstand the dangers.

From the above estimates, the Lviv region belongs to the territories with a low degree of protection. The solving problem of protection degree from dangers requires significant investment, organizational and economic, technical and other resources. Performing the Program of Civil Protection of Population and Territories of Lviv region from man-made and nature emergencies that introduced in 2016 will increase the region readiness to withstand the hazards and effectively eliminate the consequences.

References

- [1] Rud'ko H. I., Kravtsiv V. S., Samol'otov P. V., Kobel'ka M. V.: *Nebezpechni pryrodni ta tekhnopryrodni protsesy v hirs'kykh rayonakh L'vivs'koyi oblasti: stan ta prohnoz ozvytku NAN Ukrainy. Instytut rehional'nykh doslidzhen'.* – L'viv, 2001. 129 s.
- [2] UNISDR, 2009 Global Assessment Report on Disaster Risk Reduction. Available from www.preventionweb.net/english/hyogo/gar/press/documents/UNISDR_insert_2-DR-drivers_prFINAL-r.pdf (accessed 4 August 2014).
- [3] www.munichre.com
- [4] *Georges-Yves Kervern: Eléments fondamentaux des cindyniques; Editeur(s): Economica, 1995.*
- [5] http://ec.europa.eu/echo/sites/echo-site/files/swd_2017_176_overview_of_risks_2.pdf
- [6] Blaikie P.: *At Risk: natural hazards, people's vulnerability, and disasters*, Routledge, London 1994.
- [7] Chardon C.: *Etude intégrée de la vulnérabilité de la ville de Manizales (Colombie) aux risques naturels, Revue de géographie alpine*, Tome LXXXII, n°4, Grenoble, 1994.
- [8] Gilles A.: *Cybergeog: European Journal of Geography*, 2017. DOI : 10.4000/cybergeog.25297
- [9] Kuz'myn S. B.: *Problems of modern science and education*, 2015, 10, 1.
- [10] *Risk Assessment in the Federal Government: Managing the Process.* National Research Council (US) Committee on the Institutional Means for Assessment of Risks to Public Health. Washington (DC): National Academies Press (US); 1983.
- [11] Men'shykov V. V., Shvyryaev A. A., Zakharova T. V.: *Analyz ryska pry systematycheskom zahryaznenyy atmosfernoho vozdukhа opasnyu khymycheskymy veshchestvamy.* – M.: Yzd-vo Khymych. fak. Mosk. un-ta, Moscow, 2003.
- [12] *Natsional'na dopovid' pro stan tekhnohennoyi ta pryrodnoyi bezpeky v Ukraini za 2006-2016 roky: [u formati PDF].* http://www.mns.gov.ua/content/national_lecture.htm
- [13] *Kompleksna prohrama tsyvil'noho zakhystu naseleennyi i terytoriy L'vivs'koyi oblasti vid nadzvychaynykh sytuatsiy tekhnohennoho ta pryrodnoho kharakteru. L'vivs'ka oblasna rada III sesiya VII sklykannya, rishennya № 110 vid 01 bereznya 2016 r.*
- [14] *Ekolohichnyy visnyk.* <http://www.ecoleague.net/diialnist/vydannia-vel/ekolohichniy-visnyk/2016r>
- [15] <http://www.lv.ukrstat.gov.ua>
- [16] <http://loda.gov.ua>

**THE ROLE OF THE WAVELENGTH
OF LIGHT IN THE DYNAMICS
OF GROWTH OF CHLOROPHYLLSYNTHESIZING
MICROALGAE DUE TO THE ABSORPTION
OF CARBON DIOXIDE**

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Abstract. The effect of light wave length on the rate of carbon dioxide absorption by microalgae has been studied. The mechanism of transfer of carbon dioxide from the air into the internal environment of the cells of microalgae has been described. The coefficient of microalgae growth based on the mathematical model has been determined. The analytical dependence of the mentioned coefficient on the light wave length has been obtained. The optimum length of light wave has been determined to design the flow chart for eliminating carbon dioxide from industrial gas emissions by the biological method.

Keywords: photosynthesis, light wave length, microalgae, diffusion, mathematical model, kinetics.

Introduction

About 150 world leaders met in the suburb of Paris, in a township of Lai Burzhe, where a world climatic summit concerning continuous growth of carbon dioxide content in the atmosphere began on November 30, 2015. Its main task was to agree on measures, which would allow retaining the growth of temperature in our planet within the limits of 2 t °C. Scientists have already alarmed and warned that if this problem is not solved in an urgently, the middle temperature of the Earth will rise by 5 t °C till the end of the century and it will cause the threat

of global sea level rise and catastrophic consequences for all mankind.

This situation necessitates the development of effective technologies for eliminating this undesirable effect. One of the possible solutions to this problem is to use photosynthesis in industrial environment. The ability to absorb carbon dioxide from the atmosphere by plants and algae and its “storage” in the form of biomass is an objective condition for the implementation of these processes to the treatment of industrial carbon dioxide emissions. This process can be described by a reaction:



Not only plants, but also microalgae have the ability to perform photosynthesis. Moreover, the advantage of chlorophyll synthesising microalgae is that they grow quickly and absorb much more carbon dioxide than the plants, and are able to adapt to the land of adverse conditions. Photosynthesis can be implemented effectively and efficiently in a light period of a day. There is a problem of photosynthesis at night because it requires artificial lighting making industrial technologies more expensive. Therefore searching ways to reduce the cost of realization of photosynthesis in industrial technologies is the relevant problem.

One of the ways of decreasing the quantity of carbon dioxide in the atmosphere is the development of effective methods for eliminating it from industrial gas emissions, including the use of photosynthesis

which is one of the most efficient biological methods. The necessity of additional artificial lighting significantly increases the cost of environmental measures when it comes to continuous cleaning process. A significant reduction of energy costs is possible thanks to the determining the light wavelengths in the visible area of the spectrum at which the maximum absorption of the culture of microalgae is obtained. Therefore, it is reasonable to use microalgae photosynthesis at certain wavelengths of the visible spectrum of the light flux.

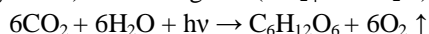
The literature contains information about the most important factors influencing the efficiency of algae photosynthesis which include temperature [2], the extent of aeration by carbon dioxide [3, 5], the illumination, the contents of macro and microelements, the alkaline-acid balance, etc. At the same time, there is little information about the impact of certain wavelengths in the visible range on the effectiveness of microalgae photosynthesis. Due to the correlation of physical and chemical values with the biological ones, you can get a deeper understanding of processes in the investigated biological object. Therefore, the study of the influence of light wavelengths in the visible area on the efficiency of photosynthesis is an interesting task.

The aim of this work is to study the influence of light wavelengths on photosynthesis processes, which accompany the absorption of carbon dioxide from the gaseous fluid by the cells of microalgae and increase their biomass.

Theoretical part

Photosynthesis is the only process in the biosphere, which leads to the increase in free energy due to the internal source. The energy stored in the products of photosynthesis is the main source of energy for the mankind. It means that the products of purposeful photosynthesis can be used for recuperation of power. For example, it can be anaerobic biodegradation with the aim of producing methane [4].

Traditionally it is believed that photosynthesis is the process of converting sunlight into energy of chemical bonds and the synthesis of organic compounds (carbohydrates) from inorganic ($\text{CO}_2 \uparrow$ and H_2O).

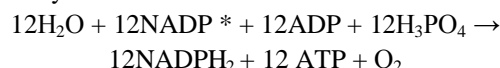


Photosynthesis is a complex multistage process; the reactions of photosynthesis are divided into two groups: reactions of the light phase and the reactions of the dark phase.

Direct experimental proof that the oxygen in photosynthesis is released from water was found in

40-ies of the last century. In addition, it was found that photosynthesis involves two groups of reactions: one, which is related to photodissociate water, release of O_2 , and the electron transfer, is a light phase; and the other, related to the reduction of CO_2 to carbohydrate, which does not depend on the light, is a dark phase.

The process, in which energy-saturated molecules and ATP compositions appear, is called the light phase of photosynthesis. The total equation of the light phase of photosynthesis:



Dark phase of photosynthesis occurs in chloroplast. The final equation of photosynthesis:



Biological objects, as a rule, are very complex and the processes occurring in them are influenced by many factors which often depend on each other. The absorption of carbon dioxide from the air by microalgae is a subject to the laws of mass transfer. At the heart of the processes of mass-exchange of microalgae cells with the environment lies a complex series arranged in a certain way in time and space of biochemical reactions. As a result of these processes the concentration of the absorbing substance, the number of single cells of the microalgae, the biomass of the microorganisms are changing and other values can also change. Thus, the absorption of carbon dioxide by microalgae is a complex heterophase process in which there occurs the mass transfer of carbon dioxide from the gas phase to conventional solid phase. This processes are characterized by the simultaneous dependence of the rate on diffusion and kinetic factors. The system "gas-liquid-cell" is three-phase, which inevitably creates additional difficulties for the description even in comparison with complex two-phase gas-liquid systems [6].

Penetration of carbon dioxide into the aqueous phase and then the diffusion transfer to the cell membrane with subsequent transfer through the membrane into the cell can be satisfactorily described by the model of mass transfer to the surface of solid particles, as cells are commonly considered to be "conventionally solid" phase. The total resistance in this case can be quite significant, therefore it is important to determine which of the all is limiting and most affects the overall speed of the process.

For the cultivation of microalgae in devices with mixers or column bioreactors the diffusion resistance at the interface "cell-liquid" can be neglected in cases where it comes to separately growing cells.. As shown in several experiments, the system with separately

developing cells of the microalgae which are in liquid environment can be influenced by mass transfer at the interface “gas-liquid”, but almost never limited by the transfer of substances into the cell or reverse transfer of metabolic products.

With sufficiently good mixing, the microalgae cells are uniformly distributed over the volume of the liquid. With this assumption the mass transfer of carbon dioxide from the gas phase into the liquid phase will flow with the speed:

$$r_{\bar{A}} = \beta_{CO_2} \cdot (\bar{C}_{CO_2} - C_{CO_2}), \quad (2)$$

and carbon dioxide which is turned into the liquid phase is consumed by the culture of microalgae, which grows with the speed:

$$r_{CO_2} = k_{CO_2} [N_K] C_{CO_2}. \quad (3)$$

With constant or little changing concentration of carbon dioxide in the gas phase, respectively, the constant concentration C_{CO_2} in the liquid phase, the system with the culture of microalgae growing in the liquid phase enters a stationary state in which the consumption of carbon dioxide by cells is fully compensated by its income from the gas phase, that is

$$r_{\bar{A}} = r_A.$$

This allows to equate expressions (2) and (3) provided that the β_{CO_2} is the surface-volume coefficient of mass-transfer from the gas phase into the liquid.

$$r_{CO_2} = r_{\bar{A}} = k_{CO_2} [N_K] C_{CO_2} = \beta_{CO_2} \cdot (\bar{C}_{CO_2} - C_{CO_2}), \quad (4)$$

The total resistance is recorded by the dependence (4), where the law of aggregate resistance is kept:

$$\frac{1}{k_{CO_2}} = \frac{1}{\beta_{CO_2}} + \frac{1}{k_{CO_2} [N_K]} \quad (5)$$

Since the overall resistance of the process of consumption of carbon dioxide – $1/k_{ef}$ is the sum of the diffusion resistance $1/\beta_{CO_2}$ and kinetic, which includes the parameters of the process of metabolism $1/k_{CO_2} [N_K]$

The process model includes a sequential component transfer from phase to phase and its consumption by the cells in the volume of the liquid phase. This leads to the conclusion about the existence of a stationary concentration of carbon dioxide, which is transferred in the phase, where its consumption occurs, namely about the constancy C_{CO_2} in time, which is determined by the expression (3). During the time when the cell concentration $[N_K]$ does not change much, the concentration of

C_{CO_2} will be constant, if C_{CO_2} , is also an invariable value, which is acceptable in practice.

The cases which are possible with significant differences in the resistances are of practical interest (5).

If the speed of the metabolism of carbon dioxide is significant due to the large quantity of k_{CO_2} or high concentrations of cells $[N_K]$, then $k_{CO_2} [N_K] \gg \beta_{CO_2}$ for the inverse values the inequality is:

$$\frac{1}{\beta_{CO_2}} \ll \frac{1}{k_{CO_2} [N_K]}. \quad (6)$$

Then (5) can be simplified because the small resistances in the amount can be neglected, in that case $k_{ef} \approx \beta_{CO_2}$ and the overall speed of the process is:

$$r_{CO_2} \cong \beta_{CO_2} \cdot \bar{C}_{CO_2} = \beta_{CO_2} \cdot \frac{1}{\gamma_{CO_2}} \cdot C_{CO_2}. \quad (7)$$

This extreme case corresponds to the diffusion regime of the process, and the nature of the dependence (7) indicates that in such circumstances $C_{CO_2} \cong 0$, in that case microalgae consume carbon dioxide, which diffuses from the gas phase while it is nearly of absent in the liquid phase. It is clear that all the factors which contribute to the increase of the coefficient of mass transfer β_{CO_2} will accelerate the overall process of cultivation due to improvement of supply the cells by the limiting substrate and carbon dioxide. This will result in an increase of the carbon dioxide concentration or its partial pressure in the gas phase.

The second extreme case is when $\beta_{CO_2} \gg k_{CO_2} [N_K]$ is achieved in the slow consumption of carbon dioxide by microalgae culture or its low concentration. Inequality

$$\frac{1}{\beta_{CO_2}} \ll \frac{1}{k_{CO_2} [N_K]} \quad (8)$$

in this case (4) can be written as:

$$r_{CO_2} \cong k_{CO_2} [N_K] \cdot \bar{C}_{CO_2} = k_{CO_2} [N_K] \cdot \frac{1}{\gamma_{CO_2}} \cdot C_{CO_2}, \quad (9)$$

The rate of consumption of carbon dioxide according to (9), is determined only by kinetic factors, therefore this mode can be called kinetic.

In these circumstances, the mass transfer ensures the maximum possible supply of carbon dioxide, which comes from the gas phase to the cells, and the current concentration of carbon dioxide is almost identical with equilibrium, which responds to saturation. Among other factors intensifying the kinetic processes are: temperature, concentration of

reagents, and for photo-kinetic, as in this case, the source of light energy.

The main material and discussion of the results

The spectrum of absorption in the visible area of the aqueous solution of *Chlorella* microalgae is presented in Fig. 1.

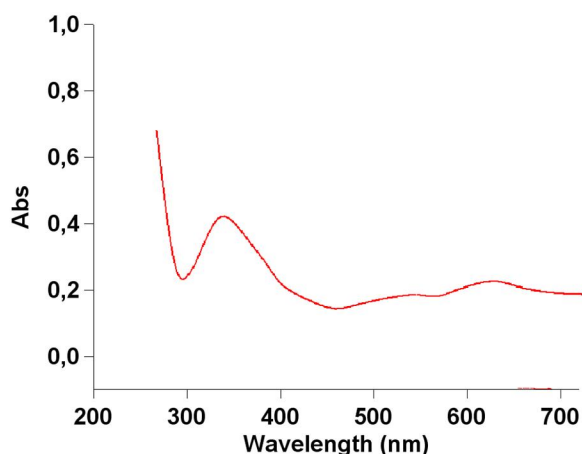


Fig. 1. The spectrum of absorption of the aqueous solution of the studied microalgae

According to the shown spectrum, it is possible to say that the greatest area of absorption has (340–400 nm) and (650–700 nm). These spectra correspond to approximately violet-blue and red light, therefore it is useful to study the absorption of the carbon dioxide in these two areas.

The object of laboratory research was the culture of green microalgae of *Chlorella vulgaris*, which is cultivated with different colours of light during 14 days in four photobioreactors with a 1.5 L volume. In the first photobioreactor the colour of the light was blue, in the second – green, in the third – yellow and in the fourth one it was red. An equal amount of inoculum with the culture of the *Chlorella vulgaris* microalgae was placed into the basic nutrient environment. The algae received the same amount of the corresponding spectrum of light and bubbling carbon dioxide in all the four photobioreactors. In the further cultivation of algae, their number increased. The pH was 6.5. The temperature of cultivation was $20 \pm 1^\circ\text{C}$. Very quickly from almost transparent content a liquid of dark green colour was formed. The selection of the solution of biomass of algae was carried out every day. The concentration of algae biomass was determined by a photocolorimetric method.

The results of experimental studies of the growth of microalgae biomass by the corresponding wavelengths are presented in Fig. 2. These are the curved lines of growth of so-called S-shaped form and allow to identify four phases of growth which take place in a specific sequence and are expressed to a greater or lesser extent: the initial, or adjustment phase, linear and stationary phases Fig. 2. Phase of settling of microalgae culture is clearly seen in Fig. 3. It is important to note that the adaptation phase for the bioreactor, which was covered in blue and red light has the lowest amount of dying culture and the highest intensity of its growth in the subsequent phases. This confirms the effectiveness of these wavelengths in the spectra of illumination during implementation of the technologies of photosynthesis in the dark period of time.

