

VARIOUS ASPECTS OF THE ASSESSMENT OF MIGRATION AND THE ROLE OF METALS IN DETERMINING THE FUNCTIONING OF AQUATIC ECOSYSTEMS

ZUBCOV Elena, ZUBCOV Natalia, BAGRIN Nina, BILEȚCHI Lucia, UNGUREANU Laurenția, ENE Antoaneta, SPANOS Thomas, CIORNEA Victor, CIORBA Petru

Abstract. The paper presents an overview of the results of multiannual investigations of the dynamics of migration of several metals in the ecosystems of the Dniester and Prut rivers – the main water courses of the Republic of Moldova. The dynamics of metals in water, suspensions, silts, aquatic plants, planktonic and benthic invertebrates, fish at different stages of development (eggs-larvae, fry, mature fish) was investigated depending on abiotic factors and under the influence of human activity. The fragmentation of the Dniester River, through the construction of several dams, and the operation of the Dniester Hydropower Complex have reduced the processes of sedimentation and self-cleaning in the river, which has reflected on the migration and circuit of metals, causing an imbalance of the native processes of metal migration, characteristic for the river ecosystems of the studied region. The impact of metals on the processes of formation of primary production and destruction of organic matter in aquatic ecosystems and on the development of fish, especially at the early stages of ontogenesis, was identified. The level of accumulation of metals in aquatic plants, planktonic, benthic invertebrates and fish is a reflection of the metal content in the aquatic environment, but also depends on the biological properties of the hydrobionts, and the overall ecological status of the aquatic ecosystem. Synergistic, additive and antagonistic interactions between different metals have been recorded. The identified regularities of the migration and accumulation of metals in the “water-solid suspensions-silts-hydrobionts” system can be used in monitoring and evaluating the functioning of aquatic ecosystems.

Keywords: aquatic ecosystem, metal, monitoring, functioning.

Rezumat. Diverse aspecte ale evaluării migrației și rolului metalelor în descifrarea funcționării ecosistemelor acvatice. Lucrarea prezintă o generalizare a rezultatelor investigațiilor multianuale ale dinamicii migrației mai multor metale în ecosistemele fluviului Nistru și ale râului Prut – arterele acvatice principale ale Republicii Moldova. A fost investigată dinamica metalelor în apă, suspensii, mълuri, plante acvatice, nevertebrate planctonice și bentonice, pești la diferite perioade de dezvoltare (icre-larve, puiet, pești maturizați) în dependență de factorii abiotici și sub influența activității umane. Fragmentarea fluviului Nistru, prin construirea mai multor baraje, și funcționarea Complexului Hidroenergetic Nistrean au diminuat procesele de sedimentare și autoepurare în fluviu, ceea ce s-a reflectat asupra migrației și circuitului metalelor, provocând un dezechilibru al proceselor native de migrație a metalelor, caracteristice pentru ecosistemele fluviale din zona de studiu. A fost stabilit impactul metalelor asupra proceselor de formare a producției primare și a destrucției materiei organice în ecosistemele acvatice și asupra dezvoltării peștilor, în deosebi, la etapele de ontogeneză timpurie. Nivelul de acumulare în plante acvatice, nevertebrate plantonice, bentonice și pești reprezintă o reflecție a conținutului de metale în mediul acvatic, dar depinde și de proprietățile biologice ale hidrobiionților, și de starea ecologică integră a ecosistemului acvatic. A fost înregistrat fenomenul de aditism, sinergism și antagonism între diferite metale. Legitățile stabilite ale migrației și acumulării metalelor în sistemul ”apă-suspensii solide-mълuri-hidrobiionți” pot fi utilizate în monitoringul și evaluarea funcționării ecosistemelor acvatice.

Cuvinte cheie: ecosistem acvatic, metal, monitoring, funcționare.

INTRODUCTION

The assessment of the functioning of aquatic ecosystems, being a fundamental scientific approach in biology and environmental protection, involves obtaining new knowledge through related *in situ* studies and laboratory modelling on the identification of the regularities of migration and circuit of chemical substances, processes of bioaccumulation and biomagnification of ecotoxicants and xenobionts, determination of the tolerance limits of hydrobionts, buffer capacity and the level of self-cleaning and secondary pollution of ecosystems.

Hydrobiological, ichthyological and ecotoxicological studies are needed to argue for compensatory measures regarding the maintenance of the biodiversity of hydrobionts, the reduction of technogenic effects and the sustainable capitalisation of aquatic ecosystems.

Metals represent a rather large group of chemical elements, extremely necessary for life, but which can transform into environmental toxicants by accumulating in water, solid suspensions, silts, aquatic plants and animals to a toxic level for aquatic ecosystems and human health.

