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ENVIRONMENTAL STATUS OF KAM'YANSKE RESERVOIR (UKRAINE)

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Abstract

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Environmental status of Kam'yanske reservoir (47°55'51.6"N 33°46'08.4"E) as one of the small water bodies belonging to southeast Ukraine was investigated. The integrated environmental assessment based on the quality indices of salt content, trophic–saprobiological indicators and specific toxic water indicators of Kam'yanske reservoir are characterised as 'satisfactory' and 'slightly polluted'. Defined bottom accumulation coefficient (BAC) shows continuing heavy metals enlargement in the upper layer of the bottom sediments and chronic pollution in ecosystem. The content of heavy metals in the muscles of industrial fish in the researched pond did not exceed maximal allowed concentration (MAC) for fish as food according to Ukrainian standards. Accumulation of heavy metals in fish was due to the peculiarities of their ways of nutrition and existing. The total contents of heavy metals in common carp was almost twice as large compared to other fish. The maximum accumulation rates set for fish muscles of essential elements – zinc and iron.

Key words: small reservoir, chemical index of water pollution, heavy metals, sediments, industrial fish.

Introduction

In Ukraine there are considerable reserves of artificial water resources including 250,000 ha of small reservoirs of different origin and purpose. In the recent years, environmental situation was deteriorated due to the growing anthropogenic load. This led to qualitative changes in the aquatic environment and had a negative impact on the ecological state of these specific artificial hydroecosystems (Pilipenko, 2007a).

Small reservoirs have gained significant distribution in the steppe zone of Ukraine to have a prominent role in shaping the economic complex components of water resources (Pilipenko, 2009; Khilchevsky, Hrebin, 2014).

In Ukraine an environmental assessment on ecosystems of different purpose small reservoirs have been conducted on the criteria of salt content, trophic–saprobiological indicators, specific indicators of toxicity and radiation exposure using environmental standards of surface water (Romanenko et al., 1998, 2001) and assessment of water quality with hydrobiological indicators (Yatsyk et al., 2010).

The conceptual principles of rational exploitation of various purpose small reservoirs were offered (Pilipenko, 2007b).

In determining the environmental conditions of small reservoirs, it is important to understand the content and distribution of heavy metals in the hydroecosystems (Rzetala et al., 2006; Siwek et al., 2012; Anim-Gyampo et al., 2013; Opp et al., 2015), hydrophysical and hydrochemical parameters of the reservoir (Mwaura, 2006; Pilipenko, 2009), environmental problems in the construction and operation of small reservoirs as well as issues related to their safety (Maksimovich, Piankov, 2012).

Degradation of ecosystems of small reservoirs progresses rapidly; therefore, all measures to their inhibition should be connected. First of all, determination of the environmental status of these water ponds is very important (Sender et al., 2014).

In this context, the aim of our research was to determine the environmental status of the Kam'yanske reservoir located in southeastern Ukraine.

Material and methods

Hydrochemical analysis of Kam'yanske reservoir water was performed by conventional standard methods (Romanenko, 2006). Measuring pH had been done with glass-electrode method. Dissolved oxygen level was measured with Winkler's method.

Ammonium ion concentrations were determined by a colorimetric indophenol titration method. Determination of nitrite nitrogen amounts in water samples had been done with basic Griess method, which relies on the reaction of nitrites with sulphanilic acid giving diazo compounds that couples with 1-naphthylamine. The reaction gives an azo dye of intense red colour. The concentration of nitrates was determined with colorimetric method after the reaction of nitrate nitrogen with sulphate-phenol reagent in an acidic environment.

The phosphate contents were analysed by modified method of Deniges–Atkins based on the extraction of phosphomolybdate $P_2Mo_7O_6*4H_2O$ with butanol and reduction with tin bivalent chloride in alcoholic solution. The extinction of the blue solution was measured with a colorimeter.

