

ENVIRONMENTAL STATUS OF THE TAROMSKY FISHERIES (UKRAINE)

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The environmental status of the nursery pond No. 2 of the Taromsky fisheries has been determined. The analysis of indicators of the hydrochemical regime of the studied pond has not reveal significant deviations from the regulatory requirements and those indicators has met the legislative norms for the cultivation of fish products. Studies have shown that the content of Cd, Pb and Fe in the water of the pond was within the maximum permissible concentrations; the content of Zn and Mn is three times higher than the permissible norms, while Ni – twice, and Cu five times higher. Insignificant concentrations of artificial radionuclides were revealed: Cs-137 and Sr-90, which do not exceed Ukrainian standards. According to the integrated index, taking into account the indices of trophic and saprobiological criteria and the content of specific substances of toxic and radiation action, the water in the pond of the Taromsky fishery belongs to the class III "Satisfactory" and "Contaminated". In bottom deposits, Fe has shown the greatest accumulation, while Ni has accumulated in the smallest amount. In fish bodies from the Taromsky fisheries, Zn has accumulated in the greatest amount. The content of Sr-90 and Cs-137 in the bodies of young fish did not exceed the standards. According to the cumulative capacity, the radionuclides in the studied fish species have shown the highest rates for Cs-137, the lowest one for Ra-226.

Key words: water soiling index, heavy metals, bottom deposits, radionuclides.

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INTRODUCTION

Fisheries in Ukraine is an integral part of the agricultural sector of the country. The productivity of fisheries depends on various factors, and the quality of the aquatic environment is one of them. Hydrochemical regime of the reservoir significantly affects the development of natural food resources and fish capacity of ponds. The decline in

water quality leads to impoverishment of the species composition and reduces the number of aquatic organisms. As a consequence, there may be a deterioration in the quality of fish products, a decrease in the productivity of farms (Andryushchenko et al. 2008). Water quality is assessed by determining the physical and chemical parameters and comparing them with the regulatory characteristics, which are based on the developed hazardous substances

maximum allowable concentration (SUC 05.01-37-385: 2006).

Currently, the problem of water pollution by heavy metals is obtaining urgent character, especially considering the significant increase of anthropogenic load on surface waters of Ukraine (Fedonenko et al. 2018). Heavy metals are conservative pollutants, which are pollutants of water bodies of increasing importance because of their stability in the environment, high biological activity and the cumulative capacity (Misliva 2010). Therefore, one of the main tasks is to study the content of various trace elements in water and hydrobionts throughout the trophic chain.

After the Chernobyl accident, most of the territories and reservoirs of Ukraine were contaminated with radionuclides. From 1950 to 1994, the Pridneprovsk chemical plant and Dneprodzerzhinsk integrated plant were engaged in enriching uranium raw materials, and radioactive waste was stored in nine tailing dumps located in clay quarries and ravines along the tributaries of the Zaporizke reservoir. The tailing dump "Dneprovskoye" is of particular risk; there are about 12 million tons of waste, which contains natural uranium and decay products of uranium and thorium series: Po-210, Pb-210, Ra-226, etc (Belokon et al. 2013). The increased radiation background resulted in contamination of many fishery reservoirs with radionuclides (Volkova et al. 2005). Thus, it becomes necessary to monitor pollution and accumulation of artificial radionuclides in water bodies and fish.

The purpose of this work was to study the features of the hydrochemical regime in the nursery pond of Taromsky fisheries, to analyse the content of heavy metals in water, bottom deposits and fish, to study the accumulation of radionuclides in water and fish products of the reservoir, determine the ecological status of ponds.

MATERIALS AND METHODS

Water and bottom deposits samples were taken from four points in the studied pond. Samples of bottom deposits were taken by the Ekman-Birge bottom sampler from the horizon of 0-5 cm. Each sample was consisted of 5 individual samples from a homogeneous area. The fish was selected during the control catches with stake net with mesh sizes from 30 to 150 mm.

Hydrochemical studies were carried out according to standard unified methods (Romanenko 2006).