Natural sources of metals in aquatic ecosystems are the parent rocks and soils of their hydrographic basins, as well as atmospheric precipitation which carry the products of volcanic eruptions. Sources of metal pollution are the metallurgical, military and chemical industry, thermal power plants, agriculture, urbanization, transport, etc.

The metal pollution of the aquatic environment is due to the fact that metals, as such, do not get destroyed or decay, but they change from one chemical or biochemical form to another, often increasing toxicity along the food chain. Some metals and their compounds are chemicals of a global concern due to their significant negative effects on human health and the environment, as Hg, which is the subject of Minamata Convention on Mercury (***. UNEP, 2013).

The migration capacity of metals in the very dynamic system "water-solid suspensions-silts-hydrobionts" is directly dependent on geographical factors, including hydrological ones, physico-chemical parameters of waters, silts, the state of hydrobiocoenoses and, last but not the least, on properties of metals and their ratio.

The ratio of metal concentrations in water, solid suspensions and silts reflects the sorption-desorption properties and the processes of self-cleaning and secondary pollution in an aquatic ecosystem.

Investigation of the biological migration of metals includes the determination of the level of their accumulation in hydrobionts, which depends greatly on the composition and biological properties of hydrobionts (algae, planktonic and benthic invertebrates), chemical parameters of water, solid suspensions and silts, gas regime, temperature, oxidation-reduction processes, pH values, mineralization, processes of additivity, synergy and antagonism between different metals, period of the year, etc.

Regrettably, the Community regulations list only Cd, Pb, Hg, Ni and their compounds as priority substances in the field of water policy (***. Directive 2000/60/EC) and set the environmental quality standards for their concentration in surface waters (Cd, Pb, Hg, Ni) and biota (Hg) (***. Directive 2008/105/EC), although it is known that several metals (e.g., Cu, Cr, Bi, Be, Ti, Tl), in rather low concentrations, can be harmful and dangerous for aquatic biodiversity and human health (ZUBCOV et al., 2013; ZUBCOV et al., 2016; GHEORGHE et al., 2017).

MATERIAL AND METHODS

Research on metals in the Dniester and Prut rivers has been carried out since the 1970s. Thousands of samples of water, suspensions, silts, biological material (plants, planktonic and benthic invertebrates, and fish), atmospheric precipitations, wastewater and samples from runoff from agricultural lands and urbanized territories were investigated. The used research scheme and methods correspond to ISO standards adapted to national ones (***. Ecotoxicological methodological guide for environmental monitoring: problematics, laboratory techniques and health risk investigation, 2021; ***. Methodological guide for monitoring the hydropower impact on transboundary river ecosystems, 2021).

Directly *in situ* or in the first 12 hours after sampling, the water samples were filtrated through membrane filters with a pore diameter of 45 microns to separate dissolved metals from those in solid suspensions. Several experimental works *in situ* and modelling in laboratory conditions were performed both to determine the influence and the level of accumulation of metals, as well as to evaluate the role of aquatic organisms in the biological migration of metals. Different methods were used: from photometric ones, of spectral emission in 1971-1990 and later – of atomic adsorption, to coupled plasma atomic emission nowadays (CIORNEA et al., 2021).

Regarding the silts, the concentration of metals was determined in aqueous solutions, obtained by centrifuging the silts, in some granulometric fractions and, according to the step by step extraction method (DEMINA et al., 2010), the concentration of metals absorbed by hydrocarbons and dissolved carbonates, of metals from mineral-organic compounds and of those in association with iron and manganese hydroxides.

The data gathered during the multiannual research have been mathematically processed according to the unanimously accepted methods in statistics, by applying the programs Excel, Statgraf, Statistica, Paradox, etc.

RESULTS AND DISCUSSIONS

Entering the aquatic ecosystems, trace metals have a very important role, being catalysts of several biochemical and biological processes. The migration capacity of metals in aquatic ecosystems and their forms of migration are conditioned both by the properties of the elements themselves and by the physicochemical particularities of the environment, which means the oxidation-reduction conditions, pH value, temperature, the presence of agents of complexation, of suspensions, the vital activity of hydrobionts. The most intense adsorption is characteristic for suspensions enriched with clay particles and organic substances. In relation to this fact, in the rivers of southern latitudes, most of the metals migrate in the form of suspended substances, while in the northern ones, on the contrary, the dissolved forms prevail over the suspended ones (ZUBCOV et al., 2016).