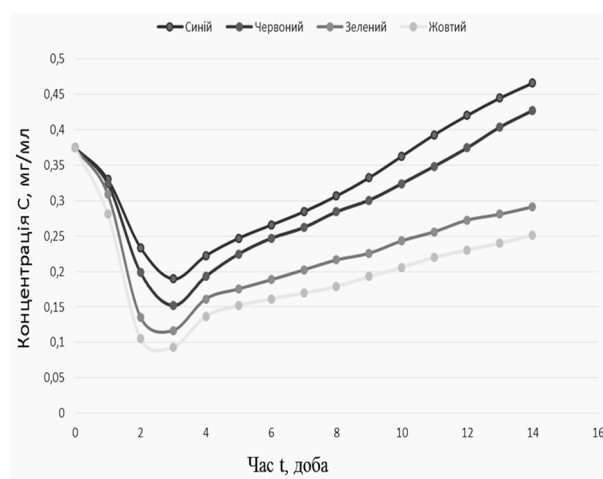


Fig. 2a. Kinetic curve lines of microalgae concentration growth

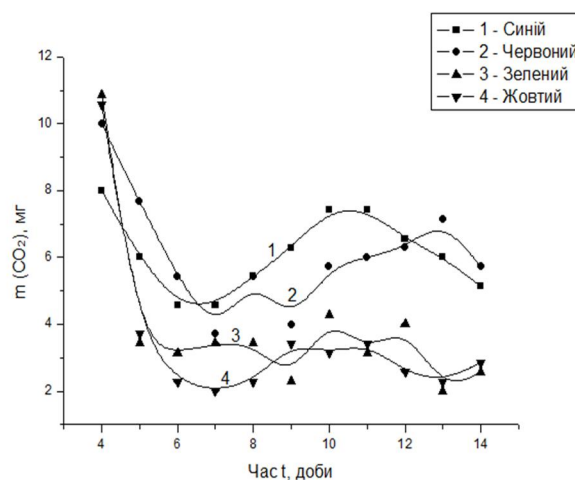


Fig. 2b. The dependence of the mass of absorbed carbon dioxide in appropriate wavelengths in the investigated limits

The basis of the processes of the cell exchange with the environment and internal metabolism is created by complex series organized in a certain way in space and time by biochemical reactions. As a result of these transformations the concentration of the target substances, the number of individual cells, biomass of microalgae and other quantities are changing. A mathematical model which describes the dependence of modification of cell concentration in the culture medium on time $N = N(dt)$ is given in [6].

As shown in Figures 2, 3, the dynamics of growth, and thus the intensity of the absorption of carbon dioxide by microalgae significantly depend on the wavelength of light. The experimental curves are well described by the famous equation:

$$N = N_0 e^{-k_M t} \quad (1)$$

where N is current cell concentration in the biomass of microalgae, N_0 is cell concentration in the microalgae biomass at the initial time $t = 0$, k_M is the coefficient of increasing microalgae biomass.

In logarithmic coordinates (1) describes a straight line, tangent of inclination of which allows to determine the growth rate k_M . The results of the transformations are shown in Fig. 3.

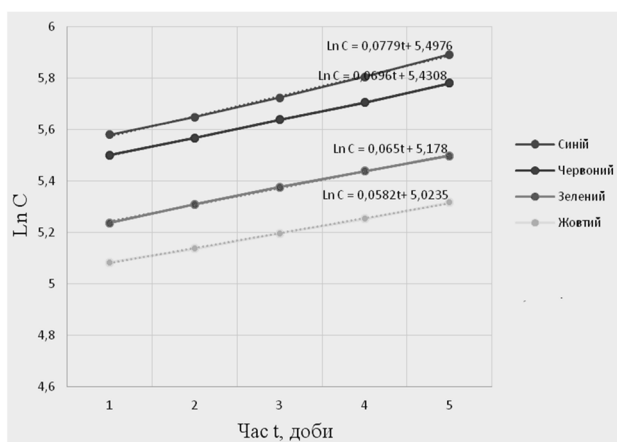


Fig. 3. Kinetic curves of increasing microalgae concentration in logarithmic coordinates with the appropriate light wavelength

Thanks to the graphic dependences, the coefficient of growth for the corresponding spectrum of light was determined, as the tangent of inclination of the experimental curves shown in Fig. 3, and recorded as analytical dependences. Accordingly, for the blue spectrum, the dependence is written: $C = C_0 e^{0,0779t}$;

- for the red spectrum: $C = C_0 e^{0,0696t}$;
- for the green spectrum: $C = C_0 e^{0,065t}$;
- for the yellow spectrum: $C = C_0 e^{0,0582t}$.

Based on the obtained values, the graph of dependence of the growth rate on the wavelength was built and the corresponding dependence was obtained (Fig. 4).

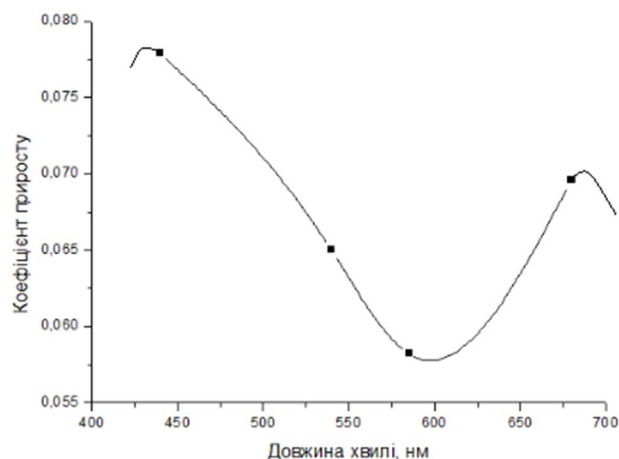


Fig. 4. The dependence of the growth rate on the wavelength

$$k = 3,2 \cdot 10^{-3} \lambda + 0,0756,$$

where λ is the light wavelength.

Conclusion

The influence of light wavelength on the dynamics of absorption of carbon dioxide by microalgae was studied. The analytical dependence $k = f(\lambda)$ of the coefficient of growth rate of microalgae on the light wavelength has been obtained.

References

- [1] Netrusov A. Y., Bonč-Osmolovskaja E. A., Horlenko V. M y dr.; Pod red. Netrusova A. Y.: Ekoloĥija mykroorhanyzmov: Učebnyk, dlja stud. Vuzov. Yzdat. centr “Akademyja”, Moskva 2004, 272. (in Russian)
- [2] Djačok V. V., Katyševa V. V., Levko O. B.: Vyvčennja vplyvu temperatury na kinetyku pohlynnnja vuhlekysloho hazu mikrovodorostjamy. Visnyk Nacional'noho universytetu “L'vivs'ka politechnika”. Chimija, tehnoloĥija rečovyn ta ič zastosuvannja., 2015, 812, 365–372.
- [3] Djačok V. V., Huhlyč S. I., Levko O. B.: Vyvčennja procesiv masoobminu pid čas realizacii bioloĥičnych metodiv očyščennja hazovych vykydiv vid vuhlekysloho hazu. Visnyk Nacional'noho universytetu “L'vivs'ka politechnika”. Chimija, tehnoloĥija rečovyn ta ič zastosuvannja, 2014, 787, 313–319.
- [4] Djačok V. V. Levko O. B.: Vyvčennja procesu masoobminu pry peretvorenni vuhlekysloho hazu u metan bioloĥičnym metodom. Ekoloĥična bezpeka, 2014, 1, 31–35.

- [5] Djačok V. V., Levko O. B.: Masoobmin v bioložičnych procesach. Visnyk NU "L'vivs'ka politechnika" Chimija, tehnoloģija rečovyn ta ič zastosuvannja, 2013, 761, 289–293.
- [6] Dyachok V., Huhlych S. Mathematical design of biological processes of complicated mass transfer Sciens and Education a New Dimension. Natural and Technical Sciences, III(5), ISSUE 41, 2015, 91–94. [7] Zolotar'ova O. K., Šnjukova Je. I., Syvaš O. O., Mychajlenko N. F. Pid red. Zolotar'ovoï O. K.: Perspektyvy vykorystannja mikrovodorostej u biotehnoloģii. Al'terpres, Kyiv 2008, 234. (in Ukrainian).

**RESEARCH OF MIGRATION PATTERNS
OF HEAVY METALS IN THE SOIL ENVIRONMENT
IN THE AREA OF PHOSPHOGYPSUM STORAGE INFLUENCE**

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Abstract. The paper is focused on the research of migration process of heavy metals in the soil environment in the area of phosphogypsum storage in Sumy region. In the profile of the gray forest soils the corresponding genetic horizons were identified. The various structures of compounds containing heavy metals were detected in the samples by the diffractometric analysis. The increased gross content of lead in comparison with the background concentration in allocated humus and illuvial horizons has been determined.

Key words: phosphogypsum, migration, heavy metals, soil, genetic horizons.

1. Introduction

The risk of entering environment (E) pollutants during the placement of waste dumps from chemical enterprises causes a need to understand the ways of contamination E, distribution in the profile of migration in the soil, impact on plants, and ultimately, on human health [1]. The main source of E contamination in the areas of placement of mineral fertilizer production on the territory of Ukraine (Armyansk, Sumy, Rivne, Vinnytsia, Kamyanskoye) are arrays of phosphogypsum dump. In particular, Sumy region has already accumulated more than 14 million tons of this waste of different genesis: phosphorite and apatite phosphogypsum.

In the areas of phosphogypsum accumulation, heavy metals (HM) as a result of washing from dumps and accelerating migration under acidic conditions are subjected to horizontal and vertical redistribution by the soil profile, which may lead to their further migration into aquifers.

2. Materials and methods

2.1. Review of the previous research

The factors contributing to migration of pollutants can be: filtration of atmospheric precipitation through the soil layer, capillary rise of moisture to the surface of the soil as a result of evaporation; diffusion of adsorbed and free ions of soil solution; transferring colloidal particles on the surface; carrying over the root systems of plants; settling on natural geochemical barriers or barriers that arise as a result of anthropogenic impact on E, etc. Processes that promote migration of substances in soils in natural conditions are different in nature and the degree of influence. Often, speed, direction and magnitude of migration depend on season, time of the day, initial conditions and soil properties such as granulometric composition, soil medium reaction, organic matter content, and temperature of individual horizons.

Among HM, which pollute soil of phosphogypsum dumps, the most dangerous are lead and cadmium (first class of danger). Usually in soils involved in agriculture, gross cadmium content does not exceed 1 mg/kg, while in contaminated areas its concentration is much higher, to 3 mg/kg of soil. Gross lead content reaches 20 mg/kg of soil at a maximum allowable concentration 100 mg/kg.

HM distribution in soil, absorption or accumulation of plants depends on the type of soil, its physical, physical and chemical properties, content of organic matter, redox conditions, antagonism or synergism between metals, their amount in pedosphere, soil temperature, vegetation type, etc.

In world practice, handling with phosphogypsum wastes is widely used in their storage in dumps.

Consequently, multi-year monitoring researches are carried out in the areas of formation of phosphogypsum dumps. Thus, in Florida Institute of Phosphate research (USA) [3] it was substantiated that the major changes in the area of phosphogypsum arrays accumulation can be characterized as a change in pH (from about 6.5 to 2.5), an increase in a number of soluble ions, especially sulphate and phosphate, inclusion of other ions such as chloride, fluoride, HM and radionuclides, and an increase amount of dissolved silica. Increasing concentration of many ligands leads to significant changes in predicted equilibrium of compound formation. Fluoride from stock solutions dumps can significantly affect modification of aluminum silicon and iron. The second major effect is appearance of ground water saturation with various solids. Low pH of contaminated solutions usually indicates that in most fresh water a part of solids falls into precipitate.

Monitoring researches of phosphogypsum dumps in India [4] indicate the development of water erosion phosphogypsum arrays, which can create cavities and instability solutions in the built dams, cause an increase in the surface runoff from dumps containing fine particles of phosphogypsum, erosion around the pipeline systems. Slopes can become more susceptible to failure and erosion with intense atmospheric precipitation.

Thus, the research of patterns of pollutants migration is relevant, in particular HM in natural components of E within the limits of possible influence of phosphogypsum dumps, which has its specific features of physical and chemical and biochemical transformations in accordance with territorial location and meteorological factors, taking into account the genesis of phosphogypsum, which are superimposed on general regularities of the transformations of these substances in biogeochemical cycles.

According to the importance, the purpose of the work was the research of HM migration process on soil profile in the area of active phosphogypsum dumps in Sumy region.

2.2/ Method of conducting field research of phosphogypsum storage area

The use of field methods allows us determine the structure of phosphogypsum dump – the boundaries of location breeding zones, the height of terraces, the area of the dump, to estimate the parameters of its spatial location in natural landscape, as well as possible directions for impact on natural objects and settlements.

Laboratory methods were oriented on establishment of laws of changing properties of phosphogypsum, depending on various factors that determine its physical and chemical characteristics such as elemental

composition, chemical and mineralogical composition, acid-base balance.

Laboratory soil samples for the analysis of HM migration from phosphogypsum into E were selected and conducted.

X-ray diffraction was used to determine the structure of material performed on the automated diffractometer DRON-4-07 based on SumDU (sensitivity of measurements is at the level of 0.1 %). When removing the structure of sample material, CuK radiation (wavelength 0.154 nm) and Breg-Brentano focusing θ - 2θ (2θ – Breg angle). were used Current and voltage value on X-ray tube set 20 mA and 40 kV. Shooting samples performed in continuous recording mode (speed 1°/60 seconds), the range of angles 2θ from 15° to 105°.

Elemental analysis of the samples was carried out on the X-ray fluorescence analyzer Elvax (Ukraine), based on SSU. Accuracy of determination of mass metal particle in the alloys is from 0.1 to 0.3%. The limits of HM impurities detection in a light matrix is not less than 10 ppm.

Measurements of pH of water extracts of phosphogypsum and soil samples were carried out in laboratory using pX-150 (ionometer) (Belarus) with glass combined electrode “EKS-10603”.

Removal of HM moving forms was carried out using ammonium acetate buffer. The content of Pb and Cd in soil solutions was determined by the atomic absorption method.

Phosphogypsum samples were taken from the dump and adjacent areas according to standard methods [5–7].

Sampling points were located on the territory of the dump and in adjacent areas, including sanitary protection zone of the dump, and beyond it. Phosphogypsum samples were taken from different sides of the dump from each terrace level, thus samples differed in terms of storage time and depth of occurrence. On re-cultivated slopes phosphogypsum samples were taken under the pre-exposed soil layer.

Soil samples were taken around the dump up to 200 m from the dump at equal intervals 50 m apart, as well as on soil profile to the soil forming rock every 10 cm. Soil samples after removal were dried under standard conditions (pressure 1 bar = 105 Pa = 750.06 mm Hg, temperature 298.15 K = 25 °C) and powdered.

As priority climatic criterion of water supply resources, nature and energy of soil formation and soil fertility for zoning forest-steppe territory, the relative indicator – hydrothermal coefficient of Selyaninov (GTK) is used, which is the ratio between the amount of precipitation in the period when the air temperature is above 10 °C, and the sum of indicated temperatures for this period, multiplied by 10 [8].

2.3. Characteristics of soil profile near the phosphogypsum dump

On a larger area of the territory around the phosphogypsum dump, a gray type of forest soils, which is characterized by loose, granular, densely penetrated roots of plants, with a humus and accumulative horizon (humus content from 3–4 % to 6–8 %) was naturally formed, which is the manifestation of advantages of the sod process.

The soils are characterized by an acidic pH on average 5.8 to 6.5 units, absence or disguise of transient horizons on the soil profile weakly – expressed eluvial and well – expressed illuvial horizons of fulvous brown color. Beyond the sanitary-protective dump zone, there is farmland where the upper soil horizons, first of all, humus-accumulative and a part of eluvial one, are plowed. All subtypes of gray forest soils on this territory are combined by acidic reaction in upper horizons, unsaturated bases and low nutrient content. It is believed that this group of soils has some unfavorable physical properties, and, first of all, weak structure.

Fig. 1 shows a photo of a soil profile section at the sampling site for analyzing contents of HM near the phosphogypsum dump.



Fig. 1. Profile of gray forest soil near phosphogypsum dumps

Soil profile was formed in places with minimal parameters $GTK\ V-IX = 1,18-1,20$, which are caused both by climatic factors and relief due to additional accumulation of waste water moisture to the values $GTK\ V-IX = 1,76$.

In the profile of gray forest soils near the phosphogypsum dump the following horizons are distinguished (Fig. 1): H_0 is dark brown turf (capacity up to 2 cm); H is humus cumulative with dark gray turf with silica powder (7–11 cm); E_1 – an eluvial one of grayish white colour, with powdered-lumpy structural composition with carbonate inclusions, contains many plants roots (18–20 cm); E_2 is transient eluvially-illuvial plated nougat with carbonate inclusions, compacted; transition is gradual (6–10 cm); I is iluvial of brown colour lobed-prismatic (32–35 cm) and P is soil forming rock with a depth of 60–80 cm [10].

Significant factor is the presence in the soil of water-soluble, and therefore mobile, fulvic acids, which causes processes of intensive washing from the soil profile of many trace elements – Fe, Mn, Zn, Cd, Pb, Sr, V, including HM. This process is also characteristic gray forest soils.

Conducted diffractometric analysis soil data revealed the presence of various structures (oxides, sulfates, phosphates, carbonates), including those containing HM, in particular – Cd, Pb. In main phase of spectrum: SiO_2 silicon oxide, $Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$ aluminosilicate compounds, iron oxide FeO .

3. Results of field research of migration of HM in soil E in the phosphogypsum storage area

Monitoring research in 2017 showed some changes in radial distribution of lead and cadmium on the soil profile in comparison with previous field research in the area of active phosphogypsum dump in Sumy region [9, 10]. Comparative analysis was carried out on gross contents and moving forms of HM. On the dump territory the soil is characterized by increased values of total lead content (Pb_v) as compared with background concentration in isolated genetic horizons (humus and iluvial) (Fig. 2).

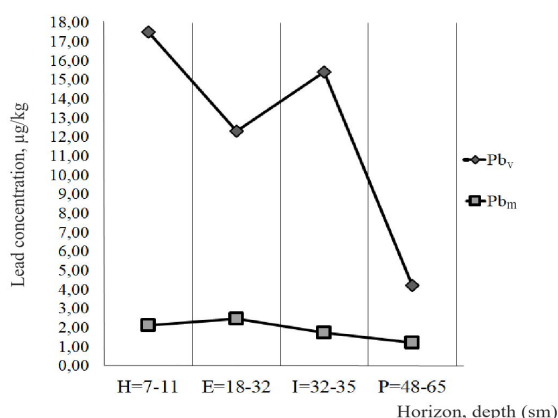


Fig. 2. Radial distribution of lead in the soil profile

Regarding lead moving forms (Pb_m), the highest values were noted in the upper 0-10 cm horizon and at a depth of 18 cm, which fluctuate between 3.5–1.76 $\mu\text{g}/\text{kg}$, then down the profile, there is a decrease in concentration to the level of 1.21 $\mu\text{g}/\text{kg}$ with MPC = 6 $\mu\text{g}/\text{kg}$.