For the toxicological analysis, the selected water was filtered through a membrane filter of 0,45 μm to separate the suspended particles and acidified with hydrochloric acid to a pH of 2,5. Further, 1 l of water samples were evaporated to dry, the residue was dissolved in 1 n nitric and 1 n hydrochloric acids (Gritsenko et al. 2012, Romanenko et al. 1998).

Samples of bottom deposits and fish were homogenized, dried at 105°C to a constant mass, and then incinerated at 450°C to produce white ash, which was treated with 1n nitric and 1n hydrochloric acid. The obtained solution was filtered through a blue ribbon filter and poured to the containers, making the volume of 10 ml.

The concentration of heavy metals in the samples was determined by atomic absorption spectrophotometer C115-M1.

The concentration of heavy metals was calculated by the formula:

$$C = \frac{K \times j \times v}{P}$$

where C is the metal concentration in the sample, mg/kg; J is the metal concentration in the analyzed solution, $\mu\text{g/ml}$; v is the volume of the diluted sample, ml; P is the ash mass, g; K is the ash ratio, g ash/g crude mass.

Table 1. The main hydrochemical indicators of the nursery pond of Taromsky fisheries

Name of indicator	Summer 2018	Regulatory value
Hydrogen index, pH units	8,03	6,5 - 8,5
Dissolved oxygen, mg/ L	4,5	8 ±2
Calcium Ca ²⁺ , mg / L	53,31	Up to 70
Sulphates SO ₄ ²⁻ , mg/L	48,0	50-70
Ammonium nitrogen, mg / L	0,085	0,01-0,07
Nitrite nitrogen, mg/ L	0,003	0,02
Nitrate nitrogen, mg / L	0,68	2,0
Phosphate phosphorus, mg/L	0,04	0,5
Permanganate oxidability, MgO/L	6,8	Up to 15,0

The content of heavy metals was expressed in mg/kg of dry and raw matter, respectively, their concentration in water in mg/l (Romanenko 2006).

To determine the specific radioactivity by the main dose-forming elements, a water sample in the volume of 23 l was acidified with concentrated nitric acid HNO₃ in ratio of 1 ml per 1 liter of water and evaporated in a water bath to a minimum volume for the purpose of concentrating radionuclides. To study the accumulation of radionuclides in young fish, whole bodies were used. The 10-40 g sample of raw tissue was crushed and dried at a temperature of 105°C in a dry oven to a constant weight.

The content of radionuclides in fish and water samples was determined using the gamma-decay energy scintillation spectrometer SEG-001 "AKP-C" and the beta radiation spectrometer SEB-01-150 and calculated by the formula:

$$C = \frac{K \times j \times v}{P}$$

where C is the concentration of radionuclides in the sample, Bq/kg; j is the concentration of radionuclides in the concentrated sample, Bq/kg; v is the volume of the diluted sample, ml; P is the weight of the dry sample, g; K is the coefficient of desiccation, g dry sample/g raw mass.

The content of radionuclides was expressed in Bq/kg per wet weight.

Bottom accumulation coefficient (BAC) and the accumulation ratio of pollutants in hydrobionts (AR) was calculated as:

$$K = \frac{C_s}{C_w}$$

where C_s is the concentration of pollutants in bottom deposits or hydrobionts, C_w is the concentration of pollutants in the water.

Environmental assessment of water quality in various categories was carried out in accordance with generally accepted methods (Gritsenko et al. 2012, Romanenko et al. 1998). The digital data were mathematically processed by General methods of variation statistics for a small sample and calculated using the Microsoft Excel-10 software package.

RESULTS AND DISCUSSION

Taromsky fisheries is one of the few functioning farms in Dnepropetrovsk region. It is located on the right bank of the Dnipro river in the forest-steppe zone, it is in line since 1963; its total area is 309,5576 hectares, including the water surface area of 105,622 hectares. This farm consists of 38 ponds, including 9 nursery ponds, 1 wintering and stock pond, 1 summer

and stock pond, 9 wintering and 18 spawning ponds. Ponds are supplied with water from the Dnipro river by the pumping station.