The ratio between the suspended and dissolved forms of metal migration in river waters is important in the evaluation of their influence on living systems, is of great importance in geochemical research and characterizes denudation processes in hydrographic basins. The relative mobility of metals, determined as the ratio of suspended forms to their total content (in water + in solid suspensions), indicates not only the state of the aquatic ecosystem, but also characterizes the direction of exogenous processes on the water catchment surface.

Human activity introduces substantial corrections in the distribution and migration of metals in aquatic ecosystems. For example, the construction of reservoirs on river course significantly changes the ratio between the suspended forms of metal migration and those dissolved both upstream and downstream of the dams. In the reservoirs, due to the reduction of the velocity of water, the sedimentation processes of suspensions intensify and with them, those of metals. As result, the importance of silts in their migration increases. The natural migration of metals in aquatic ecosystems polluted with industrial wastewater and solid waste, including plastic, household wastewater, runoff from agricultural lands, polluted atmospheric precipitation, is also affected.

In the deciphering of migration processes, especially of metals in aquatic ecosystems, the importance of investigations regarding biogenic migration and the determination of the functional role of metals in the life of aquatic plants and animals has increased. In this context, the ecotoxicological research aimed at discovering the regularities of the technogenic effect on the level of accumulation of metals in hydrobionts and, in particular, on their growth and development, should be highlighted. Thus, the investigation of the migration of trace metals in surface waters is currently considered to be one of the leading scientific directions in the field of contemporary hydrobiology, ecology, hydrochemistry, having a particular theoretical and practical importance.

All the above-mentioned directions of metal research are significant for the Republic of Moldova, where the shortage of water of a good quality is acutely felt and human action on the environment is continuously increasing. In addition, the Dniester and Prut rivers – the main water courses of the country – are bordering water bodies, because they start on the territory of Ukraine and take their waters through the densely populated regions of Ukraine, Moldova and Romania. Dam lakes have been built on both rivers and different types of hydropower plants operate, large industrial centres are concentrated in their hydrographic basins, therefore, the quality of water largely depends on human influence in these regions and nature protection measures, based on scientific elaborations and knowledge of the regularities of distribution and migration of chemical elements.

It has to be mentioned that, before the building of the Dniester Hydropower Complex (DHPC) on the territory of Ukraine, the concentrations in suspensions of about 20 permanently investigated metals were higher than their concentrations in water and, as the total concentration of metals (suspended and dissolved forms), showed a strong correlation with water discharge, which can be described by a multifunction equation of the following type:

$$y = X_0 + X_1 * Q + X_2 * S, \quad R^2 = 0.83 \dots 0.97,$$

where: y – metal concentration, $\mu\text{g/L}$; Q – water discharge in the Dniester River, m^3/s ; S – content of suspensions in water, mg/L ; R^2 – correlation coefficient.

This dependence is characteristic for the geographical area of the hydrographic basins of both rivers. Currently, there is no correlation in the Dniester River and the concentrations of most of the investigated metals in water are higher than those in suspensions. Only the concentrations of Al, Fe and Ti in over 96% of cases and of Mn and V in 40-50% of cases are higher in suspensions than in water, but even for these metals there is no obvious correlation with the water discharge and the content of suspensions.

The hydrological regime of the Dniester River has changed radically (water discharge, level, velocity, temperature, transparency) due to the operation of DHPC. Currently, especially after the operation of the Pumped Storage Hydropower Plant (PSHPP) has started, high spring floods no longer exist; in most cases the water discharge of the Dniester at the entrance on the territory of the Republic of Moldova is $100 \text{ m}^3/\text{s}$ or less, the alluvial substances have disappeared and the amount of mountain solid suspensions in the river on the territory of the Republic of Moldova has drastically decreased. As a result, the river ecosystem with running water turns into an ecosystem with stagnant water, with the formation of several areas of marshes covered with macrophytes (***. Methodological guide for monitoring the hydropower impact on transboundary river ecosystems, 2021).

In addition, the ratio between the cations of Ca, Mg, Na, K and the anions of hydrogen carbonates, carbonates, sulphates and chlorides, which in aquatic ecosystems are some of the most stable indicators, denotes the existence of irreversible processes in the hydrographic basin of the Dniester – the main source of water supply in the Republic of Moldova.

It is known that, in the native fluvial ecosystems, which are not undergoing an anthropogenic transformation (also called reference ecosystems), the origin of suspended solids, their granulometric, mineralogical and chemical composition have been and remain the main parameters in assessing the intensity of erosion-denudation processes in a hydrographic basin and an indicator of the migration capacity of chemical substances in the “water-suspensions-silts” system. Processes of absorption-sedimentation-desorption, in turn, determine the processes of self-cleaning and secondary pollution in aquatic ecosystems. The Dniester River and the Prut River are located in the same physico-geographical areas and originate from the same region of the Carpathian Mountains. The fact that the properties of a running ecosystem have been preserved in the Prut River, but the Middle and Lower Dniester is turning into an ecosystem with stagnant waters allows stating that, actually, there is a dangerous impact of the operation of DHPC.