Permanganate oxidability of organics present in water samples was determined by the Kubel method with 0.01 N solution of potassium permanganate ($KMnO_4$) in sulphuric acid at boiling medium. The colour intensity was measured at 520 nm.

Preparation of water samples for toxicological analysis was performed by conventional methods (Romanenko, 2006) and contained the following steps: water was filtered through a 0.45-μm membrane filter to separate suspended solids, especially clean acidified by hydrochloric acid to pH 2.5 and kept for laboratory processing. Thereafter, 1 l of water samples were evaporated to dryness and then the residue was dissolved in 1 N nitric and hydrochloric acids. Samples of sediments were collected with Ekman-Burge dredger from horizon of 0–5 cm. The content of heavy metals in the sample was determined by spectrophotometer C-115M1.

Collection and processing of samples was performed by conventional methods (Romanenko, 2006), whilst fish toxicological studies conducting heavy metals in the samples was determined by atomic absorption spectrophotometry after a dry ashing.

In preparation for the analysis of biological samples of fish tissue and sediments, they were homogenised, dried at 105 °C to constant weight and then incinerated at 450 °C until the white ash that was treated with 1 N nitric acid and 1 N hydrochloric acid. The solute was filtered through a filter 'blue ribbon' and transferred to a container, bringing the volume to 10 ml, after that the sample was examined for heavy metals on a spectrophotometer C-115M.

Bottom accumulation coefficient (BAC) and the accumulation rate (AR) of pollutants in aquatic organisms were calculated as follows:

$$K = \frac{Cs}{Cw} \qquad (1)$$

where Cs – the concentration of pollutants in sediments or aquatic organisms;
Cw – the concentration of pollutants in the water.

The value of chemical water quality index ($I_{Xavg.}$) is calculated as follows:

$I_{Xavg.} = (I_{Savg}. + I_{TSavg.} + I_{Tavg.}) / 3$ (2)

where $I_{Savg}.$ – the index of salt content;

$I_{TSavg}.$ – the chemical index of trophic–saprobiological indicators;

$I_{Tavg}.$ – the index of specific indicators of toxic and/or radiation exposure (Grytsenko et al., 2012).

The data was analysed as mean ± S.E.M. (standard error of the mean) at 95% reliability and significant level of $p \leq 0.05$. In order to estimate the significant differences between paired data, Student's t-test method was used.

Results and discussion

Kam'yanske reservoir is located near the Izluchyste village (coordinates are 47°55'51.6"N 33°46'08.4"E) of Dnipropetrovsk region, Sophiivka district, with a total water surface area of 298.0 ha, total volume of 16.2 million m^3, storage capacity of 14.7 million m^3 and average depth of 6.5 m (Fig. 1).

The reservoir formed by earthen dam of 21 m height on a small river Kam'yanka, the Dnieper right tributary of second order. The riverbed is rocky; the outputs of crystalline rocks such as granite, which determined the name of the river, are on the banks. Basin located on the area of granite and magmatite contains the deposits of iron ore and construction materials that are represented with granite, quartzite, refractory clays and building sand. Complex hydrogeological conditions cause poor groundwater quality (higher than normal dry residue, water tight) and affect the formation of the chemical composition of surface waters. Power supply reservoir is formed from Kam'yanka river, drain surface water from rain and snowmelt, groundwater sources. For beam, Shyroka effluents from sewage treatment plants from Kryvyi Rih city are carried out.

Kam'yanske reservoir was built in 1976 on an individual government project as a public storage of treated wastewater of Kryvyi Rih with their subsequent use for irrigation of crops and at present is also used for fish farming. Ichthyofauna of reservoir is represented by indigenous and invasive species: pike, perch, bream, Prussian carp, roach; carried stocking common carp, grass carp, silver carp.

