



Dependence of the artificial reservoir pollution with heavy metals on anthropogenic factors

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Abstract

The article presents the research results of the heavy metals content in artificial reservoirs located at different distances from a number of pollutants of anthropogenic origin. The manuscript provides data on the dependence of the concentration of copper, zinc, lead, iron, cadmium in pond water on their location on highways and arable land. The location near these anthropogenic factors of artificial reservoirs pollution causes the accumulation of heavy metals in the water leading to significant exceedances of permissible levels for the catch of commercial fish, poses a significant threat to the environmental situation and safety of aquaculture. Research has also revealed that fish farming technology used in the farm also determines the ingress and accumulation of heavy metals in the reservoir. In particular, it was found that the operation of non-letting ponds, the use of cascades near the highway and arable land increases the accumulation of heavy metals. According to the results of our research, the content of heavy metals in a pond located at a short distance from the road and agricultural land indicate a high increase in the concentration of toxicants in water. It was established that the concentration of Kuprum was in the water thickness – 0.085 mg/dm³, and at the bottom of the reservoir 0.095 mg/dm³ at MPC 0.001 mg/dm³. The Zn content in the water thickness was 0.119 mg/dm³, in the deep layers of the reservoir – 0.127 mg/dm³, exceeding the maximum allowable concentrations of 11.9 and 12.7 times, respectively. Mangan in the water thickness of the reservoir located near anthropogenic pollutants was 0.091 mg/dm³, and near the bottom of the reservoir – 0.034 mg/dm³ at the MPC – 0.01 mg/dm³. Fe in the water of an artificial reservoir located near the field and road exceeded the maximum allowable concentrations for this chemical element by 20 times regardless of the layer of its selection.

Keywords: heavy metals, anthropogenic pollutants, artificial reservoirs.

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1. Introduction

For many years, the territory of Ukraine has been subject to various factors of environmental pollution, primarily anthropogenic. This is due to various reasons, in particular, the population of Ukraine, which is only about 1 % of the world's population, accounts for about 5 % of world production and processing of mineral resources. In addition, about 50 % of the crop is grown on arable land treated with various chemical plant protection products. A large number of toxic metals in the form of ballast enters the soil at the same time with mineral fertilizers, they can get into water bodies from highways, fields, and industrial waste (Zhovinskiy & Kuraeva, 2002).

According to most scientists (Nriagu, 1989; Pacyna, 1996; Arruti et al., 2010), heavy metals are a vague group of chemical elements with metallic properties, which usually includes transition metals, some metalloids, lanthanides and actinides. Some scientific studies (Arora et al., 2008; Fu & Xi, 2020) list more than five dozen heavy metals. As a result, the

number of items belonging to this group varies widely. Heavy metals are generally characterized by high chemical resistance, high biological toxicity, the ability to accumulate in living organisms and adversely affect their health. Numerous characteristics are used as criteria, namely atomic mass, density, toxicity, prevalence in the natural environment, the implementation degree in natural and man-made cycles.

The most dangerous are cadmium ions (Cd), a natural insignificant trace element. Its tendency to bioaccumulate in living organisms is becoming dangerous, and its presence in the environment is a cause for concern (Kalman et al., 2010; Liao et al., 2011; Sfakianakis et al., 2015; Bashchenko et al., 2021; Slobodian et al., 2021). Copper (Cu) is an important trace element for cellular metabolism in living organisms due to the presence of a key component of metabolic enzymes (Monteiro et al., 2009). However, it can be extremely toxic to intracellular mechanisms in aquatic animals at high concentrations (Hernández et al., 2006; Abdel-Tawwab et al., 2007). Iron (Fe) is a major component of industrial and mining

effluents in the aquatic environment. Black iron (Fe^{2+}) is considered more toxic to fish than the ferric form (Fe^{3+}) (Decker & Menendez, 1974). Lead (Pb) is a stable heavy metal that is characterized as a priority hazardous substance (Sfakianakis et al., 2015). Pb is a natural substance that occurs in the environment, but its concentration increases significantly due to anthropogenic sources which include the extraction of base metals, production of batteries, paints, and gasoline (Monteiro et al., 2011). Zinc (Zn) is the second most common trace element after Fe, it is an important trace element for living organisms because it is involved in the synthesis of nucleic acids and is found in many enzymes. Its excess causes damage to nerve cells, kidneys, hematopoietic organs, it also leads to intoxication and organic changes (Sfakianakis et al., 2015). Manganese (Mn) is the 14th most abundant element on Earth, accounting for 0.03 % of the total number of crust atoms. The average manganese content in the earth's crust is 0.1 %, and 0.06–0.2 % in most volcanic rocks where it is scattered. Manganese ranks third in the Earth's crust after iron and titanium among heavy metals (Gainey & Kenyon, 1990).