The results of the investigation of the migration of metals in the “water-solid suspensions-silts-hydrobionts” system demonstrate that the adsorption and sedimentation processes in the Dniester River do not correspond to the regularities of the functioning of a river ecosystem in the given region. Human factor, which has become dominant, influences the direction and forms of migration of chemical substances, diminishing the natural processes of self-cleaning, and the modification of the hydrological regime causes an imbalance not only in the circuit and migration of metals, but also in the functioning of hydrobiocoenoses. Especially, the productivity of hydrobionts and the reproduction of fish are affected.

Silts are the most stable components of aquatic ecosystems, being also metal accumulators. Concentrations of Zn, Cu, Pb, Ni, Mo and V in silts are 2-7 times higher than those in soils of the region. The concentration of metals in silts is directly correlated with the amount of clay particles of a diameter of less than 0.01 mm ($r=0.86-0.97$). The range of oscillations of the distribution of metals in the silt fractions depends on their size (Fig. 1).

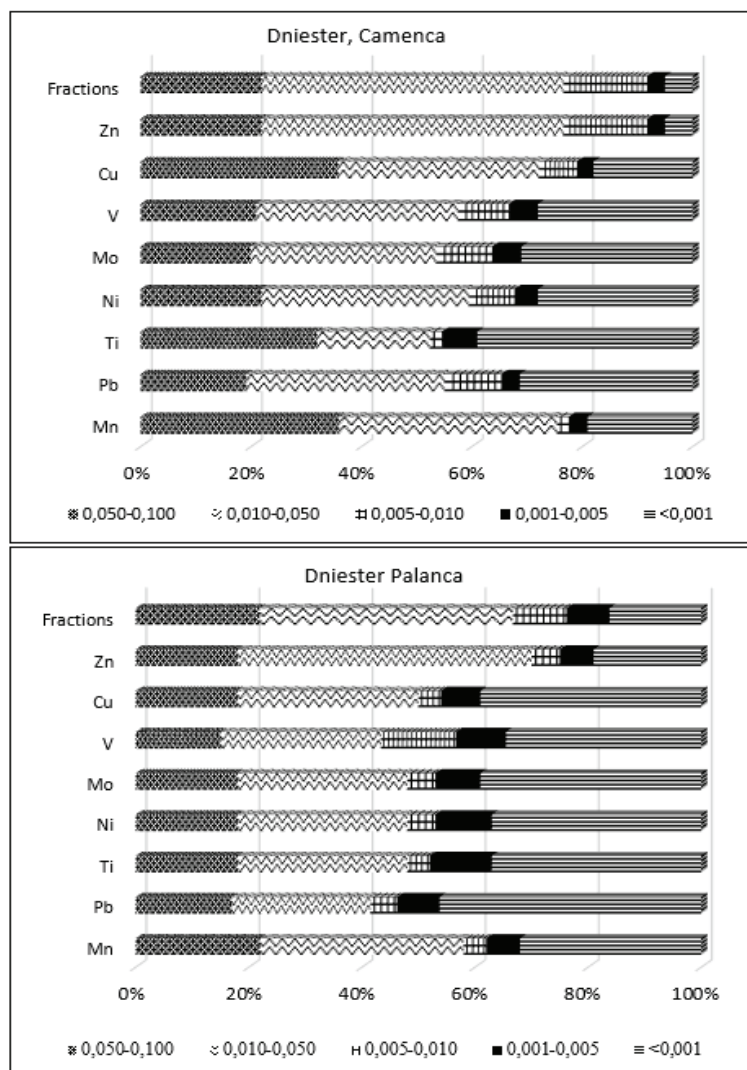


Figure 1. The ratio of metal content in the granulometric fractions of silts from the middle (Camenca) and lower (Palanca) sectors of the Dniester River.

The amount of mobile and accessible forms of metals for hydrobionts is higher in the silts of the middle sector of the Dniester compared to those of the lower sector. A negative correlation was found between the total content of mobile forms of metals and the amount of fine clay particles and that of organic substances ($r = -0.83 \dots -0.92$).