In the upper horizon there was also cadmium accumulation the amount of which down the profile decreases to the illuvial horizon (Fig. 3).

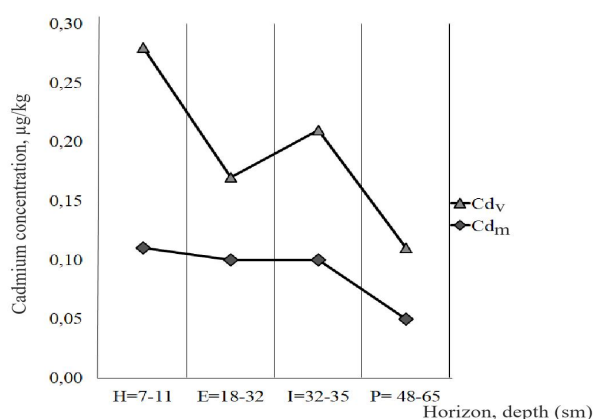


Fig. 3. Radial cadmium distribution in the soil profile

Total cadmium (Cd_v) content in the upper horizons remains approximately equal to 0.25–0.33 mcg/kg , then at a depth of 18–32 cm it decreases to 0.17 $\mu\text{g}/\text{kg}$ and at a depth of 32–35 cm. its concentration slightly increases. In the case of moving forms (Cd_m), their value is significantly less than MPC (1-2 $\mu\text{g}/\text{kg}$) with a gradual decrease in horizons within the range of 0.11–0.05 $\mu\text{g}/\text{kg}$.

4. Conclusions

The research describes the soil profile of the area of active phosphogypsum dump location. The conducted diffractometric analysis of soil data revealed the presence of various structures (oxides, sulfates, phosphates, carbonates), including those containing HM, in particular – Cd, Pb. In the main phase of spectrum there are: SiO_2 silicon oxide, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ aluminosilicate compounds, and FeO iron oxide.

Comparative analysis of gross content and moving forms of HM in the soil on the dump territory is characterized by higher values of total lead content compared with the background concentration in isolated humus and illuvial genetic horizons. In the upper horizon, cadmium accumulation was also observed, the amount of which decreases to the illuvial horizon down the profile. Lead and cadmium concentration does not exceed the MPC, which is related to the possibility of

absorbing these cations by soil complex of gray forest soils rich in clay minerals and humus, which causes soil to perform a buffer function to protect ecosystems.

References

- [1] Liubimova I. I. Vliianie potentsialno opasnykh khimicheskikh elementov, soderzhachikhsia v fosfogipse, na okruzhaiuchuiu srediu / I. I. Liubimova, T. I. Borisochkina. – M.: Pochv. in-t im. V. V. Dokuchaeva RACKH, 2007. – 45p.
- [2] Endovitskii A. P. Sostoianie svitsa I kadmia v chemozieme posle vnesenia fosfogipsa / A. P. Endovitskii, V. P. Kalinichenko, T. M. Minkina // Pochvovedenie. – 2014. No. 3. – P. 340–350.
- [3] How does phosphogypsum storage affect groundwaters? Prepared for Florida Insitute of Phosphate research FIPR Project No 94-05-042, 1998, 208 p.
- [4] Guidelines for Management and Handling of Phosphogypsum Generated from Phosphoric Acid Plants Final Draft Report. Central pollution control board (Ministry of Environment & Forests) Parivesh Bhawan, East Arjun Nagar, 2012. 46 p. – available at: www.cpcb.nic.in
- [5] Okhorona navkolyshniago pryrodного seredovishcha ta ratsionalne vikoristannia prirodnikh resursiv. Yakist dovkilliu. Vidbir prob hruntiv ta vidkhodiv pri zdiisnenni khimiko-analitichnogo kontroliu prostorovogo (zagalnogo i lokalnogo) zabrudnennia obektiv navkolishniago pryrodного seredovishcha v raionah vplivu promislivih, silskogospodarskih, gospodarsko-pobutovih i transportnih dzherel zabrudnennia. Instruktisiia. – [Chunnii vid 2005-03-01]. – Kiiv : Ministerstvo ohoroni navkolishniago pryrodного seredovishcha Ukraini, 2005. – 24 p.
- [6] Yakist gruntu. Vidbir prob. Chastina 1: DSTU ISO 10381 – 1: 2002. – ISO 10381-1:2002. – [Chunnii vid 2006-04-01]. – Kiiv : Depzhspozhivstandart Ukraini, 2002. – 38 p.
- [7] Ohrana prirodi. Pochvi. Metodi otbora i podgotovki prob dlia himicheskogo, bakteriologicheskogo, gelmintologicheskogo analiza: GOST 17.4.4.02–84. – Utv. MZ SSSR ot 19 dekabria 1984 g. – No. 4731. – Moskva : Izdatelstvo standartov, 1984. – 8 p.
- [8] Bozhko L. Yu. Otsinka vplivu ekstremalnih yavishch na produktivnist silskogospodarskih kultur / L. Yu. Bozhko ; MON Ukraini ; Odes. derzh. ekolog. un-t. – Odesa : Ekologiya, 2013. – 240 p.
- [9] Plyatsuk L. D. Modeluvannia tehnogenного zabrudnennia gruntiv raionu vidvalu fosfogipsu / L. D. Plyatsuk, I. O. Trunova, R. A. Vaskin // Visnik Kremenchutskogo derzh. politeh. univ-tu. – 2006. – No. 6 (41). – P. 123–126
- [10] Plyatsuk L. D. Sistemni podhod k ekologicheskomu monitoringu v paione rozmeshchenia otvala fosfogipsovih othodov / L. D. Plyatsuk, Ye. Yu. Chernysh, E. N. Yakhnenko [etc.] // Ekologicheskii vestnik (Minsk). – 2015. – No. 4(34). – P. 77–85.

ENVIRONMENTAL HAZARD OF UNCONTROLLED ACCUMULATION OF INDUSTRIAL AND MUNICIPAL SOLID WASTE OF DIFFERENT ORIGIN IN UKRAINE

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Abstract. The analysis of the generation, recycling and landfilling of waste in Ukraine is carried out. Significant generation of various wastes leads to their storage on the ground surface, as it is the most widespread way of waste treatment in Ukraine. Frequently, the stored waste burns (waste heaps, waste coal, landfills), causing significant accumulation of hazardous substances in the environment. The main way of environmental hazard reducing in the landfill area is the implementation of an effective policy of prevention of waste generation at the local authority level and state control over the waste disposal sites.

Key words: waste, municipal waste, environmental safety, environmental hazard, environment

Introduction

Every country in the world faces a waste management problem. Even if some countries have

fixed the problems with the recycling of municipal waste, then the handling of industrial and hazardous waste is merely under consideration. Ukraine has accumulated about 36 billion tons of waste, or more than 50 thousand tons per 1 km², among them only 30 % of industrial and 4 % of municipal waste are utilized. The volume of the generation, placement, recycling and disposal of waste is constantly updated, taking into account the criteria for their assigning to different types and classes of hazard [1].

There is a number of classifications of man-made wastes based on different principles, approaches, methods of analysis. In our opinion, from the position of environmental hazard caused by solid waste, it makes sense to classify them according to technological and organizational measures that should be taken for minimizing of this environmental hazard. A simplified classification system of solid man-made waste is shown in Fig. 1.

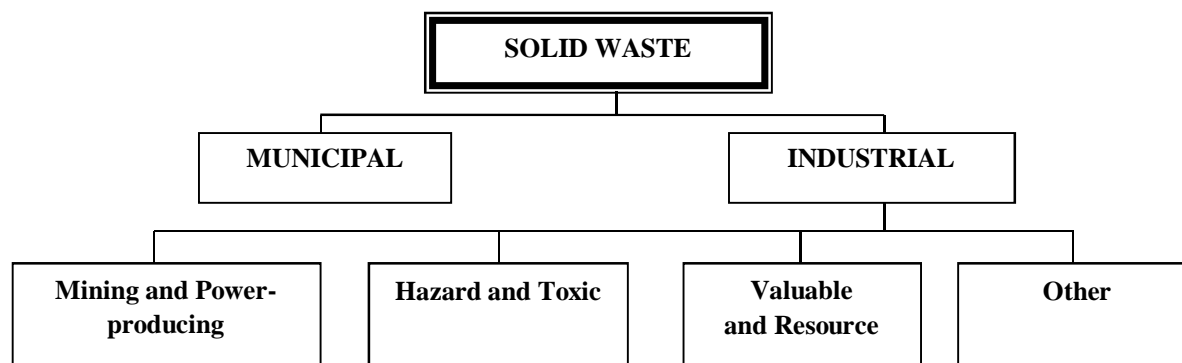


Fig. 1. Solid wastes classification according to technological and organizational measures that should be taken for minimizing of environmental hazard

Mining and power-producing waste include coal-mining waste, phosphogypsum, tailings (sulphuric, phosphorous, potash ore, etc.), slags of thermal power plants, slurry, sludge, etc. These wastes are characterized by large-tonnage. In order to avoid the environmental hazard caused by their accumulation only technologies of large-tonnage application (production of building materials, highways construction, use as a waste fill on coffins and dead pits, etc.) are suitable.

Hazardous and toxic wastes include radioactive, toxic, medical and other types of waste. A significant threat to the environment and biota is made up by medical waste containing hazardous pathogens and opportunistic microorganisms. Every year, the state produces 350 thousand tons of medical waste, which creates a high risk of spreading of infections and diseases [2]. Such a situation with the wastes generation leads to an increase of the regional environmental hazard and affects the national security of the state. Recycling technologies of hazardous and toxic wastes are special cost technologies that provide the maximum completeness of waste disposal.

Recycling technologies of valuable and resource waste are the special technologies, individual for each type of waste that provides the maximum recovery of valuable components. With the development of innovative technologies of processing to this category may be added the waste, which currently are stocked in man-made deposits.

For processing of other waste there are special technologies, individual for each type of waste according to its physical and chemical characteristics and volume of accumulation.

Human life is also concerned with huge amount of solid municipal waste (SMW). Significant growth of resources and goods consumption around the world in recent decades contributes to it. The best ways of SMW processing are:

- elemental or separate waste collection, which is an optimal solution of the problem of their disposal and the comprehensive recycling of secondary raw materials.
- exportation to sanitary-industrial zones, where they are sorted for obtaining of secondary raw materials and burned in special furnaces for power generation.
- processing of solid municipal waste by burial on special landfills.

Existing municipal landfills are considered to be one of the most hazardous objects for environment and human health. In this regard, almost all Ukrainian cities are involved in intensive discussion of the prospects of landfill closure and switching to another waste management technology. The alternatives in the new technology are:

- A new landfill designed and operated in accordance with Ukrainian and EU norms and also gives an opportunity of biogas power generation\$

- Waste recycling plant, where garbage from the collection system passes through the preliminary separation stage where valuable components are extracted, and then are either applied to an anaerobic digestion, or burned, or stored at the SMW landfill. It is also possible to apply different methods of processing to different group of waste;

- An incineration plant where all garbage from the collection system is burned. Solid residue and dust captured by the waste gas treatment system are stored at a SMW landfill according to the hazard class of the waste.

Presently, only 3.5 % of solid municipal waste is burned at two waste incinerators. About 0.1 % of municipal waste is hazardous. The most hazardous components of landfills are filtrate, biogas and biodegradable waste products. Filtrate, accumulated at the foot of the landfills, is rich in hazardous substances and heavy metals, that have a destructive effect on the environment [3–5]. Biogas, released from the landfill site, leads to local combustion and even explosions [6–8].

Aim, methods and tasks of the research

The aim of the work is to determine the specifics of waste management in Ukraine and their impact on environmental safety. According to the aim it was supposed to solve the following tasks:

- carry out an analysis of the generation, processing and disposal of waste in Ukraine;
- establish the volume of municipal waste generation per person;
- propose the ways to overcome the environmental problems caused by waste.

In the process of research, the following methods were used: comparative ecology, mathematical-statistical, system analysis and methods of logistic reasoning. The results were processed using mathematical programming in the MS Excel package.

Results of the research

In Ukraine there is a tendency to increase the amount of municipal waste generation. Having considered the statistics on waste generation, it should be noted that since 2014 the amount of waste per year has decreased. The reason is the exclusion from calculations the municipal waste in annexed territories. Data on the waste generation over the years is shown in Fig. 2.

It should be noted that the amount of municipal waste per person increases every year. Figure 3 shows that the amount of municipal waste per person has slightly decreased, but these data do not consider the generation of municipal waste in annexed territories.

In 2014–2016 there was an increasing tendency of the amount of burnt waste (at 2 waste incinerators).

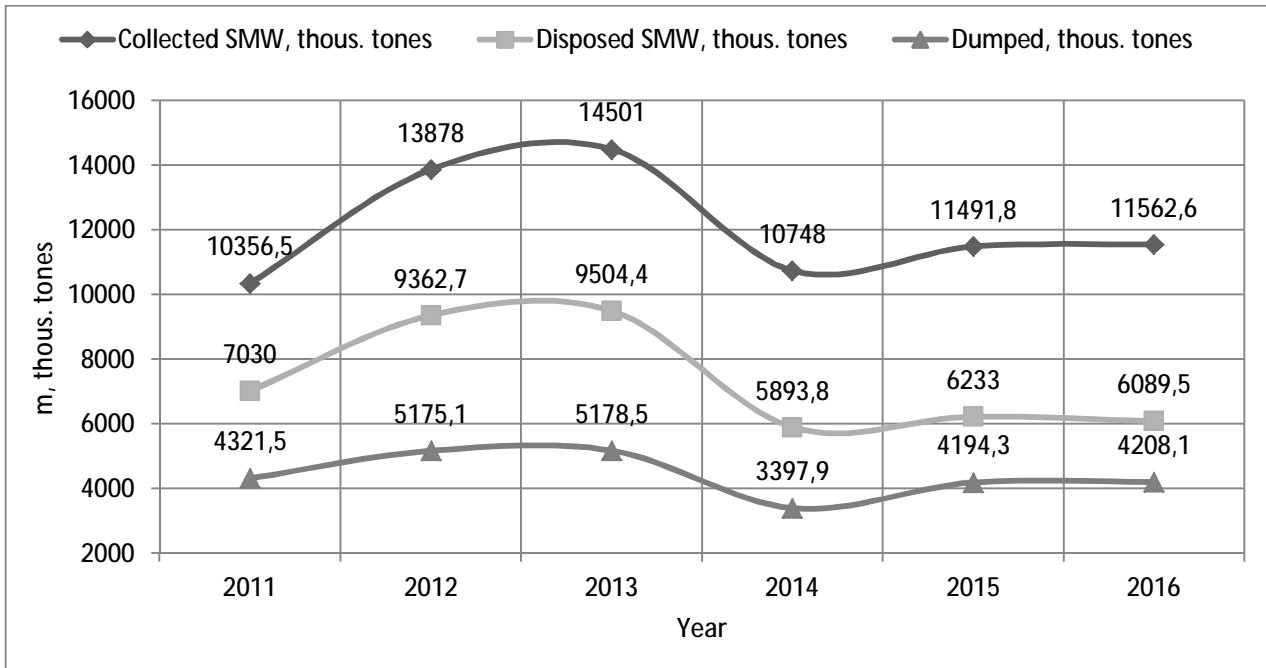


Fig. 2. Municipal waste management in Ukraine in 2011–2016

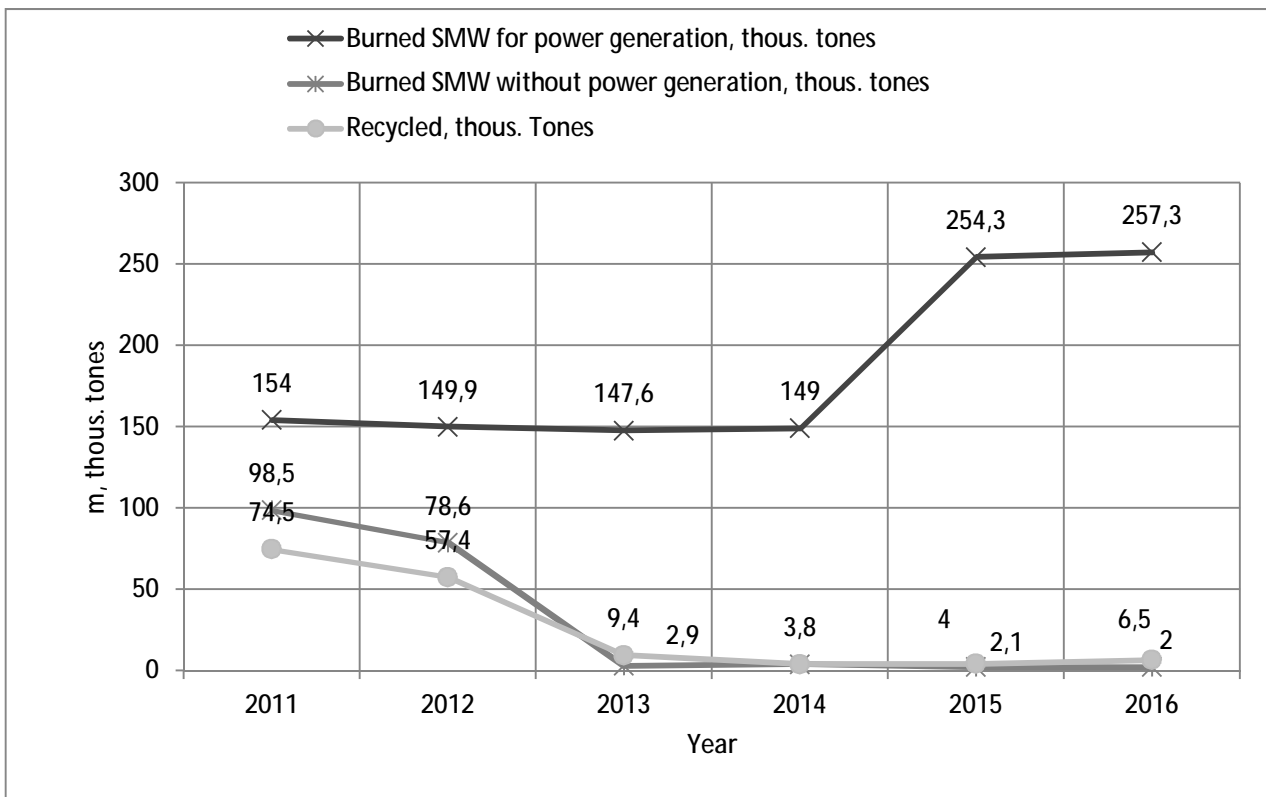


Fig. 3. Dynamics of incineration and recycling of municipal waste in Ukraine during 2011–2016