Currently, the farm uses only 2 ponds. Fish-farming in the farm is held in pond No. 2 with an area of 7,9 ha (48,464631,34.775550); its total water surface area is 7,26 ha, length is 825,00 m, average width is 88,00 m, average depth is 1,08 m. Bottom deposits of the nursery pond are represented by clay silt; silt thickness is 0,4-0,5 m. The bed of the pond is flat, the bottom relief is directed towards the overflow spillway. In this pond stocking material of carp and catfish is grown (fingerlings).

The results of hydrochemical studies of the nursery pond are given in Table 1.

An important indicator of water quality in fish farming is the hydrogen index. The pH value affects the development and vital activity of aquatic plants and plankton, consistency of the elements migration, the process of converting different forms of nutrients (Khilchevsky et al. 2012). In summer, the pH of the pond indicated a slightly alkaline environment and corresponded to the regulatory characteristics of fishery water bodies (SUC 05.01-37-385: 2006).

An important factor for vital activities of fish is the content of dissolved oxygen in water consumed by fish. Oxygen regime in the nursery pond in the summer was satisfactory and was within the fishery rules.

The content of calcium in water is limited by its consumption by hydrobionts, especially molluscs. Also, the concentration of calcium in the water is directly dependent on the sulfate regime because there is a possibility of formation of slightly soluble CaSO_4 (Fedonenko et al. 2018). Summer indicators of calcium content did not exceed the regulatory values.

Sulphate concentrations in the aquatic environment are subject to seasonal variations and usually correlate with changes in total water mineralization (Petin, 2006). The summer

sulphate concentration in the nursery pond was within acceptable limits.

Biogenic substances, which include nitrogen and phosphorus compounds, provide biological productivity of fishery water bodies, which is especially important in the cultivation of fish products.

In natural waters nitrogen is in the form of inorganic and various organic compounds. Inorganic nitrogen compounds are: ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) ions. Ammonia is released during the fish life as the final product of metabolism of nitrogen-containing substances (Goncharova 2013). In the studied pond, the content of ammonium nitrogen in the summer was slightly higher than the regulatory requirements. This indicates an increased content of decomposition products of organic substances in water.

Nitrites are intermediate products in the system of bacterial processes of oxidation of ammonium to nitrates and back. Generally, the amount of nitrites in the water is insignificant (Khilchevsky 2012). The concentration of nitrates in the pond water did not exceed the standard values.

The concentration of nitrates in the water is subject to seasonal fluctuations. In the researched pond, the summer concentrations of nitrates met the fishery rules.

Phosphorus compounds limit the development of phytoplankton. The content of polyphosphates in the summer in the growing pond was within acceptable limits.

Permanganate oxidability characterizes the presence in water of easily oxidized organic substances in a dissolved or suspended state (Andryushchenko et al. 2008). In summer, the indicator of permanganate oxidation in the pond met the normative indicators.

The analysis of indicators of the hydrochemical regime of the studied pond in the Taromsky fishery during 2018 did not reveal significant

deviations from the regulatory requirements and met the legislative norms for the cultivation of fish products.

One of the pollutants of water bodies are heavy metals, characterized by high toxicity, biochemical activity and the ability to be accumulated. The increased content of pollutants in water and deposits poses a threat of abnormal development of various hydrobionts.

Heavy metals tend to redistribute in various elements of the aquatic environment, accumulating in the components of the aquatic system, including fish. This is the danger of entering heavy metals the human body through the trophic chains.

According to the content in the water of the pond № 2 metals form the following decreasing series: Fe> Pb> Mn > Zn> Ni> Cu>Cd (Fig. 1).

Analysis of the study results showed that the content of Cd, Pb and Fe in the water of the pond was within the maximum permissible concentrations. The content of Zn and Mn is three times higher than the permissible norms, Ni twice, and Cu five times higher (SUC

05.01-37-385: 2006). This fact may be due to the income of elements not only together with the water intake from the Dnipro river, but also together with the surface runoff from the agricultural areas of Taromsky village.