The most mobile component of silts is their aqueous solution, where the concentrations of metals, except for the case of V, is higher compared to those in water layers. The migration of the investigated metals in the “water-silt solution” system, as well as in the “water-silts” system, takes place from top to bottom in running ecosystems. Reverse processes were recorded in the cooling reservoir of the Cuciurgan Thermal Power Plant, where silts represent not a potential, but a real source of secondary pollution with metals, especially in the summer period, when the deficiency of dissolved oxygen occurs and the processes of sulphate-reduction become more intense, with the elimination of hydrogen sulphide (H_2S) in water layers.

The biogenic migration of metals in aquatic ecosystems represents the cycle of metals with the participation of microorganisms, algae (micro- and macro), macrophytes, planktonic invertebrates, benthic invertebrates and fish. The study of biogenic migration of metals is an important aspect of monitoring and assessing the functioning of aquatic ecosystems, which provides scientific support for the sustainable management of aquatic resources and the development of directed aquaculture (ZUBCOV et al., 2016).

Experimental research has been carried out directly *in situ* during the vegetation period regarding the evaluation of the influence of metals (Cu, Zn, Mn, Ni, Mo, V, Pb, Cd) on the primary production of phytoplankton and the bacterial destruction of organic matter. Solutions of metal salts were used in the experiments, therefore, the large majority of metals were in ionic form, which is considered to be the most toxic. However, the presence of suspended substances in water, of organic compounds, probably plays the determining role in the processes of redistribution of metals and reduction of their toxicity. The analysis of the results confirmed that Mo and V in concentrations up to 9-12 $\mu g/L$, Pb and Ni - up to 10-25 $\mu g/L$, Cu, Zn, Mn - up to 20-25 $\mu g/L$ practically do not change values of primary

production and destruction of organic matter. Even more, Zn and Mn concentrations of up to 70 $\mu\text{g/L}$ increase the values of primary production.

Based on the concept of the buffering capacity of aquatic ecosystems, the concentrations of metals indicated above are considered to be ecological or favourable for the functioning of ecosystems. Concentrations of metals that gradually decrease the values of primary production and destruction of organic matter can be characterized as admissible, and water bodies can be assigned to the category of polluted ones. Concentrations that suddenly diminish production-destruction processes or completely block them refer to those critical for aquatic ecosystems and, in the given case, water bodies can be assigned to the category of heavily polluted ones. It should be noted that these concentrations have been shown to be critical for the growth and development of fish larvae.

Aquatic plants are able to accumulate quite high concentrations of metals, which allow their use as monitor organisms. The dynamics of metal accumulation has a seasonal character, as a reflection of the dynamics of metals in the aquatic environment (Fig. 2).

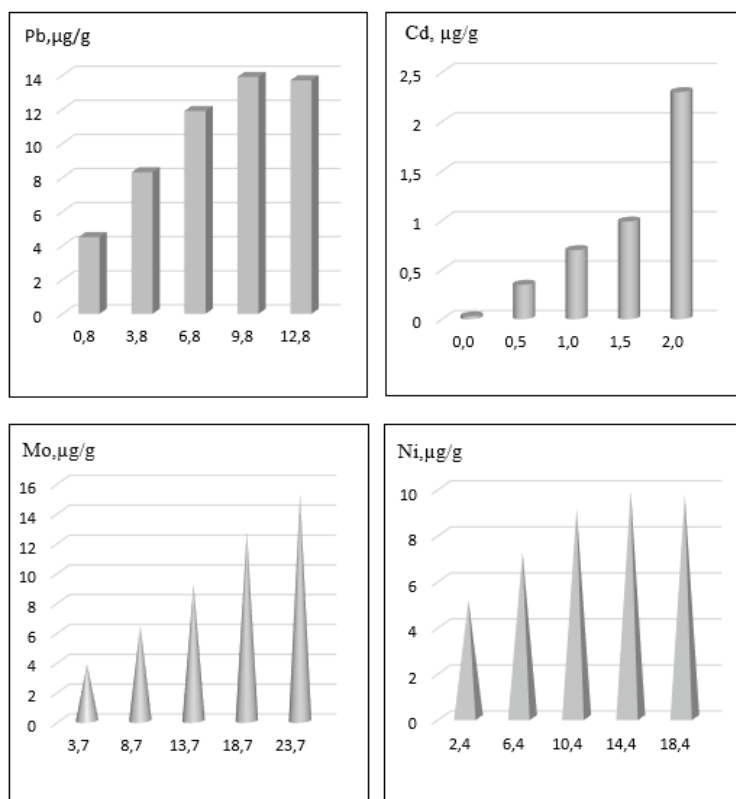


Figure 2. The dependence of the accumulation of metals ($\mu\text{g/g}$) in *Ceratophyllum demersum* on their concentration in water ($\mu\text{g/L}$) in a laboratory experiment.