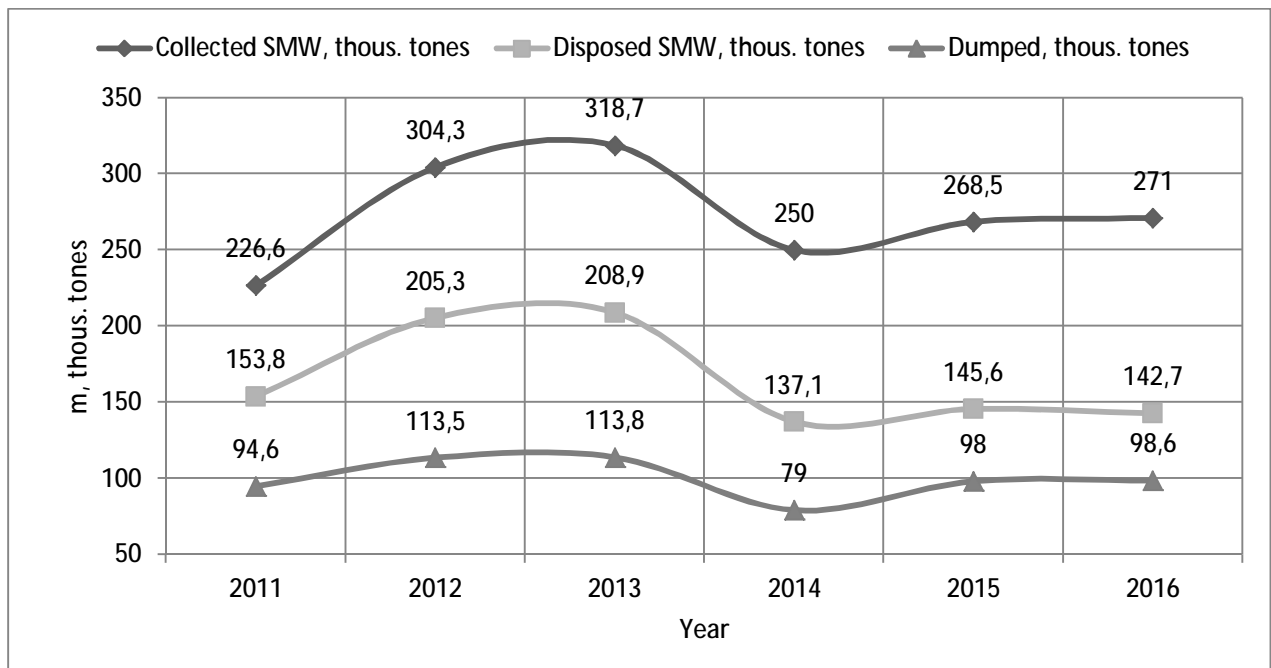


Fig. 4. Dynamics of municipal waste generation annually per person in Ukraine

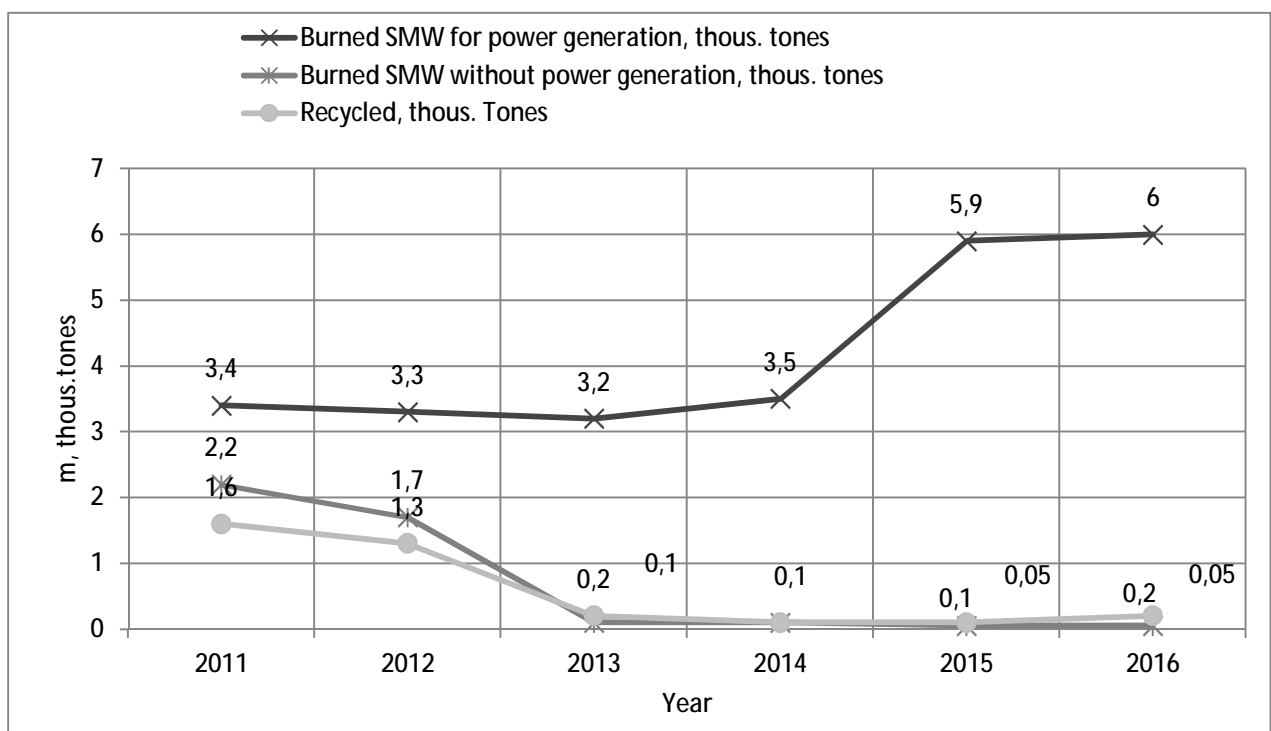


Fig. 5. Dynamics of incineration and recycling of municipal waste per person in Ukraine during 2011–2016

The total amount of accumulated hazardous waste in Ukraine is about 1.6 billion tons. Presently, chemical crop protection products are stored in breach of legal requirements for environmental and technological safety in 4075 warehouses. The incorrect storage of specific waste generated in medical service, veterinary practice, related researches, and after getting to the municipal waste

containers and landfills may lead to various infectious diseases [1].

Totally in 2017 366423.5 thousand tons of waste of I-IV classes were formed, recycled – 96057 thousand tons, burned – 1105 thousand tons, disposed to special places or objects – 193607.9 thousand tones (Fig. 6). It should be noted that the given data doesn't include the temporarily occupied

territories in the Donetsk and Luhansk districts and the Autonomous Republic of Crimea.

The development and management of waste of hazard classes I to IV in 2017 is given in Table 1. It should be noted that mostly the following types are

formed: industrial waste sediments, iron-and-steel waste, vegetable waste, animal excrement, urine and manure, household and similar waste, mixed and non-differentiated materials, mineral and mixed construction waste, mine soil.

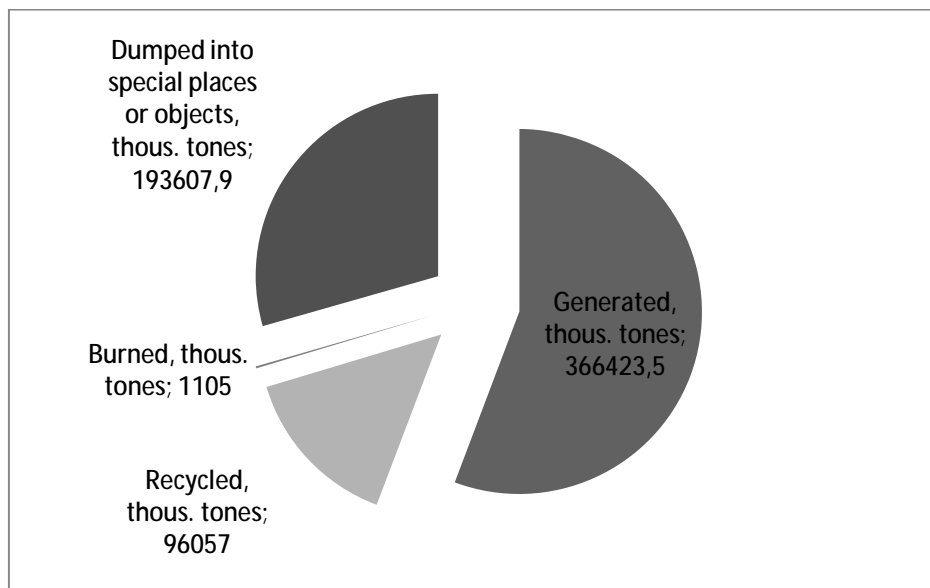


Fig. 6. Structure of waste management measures in 2017

Table 1

Development and management of waste of hazard classes I to IV in 2017

Type of Waste	Generated, th. tones	Processed, th. tones	Burned, th. tones	Disposed, th. tones
1	2	3	4	5
Waste solvents	1.2	0.4	0.2	0.0
Waste of acids, alkali or salts	213.1	78.9	4.2	102.5
Waste oils	18.0	18.2	1.0	0.2
Chemical waste	848.3	9.8	16.0	787.3
Industrial sewage sludge	3644.1	609.7	2.4	389.0
Spent slurry and liquids of waste treatment facilities	974.6	64.4	0.1	940.5
Biological and medical service wastes	0.8	0.1	1.4	0.0
Iron-and-steel waste	3555.2	3041.3	0.1	773.1
Nonferrous waste	29.2	5.9	0.0	0.0
Mixed ferrous and nonferrous waste	9.1	2.1	0.0	0.9
Glass wastes	34.4	3.4	0.0	0.3
Wastepaper	185.0	31.5	0.3	2.9
Rubber wastes	26.5	6.1	0.2	1.1
Plastic wastes	64.4	13.7	1.0	2.4
Wood waste	814.8	57.9	374.3	17.9
Textile wastes	21.0	1.1	0.3	0.3
Waste containing polychlorinated biphenyl	0.2	0.0	0.1	–
Unfit equipment	16.0	1.0	0.1	0.1
Non-serviceable vehicle	1.7	0.0	0.0	–
Waste accumulators and batteries	5.7	35.1	0.0	0.0
Animal waste and mixed food waste	589.4	311.2	4.1	8.1
Phylogenetic waste	8678.7	2425.9	414.3	54.5
Animal excrement, urine and manure	3651.6	2614.0	–	52.7
Municipal waste	6605.7	16.6	283.8	6589.9
Mixed and non-differentiated materials	10798.2	1459.9	0.9	2834.8
Sorting residuals	62.3	1.6	0.0	17.3

Continuation of table 1

1	2	3	4	5
General residuals	513.1	40.6	–	209.8
Mineral and mixed construction waste	975.5	387.0	0.0	1109.9
Other mineral waste	265739.8	68755.2	0.1	138932.8
Incineration waste	12901.5	4070.1	0.0	7133.9
Soil waste	367.3	80.9	0.0	156.8
Mullock	45028.0	11913.0	0.0	33478.6
Hardened, stabilized or glazed waste; mineral processing waste	49.1	0.4	0.1	10.3
Total	366423.5	96057.0	1105.0	193607.9

It should be noted that the significant formation of various wastes leads to their storage on the ground surface, since in Ukraine this is the most widespread way of waste treatment. Frequently, the stored waste burns (waste heaps, waste coal, landfills), causing significant accumulation of hazardous substances in the environment.



Fig. 7. Burning of Ternopil city landfill

According to the “Waste Management Concept for 2013–2020”, the main reasons for the problem of municipal waste treatment are: the imperfection of the mechanisms of collection, transportation, storage, treatment, recycling, disposal, neutralizing and land burial of waste, which leads to the accumulation increase; the absence of environmentally safe methods and techniques of waste management, which leads to an increase in man-made and environmental risks; low rates of implementation of low-waste technologies, development of waste management infrastructure, especially for hazardous waste; imperfection of legislation and state regulation system in the field of waste management; the absence of a single body authorized with waste management functions [1].

Conclusions

Waste management in Ukraine involves a single final stage – storage on an open area. As a result,

landfills, waste heaps, tailings ponds, slurry reservoirs are located on the territory of the whole country. It leads to an increase of the regional environmental hazard level. This situation is primarily caused by the lack of appropriate processing plants and technologies. The main way of environmental hazard reducing in the landfill area is the implementation of an effective policy of prevention of waste generation at the local authority level and state control over the waste disposal sites.

References

- [1] Rozporyadzhennya Kabinetu Ministriv Ukrainy vid 3 sichnya 2013 r. № 22-r “Pro skhvalennya Kontseptsiyi Zahal'noderzhavnnoi prohramy povodzhennya z vidkhodamy na 2013–2020 roky”.
- [2] Zakon Ukrainy “Pro Osnovni zasady (stratehiyu) derzhavnnoi ekolohichnoi polityky Ukrainy na period do 2020 roku” No. 2818-VI vid 21 hrudnya 2010 roku. Vidomosti Verkhovnoi Rady Ukrainy (VVR), 2011, No. 26. – S. 218.
- [3] Malovanyy M., Sereda A., Sliusar V. Ways to Minimize Environmental Hazards From Pollution of the Environment in the Zone of Influence of the Hrybovychi Landfill. *Environmental problems*. 2017. V 2, N 2. P. 65–70.
- [4] Two-stage landfill leachate treatment in aerated lagoons and at a municipal wastewater treatment plant/ Malovanyy M., Zhuk V., Sliusar V., Sereda A. *Eastern-European Journal of Enterprise Technologies*. 2018. № 1(10). P. 11–18.
- [5] Analiz perspektyv aerobnoho ochyshchennya infil'trativ smittyezvalyshch ta polihoniv tverdykh pobutovykh vidkhodiv / Moroz O. I. ta in. *Naukovyy visnyk NLTU Ukrainy*. 2017. Vyp. 27(3). S. 83–88.
- [6] Popovych V. V., Kucheryavyy V. P. (2015). Ekolohichna nebezpeka fil'tratsiynykh vodoyv smittyezvalyshch. *Visnyk LDUBZHD*. 12. 77–84.
- [7] Popovych V. V. (2016). Snyzhenye tekhnohennoho presynga polyelementnykh anomalyy devastirovannykh landshaftov putem fyto-melioratsiynogo vosstanovlennya. *Biolohichnyy visnyk MDPU*. 1. 94–114.
- [8] Popovych V. V. (2013). Devastovani landshafty v zoni nahromadzhennya tverdykh pobutovykh vidkhodiv i yikh fito melioratsiya. *Landshaftna arkhitektura i suchasnist'*. 23.9. 376–380.

STUDY OF AN ISSUE OF PROVIDING THE PEOPLE OF TOPORIV VILLAGE WITH DRINKING WATER

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Abstract. Monitoring findings regarding fluorine concentration in drinking water of Toporiv Village in Busk District of Lviv Region are analyzed. Reasons for biogeochemical endemic of hypoplasia and fluorosis in the local population are found. The quality of drinking water has been investigated by means of biotesting using flax and lupine seeds.

Key words: drinking water, fluorine, defluorination, biotesting, teeth affection.

Introduction

Consumption of drinking water containing high concentrations of harmful compounds, in particular fluorine, results in deterioration of people's health. There are four concentration levels for each element: deficit, optimal, increased (acceptable) and very high (lethal) [1]. Microelements in certain doses are necessary for functioning of the human body, but their excess in the environment may cause various diseases or affections of the entire body. It is known that both lack and excess of fluorine in food and drinking water affect the human body, resulting in different diseases. Fluorine in the body is in a bound state, usually in a form of poorly soluble salts of calcium, magnesium, and iron. Fluorine compounds are present in all tissues of the human body. Around 99% of total fluorine is in bones and the tooth enamel. Fluorine content in water in the amount of 0.7 to 1 mg/dm³ contributes to normal development and mineralization of bones and teeth. Lack of fluorine in drinking water (below 0.6 mg/dm³) causes tooth cavity. Excessive fluorine (above 1.5 mg/dm³) leads to fluorosis of teeth and bones, muscle-skeleton

disorders, hepatitis, neurocirculatory asthenia, myocardosis, gastritis, rhinitis, ECG alterations, pulmonary tissue calcification, and slowdown in growth and sexual development [2]. Therefore, ensuring ecological safety of water resources is an urgent issue.