According to the research on hydrochemical parameters, high concentrations of solids (content of dissolved solids) – 6,355.00 mg/dm^3 – and nitrogen nitrate – 3.48 mg/dm^3 – were set. High rates of salinity in the Kam'yanske reservoir water might be explained within the presence of highly reservoir line sources that have significant contribution to the supply of the reservoir. Elevated level of nitrates is associated with excessive use of fertilisers on farms and washings away from the fields located on the banks of the reservoir.

Fig. 1. The scheme of Kam'yanske reservoir.

According to the ‘Environmental Assessment Method of surface water for different categories’ (Romanenko et al., 1998) and ‘Common Implementation Strategy for the Water Framework Directive (2000/60/EU), Guidance document № 10’, the environmental assessment of water quality on parameters of chemical composition had been done in Kam’yanske reservoir (Table 1).

T a b l e 1. Environmental characteristic of the water quality on chemical composition in Kam’yanske reservoir , M ± m, n = 5.

Indicator of chemical composition of water	Class of water quality				
	I High	II Good	III Moderate	IV Poor	V Bad
Hydrogen index, pH		7.9 ± 0.16			
Dissolved oxygen content, mg/dm³		8.15 ± 0.12			
Ammonia nitrogen, mg/dm³			0.95 ± 0.03		
Nitrite nitrogen, mg/dm³		0.03 ± 0.001			
Nitrate nitrogen, mg/dm³					3.48 ± 0.01
Phosphate phosphorus, mg/dm³			0.11 ± 0.01		
Permanganate oxidability, mgO/dm³		7.44 ± 0.11			
Total iron, mg/dm³					9.64 ± 0.15
Zinc, mg/dm³			0.071 ± 0.0035		
Copper, mg/dm³			0.022 ± 0.0011		
Lead, mg/dm³					0.14 ± 0.007
Cadmium, mg/dm³					0.021 ± 0.0011
Manganese, mg/dm³		0.022 ± 0.001			

It can be concluded that by the criteria of salt content (salinity), Kam’yanske water reservoir is classified as brackish α-mesohaline according to the quality of II class 4 category. For the majority of the environmental and health criteria, Kam’yanske reservoir water state can be classified as I–II classes ‘high–good’. In terms of permanganate oxidation of water belongs to II class 3 category of ‘good water’. The concentrations of phosphate and ammonia nitrogen in water determine its belonging to III class 5 category – ‘satisfactory and moderate’. For large excess of nitrate nitrogen, Kam’yanske reservoir water quality belongs to 7 class V category – ‘very bad’. Increasing levels of nitrates and phosphates in water is a negative sign because it accelerates eutrophication and promotes the processes of algal blooms, siltation and overgrowing the bottom of the reservoir.

Based on these data, we assessed the water quality of the Kam’yanske reservoir on specific indicators of toxic effects. For the content of manganese, researched water belongs to the II class and 2 category and has been characterised as ‘good’ and ‘clean’. For the contents of zinc and copper, water belongs to III class 5 category – ‘satisfactory’; for the content of lead, it belongs to ‘dirty – moderately polluted’; and for the cadmium and total iron contents, it belongs to the V class 7 category of water quality – ‘very bad’ and ‘very dirty’. Thus, significant influence on the elemental composition of the Kam’yanske reservoir water has anthropogenic factor and natural geochemical conditions.

This data made it possible to calculate the chemical index of water quality, including code quality salt content, which was equal to 4; trophic–saprobiological indicators – 3.71; and for the indicators of specific toxic effects – 5.5. So balanced (averaged) chemical index was 4.4, characterising the quality of the Kam'yanske reservoir water as 'satisfactory' and 'slightly polluted'.

One of the objective and reliable indicators of water pollution and the total anthropogenic loading is the content of heavy metals in the sediments. Kam'yanske reservoir sediments are clayey silt, which in the case of sustained flow of water masses accumulate the most fine fractions suspensions and dying phytoplankton that is why there is a high content of organic substances. Clay mules are active accumulators of heavy metals due to their high sorption capacity. Therefore, reservoir sediment could be considered as an indicator of pollution of whole hydroecosystem. Heavy metals accumulated in the sediments adversely affect the water quality because of their transition into the water column and secondary pollution.