Similar relationships were obtained for phytoplankton, which opens the possibility of growing green microalgae as a food source for herbivorous fish at early ontogenetic stages with the addition of metals-trace elements.

As plants have a high resistance to toxic concentrations of metals and an intense growth, they serve as biofilters in water self-cleaning processes. At the same time, aquatic plants can be a source of secondary pollution of aquatic ecosystems, thus, they play an enormous role in the migration and circuit of chemical elements in aquatic ecosystems. The use of aquatic plants to assess the level of pollution with heavy metal has a range of advantages compared to direct determination in water. The analysis of the accumulation of microelements in plants also allows solving the problem of their accessibility in water for living organisms in general and, in particular, for microalgae.

An intense coverage of the Middle and Lower Dniester with macrophytes, especially with filamentous algae, which were previously observed only at shallow depths in reservoirs and on some river sectors, was recorded in the last years. Nowadays, they practically cover compactly the most part of the river. Relating to this fact, the knowledge about the accumulation of metals in aquatic plants has a special scientific and practical value.

An important role in solving the problems of biomonitoring metals in the evaluation of the ecological state and, especially, in deciphering the native processes of functioning of aquatic ecosystems belongs to the determination of the level of accumulation of chemical substances in aquatic invertebrates, which have the highest share in the biodiversity of aquatic ecosystems and play the role of intermediate or even final links in the trophic chains. The results of the investigations demonstrated that invertebrates, with some exceptions, are much more sensitive, compared to plants, to metal pollution and form the most diverse ecological links.

The evaluation of the role of zooplankton in the functioning of aquatic ecosystems has proven to be a difficult task. For example, taking a necessary weighed amount of biological sample proved to be difficult; therefore, we investigated the accumulation of metals in *Daphnis sp.* (Crustacea, Cladocera). All investigated species in fact are macroconcentrators of metals in a wide range. Some modelling with daphnia was also carried out *in situ* - in fish ponds and in the ponds for cultivation of live feed of the fish farms located in the lower sector of the Dniester. An obvious correlation ($r=7.5-8.0$) was identified between the content of most of the investigated metals (Zn, Cu, Mn, Mo, Co, Ni, Fe) in the daphnia body and their concentrations in water. For example, one week after the addition of some metal salts in the water of ponds for raising daphnia, the concentration of these metals in the daphnia body increased suddenly (Fig. 3).

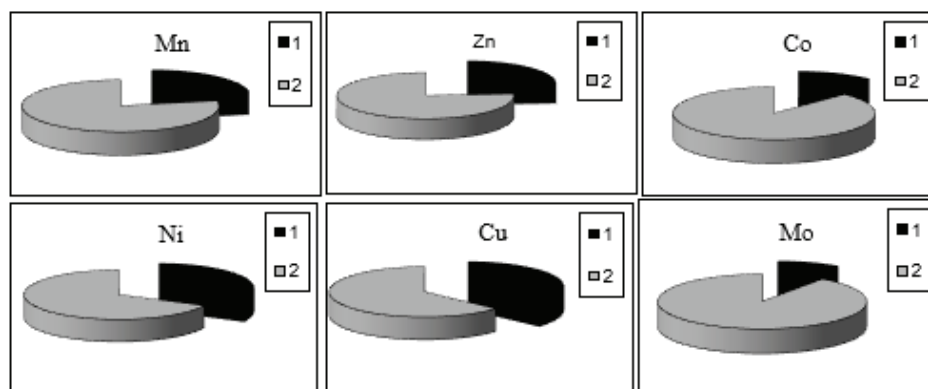


Figure 3. The ratio between the concentrations of metals in *Daphnis sp.* from the ponds for cultivation of live feed for fish before the addition of salts with a determined content of metals (1) and 7 days later (2)

The range of oscillations in the metal concentrations in benthic invertebrates is very large and is conditioned both by the variation in the environmental conditions, the biological importance of the metals, as well as by the taxonomic and age peculiarities of the hydrobionts.

In order to evaluate the influence of the aquatic environment on the level of metal accumulation in molluscs, a series of laboratory experiments was carried out with *Dreissena polymorpha*, *Unio pictorum* and other molluscs. It should be mentioned that the level of accumulation of metals in the shells is in a close correlation with their content in water ($r>0.98$), this correlation being described as quite veridical by the equation of linear dependence. The correlation between the accumulation of metals in soft tissues and their content in water ($r=0.84-0.95$), in most of the cases, corresponds to polynomial equations. It is assumed that the accumulation processes in shells are determined by the intensity of physico-chemical adsorption, but in the soft tissues of the body the accumulation of metals depends more on metabolic processes. On the example of unionid mussels, it was revealed that the content of all metals was minimal in the body and foot muscles; the higher concentrations were recorded in the gills (Mn, Co, Ni, Zn) and mantle (Al, Pb, Ti, Mo, V, Cu, Cd). The content of Co, Mn, Zn, Mo, Cu in mollusc eggs was found to be higher, compared to that in soft tissues, the level of Ni, Ti, Al, V – lower, and of Pb and Cd – close to analytical zero. There may be some regulatory mechanism that protects the developing eggs of animals from the adverse effects of toxic heavy metals.