The fluorine circulation in nature involves lithosphere, hydrosphere, atmosphere and biota. Widely spread soluble fluorine-containing compounds in rocks and soils make fluorine present in natural water used for public water supply. Fluorine concentration in natural water varies within a wide range (from 0.01 to 27 mg/dm³) and depends on solubility of its compounds. Ground waters get saturated due to their contact with fluorine-rich rocks like fluorspar, aluminosilicates, apatites, phosphorites, etc. Fluorine contained in mineral thermal water is related to magmatic processes in volcanic formations. Surface water gets contaminated by emissions and discharges from certain productions – during processing apatites into superphosphate fertilisers, coal washing, glass melting as well as application of fluorine-containing mineral fertilisers and silicon-fluoride salts as insecticides by agribusiness.

Migration capability of fluorine in natural water depends on the content of calcium ions in it, forming low-solubility compounds together with fluorine ions. The increased pH causes higher fluorine mobility. Fluorine content in river water varies within 0.05 to 1.9 mg/dm³, in atmospheric precipitations within 0.05 to 0.54 mg/dm³, and in ground water within 0.3 to 4.6 mg/dm³. Concentration of fluorine in thermal water in certain cases reaches up to 10 mg/dm³, and fluorine content in the oceans is around 1.3 mg/dm³ [3].

Ground (artesian and well) water is richer in fluoride ions as compared to surface water, and sources of concentration of fluoride ions exceeding the maximum allowable concentration are more common for it.

Today, there are norms for drinking water applied in Ukraine and around the world as to fluorine intake by the human body, which are presented in Table 1.

People may also consume daily mineral water for drinking. Table 2 presents fluorine norms for mineral water. It should be mentioned that EU Directives require additional marking if mineral water contains more than 1 mg/dm³ (“contains fluoride”) as well as more than 1.5 mg/dm³ (“product not intended for babies and children under seven”).

Table 1

Fluorine Norms for Drinking Water [4]

WHO	USA		European Union (Directive 98/83/EC)	Ukraine (DSanPiN 2.2.4.-005-98) (by climatic zones):
	(FDA, 2002, 21CFR Part 165.110)	IBWA Model Code		
1.5	1.4-2.4 (based on local air temperature at place of water distribution)	3.0	1.5	IV – up to 0.7 III – up to 1.2 II – up to 1.5

Table 2

Fluorine Norms for Mineral Drinking Water [4]

USA		European Union (Directives 2009/54/EC, 2003/40/EC CODEXSTAN 108-1981, Rev. 2-2008)	Ukraine (DSTU 878-93, DSTU 42.10.02-96)	
(FDA, 2002, 21CFR Part 165.110)	IBWA Model Code		table water	medicinal table water
1.4-2.4	3.0	5.0	1.5	10.0

In order to bring fluorine content to normal limits, mineral drinking water is allowed to be fluorinated and defluorinated. At that, with defluorination of mineral water, preservation of its basic chemical composition is mandatory.

Nowadays, methods of removal of fluorine ions from water are a matter of study of many scientists.

In practice, there are different methods used for water defluorination. Most of them can be divided in two groups:

1. Precipitation methods:

A) contact-sorption methods of precipitation with ammonium salts, magnesium oxy-hydrate, and tricalcium phosphate, based on sorption of fluorine by different solutions;

B) defluorination by electrocoagulation and electroflotation, based on anodic dissolution of electrodes;

2. Methods based on volumetric ion-exchange sorption:

A) fluorine is removed by filtration through fluorine-selective materials (activated alumina, phosphate (bone coal, tricalcium phosphate, hydroxyapatite, superphosphate, etc.) or magnesium sorbents, activated carbon, ionites, and clinoptilolite;

B) Hyperfiltration method.

Experimental Part

The experiments were aimed at finding implication of the increased fluorine content for the incidence of teeth affection in the people of Toporiv Village in Busk District of Lviv Region as well as defining the quality of drinking water by biotesting.

First cases of hypoplasia of the enamel among the population of Toporiv were revealed in 1996. In order to find the reasons for this pathology, at the beginning of 1997, Busk District Sanitary-Epidemiological Station

initiated detailed study of the composition of the local ground water.

Wells are one of the most common sources of water intake for household and drinking needs in this region, as they are present almost in each household. By chemical composition, the well water is sulphate-fluoride-chloride- hydrocarbonate-sodium water with 0.63 g/dm^3 mineralisation. The water meets standards of DSanPiN 2.2.4-171-10 "Hygienic Requirements for Drinking Water Intended for Consumption by People".

Artesian Well No. 1 is located in Lviv Region, Busk District, Toporiv Village. The intended purpose of the artesian well (according to the water use needs and the classifier of minerals) is the water use for household and drinking. The artesian well is 58.0 m deep with the aquifer in upper cretaceous deposits formed by grey fractured marl. By chemical composition, the water is sulphate-fluoride-chloride-hydrocarbonate-sodium water with 0.88 g/dm^3 mineralisation. The water meets standards of DSanPiN 2.2.4-171-10 "Hygienic Requirements for Drinking Water Intended for Consumption by People".

All the existing sources of water supply in the Toporiv area were found to have excessive fluorine content. According to medical examination data as of 29 October 1997, hypoplasia of the enamel of different

severity was diagnosed in over 80 students in the Toporiv area. Based on studies conducted by the Busk District Sanitary-Epidemiological Station and an analysis of their statistical materials, we can make a conclusion that the excessive fluorine concentration in drinking water in the specified period is related to the beginning of uncontrollable tapping by the local people in the water main and the use of service water for drinking needs due to drying out of a number of wells in Toporiv.

Many researches also show that calcium and fluorine are antagonists. Therefore, low calcium content in drinking water combined with high fluorine concentration may provoke biogeochemical endemic hypoplasia and fluorosis. At the same time, the lowest calcium content in water of the cretaceous aquifer is noticed just within Chervonohrad water intake [3].

During 2011-2017, authorized entities (the Sanitary-Epidemiological Station and Lviv Regional Laboratory Centre) sampled the water directly in Well No. 1 as well as at different points of the water-supply main at the following addresses: 8 Shkilna St. (a school), 37 Krakova Str. (a residential building) and 2 Shpytalna Str. (an outpatient clinic) and submitted for an analyses to Lviv Regional Laboratory Centre (see Fig. 1).



Fig. 1. Diagram of the water-supply main in Toporiv Village.
Points of sampling of main (1) and well (2) water

The results of drinking water sampling for fluorine content are given in Table 3. Observed fluorine exceeds the MAC 1.2-2.6 times. Fluorine concentration dynamics in water is a variable value, so a number of people who have had fluorosis symptoms and general deterioration of health, caused by excessive fluorine, varies.

During 2010–2017, there were 32 % of the people diagnosed with fluorosis (with the population of 1043 people): 23 % of the children and 9 % of the adults. The tendency to decline in morbidity is due to the fact that after making the population acquainted with the

contamination issue, the utilization of the main water supply has been reduced in favour of mine and home wells up to 35 metres deep, where fluorine concentration is within normal limits.

In 2017 water samples were also used in a test to determine the impact of fluorine on biosensitive plants (bioindicators). It involved sprouting of plant test-systems: flax and lupine seeds. There were 25 seeds of each of the test samples. 25 seeds were put in each of the 3 double-dishes and topped with tested (well, main and filtered) water during 7 days. The test results are presented in Fig. 2–6.

Table 3

Monitoring Data on Fluorine Concentration in Drinking Water (2011-2017)

Sampling site	Concentration of fluorides in water, mg/dm ³				
	2011	2014	2015	2016	2017
Water-supply main	3.89	3.59	1.12	1.33	2.70
Well No. 1	4.01	3.62	1.24	1.81	3.27

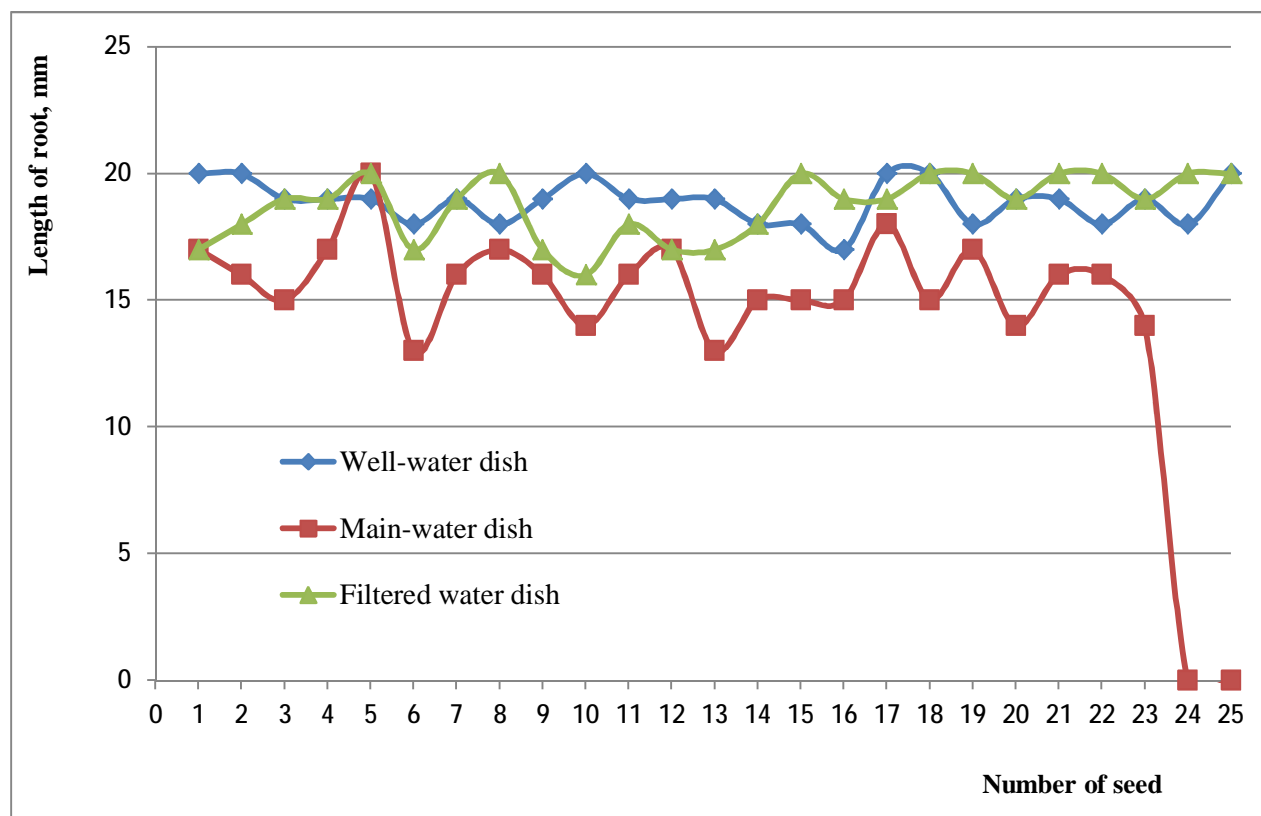


Fig. 2. Flax seed sprouting dynamics

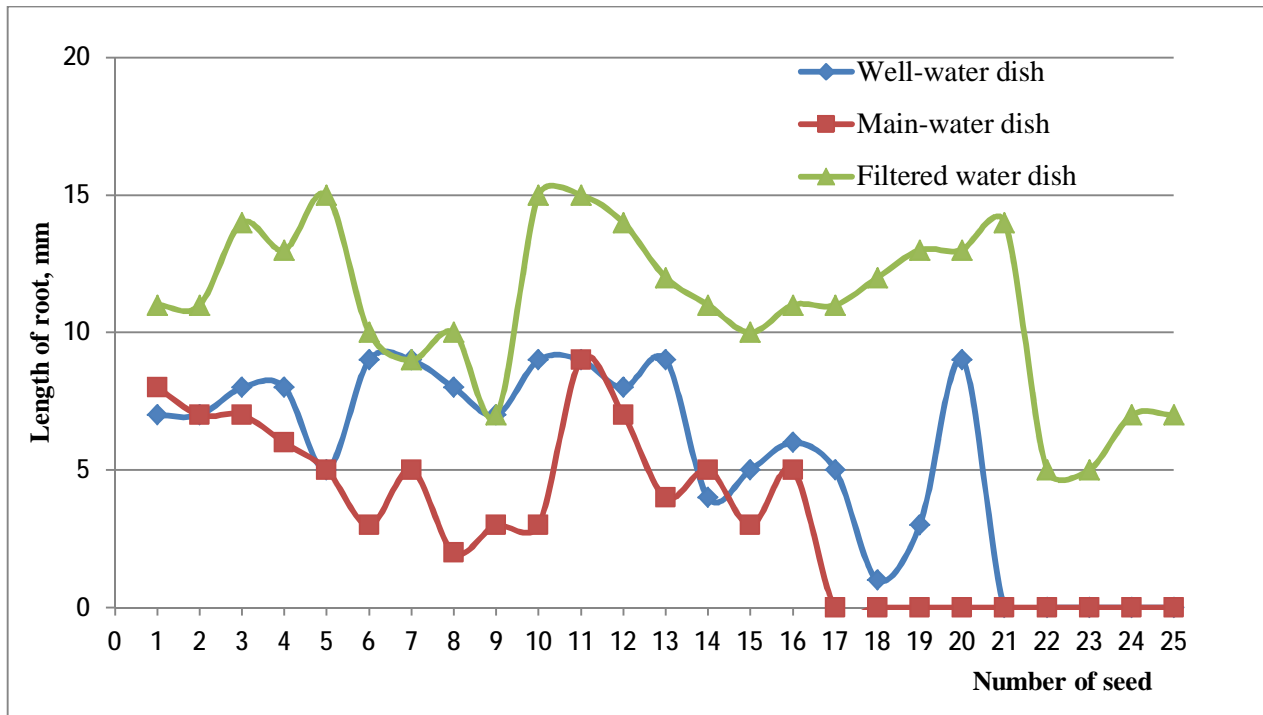


Fig. 3. Lupine seed sprouting dynamics

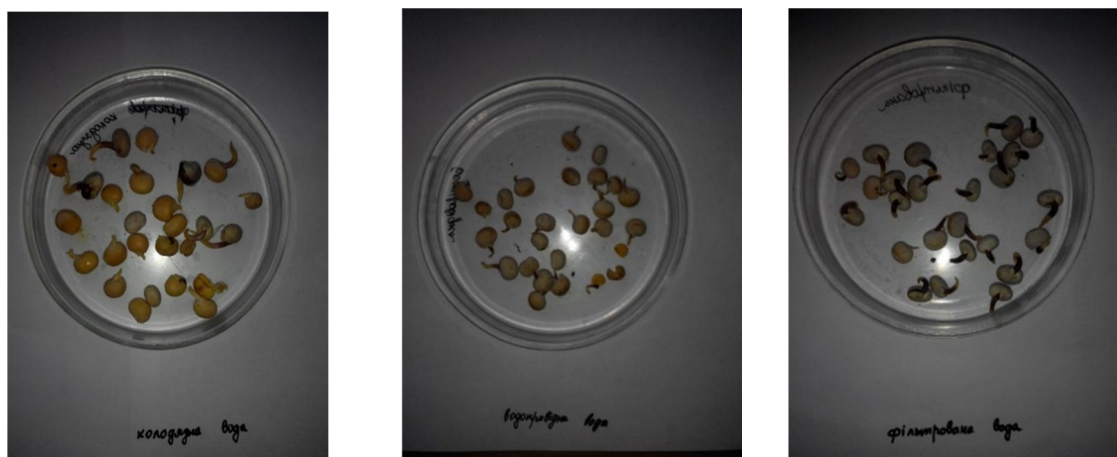


Fig. 4-6. Double-dishes with sprouted lupine seeds in well, main and filtered water

Test Results

The biotesting method is simple and inexpensive. It does not require special equipment, and allows visual evaluating of toxic impact of a pollutant on life processes of the bioindicator. It is suitable for evaluating water with low contaminant concentration and covers the synergism effect. The results received in the test during 7 days and presented in Fig. 2-3 demonstrated the average length of roots of the sprouted flax of 17-20 mm and destruction of 2 plants in the main water. Lupine turned out to be more sensitive, and the action of the main water on the lupine seeds was more intensive. The average length of roots of the sprouted lupine in the filtered water varied from

11 to 15 mm. In the well-water dish, we observed destruction of 5 lupine seeds (20 %). In the main-water dish, 36 % of the seeds died and the remaining ones almost did not sprout. Thus, we observed the reduction of flax and lupine radicles in size in the main water as compared to the reference sample.

Conclusions

Based on our analysis of the monitoring data and experimental studies, we found that the situation with drinking water in Toporiv Village is unsatisfactory and unstable as to fluorine content during the last seven years. We observed destruction of plants in the well and main fluorine-contaminated water, while in the filtered

water they developed normally. The biotesting results should be accompanied by chemical analytical studies. In order to eliminate the high incidence of fluorosis, it is necessary to prohibit the use of the service water-supply main in Toporiv for drinking needs and urgently develop defluorization technology. This would allow decreasing the incidence of fluorosis in the local population. The District State Administration must keep activities on elimination of consequences related to the toxic impact of the increased fluorine concentration in the water-supply main under control.

References

- [1] Kovda V.A. Biogeohimiya pochvennogo pokrova. – M.: Nauka. – 1985. – 264 c.
- [2] Grebnyak M. P., Grebnyak V. P., Grmachenko O. B., Pavlovich L. V. Zabrudnennya hruntu himichnimi elementami: faktori riziku, negativnij vpliv na zdorovya. // *Dovkillya ta zdorovya*. No. 3 (42) - 2007. – C. 22–28.
- [3] H. I. Rudko, O. O. Matsiyevska. Doslidennya hidrogeohimichnyh pokaznykiv pidzemnoyi hidrosfery zahidnyh regioniv Ukrainy na vmist mikroelementiv. // *Visnyk Natsionalnogo universytetu "Lvivska politehnika"*. – 2009. No. 655 : Teoriya ta praktyka budivnytstva. – P. 250–256.
- [4] Kysylevska A. Yu. Suchasni vymogy do normuvannya ftoru v mineralnyh ta pytnykh vodah. // *Zbirnyk tez dopovidey VseUkrainskoyi naukovo-praktychnoyi konferentsiyi*. – Odesa : ONAHT. – 2011 – P. 21–22.