The result of the Chernobyl accident was a vast area of radioactive contamination, which led to the contamination of drainage areas of the Dnipro, including many fishery reservoirs with artificial radionuclides. Ichthyofauna is the last chain in the trophic system before human consumption. The concentration of radionuclides in water is essential for the formation of radioactive contamination of hydrobionts (Belokon 2009).

Small concentrations of artificial radionuclides were observed in the water of the studied reservoir of the Taromsky fishery: Cs-137-0,13 Bq/l and Sr-90 – 0,04 Bq/l. These indicators do not exceed the Ukrainian standards of permissible levels for these radionuclides in water (GN-2006). Concentrations of natural radionuclides in water showed the following results: Ra-226 – 2,60 Bq/l, Th-232 – 1,99 Bq/l, K-40 – 4,85 Bq/l. The level of natural radionuclides is often higher than such of artificial ones due to the high

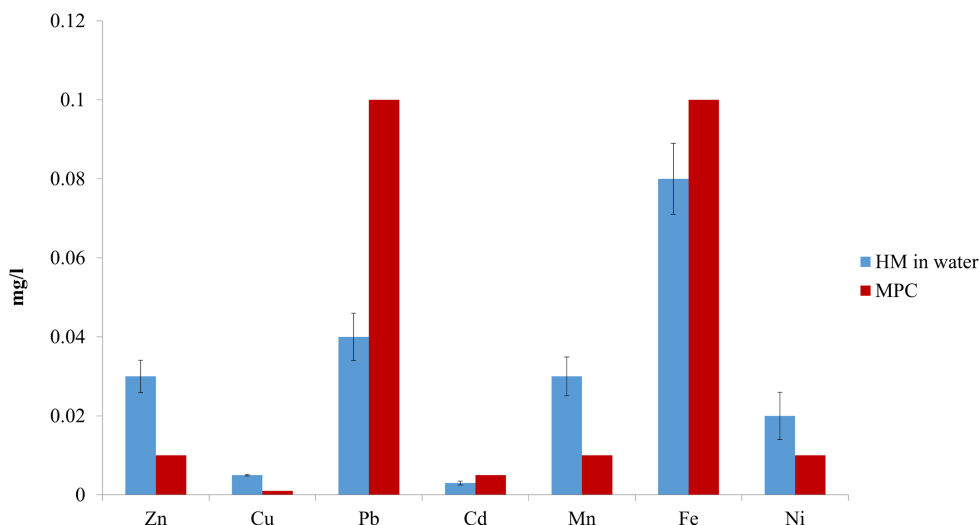


Fig.1 The content of heavy metals in the water of the nursery pond of the Taromsky fishery, M ± m, n = 5.

Table 2. Ecological characteristic of water quality in the nursery pond of Taromsky fisheries on environmental and sanitary criteria

Name of indicator	Purity level	
	Class	Category
Hydrogen index, pH units	II	3
Dissolved oxygen, mg/ L	IV	6
Sulphates SO_4^{2-} , mg/L	I	1
Ammonium nitrogen, mg / L	I	1
Nitrite nitrogen, mg/ L	I	1
Nitrate nitrogen, mg / L	III	4
Phosphate phosphorus, mg/ L	II	3
Permanganate oxidability, MgO/L	II	3

Table 3. Classification of water quality in the nursery pond of Taromsky fisheries according to the criteria of the content of specific substances of toxic and radiation action, $M \pm m$, $n = 5$

Name of the indicator, unit of measurement	Value of indicator	Purity level	
		Class	Category
Iron total, mg/l	0,08±0,009	II	3
Cadmium, mg/l	0,003±0,0005	IV	6
Copper, mg/l	0,005±0,0002	III	4
Zinc, mg/l	0,03±0,0041	III	4
Lead, mg/l	0,04±0,006	III	4
Nickel, mg/l	0,02±0,006	III	4
Manganese, mg/l	0,03±0,0049	II	3
Cesium-137, Bq/l	0,13±0,004	III	4
Strontium-90, Bq/l	0,04±0,0002	III	4

concentration of accumulation in ecosystems (Belokon, 2009). Level of Radium-226 in water exceeds allowable level by 2.5 times (NRBU-97).