Accumulation processes in fish are even more complicated, as the content of metals in fish organs and tissues is a function of the composition of the environment (ZUBCOVA, 2011; ZUBCOV et al., 2012; 2016). Mature fish possess a fairly developed homeostatic mechanism, which regulates the processes of accumulation and redistribution of metals between different organs, depending on the plastic and generative metabolism of the fish and the need for one or another metal. The intense processes of accumulation of biologically important metals in the gonads dominate in the period preceding spawning, accompanied by a decrease in their concentrations in the skeletal muscles. In the growth period, an opposite phenomenon is observed. The content of metals in fish eggs and larvae is an accurate reflection of that of metals in water ($r=0.90-0.98$), but it also depends on the metabolic peculiarities of the species. Thus, fish eggs and larvae can be used in the monitoring of aquatic ecosystems and in the investigation of metal toxicity. At the juvenile stage the level of bioconcentration of metals is determined more by the metal content in their nutrition and less by the content in the water (ZUBCOV et al., 2012).

The experiences carried out in the last years showed that the metal tolerance has decreased by 5-10 times in the waters of the Dniester River. This phenomenon is conditioned by the fact that the content of suspended solids in the river water has decreased considerably. Modelling works with the estimation of production-destruction processes, as well as those with eggs, larvae, fish fry and some invertebrates allowed for the observation of antagonistic, synergistic and additive effects at the interaction of different metals. For example, experiences have shown that Mo, V, Ni increase and Mn decreases the toxicity of Cu and Zn. Co and Fe, Cu and Zn demonstrated antagonism, and Cd and Pb manifested as additive toxic metals.

CONCLUSIONS

Solid suspensions and silts of the investigated aquatic ecosystems represent native accumulators of metals, which contents are, in most cases, higher than in the parent rocks and soils of the region. The adsorbed metals, easily soluble metal carbonates and metals from the associations of amorphous hydroxides of Fe and Mn in silts form 56-78% of the mobile and accessible metals for hydrobionts. The dynamics of the total content of metals (in water + in solid suspensions), in silt aqueous solutions, their distribution in the granulometric fractions of silts and the dependence of different forms of metal migration on the amount of dispersed clay particles and that of organic substances are established ($r=0.78-0.99$). The migration of metals in the “water- suspensions-silts” system takes place from top to bottom, except for some isolated cases, as that of the cooling reservoir of the Cuciurgan Thermal Power Plant, where the reverse phenomenon is observed.

The building of hydrotechnical constructions and the operation of hydropower plants changed the ratio between the dissolved and suspended forms of metal migration; the concentrations of suspended forms downstream the dams of the Dniester Hydropower Complex have reduced drastically – by tens of times. There is no longer any correlation with the hydrological parameters – the water flow and the amount of suspensions – in the Middle and Lower Dniester.

Aquatic plants are macro-accumulators of metals and can be used in their biomonitoring, as well as biofilters for the treatment of wastewater and surface runoff. However, they can also become sources of secondary pollution with metals. The accumulation of microelements in aquatic plants is determined by their dynamics in water, silts and has a seasonal character.

The dynamics and mechanism of metal accumulation by the dominant species of aquatic invertebrates are evaluated and the functional dependence of the level of metal accumulation in invertebrates on the dynamics of metals in the aquatic environment is established. In mollusc shells, the accumulation of metals depends more on sorption processes, but in soft tissues it also depends on the metabolic processes of these aquatic invertebrates.

Data on the quantitative parameters of the algal and invertebrate communities together with those on the level of metals allow to determine the contribution of the main groups of hydrobionts to the biogenic migration and cycle of metals in aquatic ecosystems.

The processes of metal accumulation in the organs and tissues of fish starting from the stages of early ontogenesis up to sexually mature fish have a rather complicated and diverse nature, conditioned by the complex of environmental factors and the physiological-biochemical status of the organisms.

The results of multiannual field and experimental research served as the basis for specifying the impact of metals on production-destruction processes, the growth and development of fish, for determining the buffer capacity of aquatic ecosystems and water quality.