FINAL-TREATMENT OF WASTEWATER FROM THE PRODUCTION OF EDIBLE OILS

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Abstract. The adsorption method of after-treatment of wastewater from the production of vegetable oils was investigated. The reasons of choice the activated carbon as adsorbent was justified. The statics and the kinetics of the adsorption process by activated carbon the organic component from the wastewater of oil production after extraction cleaning was investigated. The experimental data based on the theory of Freundlich and Langmuir were processed and the main constants of the process were defined.

Key words: wastewater, adsorption, activated carbon, isotherm, statics, kinetics.

Statement of the problem

Today the problem of wastewater treatment of the edible oil's production, along with the quality of the final product of production is an important task. It is also conditioned by the introduction of more modern and efficient technological processes, and the development of new approaches to the organization of non-waste or low-cost resource and energy-saving technologies. All this justifies a more serious attitude to the problems of the disposal of waste products [3, 4].

The production of edible oil's increases year by year in proportion to the demand, more and more enterprises of this profile emerge, thus the total amount of emissions including wastewater increasing. For Ukraine, the topic of wastewater from the production of oils is relevant because our country occupies the first place in the world ranking of growing sunflowers, consequently, the production of oil. As Ukraine is one of the major sunflower producers and their processors, the issue of wastewater treatment of the oil's production is very relevant today.

In the process of vegetable oil's production, a large amount of wastewater arises in the form of emulsions. Such systems are stable over a long period of time. They are not destroyed by the mechanical method [5, 6]. They are poorly biodegradable due to large volumes of wastewater and a significant amount of organic components in them [2–4]. In

such circumstances, it is appropriate to use liquid extraction to clean such wastewater [1, 7]. The feasibility of using extraction for wastewater treatment is determined by the concentration of organic impurities in them. In the general case, for most substances, it can be assumed that at the concentrations of more than 3–4 g/l, it is more expedient to withdraw them by extraction than adsorption. At concentrations, less than 1 g/l the extraction should be used in special cases.

The absolutely insoluble liquids are absent in water, that's why in the process of extraction, the part of the extractant dissolves in wastewater and becomes a new pollutant. Therefore, it is necessary to remove the extractant from the conditionally purified water. This also needs to be done to reduce the consumption of the extractant. In addition, extraction cleaning is not always appropriate to achieve high purification efficiency. In these cases, the adsorption method of purification is used. The advantage of the method is the high efficiency, – and the possibility of purification of wastewater, which contains several substances and recovery from these substances.

The analysis of recent researches and publications

In most enterprises of oil production in Ukraine, industrial effluents cannot be purified and hundreds of tons of pollutants are dumped into water bodies. Treatment facilities, as a rule, have been built long ago and are designed according to the requirements of domestic wastewater treatment. Such facilities partially reduce the size of the general BOD (biochemical oxygen demand), or just pass through wastewater, and at worst case, rots in them and further poisoning before dumping into water bodies. Such industrial wastewater is mostly contaminated with organic substances, as the result treatment facilities are unable to clean them up to the level of sanitary requirements. Significant environmental hazards create pollution of surface water with organic substances

from wastewater of edible oil's production. These substances, getting into the body of water, contribute to contamination with pathogens, algal bloom and, - have a negative impact on flora and fauna. For many companies, proper treatment of wastewater is a serious problem. Increasingly, companies have the problem of finding treatment facilities efficient and reliable in use, which guarantee a stable, high quality of cleaning.

The literature contains data about liquid-extraction wastewater treatment, which significantly reduces the level of pollution of wastewater from the vegetable oil's production, but there is always a certain amount of extractant. Therefore, to resolve the problem, it is advisable to use adsorption purification.

The aim of this work is to study the statics and kinetics of adsorption purification of wastewater at companies of vegetable oil's production.

Theoretical part

The adsorption method is used for the deep purification of wastewater from dissolved organic substances, as well as in local installations if the concentration of these substances in water is low or they are highly toxic. The most universal from adsorbents is activated carbon, but it must have certain properties.

The activated carbon, as a rule, poorly interacts with water molecules and well – with molecules of organic substances. It has a relatively coarse pore with an effective radius in the range of 0.8–5.0 mm, or 8–50 Å, so its surface is available for large and complex organic molecules. With a small time of contact with wastewater, activated carbon has a large adsorptive capacity, high selectivity, and low containment during regeneration. Actually, the latter condition ensures limited costs for the adsorbent regeneration. Coal is mechanically strong, quickly getting wet with water, has a definite granulometric composition. In the process of purification, fine-grained adsorbents with particles of 0.25–0.5 mm in size and less highly dispersed coal with particles of 40 microns are used.

It is important that coal has a small catalytic activity in relation to oxidation, condensation, and other reactions, because some organic substances that are contained in wastewater tend to oxidizing and gumming. These processes are accelerated by catalysts. After gumming, the substances clog the pores of the adsorbent, which complicates its low-temperature regeneration. Finally, activated carbon has a low cost, and does not decrease its adsorption capacity after regeneration, which guarantees a large number of cycles of operation. The raw material for the manufacture of activated carbon can be any carbonaceous material: coal, wood, polymers, food waste and pulp and paper industries and others.

The adsorption capacity of activated carbon is a consequence of a highly developed surface and high porosity. If there are several components in wastewater,

then for determining the possibility of their joint adsorption for each substance, find the values of the standard differential free energy ΔF° and determine the difference between the maximum and minimum values. Assuming $\Delta F^\circ_{\max} - \Delta F^\circ_{\min} < 0.5$ kJ / mole, the joint adsorption of all components is possible. If this condition is not respected, the treatment is carried out sequentially in several stages.

The rate of adsorption process depends on the concentration of the pollutant in wastewater, the nature and the structure of pollutants, the temperature of wastewater, the type, and properties of activated carbon. Usually, the adsorption process consists of three stages: the transfer of pollutants from wastewater to the surface of the adsorbent grains (external diffusion area), the adsorption process, the transfer of pollutants inside the grains of the adsorbent (the internal diffusion area). It is believed that the speed of adsorption is large and does not limit the overall speed of the process. Therefore, the limiting stage may be external or internal diffusion. In some cases, the process is limited by both these stages.

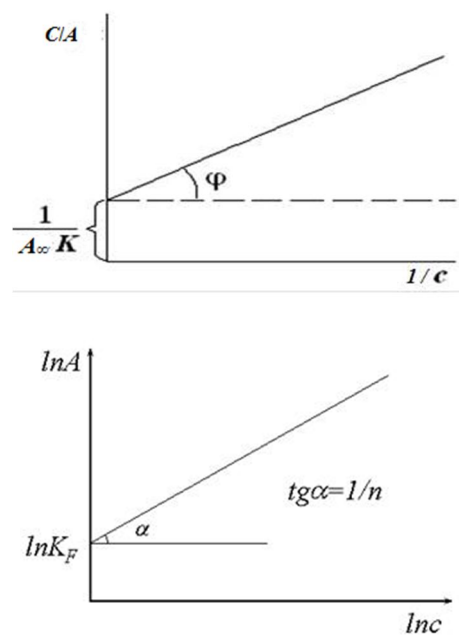


Fig. 1. Determination of Langmuir and Freundlich adsorption isotherms constants

In the external diffusion area, the rate of mass transfer is mainly determined by the turbulence intensity of the stream, which depends on the rate of wastewater. In the medium diffusion area, the intensity of the mass transfer depends on the type and the pores size of adsorbent, the shape and diameter of its grains, the size of the adsorbent molecules, and the mass transfer coefficient. All these circumstances determine the conditions in which adsorption treatment of wastewater goes with optimal speed. The process should be carried out in such hydrodynamic regimes, that it is limited in the internal diffusion area, the resistance of which can

be reduced with changing the structure of the adsorbent and reducing the diameter of the grain.

Substances that are well adsorbed from aqueous solutions by activated carbons have a convex isotherm of adsorption, and poor adsorbing – concave. The isotherm of adsorption of substances in wastewater is determined by experimental methods [1, 8].

The most important stage in the process of adsorption purification is the regeneration of activated carbon. Biological methods of coal regeneration, in which the adsorbed substances are biochemically oxidized, are increasingly developed today. This method of regeneration significantly extends the use of the sorbent.

The methodology of research

To study the adsorption capacity of activated carbon for wastewater contaminants of vegetable oil's production, 200 cm³ of wastewater after chemical purification (the destruction of stable emulsion "oil-water" by chemical substances) were placed in glass flasks, at different initial concentrations ($C = 0.025\text{--}35\text{ g/dm}^3$), and added the same amount of sorbent (~ 10g). The range of pollutants concentrations was the same as in industrial wastewater. The flasks were hermetically sealed and left in the mixing regime for two days at a temperature of + 20 °C. The sorbent was separated from the solution, which was analyzed for the content of pollutants by photocolometric method at a wavelength of 490 nm according to the known method [9].

The main material and discussion of the results

The adsorption method of extraction residual amount of the pollutant and the extractant was chosen for research. This method allows to removing of residual concentrations of pollutions. The activated carbon was selected as a sorbent. It has the ability to absorb pollutants of organic origin. In mixing the adsorbent with wastewater, activated carbon was used in the form of particles of 0.1 mm and less.

The adsorption of activated carbon in the form of the isotherm is shown on the graphic (Fig. 2). The isotherm describes the equilibrium between the pollutant in wastewater which must be treated and the amount of pollutant in the activated carbon.

The adsorption equilibrium in the solid adsorbent-solution system describes the equations that are given in the literature [1, 8]. We used two models that describe adsorption isotherms. One of the models is represented by the Freundlich equation:

$$A =$$

where A is a value of adsorption, $mg/gads$; C – equilibrium concentration of adsorbed substance in wastewater, g/dm^3 ; k, n are constants.

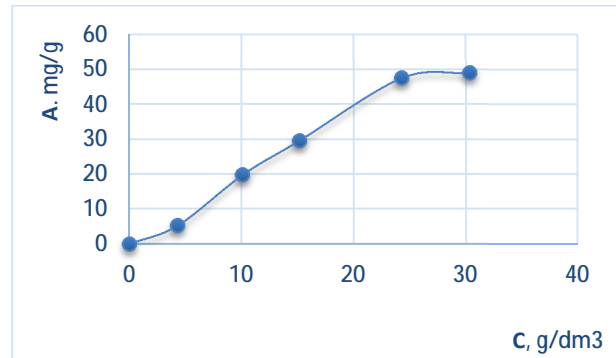


Fig. 2. The isotherm of adsorption wastewater pollutants in sunflower oil's production by activated carbon

To determine the constants of the Freundlich equation (k, n), the equation was given to the linear form by taking their logarithm:

$$\ln A = \ln k + 1/n \ln c;$$

From the graph built in the coordinates $\ln A = f(\ln c)$, we find $\text{tg} \alpha = 1/n$ and $\ln k$ as the distance which cuts the experimental straight line on the Y-axis. Experimental data in linear coordinates $\ln A = f(\ln c)$ according to Freundlich equation are presented in Fig. 3.

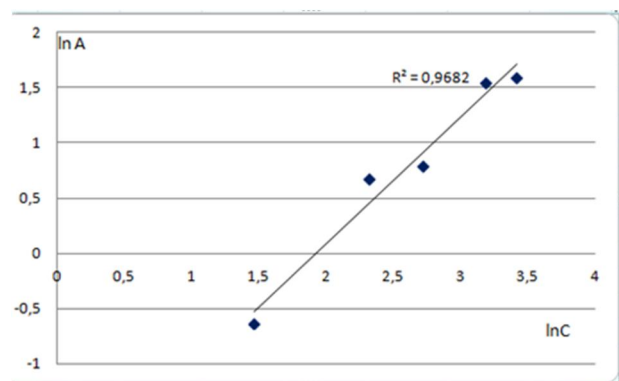


Fig. 3. The isotherm of adsorption in linear coordinates.

The experimental data on Fig. 3 represent a straight-line correlation and this indicates a satisfactory description of the isotherm of adsorption by the Freundlich equation. The correlation coefficient of experimental and theoretical data is 0.96, which indicating the reliability of experimental data.

The final form of the Freundlich equation for the adsorption process with using activated carbon:

$$A = 1.045C^{1.1836};$$

However, we believe that there is sorption in the form of a monomolecular layer of adsorbate and this process is better described by the Langmuir equation. Therefore, we have analyzed the obtained isotherms of adsorption according to this theory.

where A – is the static activity of the adsorbent which was determined, $mg/gads$; A_{∞} – the maximum possible value of adsorption (the value of adsorption

at full saturation of the monolayer) k – the constant of adsorption equilibrium.

To calculate the limiting adsorption of the organic pollutant (A_{∞}) we use the linearity Langmuir equation [2, 3].

$$A_{\infty} = \frac{C}{k} \left(\frac{1}{A} - \frac{1}{A_{\infty}} \right)$$

where A_{∞} - the static activity of the adsorbent, which determined:

$$A_{\infty} = \frac{1}{k} \left(\frac{1}{A} - \frac{1}{A_{\infty}} \right)$$

The graph in the coordinates $C/A = f(1/C)$ was constructed and the angular coefficient of the slope of the line $k = \Delta C / \Delta (C/A^*)$, which is equal to the limit of the adsorption of was find.

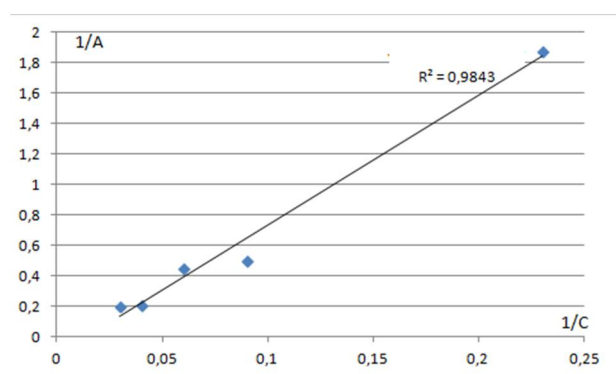


Fig. 4. The Langmuir isotherm of adsorption in linear coordinates

The isotherm of adsorption pollutants from wastewater of sunflower oil's production after chemical treatment (the destruction by chemical substances of a stable emulsion "oil-water"), by activated carbon is described by the Langmuir equation:

The correlation coefficient of the experimental and theoretical data R^2 is 0,96–0,98, which indicates a more reliable description of the experimental data by Langmuir isotherm. The selection criterion of the theoretical model was the maximum value of Fisher's criterion (F) and the maximum value of the determination coefficient.

To develop the technological process of sorption, it is necessary to determine the optimal contact time of the sorbent in the mixing reactor. The results of research about the kinetics of sorption by activated carbon are shown in Fig. 5/

The shape of the kinetic curves shows that the process of sorption most actively at the initial stage of the process, namely during the first hour of the experiment. The sharpest decrease of kinetic curves is observed after 30 minutes of the experiment, and from 30–60 minutes continue to fall. For 1 hour of sorption, the process is completed, as the linear origin of lines shows. Therefore, the optimal and most effective time for recovering the pollutants is 1 hour.

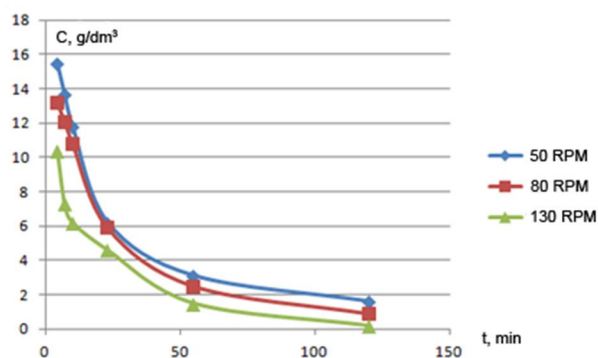


Fig. 5. Kinetics of adsorption the pollutants from wastewater of vegetable oil's production.

As shown on Fig. 5, the kinetics of adsorption the pollutant significantly depends on hydrodynamics. Intensification of the hydrodynamic conditions increases the adsorption rate, which allows us to assert the external diffusion area of the sorption process.

Conclusion

The statics and kinetics of adsorption method of after-treatment of wastewater from the production of vegetable oil was studied. The study established that the experimental isotherm of adsorption is the best described by the Langmuir equation, and the process of adsorption proceeds by the external diffusion mechanism. In such circumstances, the degree of wastewater treatment corresponds to safe hygiene practices.

References

- [1] Zapol's'kyj A. K., Kly'menko N. A., Astrelin I. M. ta in.: Fyzy'ko-ximichni osnovy` texnologiyi ochy'shennya stichny`x vod. Libra, Kyiv 2000, 552.
- [2] Py'ly'penko A. T., Vaxny'n Y'. G., Goronovsky`j Y'. T. y` dr.: Kompleksnaya pererabotka my`neraly`zy`rovanny`x vod. Naukova dumka, Kyiv 1994, 284.
- [3] Domarecz`ky`j V. A. Ostapchuk M. V., Ukrayinecz` A. I. za red. d-ra texnichny`x nauk, prof. A.I. Ukayincyay: Texnologiya xarchovy`x produktiv. Pidruchny`k. NUXT, Kyiv, 2003, 572.
- [4] Zapol's'ky`j A. K. Ukrayinecz` A. V. Ekologizaciya xarchovy`x vy`robny`cztv. Vy`shha shkola, Kyiv, 2005, 423.
- [5] Maraxovs`ka A. O., Visny`k NU "LP", 2013, 761, 297.
- [6] Holodovs`ka O., Marakhovs`ka A., Dyachok V.: Pat. UA 111389, Publ. Oct. 11., 2016.
- [7] Dyachok V., Marakhovska A., Marakhovska S., Chemistry & Chemical Technology, 2018, 12, 1, 114.
- [8] Parfy't G., Rochester K.: Adsorbcy`ya y`z rastvorov na poverxnostyax tverdyy`x tel. My`r, Moskva, 1986, 488.
- [9] Lur'e Yu. Yu. Analy`ty`cheskaya xy`my`ya promy`shlenny`x stochny`x vod. Xy`my`ya, Moskva, 1984, 447.