Cadmium in water bodies can be caused by its industrial use (batteries, galvanic coating, plastic stabilizers, and pigments), which leads to pollution of aquatic habitats (Järup, 2003). The use of fertilizers and agrochemicals, wastewater from agricultural lands can also cause water pollution (ATSDR, 2003). The increase in the concentration of copper in artificial and natural reservoirs is due to the widespread use of fungicides, algaecides, molluscicides, insecticides and waste disposal (Michael, 1986). Iron is a major component of industrial and mining effluents in the aquatic environment. Therefore, the anthropogenic factor of water pollution is a determining one. The concentration of lead in water bodies can increase significantly due to anthropogenic sources, which include the extraction of base metals, production of batteries, paints and gasoline (Monteiro et al., 2011). This heavy metal can enter water from industrial and smelting effluents; from the dissolution of old lead plumbing, pesticides, and also from municipal wastewater (Sorensen, 1991; Sepe et al., 2003). Common sources of zinc in water bodies are galvanized metal products, zinc chloride used in plumbing and paints. On the contrary, the entry of manganese into water bodies is abiogenic, it is due to the presence of iron-manganese ores and other minerals that contain manganese compounds. However, this element can get into surface waters due to the activities of metallurgical plants and chemical companies.

Heavy metal ions are contained in the body of various species of aquatic organisms in small quantities, they play an important role in various organ systems of fish, they may be responsible for growth, development, regulation of respiratory function, hematopoiesis, muscle and bone formation in fish, reproduction and many other functions (Yanovych & Yanovych, 2014). Fish are particularly vulnerable and highly susceptible to pollution, because they cannot avoid the harmful effects of pollutants (Yarsan & Yipel, 2013; Saleh & Marie, 2014). Higher aquatic organisms are more sensitive to many toxicants than invertebrates, they are a convenient object of testing to determine the state of the ecosystem (Adams & Ryon, 1994; Zaki et al., 2014). Contamination by heavy metals and metalloids of water and bottom sediments in higher concentrations poses a serious threat due to their toxicity, long-term stability, bioaccumulation and biological increase in the food chain (Eisler, 1993; Has-Schön et al., 2006). Fish are considered to be the most significant bioindicators in aquatic systems for assessing the level of metal

pollution (Rashed, 2001; Authman, 2008). Higher hydrobionts are at the end of the aquatic food chain and can accumulate metals and transmit them to humans through food that causes chronic or acute diseases (Al-Yousuf et al., 2000). Therefore, the study of the dependence of heavy metal pollution of artificial reservoirs on various anthropogenic factors is important and relevant.

The aim of the study was to research the dependence of the pollution level of artificial reservoirs on such anthropogenic factors as fish farming technology, distance to major pollutants, namely roads and arable land.

2. Materials and methods

The objects of the study were water samples of artificial reservoirs of the Dobrobut private farm in the Haisyn district of the Vinnytsia region. The samples were taken from the bottom and the water column from each artificial reservoir in two artificial reservoirs in October to determine the content of heavy metals according to the Order of the State Emergency Service of Ukraine No. 30 of January 19, 2016 On approval of the Instruction on sampling and hydrobiological analysis by hydrometeorological stations and posts (Order No. 30, 2016) and DSTU ISO 5667-6-2001 (DSTU ISO 5667-6: 2009).

The topography of the experimental artificial reservoirs of the farm is presented in the figure.



Fig. 1. Artificial reservoirs of the Dobrobut private farm

The distance from the first researched reservoir to arable land is 37.2 m and to the road is 87.9 m; the distance from the second researched reservoir to arable land is 514.9 m, and to the road was 123.1 m. This farm is not fully systematized. Carp and silver carp are bred here. The ponds are cascading. Pond No. 1 is non-descending pond No. 2 is descending.