ACKNOWLEDGEMENT

The research was carried out in the framework of the national project no. 20.80009.7007.06 AQUABIO (the State Programme 2020-2023), and international projects BSB27 Monitox and BSB165 HydroEcoNex (Joint Operational Programme Black Sea Basin 2014-2020, financed by the European Union).

REFERENCES

- CIORNEA V., ZUBCOV ELENA, BAGRIN NINA, CIORBA P., ENE ANTOANETA, ZUBCOV NATALIA. 2021. Inductively coupled plasma atomic emission spectrometry (ICP-OES) for environmental analysis. In: *High-performance analytical techniques for the monitoring of toxicants in environment*. (Ed. A. Ene). Edit. Casa Cărții de Știință. Cluj-Napoca: 37-44.
- DEMINA LIUDMILA L., GORDEEV V. V., GALKIN S. V., KRAVCHISHINA MARINA D., ALEKSANKINA SVETLANA P. 2010 The biogeochemistry of some heavy metals and metalloids in the Ob River estuary – Kara Sea section. *Oceanology*. Springer. Moskva. **50**(5): 771-784 [in Russian].
- GHEORGHE ȘTEFANIA, STOICA CATALINA, VASILE GABRIELA GEANINA, NIȚĂ-LAZĂR M., STĂNESCU ELENA, LUCACIU IRINA EUGENIA. 2017. Metals toxic effects in aquatic ecosystems: modulators of water quality. In: *Water quality*. (Ed. H. Tutu). InTech. <http://dx.doi.org/10.5772/65744> (accessed April 9, 2023).
- ZUBCOV ELENA, ZUBCOV NATALIA, ENE ANTOANETA, BILEȚCHI LUCIA. 2012. Assessment of copper and zinc levels in fish from freshwater ecosystems of Moldova. *Environmental Science and Pollution Research*. Springer. Berlin. **19**(6): 2238-2247. <https://doi.org/10.1007/s11356-011-0728-5> (accessed April 3, 2023).
- ZUBCOV ELENA, BILEȚCHI LUCIA, ZUBCOV NATALIA, PHILIPENKO ELENA, BORODIN NATALIA. 2013. The metal accumulation in aquatic plants of Dubăsari and Cuciurgan reservoirs. *Oltenia. Studii și comunicări. Științele Naturii*. Muzeul Olteniei Craiova. **29**(2): 216-219.
- ZUBCOV ELENA, TODERAȘ I., ZUBCOV NATALIA, BILEȚCHI LUCIA. 2016. Repartizarea, migrația și rolul microelementelor în apele de suprafață. In: *Microelementele în componentele biosferei și aplicarea lor în agricultură și medicină*. (Coord. S. Toma). Edit. Pontos. Chișinău: 78-107.

- ZUBCOVA NATALIA N. 2011. *Patterns of accumulation and the role of microelements in fish ontogenesis*. Edit. Știința. Chișinău. 88 pp. [in Russian].
- ***. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (OJ L 327, 22.12.2000, p. 1). Available at: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02000L0060-20141120&from=EN> (accessed: April 10, 2023).
- ***. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (OJ L 348, 24.12.2008, p. 84). Available at: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02008L0105-20130913&from=EN> (accessed: April 10, 2023).
- ***. *Ecotoxicological methodological guide for environmental monitoring: problematics, laboratory techniques and health risk investigation*. 2021. (Eds. E. Zubcov & A. Ene). S. n. Chișinău. 112 pp.
- ***. *Methodological guide for monitoring the hydropower impact on transboundary river ecosystems*. 2021. (Eds. E. Zubcov & L. Bilețchi). Chișinău. 80 pp.
- ***. UNEP. 2013. Minamata Convention on Mercury: 30. Available online at: <https://www.unep.org/resources/report/minamata-convention-mercury> (accessed: April 13, 2023).

Zubcov Elena, Zubcov Natalia, Bagrin Nina, Bilețchi Lucia, Ungureanu Laurenția, Ciornea Victor, Ciorba Petru
Moldova State University, Institute of Zoology, 1, Academiei Str., Chișinău, Republic of Moldova.
E-mails: ecotox@yahoo.com; natzubcov@mail.ru; nina.bagrin327@gmail.com; lucia_biletski@yahoo.com;
ungur02laura@yahoo.com; victor.ciornea@gmail.com; petrucio1992@gmail.com

Ene Antoaneta

“Dunărea de Jos” University of Galați, Romania.
E-mail: antoaneta.ene@ugal.ro

Spanos Thomas

International Hellenic University (IHU), Kavala, Greece.
E-mail: tspanos@chem.ihu.gr

Received: April 14, 2023
Accepted: August 10, 2023