**ADSORPTION OF Cu (II) and Cr (III) IONS
FROM AQUEOUS MEDIUM
IN FIXED BED COLUMN**

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Abstract. The adsorption of Copper (II) and Chromium (III) from aqueous solution by natural zeolite was investigated in fixed bed column. The effects of selected operating parameters such as flow rate and bed depth were evaluated. The breakthrough data are fitted well to Bed Depth Service Time (BDST) and Thomas models with high correlation coefficient, $R^2 = 0,91$. The results showed that zeolite can be an effective adsorbent for Copper (II) and Chromium (III) removal.

Key words: copper, heavy metals, adsorption, wastewater

1. Introduction

The contamination of wastewater by toxic heavy metals is a worldwide environmental problem. Heavy metals are classified as toxic materials due to their non-biodegradability and bioaccumulation tendency in living organisms. Its excessive amount causes health problem in animals, plants and humans. These metals pollutants get to surface waters through different industrial enterprises activities. A number of techniques e.g. chemical precipitation, adsorption, ion exchange, and biological treatment have been applied. Although these techniques have been widely used, they possess limitations such as are high O&M cost and formation of by-products [1, 2]. Cu (II) and Cr (III) are essential for some biosynthesis in human body and are well-known as micronutrients for animals and plants, but they are toxic at high concentration. Recently, there is a growing interest in using

zeolites as an adsorbent to remove heavy metals from wastewater. This method has been widely investigated as an alternative to current costly wastewater treatment methods [3, 4].

In previous publications the experimental studies of adsorption of heavy metal ions in static conditions were presented. The theoretical preconditions of the mechanism of sorption extract of cuprum and chromium from the investigated solution by clinoptilolite of Sokirnitsya deposit were defined. It has been established that the selectivity of metal extraction has an effect on the radius of the metal atom and the solubility of its compounds. The conditions of deposition of compounds of heavy metals have been established and a diagram of the composition of the investigated two-component system depending on the acidity of the medium was constructed [5, 6, 7].

2. Experimental studies

2.1. Characteristics of zeolite

The surface of zeolite after the adsorption of heavy metals was analyzed by X-ray fluorescence analyzer [8].

2.2. Adsorbent

For research the zeolite of Sokyrnytsya deposit (Ca-clinoptilolite) with the size ranging from 2–3 mm was used.

2.3. Adsorbate

Model solution of Cu (II) was prepared by dissolving of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in distilled

water. Model solution of Cr (III) was prepared by dissolving of chromium nitrate $\text{Cr}(\text{NO}_3)_3$ in distilled water. The initial concentration of the solution was 2.030 g/l. Concentrations of Cu (II) and Cr (III) in solutions were determined by atomic absorption spectroscopy.

2.4. Column Set-up

A glass column with a diameter of 1 cm and a height of 50 cm was used. A known amount of adsorbent was placed into the column at the required adsorbent bed depth. Two cm thick fibreglass was placed at the bottom of the column to prevent the adsorbent media from leaching into and clogging the drainage area, as well as on the top of the adsorption column to increase the distribution of the solution onto the adsorbent surface and maintain a constant flow rate. The initial concentration of Cu (II) and Cr (III) solutions at 2,03 mg/l were pumped downward into the column. Lower concentration of metal ions solution was used to obtain a breakthrough curve as industrial effluents discharge are within this range

[9, 10]. The column was operated until the concentration of metal ions in the effluents reached the value of about 2,03 mg/l. The column study was carried out at room temperature and all column experiments were performed in triplicates.

3. Results and Discussion

Analyzing the results of X-ray fluorescence analysis of the zeolite surface after adsorption of copper and chromium ions (Fig. 1), we see that copper ions are much better absorbed by the sorbent than chromium ions. Despite the uniform concentration of chromium and cuprum ions in the solution, selective extraction of Cu^{2+} occurs. As can be seen from the results of experimental studies, the concentration of copper ions on the surface of the sorbent increases from 0.682 % by weight at a concentration of 0.01 g/l to 47.380 % by weight at a concentration of 1 g/l. The concentration of chromium ions on the surface of the sorbent after adsorption was little dependent on the increase of Cr^{3+} concentration in the initial solution.

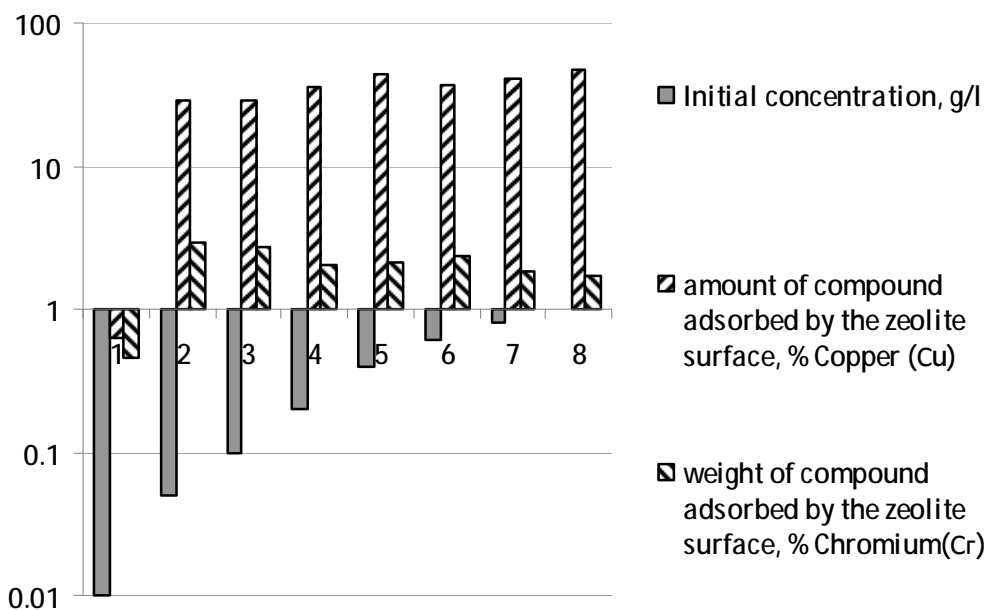


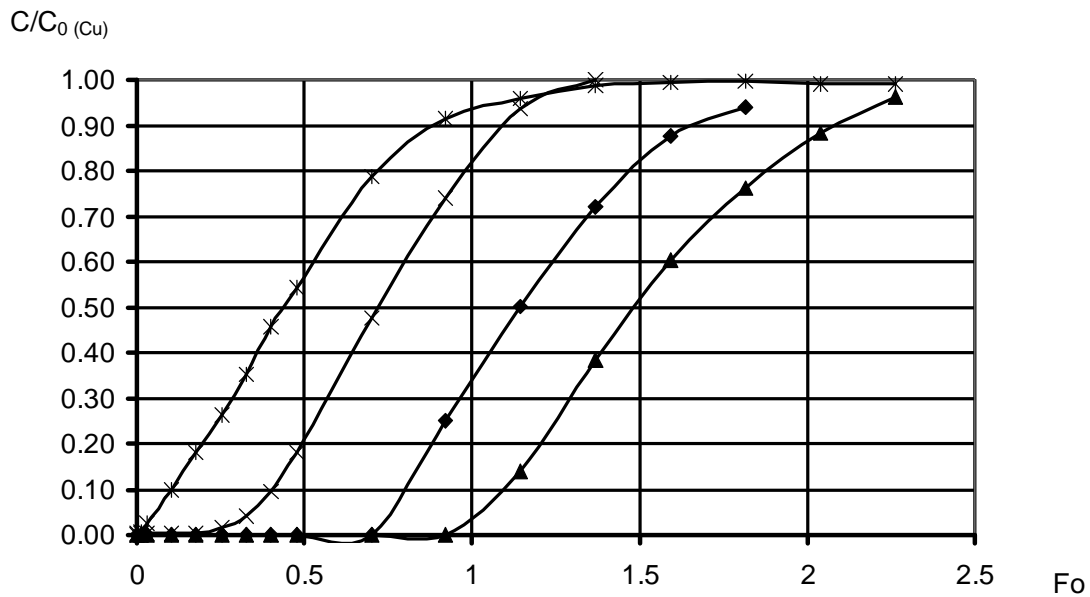
Fig. 1. The amount of copper and chromium ions on the surface of the sorbent after adsorption test solution

Effect of Bed Depth on Breakthrough Curve

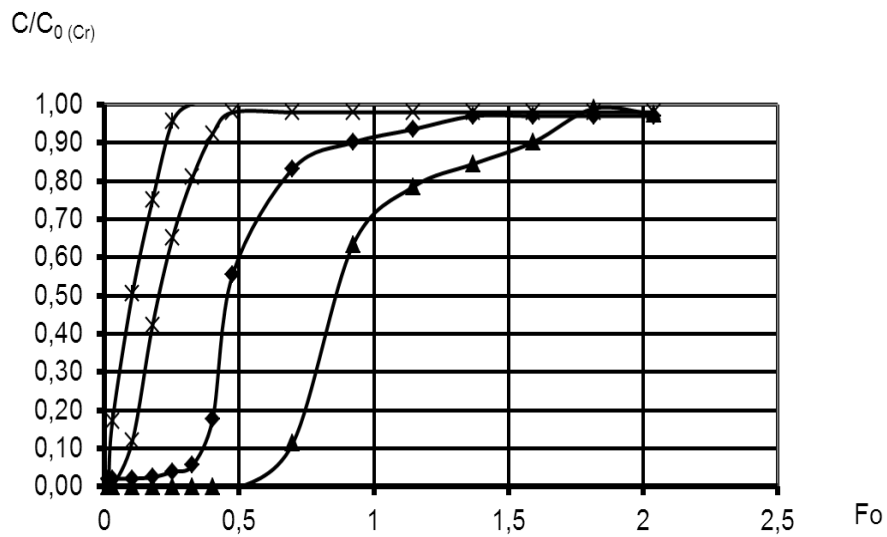
Adsorption of heavy metals in the fixed bed column largely depends on the quantity of adsorbent in the column. As the bed depth increased, the volume of the treated solution and the amount of cuprum and chromium removal increased, respectively.

It can be seen that the breakthrough time (t_b) and exhaustion time (t_e) increase with an increase in bed depth. Fig. 2 illustrates breakthrough curves obtained at different bed depth (2, 5 and 7 cm) with a constant concentration of 1 g/l and a flow rate of 4 ml/min. With the increase in the bed depth from 2

to 7 cm, the slope of the S-shaped curve decreased, indicating that the initial curve becomes steeper since the height of the layer was increased, when the bed depth decreases.



a



b

Fig. 2. Effects of different bed depth on the breakthrough curve of Cu (II) (a) and Cr (III) (b) adsorption onto zeolite at 4 ml/min flow rate:
* – 1 sm; x – 2 sm; ◆ – 5 sm; ▲ – 7 sm;

Table 1

**Experiment constant of BDST model
for Cu (II) and Cr (III) adsorption onto zeolite
($C_0 = 2,030$ g/l, flow rate = 4 ml /min)**

Bed depth (sm)	a* Cu (mg/g)	tb Cu(min)	te Cu(min)	a* Cr (mg/g)	tb Cr(min)	te Cr(min)
2	8.93E+01	20	80	2.55E+01	2	30
5	9.91E+01	43	120	7.47E+01	15	55
7	9.49E+01	62	145	8.56E+01	30	80

The calculation of theoretical breakthrough curves was carried out on the following dependencies:

For the mathematical expression of the dependence between the concentration of copper and chromium ions and the time of sorption at a certain flow rate, we have used the Thomas (1) model, which is the simplest and most convenient. The equation of the output curve for a layer of low altitude was described by the following expression:

$$\frac{C}{C_0} = 1 - ae^{-\lambda Fo}, \quad (1)$$

where λ is the model constant, 1 / s; a – coefficient of proportionality;

$$Fo = \frac{D^* t}{R^2} - \text{Fourier criterion};$$

D – coefficient of internal diffusion of heavy metals ions in the grain of adsorbent, m^2 / s ; R – radius of the grain of adsorbent, m; t – time, s.

Values of $\frac{C}{C_0}$ for other bed depths Z was obtained

on the basis of Laplace transformations, according to which a certain function N corresponding to the concentration varies according to the dependence [11]. Dependence (1) can describe the breakthrough curve for the bed depth Z-2cm.

$$N_n'' = \frac{1}{p} (pN^1)^n, \quad (2)$$

де

$$N' = \frac{\lambda}{p(\lambda + p)}; \quad N'' = \frac{\lambda''}{p(\lambda + p)^n};$$

p – Laplace parameter.

The transition to the original of the function was performed on the basis of transition tables from the image to the original. The original of the approximate solution has the form:

$$\left(\frac{C}{C_0}\right)_n = 1 - \left[\lambda Fo + \frac{(\lambda Fo)^2}{2!} + \dots + \frac{(\lambda Fo)^{n-1}}{(n-1)!} \right] e^{-\lambda Fo}, \quad (3)$$

where n – layer targets lengths n = 2,3 ...

$$Z_2 = nZ_1.$$

After logarithm we get:

$$f(t) = 1 - e^{-aFo} \quad (1)$$

$$\begin{aligned} \frac{x''}{x'} = 2; \quad f_2 &= 1 - e^{-aFo} (1 + aFo) \\ \frac{x''}{x'} = n; \quad f_n &= 1 - e^{-aFo} \left(1 + aFo + \dots + \frac{aFo^{n-1}}{(n-1)!} \right) \end{aligned} \quad (2)$$

Analyzing experimental data, we see that in the initial moments of time, the experimental and theoretical curves coincide, but due to the large porosity of the granular layer (0.3), the solution is quickly filtered through the sorbent layer and the exhaustion time is almost equal to the breakthrough time. This process is described by the model of ideal displacement.

Conclusions

The elemental composition of the sorbent surface was investigated according to X-ray fluorescence method after absorption of heavy metals from a two-component system containing Cu^{2+} and Cr^{3+} ions. The mechanism of sorption of copper and chromium from a solution was theoretically grounded. It has been established that the selectivity of metal extraction has an effect on the radius of the element and the solubility of its hydroxides. The conditions of precipitation of the hydroxides of the corresponding metals were calculated and the logarithmic diagram of the composition of the two-component system was constructed, depending on the pH.

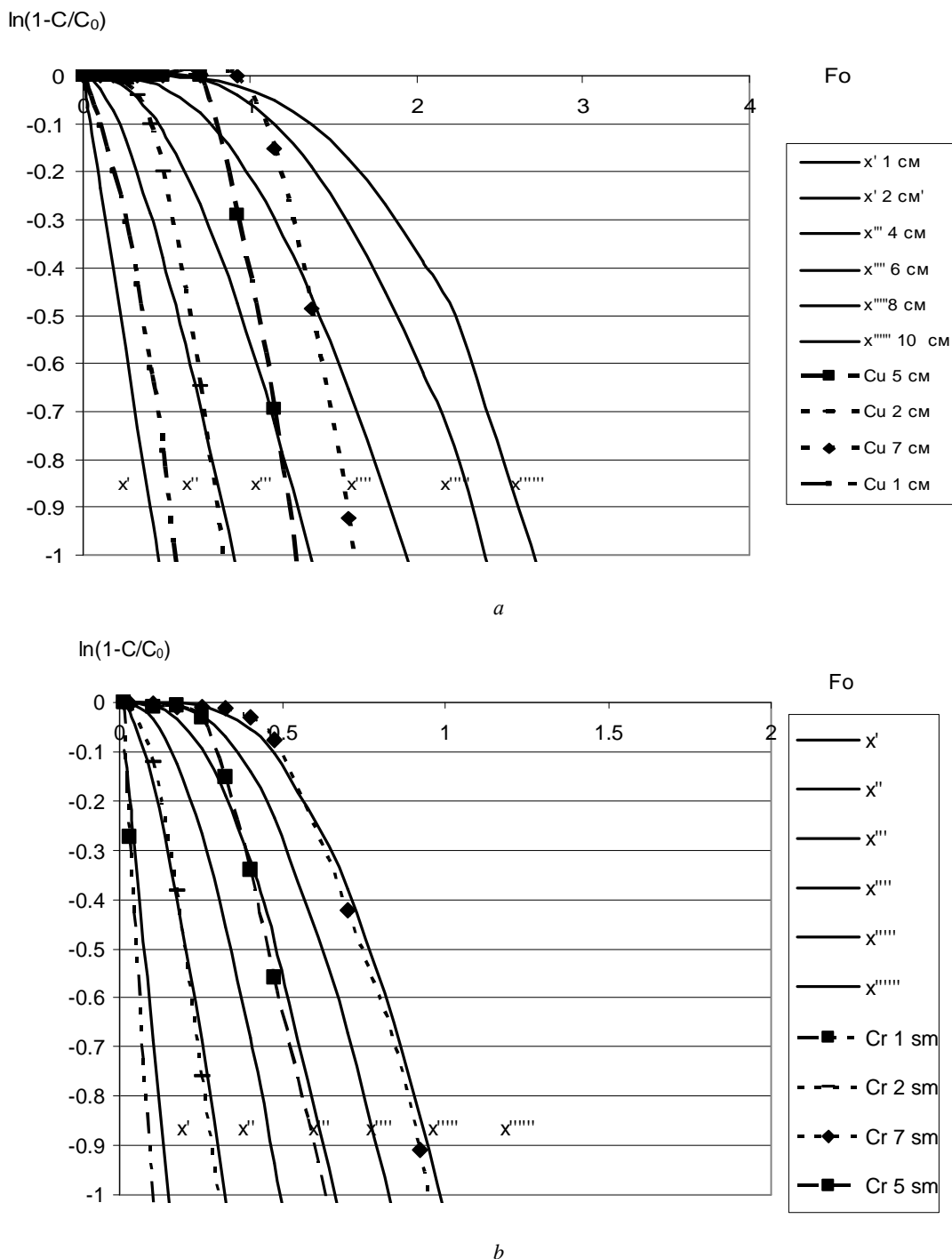


Fig. 1. Comparison of theoretical breakthrough curves of adsorption with experimental results in logarithmic coordinates

a – for Cu^{2+} ; b – for Cr^{3+} , where * – 1 cm; x – 2 cm; \diamond – 5 cm; \blacktriangle – 7cm

References

[1] Wang S., Peng Y. Chem. Eng. J. 2010, 156, 11. <https://doi.org/10.1016/j.cej.2009.10.029>

[2] Gomonay, V., Golub N., Gomonay P. Book of Proceedings of the International Regional Seminar “Environment Protection: Modern Studies in Ecology and Microbiology”, 1997, 2.