According to the obtained hydrochemical parameters, the water quality of the studied pond was assessed according to trophic and saprobiological (ecological and sanitary) criteria (Table 2) and to the content of specific substances of toxic and radiation action (Table 3).

Analysis of the environmental assessment of the pond water showed that the classification of indicators such as sulfates, ammonium nitrogen

and nitrite nitrogen allows to characterize the water as “Excellent” - class I, category 1. The pH content of the water allows to assign water class II, category 3 - “Good”. According to such indicators as permanganate oxidability and phosphates, the water quality in pond No. 2 corresponds to class II, category 3 - “Good”. In terms of nitrate nitrogen in water, it is possible to characterize water as “Satisfactory” - class III, category 4. The content of dissolved oxygen corresponds to class IV, category 6 - “Bad”.

According to the content of copper, zinc, lead and nickel water in pond No 2 belongs to class III “Contaminated” and category 4 “Slightly contaminated”. By the content of cadmium

Table 4. Content of heavy metals in bottom deposits of the Taromsky fishery pond (mg/kg of dry weight), $M \pm m$, $n=5$

Heavy metals/ Indicators	Zn	Cu	Pb	Cd	Mn	Fe	Ni
Bottom deposits	52,21± 6,8	14,36± 2,2	25,67± 4,9	3,36± 0,98	160,26± 21,3	9244± 410, 3	20,23± 3,7

Table 5. Average values of the CBA coefficient in the deposits of the nursery pond of Taromsky fisheries

Heavy metals/ Indicators	Zn	Cu	Pb	Cd	Mn	Fe	Ni
CBA	1740	2872	642	1120	533	115550	101

water belongs to the IV class and 6 category - "Dirty". According to the content of iron and manganese pond water belongs to class II "Clean" and category 3 "Quite clean". The anthropogenic factor and natural geochemical conditions had an impact on the formation of the elemental composition of the water in the pond of the Taromsky fishery.

It was found that by the content of cesium-137 and strontium-90 water is characterized as class III - "Contaminated", category 4 - "Slightly contaminated".

According to the integral quality indicator the water of the pond in Taromsky fisheries belongs to class III "Satisfactory" and "Contaminated".

Bottom deposits play the role of a depositing medium, as they have the ability to accumulate various chemical elements and participate in the processes of self-purification of the reservoir. However, they have the ability to secondary pollution of the aquatic environment.

Deposits analysis is important for fisheries. Heavy metals accumulating in bottom sediments can negatively affect benthic organisms, lead to changes in their qualitative and quantitative composition. Thus, heavy metals affect benthic fish not only through the aquatic environment, but also through forage objects.

According to the content in the bottom deposits of the pond No 2 metals form the following decreasing series: $Fe > Mn > Zn > Pb > Ni > Cu > Cd$ (Table 4).

The results of the research allow us to note that Fe occupies a leading position in composition both in water and in bottom deposits. Whereas Cu and Cd are found in the lowest amounts in both water and bottom deposits of the studied pond.

The coefficient of bottom accumulation (CBA) was calculated as the ratio of metal content in bottom deposits to their content in water and characterizes the processes of accumulation of toxicants in bottom soils (Table 5).

According to the results, the coefficients of bottom accumulation of heavy metals varied widely. Fe had the greatest accumulation in bottom deposits, the coefficient of bottom accumulation was 115550. This may be due to the high content of this element in the sediments. The lowest accumulation was in Ni, which bottom accumulation coefficient was 101.

The study of the content and accumulation of heavy metals and radionuclides in the bodies of young fish is of particular interest, as it is the final product of the fishery activities of the enterprise.