The proximity of the location of ironstone and iron intake from groundwater contributes to the accumulation of sediments in Kam'yanske reservoir, the content of which is 7,020.48 ± 351.024 mg/kg (Table 2).

T a b l e 2. The contents of heavy metals in the sediments of Kam'yanske reservoir, mg/kg, M ± m, n = 5.

Heavy metals	**Zinc**	**Copper**	**Lead**	**Cadmium**	**Manganese**	**Iron**
Concentration, mg/kg	42.90 ± 2.145	3.02 ± 0.151	16.74 ± 0.837	0.29 ± 0.0145	52.68 ± 2.634	7,020.48 ± 351.024
BAC	604	145	117	14	2395	728

To characterise the processes occurring in the reservoir, BAC was calculated by taking into account the ability to accumulate heavy metals in the sediments.

Analysis of the results showed that manganese has the highest level of accumulation in the sediments, when BAC is 2,395, which might be because of the fact that most of migrations are conducted in suspended state (Ostrovskaya, 2000).

At present, the foundation Kam'yanske reservoirs fishery up four- and five-year individuals of common carp (*Carassius gibelio*, Bloch 1782), European perch (*Perca fluviatilis*, Linnaeus 1758), pike-perch (*Sander lucioperca*, Linnaeus 1758) and silver carp (*Hypophthalmichthys molitrix*, Valenciennes 1844).

Toxicological researches have shown that the concentration of all investigated metals in fish muscle is relevant to health standards (GSTU 2284:2010, 2012).

In researched fish muscles, the content of zinc and iron was observed to be higher than other heavy metals. Perhaps this is due to the fact that they are physiologically active metals participating in the life-sustaining activity of aquatic organisms (Fig. 2).

Fishes are able to absorb iron directly from water through gills, but the main source of it in the organism is the food (Romanenko, 2001). The iron content in the muscles of fish depends on the species and sex characteristics and season (Fedonenko et al., 2012).