The content of heavy metals was determined by atomic adsorption spectrophotometry using the Analytik Jena NovAA400R device according to GOST 30178-96. The results of studies with maximum allowable concentrations for fish ponds are the following: 0.001 mg/dm³ of Cu; 0.01 mg/dm³ of Zn; 0.01 mg/dm³ of Mn; 0.1 mg/dm³ of Fe; 0.1 mg/dm³ of Pb; 0.005 mg/dm³ of Cd.

Statistical processing of research results was performed using Microsoft office Excel 2019. The calculations were done according to generally accepted methods.

3. Results and discussion

3.1. Results

We found that the presence of heavy metals in artificial reservoirs was due to anthropogenic action. Thus, the quality

of water in the research ponds of the private farm Dobrobut does not meet the maximum allowable levels of heavy metals concentration for fisheries. The content of Pb and Cd in the water column and at the bottom were within normal limits in

the experimental reservoir No. 1, and there was no excess of the MPC in the water column and Pb at the bottom in the experimental reservoir No. 2 (Table 1).

Table 1

The concentration of heavy metals depending on a number of anthropogenic factors ($M \pm m$, $n = 3$)

The concentration of heavy metals depending on the layer of the reservoir, mg/dm ³	Artificial reservoir		Deviation of indicators of reservoirs No. 1 to No. 2:	
	No. 1 (non-descending, located close to anthropogenic pollutants)	No. 2 (descending, distant from anthropogenic pollutants)	absolute, mg/dm ³	relative, %
Copper:				
- water column	0.085 ± 0.009**	0.056 ± 0.004	+0.029	+51.8
- bottom layer	0.095 ± 0.009	0.071 ± 0.005	+0.024	+33.8
Zinc:				
- water column	0.119 ± 0.010**	0.075 ± 0.004	+0.044	+58.7
- bottom layer	0.127 ± 0.007**	0.093 ± 0.003	+0.034	+36.6
Manganese:				
- water column	0.091 ± 0.005**	0.069 ± 0.003	+0.022	+31.9
- bottom layer	0.034 ± 0.004****	0.623 ± 0.002	-0.589	-94.5
Iron:				
- water column	1.93 ± 0.10****	0.45 ± 0.02	+1.48	+328.9
- bottom layer	0.29 ± 0.07****	4.55 ± 0.11	-4.26	-93.6
Lead:				
- water column	0.017 ± 0.005***	0.071 ± 0.004	-0.054	-76.1
- bottom layer	0.034 ± 0.006***	0.076 ± 0.002	-0.042	-55.3
Cadmium:				
- water column	0.0022 ± 0.0004****	0.0077 ± 0.0008	-0.0143	-185.7
- bottom layer	0.0074 ± 0.0003**	0.0093 ± 0.0006	-0.0019	-20.4

Note: ** – $P < 0.05$, *** – $P < 0.01$, **** – $P < 0.001$

The results of studies of the heavy metals content in an artificial reservoir located at a short distance from the road and arable land indicate an excess of toxicants in the water, regardless of the layer of its selection. Thus, the concentration of copper was 0.085 mg/dm³ in the water column, and 0.095 mg/dm³ at the bottom of the reservoir at an MPC of 0.001 mg/dm³. The concentration of Zn was 0.119 mg/dm³ in the water column, and 0.127 mg/dm³ in the deep layers of the reservoir, exceeding the maximum allowable concentrations was 11.9 and 12.7 times, respectively. The Manganese content was 0.091 mg/dm³ in the water column of the reservoir located near anthropogenic pollutants and 0.034 mg/dm³ near the bottom of the reservoir at a maximum concentration limit of 0.01 mg/dm³. The concentration of Fe in the water of the artificial reservoir located near the field and the road exceeded the maximum allowable concentrations for this chemical element by 19.3 times, regardless of the layer of its selection.