Table 6. The content of heavy metals in bodies of fish from Taromsky fisheries, mg/kg of raw weight, $M \pm m$, $n = 5$

Heavy metals/Fish species	Zn	Cu	Pb	Cd	Mn	Fe	Ni
Common carp	1,29± 0,01	0,07± 0,006	39,16± 0,07	0,51± 0,05	0,79± 0,004	29,62± 0,08	4,93± 0,05
Catfish	1,43± 0,05	0,09± 0,004	47,83± 0,02	0,71± 0,03	0,58± 0,019	6,99± 0,01	4,88± 0,07

Table 7. The coefficients of accumulation of heavy metals in fish from Taromsky fisheries

CBA/ Fish species	Zn	Cu	Pb	Cd	Mn	Fe	Ni
Common carp	32,25	23,33	1305,33	17,00	158,00	370,25	246,50
Catfish	35,75	30,00	1594,33	23,67	116,00	87,38	244,00

Analysis of the content of heavy metals in fish tissues of the studied pond revealed some features of their distribution and accumulation in the body of the studied objects of fisheries (Table 6).

Evaluation of the data showed that zinc dominates in accumulation in the organisms of the studied fish. Zinc plays an important biological role in the metabolism of fish, affects the growth and development of fish and is an activator of a number of enzymes (Shkodin, 2011). The content of zinc in the body of catfish was little more than in the body of carp.

Iron is actively involved in various metabolic processes, especially in the process of transport, deposition and exchange of oxygen (Yanovych, 2014). The concentration of iron ions in the body of a carp was 3 times higher than in catfish.

The Nickel content in the bodies of carp and catfish was almost equal. A similar picture is shown by the analysis of the concentration of lead in fish organisms.

Copper is necessary for fish for the synthesis of red blood cells, as it is part of the liver proteins and a number of oxidative enzymes (Mileva,

2016). Levels of copper in carp was by 36,2 % more than in the catfish.

Manganese plays an important role in the activation of various enzymatic reactions, the level of absorption of this trace element from water is quite high (Watanabe, 1997). Manganese content in the body of carp is 28,2 % less than in the body of catfish.

Cadmium activity is closely related to zinc activity, so cadmium can replace it in many important enzymatic reactions. (Komarovskiy 1996) the level of cadmium in carp is 22,2% lower than in catfish body.

Heavy metals content in body of carp from Taromsky fisheries decreases in the ranked row as follows: $Zn > Fe > Ni > Pb > Cu > Mn > Cd$, which can be compared with the content of the same heavy metals in the body of catfish, where the series looks like this: $Zn > Fe > Ni > Pb > Mn > Cu > Cd$.

The process of accumulation of heavy metals in fish organisms is estimated by the biological accumulation coefficient. The biological accumulation coefficient was determined for each fish species (Table 7).

Table 8. The accumulation coefficients of natural and artificial radionuclides in juvenile fish from Taromsky fisheries

CBA/Fish species	Cs-137	Sr-90	Ra-226	Th-232	K-40
Common carp	43, 69	42,27	14,,00	19,08	19,02
Catfish	38,38	38,25	8,.86	14,34	14,17

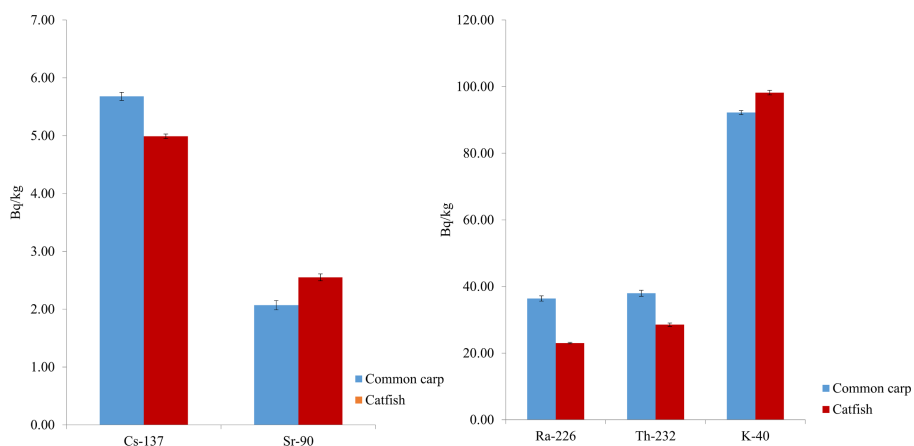


Fig. 2 The levels of artificial and natural radionuclides in fish from Taromsky fisheries, Bq/kg, $M \pm m$, $n = 5$.