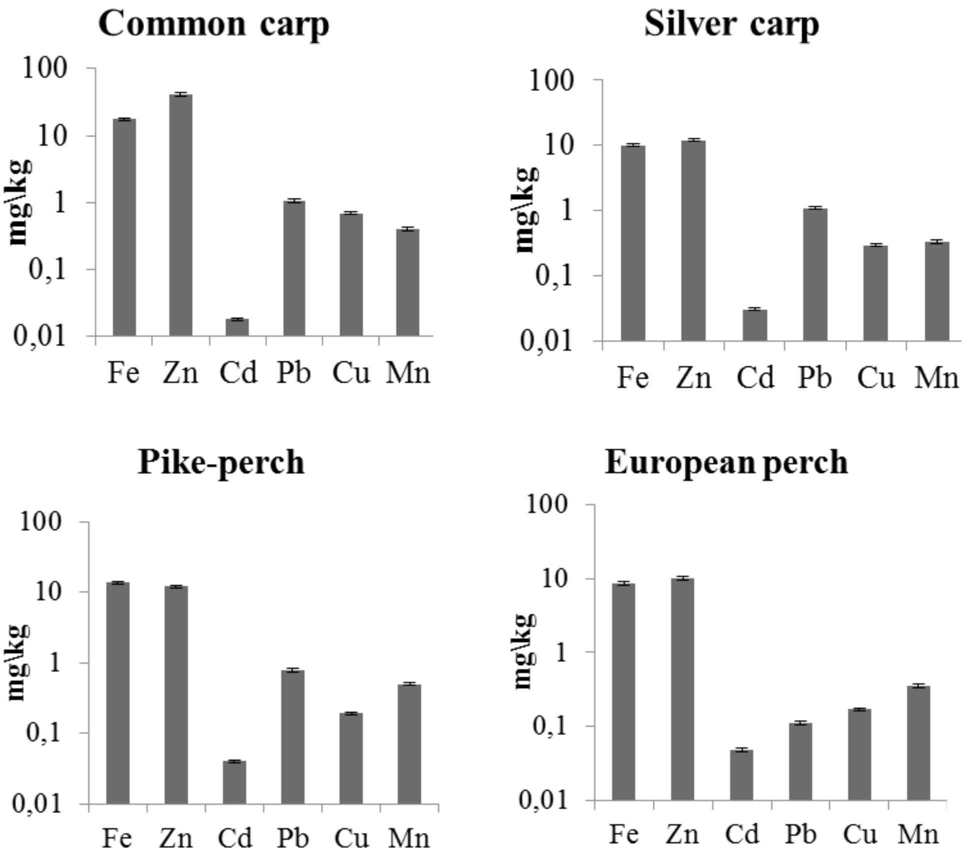

Fig. 2. The contents of heavy metals in fish muscles in Kam'yanske reservoir, mg/kg wet weight, M ± m, n = 5.

The highest iron content was observed in the muscles of common carp (17.54 mg/kg) and was higher compared to the pike-perch muscle by 22% and European perch and silver carp muscle by 47% ($p \leq 0.05$).

Zinc enters the organism via water and fish food, and the first way is more important for the high zinc content in the water. The content of zinc in the muscles of common carp (41.16 mg/kg) was higher compared to other researched fish muscle by 70% ($p \leq 0.05$). That is connected with the both nutrition and habitat types of common carp, which constantly contacts with the bottom sediments.

The physiological role of cadmium is poorly researched, because, despite its salts are highly toxic, it is necessary for the fish. Cadmium does not belong to the organism's vital elements. However, it could be claimed that its low concentrations stimulate cell division. Amongst the most researched fish, the cadmium concentration was observed in the European perch (0.048 mg/kg). Its content in European perch muscles is higher than that in pike-perch for 17%, in silver carp for 38% and in common carp for 63% ($p \leq 0.05$) (Fedonenko et al., 2012).

The toxicity of lead is slightly lower than cadmium. It belongs to one of the most dangerous pollutants because it has a lengthy action. Lead, judging by various biological indicators, is a strong inhibitor of cellular metabolism and might increase the toxicity of other metals. It is known that prolonged exposure to fish that are on top of the food chain, even small concentrations of lead could increase toxic effects but not adapting to it (Fedonenko et al., 2008). In Kam'yanske reservoir, silver carp muscle has the largest lead content than other fish species (1.09 mg/kg), and it was higher compared to the levels of pike-perch muscle by 28% ($p \leq 0.05$). Also the lead content in the muscles of silver carp was higher than that in European perch and common carp muscle, on an average, by 91% ($p \leq 0.05$).

Copper is present in all organisms and one of the trace elements necessary for their normal growth. Copper is very important for increasing the immune, biological and harmful effects resistance from the environmental factors in the growth process. Compared with other types of fish, the concentration of copper is the highest in the common carp, 0.69 mg/kg wet weight and higher compared to the levels of silver carp muscle by 58% ($p \leq 0.05$). This little amount of metal content is possibly related to the fact that its metabolic antagonists are iron and zinc, which are accumulated in high concentrations in the muscles of fishes researched in Kam'yanske reservoir. Compared to other fish species, the metal content observed in common carp muscle more than that in pike-perch and European perch by 72 and 75% ($p \leq 0.05$), respectively. Thus, the level of fish organism supply depends on following factors: biochemical features habitats, climatic and hydrochemical factors and physiological state of zinc and iron in the body of the fish.