Studies of the heavy metals content in the water of the pond, which is lower in cascade and ten times more distant from anthropogenic pollutants have shown other results. Thus, the concentration of Cu was 0.056 mg/dm³ in the water column, and 0.071 mg/dm³ near the bottom at a maximum concentration limit of 0.001 mg/dm³. The content of Zinc was 0.075 mg/dm³ in the water column of the pond No. 2, and 0.093 mg/dm³ in the deep layers of the reservoir at a rate of 0.01 mg/dm³. The concentration of Mn was 0.069 mg/dm³ in the water column, and 0.623 mg/dm³ in the bottom layer. It was experimentally found that the concentration of iron exceeded the MPC by 4.5 times and was 0.45 mg/dm³. The content of this metal was 4.55 mg/dm³ at a maximum concentration limit of 0.1 mg/dm³ in water samples near the bottom of the reservoir. The concentration of Pb was 0.071 mg/dm³ in the water column and 0.076 mg/dm³ in the deep layers of the

reservoir. Exceedances of maximum permissible concentrations were 1.54 and 1.86 times, respectively.

3.2. Discussions

Studies have shown that the water of artificial reservoirs was contaminated with heavy metals, regardless of the distance to the selected anthropogenic factors. However, the general trend of dependence can be outlined as follows: the closer the pond is to the road and arable land, the more copper, zinc, manganese and iron fall into the water. Thus, a significant ($P < 0.05$) excess of Cu concentration (by 0.029 mg/dm³ or 51.8%) was found at insignificant distance to the specified pollution factors in the water of the artificial reservoir in comparison with the remote pond (control). The zinc content exceeded the control values by 36.6–58.7%, and the difference was significant ($P < 0.05$). During the analysis of Manganese content, it was found that in the water column its concentration exceeded the indicators from the pond away from the sources of pollution by 31.9% ($P < 0.05$), and contained less than half of it in the bottom layers. This may be explained by the fact that manganese in the first pond, entering the wastewater from the transport network and the field, does not have time to accumulate in the bottom sediments, and with the flow of water enters the second pond and deposited in silt. Therefore, its concentration in the second reservoir in the layers of water at the bottom increases due to technological factors. We found a similar relationship studying the iron accumulation. Its concentration in the water column of the pond located close to the road and the field exceeded the control values almost three times, and was by 93.6% lower ($P < 0.001$) in the bottom sediments. This may indicate the migration of this element in the wastewater from the highway and arable land into the reservoir and its sedimentation in the bottom sediments downstream.

Another pollution dynamics is set by the lead level. This heavy metal was found in higher concentrations in an artificial reservoir remote from a number of studied anthropogenic factors. In particular, the content of Pb exceeded the indicators of water from the middle and deep layers of the first pond by 76.1 % and 55.3 %, respectively ($P < 0.01$). Cadmium was detected in a concentration higher by 0.042 mg/dm³ and 0.014 mg/dm³, respectively ($P < 0.01$, $P < 0.05$) than the first pond. The explanation for this excess, in our opinion, may be an abiogenic factor, i.e., the natural mineralization of the soil with lead ores, which are known to be rich in inclusions of natural cadmium compounds as a concomitant mineral.

4. Conclusions

1. The distance of the reservoir to anthropogenic pollution factors and farming technology determine the water pollution level by heavy metals. It was experimentally proved that the maximum permissible concentrations were exceeded for Cu, Zn, Mn, Fe, except for Pb and Cd in artificial reservoirs No. 1 and with the exception of Pb in artificial reservoirs No. 2.

2. With increasing the pond distance to the road (1.5 times) and arable land (13.8 times) decreases the level of manganese accumulation (94.5 %, $P < 0.001$) and iron accumulation (93.6 %, $P < 0.001$) in the water of the bottom layer.

3. It has been experimentally proved that the level of pollution of Dobrobut reservoirs with lead and cadmium does not depend on the anthropogenic factors we have studied, and is probably determined by natural mineralization.

Prospects for further research. In the future, we will conduct comprehensive study of current issues of dependence of heavy metal pollution of artificial reservoirs of Vinnytsia region on anthropogenic factors. In particular, it is planned to study the dynamics of heavy metals in bottom sediments, natural forage base and commercial fish depending on the distance of water bodies to transport networks, arable land and fish farming technology.

Conflict of interest.

The authors state that there is no conflict of interest.

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