Comparative analysis of the coefficients of biological accumulation of heavy metals in bodies of fish from Taromsky fisheries showed fluctuations in its values over a wide range. The greatest accumulation in the studied species had such metal as zinc. It shows its high biophilia and ability to intense biological accumulation in the tissues of fish (Sharamok, 2017). Moderate accumulation coefficients were observed in nickel and copper.

The accumulative capacity of carp in relation to iron was 4,2 times, and in relation to copper 1,4 times higher compared to catfish. The cumulative capacity of catfish in relation to zinc was more than 1,2 times compared to carp.

According to the cumulative capacity, the metals in the bodies of the studied fish are arranged in a certain sequence:

Common carp: $Zn > Fe > Ni > Cu > Pb > Cd > Mn$;

Catfish: $Zn > Ni > Cu > Fe > Pb > Cd > Mn$.

The average content of Cs-137 and Sr-90 in fish of the Taromsky fishery according to the results of these studies was significantly lower than the standards established by the legislation (GN-2006) (Fig. 2).

The content of Cs-137 carp was slightly higher than that of catfish. On the contrary, the concentration level of Sr-90 was higher in catfish than in carp.

Literature data show that levels of accumulation of environmentally important radionuclides, such as Cs-137 TA Sr-90, are closely related to the level of consolidation of food and water concentrate. Thus, Cs-137 is deposited mainly in the muscles of fish (regardless of the ways of getting into the body), and Sr-90 is characterized by accumulation in the bones of fish (Prosyaniuk 2015, Zarubin et al. 2013).

The concentrations of natural radionuclides that form the radiation background of the natural ecosystem are analyzed (Figure 2).

The Ra-226 content in carp bodies was 58% higher than in catfish bodies. Moreover, the level of Th-232 in carp was 33% higher than that in catfish. However, the catfish had a higher K-40 content in the body than the carp.

The ranked number of contents of artificial and natural radionuclides in juvenile carp and catfish will look identical: K-40>Th-232>Ra-226>Cs-137> Sr-90. In organisms of both fish species, the leading role in terms of content belongs to K-40, and the content of Sr-90 is minimal.

The level of accumulation of various radionuclides depends on the species of fish, its age, nature of nutrition, physiological characteristics of the organism, as well as on the temperature regime of the reservoir, its hydrochemical parameters and factors (Ananieva 2017).

According to the obtained data on the concentration of radionuclides, coefficients of their accumulation can be calculated (Table 8).

According to the cumulative capacity, the radionuclides in the bodies of the studied fish species are arranged in a certain sequence, the same for carp and catfish: Cs-137>Sr-90>Cs-137>Th-232>K-40>Ra-226. The highest rates were recorded for Cs-137, the lowest for Ra-226.

FINDINGS

The analysis of indicators of the hydrochemical regime of the pond No 2 in the Taromsky fishery during 2018 did not reveal significant deviations from the regulatory requirements for the cultivation of fish products.

Ecological quality of water in the studied pond by an integral indicator of quality belongs to the class III "Satisfactory" and "Polluted".

The coefficients of bottom accumulation of heavy metals varied widely. In bottom

sediments Fe was accumulated in the greatest amount, while Ni in the smallest.

In the studied fish species zinc revealed the greatest accumulation. Moderate accumulation coefficients were observed in Nickel and Copper. The accumulative capacity of carp in relation to iron was 4.2 times higher compared to catfish. The cumulative capacity of catfish in relation to zinc was more than 1.2 times compared to carp.

The content of Sr-90 and Cs-137 radionuclides in the water of pond No. 2 and in the bodies of young fish did not exceed the permissible levels of radioactivity provided for by the Radiation Safety Standards of Ukraine. According to the cumulative capacity, the radionuclides in the studied fish species have shown the highest rates for Cs-137, the lowest for Ra-226.

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