[3] Han, R., Zou, L., Zhao, X., Xua, Ya., Xua, F., Lia, Y., Wanga, Yu. Chemical Engineering Journal., 2009, 149. <https://doi.org/10.1016/j.cej.2008.10.015>

Galarneau, A., Renzo F. Di, Fajula F., Vedrine, J. – Elsevier Science, Surface Science and Catalysis. – 2001. – 443 r.

- [4] Warchol J., Matlok M. et al. *Micropor. Mespor. Mater.* 2012, 153, 63.
<https://doi.org/10.1016/j.micromeso.2011.12.045>
- [5] Sydorчук O. V., Gumnitsky Ya. M. *Visnyk L'vivskoho derzhavnoho universytetu bezpeky zhyttyediyal'nosti.*, 2013, 7.
- [6] Sabadash V., Hyvlyud A., Gumnitsky Ya. *Chem. Technol.*, 2016, 2.
- [7] Sabadash V., Gumnitsky J., Mylyanyk O., Lyuta O. *Scientific Bulletin of UNFU.* 2017, 27, 117.
doi: <https://doi.org/10.15421/40270326>
- [8] Lur'e Yu. Yu. *Spravochnyk po analytycheskoy khymyy.* Moskva., 1989.
- [9] Lee I., Kuan Y., Hcern J. J. *Chinese Inst. Chem. Eng.*, 2007, 38, 71. <https://doi.org/10.1016/j.jcice.2006.11.001>
- [10] Wang S., Peng Y.: *Chem. Eng. J.* 2010, 156, 11.
<https://doi.org/10.1016/j.cej.2009.10.029>.
- [11] Hasfalina C. M., Maryam R. Z., Luqman C. A., Rashid M. *cAPCBEE Procedia*, 2012, 3, 255.
doi: [10.1016/j.apcbee.2012.06.079](https://doi.org/10.1016/j.apcbee.2012.06.079)

THE LIFE PATH AND SCIENTIFIC PRIORITIES OF PROFESSOR OLEKSANDR MOROZ

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Abstract. The life path and the range of scientific interests of Professor Oleksandr Moroz are described. The main results of scientific research in the field of the influence of vertical refraction on the accuracy of astronomical and geodetic measurements are shown.

Key words: atmosphere, leveling, fluctuations of images, refraction, temperature gradients.

Oleksandr Moroz was born on July 3, 1955 in the village of Ilinka Khankai district, Primorsky Territory, Russia in the family of Ukrainians. In 1959, the family returned to Ukraine to the village of Petrivka-Romenska in Gadyach district of Poltava region. His father, Ivan Danylovykh, worked as a driller at the Glinsko-Rozbyshiv Drilling Office, and his mother, Anna Ivanivna, was a housewife.

After graduating from Petrivka-Romenska secondary school in 1972, Oleksandr Ivanovych entered

Poltava Oil Exploration College and in 1973, he joined the Soviet Army. He served in Strategic Missile Forces as a geodesist, which determined his further life path.

After demobilization in the autumn of 1975, he entered the preparatory department of Lviv Polytechnic Institute. In 1976, O. I. Moroz became a first-year student of the Geodesy faculty in the field of Applied Geodesy. During his studies he was actively engaged in social and scientific work, and since the third year of his study he has worked as a part-time worker at the MNDL-18, where he performed field and office geodetic works. He was a Leninist scholarship holder and a Komsomol organizer of Lviv Polytechnic. After graduating from Institute in 1981, he was directed to work at the MNDL-18 as an engineer.

In 1984 Oleksandr Ivanovych Moroz entered the postgraduate course at Lviv Polytechnic Institute and was sent to study at Dresden Technical University, where in 1987 he defended his Ph.D. thesis on the topic "Investigation of Leveling Refraction in the Surface Layer of the Atmosphere on the Basis of Oscillations of Images". On returning to Lviv, he worked as an assistant, senior lecturer and assistant professor at the Department of Geodesy of Lviv Polytechnic. In 1988, by the order of the rector, O. I. Moroz was appointed Head of the Educational Department of Polytechnic Institute, where he has worked for five years. On April 1, 1993, he was selected by competition for the post of Head of the Department of Geodesy. Oleksandr Ivanovych has worked in this post for 21 years.

In 2003 he defended his doctoral dissertation on the topic "Theoretical Foundations of Vertical Refraction, Methods of Its Determination, Calculation and Forecasting", and in the following year he received the title of Professor of Geodesy.

In 2011, O. I. Moroz was appointed, and subsequently elected Director of V. Chornovil Institute of Ecology, Environmental Protection and Tourism, which in 2017 was renamed the Vyacheslav Chornovil Training and Research Institute of Sustainable

Development of Lviv Polytechnic National University, where he works until now.

The range of scientific interests of Oleksandr Ivanovych is related to the study of the influence of the atmosphere on the accuracy of astronomical and geodetic measurements, namely the definition and calculation of vertical refraction during geodetic measurements. They revealed the patterns of fluctuations of abnormal vertical temperature gradients.

The Earth's atmosphere is an optically heterogeneous medium, so the ray of light between two points does not pass directly but through rather complex spatial curve. During the angular measurements, the refractive index is the angle between the tangent to the beam at the starting point and the chord connecting the initial and final points of the beam. The projection of this angle into a sloping plane passing through the initial and final points of the beam is called the angle of vertical refraction or vertical refraction,

and its planned projection is the angle of horizontal refraction or horizontal refraction. The value of vertical refraction, usually, is several orders of magnitude higher than the horizontal one.

The general vertical refraction is determined by the formula of the following differential equation:

$$d\sigma_B = \frac{1}{n} \frac{dn}{dz} \cos \alpha dl \quad (1)$$

which indicates that the common refractive angle $d\sigma_B$ is the function of the gradient of the order index in the direction of the straight line (Fig. 1).

By formula (1) the total vertical refraction, as well as partial refraction angles can be defined, if we assume that the ray is refracted at one point. During the propagation in the atmosphere, the light beam continuously and alternately refracts on its path. In order not to build many auxiliary spheres for defining refraction, it is expedient to have its integral equation.

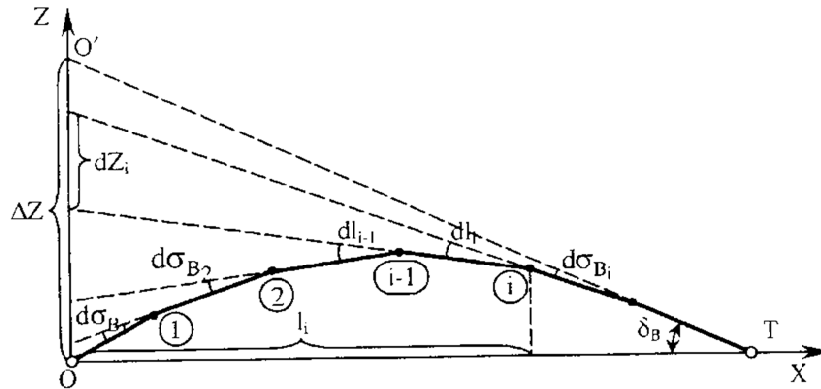


Fig.1

At the point O of the origin of the coordinates there is a sight target, and at the point T a receiver is installed – an optical device, for example, a theodolite. Due to the curvature of the beam in the vertical plane, the point O due to the refraction will be visible through the optical tube in the position O' . Due to the fact that OO' and angle σ_B are small, with a sufficient degree of accuracy it can be assumed, that $X_T = L$, $x_i = l_i$. The change in the direction of the beam by the angle $d\sigma_B$ due to the movement of light from the point $(i-1)$ to the point i and projection on the OZ axis is like the change of the apparent position of the point O on OZ_i and

$$dZ_i = l_i d\sigma_{B_i} \quad (2)$$

Substituting in (2) the value $d\sigma_{B_i}$ from (1) we get

$$dZ_i = \frac{1}{n} \frac{dn}{dz} l_i \cos \alpha dl_i \quad (3)$$

Moving the beam of light along the trajectory from the point O to T corresponds to the segment on the OZ axis,

$$\Delta Z = \int_0^L \frac{1}{n} \frac{dn}{dz} l \cos \alpha dl, \quad (4)$$

which is an angular partial refraction δ_B . Since the angle δ_B is small, you can write

$$\sigma_B = \frac{\rho \Delta Z}{L} \quad (5)$$

Taking into account (4), the equation of the partial angle of the vertical refraction has the form

$$\delta_B = \rho \frac{\cos \alpha}{L} \int_0^L \frac{1}{n} \frac{dn}{dz} l dl \quad (6)$$

For the trails close to the horizon $|\alpha| \leq 6^\circ$, that's why

$$\sigma_B = \frac{\rho}{L} \int_0^L \frac{1}{n} \frac{dn}{dz} l dl \quad (7)$$

It is expedient to express the change in the refractive index in the functions of temperature T and pressure P . The humidity is usually neglected. To do this, you need to differentiate the equation of the refractive index of the air ($n - 1 = 78.85 \frac{P}{T} 10^{-6}$).

In this case, the influence of humidity is neglected. We'll get

$$\frac{dn}{dz} = \frac{78.85}{T} \frac{dP}{dz} 10^{-6} - \frac{78.85}{T^2} P \frac{dT}{dz} 10^{-6} \quad (8)$$

As $\frac{dP}{dz} = \frac{dP}{dh} \frac{dT}{dz} = \frac{dT}{dh}$, taking into account that $\frac{dP}{dz} = 0,0342 \frac{P}{T}$ GPA/m, dependence (8) will be

$$\frac{dn}{dZ} = -78.85 \cdot 10^{-6} \frac{P}{T^2} \left(0.0342 + \frac{dT}{dh} \right). \quad (9)$$

Substituting (9) into (7), assuming that $n \approx 1$ with an accuracy of 0.0001, it can be recorded

$$\delta_B = -\frac{\rho}{L} \int_0^L 78.85 \cdot 10^{-6} \frac{P}{T^2} \left(0.0342 - \frac{dT}{dh} \right) l dl, \quad (10)$$

or

$$\delta_B = -0,278 \frac{P}{T^2} L - \frac{\rho}{L} \int_0^L 78.85 \cdot 10^{-6} \frac{P}{T^2} \gamma l dl. \quad (11)$$

As usual, the temperature gradient is divided into a normal and abnormal components, ie, $\gamma = \gamma_H + \gamma_{aH}$, therefore (11) will be

$$\delta_B = -0.278 \frac{P}{T^2} L - \frac{\rho}{L} \int_0^L 78.85 \cdot 10^{-6} \frac{P}{T^2} (\gamma_H + \gamma_{aH}) l dl. \quad (12)$$

Because $\gamma_H = const$

$$\delta_B = -0.278 \frac{P}{T^2} L - 8.13 \frac{P}{T^2} L \gamma_H - \frac{\rho}{L} \int_0^L 78.85 \cdot 10^{-6} \frac{P}{T^2} \gamma_{aH} l dl. \quad (13)$$

Taking into account that $\gamma_H = 0.098$ grad/m, and also, having multiplied and divided the last summand (13) by $2L$, we get

$$\delta_B = -0.278 \frac{P}{T^2} L - \frac{0.080P}{T^2} L - 78.85 \cdot 10^{-6} \rho \frac{2L}{2L^2} \frac{P}{T^2} \int_0^L \gamma_{aH} l dl. \quad (14)$$

After introducing the notion of abnormal equivalent mean temperature gradient $\gamma_{aH.e.cep}$, which can be expressed as

$$\gamma_{aH.e.cep} = \frac{2}{L^2} \int_0^L \gamma_{aH} l dl. \quad (15)$$

dependence (14) can be written as follows

$$\delta_B = -0.278 \frac{P}{T^2} L - 0.080 \frac{P}{T^2} L - 8.132 \frac{P}{T^2} L \gamma_{aH.e.cep}. \quad (16)$$

The first term on the right side of equation (16) expresses the share of refraction, which depends on the vertical pressure gradient; the second is a component due to the normal temperature gradient; and the third component is due to an abnormal temperature gradient.

In short, taking into account the value of γ_H the dependence (16) looks like this

$$\delta_B = 8.132 \frac{P}{T^2} L (0.0244 + \gamma_{aH.e.cep}), \quad (17)$$

or

$$\delta_B = 0.198 \frac{P}{T^2} L - 8.132 \frac{P}{T^2} L \gamma_{aH.e.cep}. \quad (18)$$

In (18), an abnormal refraction sign in a thermally turbulent atmosphere is taken into account.

In addition, the relationship between abnormal refraction and the thermal turbulence of the atmosphere has been established.

Thermal turbulence and abnormal refraction exist only simultaneously, because they are caused by the same physical phenomena, and they are based on natural processes.

Visible swings of fluctuations of the images of sight targets in sight of the visual tube of a geodesic device or the trace of a laser beam are equivalent, that is, medium-wave fluctuations, which inform about fluctuations of temperature gradients along the entire path of the beam from the sight target or from the source of radiation to the receiver.

The reason for the vertical fluctuations of the images of sight targets in the optic tubes or the generated beam is, for the most part, the fluctuations of the vertical abnormal equivalent temperature gradient $-\gamma_{aH.e}$.

The geometric content of the theory of determining abnormal vertical refraction by the fluctuations of images of sight targets is shown in Fig. 2 where $\delta_{aH.e.cep}'' = \frac{\Delta \delta_{max}''}{2}$

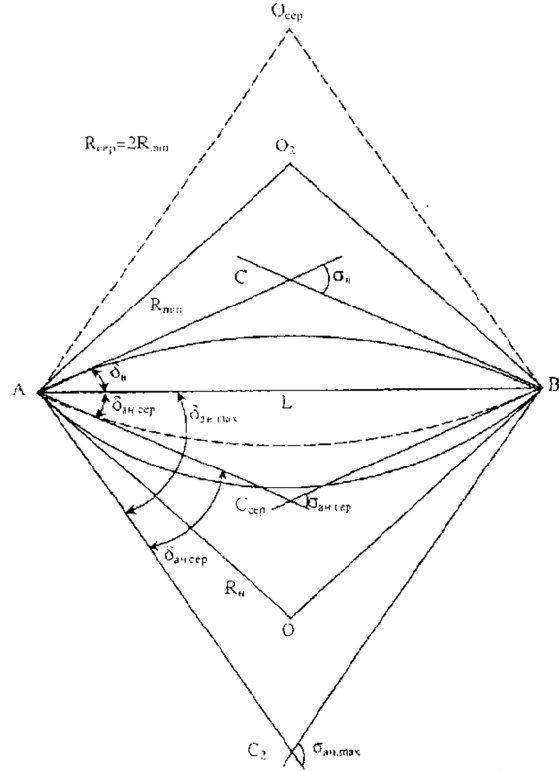


Fig. 2

Based on the above stated, a general conclusion is made that abnormal vertical refraction is based on the

laws of fluctuations of abnormal vertical temperature gradients, which justifies the unity of atmospheric turbulence and abnormal vertical refraction.

Professor O. I. Moroz is the author of 6 textbooks, monographs, 120 scientific articles and 40 methodological developments. He has got 25 author's certificates for inventions. He lectures on Geodesy and Topography for students of the Institute of Geodesy, as well as Tourist Topography for students of the V. Chornovil Institute of Sustainable Development of Lviv Polytechnic National University. O. I. Moroz supervises the training of postgraduate students; under his supervision two theses were defended.

He was awarded the breastplate of the State Service of Geodesy, Cartography and Cadastre “Honorary Geodesist of Ukraine” (2005), and the honorary title “Honoured Worker of Science and Technology of

Ukraine” by the Decree of the President of Ukraine in 2008.

References

- [1] Moroz O. I. Vyznachennya ta vrakhuvannya vertykal'noyi refraktsiyi pid chas heodezychnykh vymiryuvan'. Monohrafiya. – L'viv: Vydavnytstvo Natsional'noho universytetu «L'vivs'ka politehnika», 2003. – 224 s.
- [2] Moroz O. Osnovni polozhennya teoriiy fluktuatsiynoho metodu vyznachennya anomal'noyi vertykal'noyi refraktsiyi / O. Moroz, O. Ostrovs'kyy. – L'viv: Zbirnyk naukovykh prats' “Suchasni dosyahnennya heodezychnoyi nauky ta vyrobnytstva”, 2002. – S. 110-120.
- [3] Moroz O. Y. Teoryya y praktyka fluktatsyonnoho metoda opredelenyya vertykal'noyi refraktsiyi. / O. Y. Moroz, A. L. Ostrovs'kyy. – Moskva: Yzvestyya vuzov. Heodezyya y aérofotos"ëmka, 2000. – № 3 – S. 11–39.