Aquatic organisms get manganese from water and food objects. There is a selective ability of aquatic organisms' individual taxonomic groups to its accumulation. In manganese exchange, there are species features (Fedonenko et al., 2008). It is considered that the level of manganese absorption from the water is high enough. Biological activity of manganese in aquatic ecosystems depends on the pH, the presence of organic and other complexing agents, the concentration of suspended components and oxidation-restorative properties of water. Therefore, the role of manganese in water bodies could only be considered by these factors. The highest concentration of manganese in comparison with other fish species in the reservoir is observed in pike-perch (0.496 mg/kg) and is larger compared to the levels of the body other researched fishes by 28% ($p \leq 0.05$). Perhaps this is due to the fact that pike-perch has more predatory lifestyle and feeds on small fish, which in turn can be a source of manganese for them.

Comparative analysis of the heavy metals accumulation factors in the muscle of different fish species in Kam'yanske reservoir showed its value in a wide range, which is primarily due to the eating habits and their habitat. Some kinds of fish have relatively high rates of accumulation of zinc and iron (Table 3). First of all, the essential elements were accumulated – zinc and iron. Some species distinguished relatively high rates of accumulation: zinc in the common carp and iron in European perch, pike-perch and silver carp ($201 < AR < 1,000$). Also, there is a moderate rate of accumulation of zinc in fishes such as European perch, pike-perch and silver carp (51 < AR < 200). It is also important that common carp had extremely high rates of iron accumulation (AR < 1,000).

T a b l e 3. Accumulation rates (AR) of heavy metals in fish muscle in Kam’yanske reservoir.

Kind of fish	**Accumulation rate (AR) values**					
	Zinc	**Copper**	**Lead**	**Cadmium**	**Manganese**	**Iron**
Common carp	579.71	31.36	0.43	0.86	18.09	1,031.76
European perch	141.07	7.72	0.79	2.29	16.0	502.94
Pike-perch	183.21	8.64	5.57	1.9	22.55	805.29
Silver carp	168.87	13.18	7.79	1.43	14.9	586.47

Heavy metals are ranked based on the their rate of accumulation in fish muscles as follows:
Common carp: Zn > Fe > Cu > Mn > Pb > Cd;
European perch: Zn > Fe > Mn > Cu > Pb > Cd;
Pike-perch: Fe > Zn > Pb > Mn > Cu > Cd;
Silver carp: Zn > Fe > Pb > Mn > Cu > Cd.

The maximum content of heavy metals in fish muscle was observed in common carp, the minimum in European perch. The total content of heavy metals in common carp was almost twice as large compared to other fish.

Thus, the heavy metals in industrial fish in Kam’yanske reservoir depended on the type of food and their habitat. The maximum content of heavy metals was observed in common carp, which coincides with the data obtained earlier (Fedonenko et al., 2012). It was revealed that the metals that are essential to the flow of physiological processes were first accumulated in the body of fishes in Kam’yanske reservoir.

Conclusion

By the integrated environmental assessment using chemical water quality index of Kam’yanske reservoir, it is characterised as ‘satisfactory’ and ‘slightly polluted’.

BACs of heavy metals varied widely (from 14 for cadmium to 2,395 for manganese). Calculated BAC values indicate the continued accumulation of the researched toxic substances in the upper layer of the bottom sediments and the chronic pollution in ecosystem, which indicates that the degree of anthropogenic pollution exceeds the level of the self-cleaning ability of the Kam’yanske reservoir ecosystem. Bottom sediments can be a permanent source of secondary pollution by returning pollutants to the aquatic environment.

The researched features of the Kam’yanske reservoir must be taken into account along with the chemical treatment and measures carried out to preserve its ecosystem and water management.

The content of heavy metals in the muscles of industrial fish in the researched pond did not exceed MAC for fish as food according to the Ukrainian standards.

Accumulation of heavy metals in fish is connected to the peculiarities of their ways of nutrition and existing. The total content of heavy metals in common carp was almost twice as large compared to other fish. Maximum rates of accumulation in fish muscles are set for zinc and iron (essential elements), which are necessary for normal physiological processes of the organism.

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