THE DYNAMICS OF TRACE ELEMENTS IN DNIESTER RIVER ECOSYSTEMS

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Abstract. *The goal of this research was to investigate the dynamics of trace metals (Cu, Zn, Mn, Co, Ni, Mo, V, Pb, Cd etc) in water, sediments, and the accumulation in the plants, invertebrates and organs and tissue of Cyprinidae and Percidae fish from Dniester river ecosystems. The interrelationships of abiotic and biotic factors and the effects of impaired water quality on biota were studied. The use of fertilizers and pesticides for agricultural purposes affects directly the dynamics of Cu, Zn, Mn in aquatic systems (r=0.70-0.92), and the pollution is intensified by the dismembered relief, the peculiarities of rainfall and intensive erosion processes. All these led to a continuing increase in trace element content downstream the rivers. The discharged wastewaters from industry contribute to freshwater pollution with Ni, Zn, Cu, Ag and Cd (r=0.73) and change the ratio of dissolved and suspended forms of trace elements, this being characteristic especially for Chisinau, Bender, Tiraspol, Soroca, during low water period. The zone of confluence of Dniester river with its tributaries – Raut Bic were observed increase the concentration of trace metals (Ni, Pb, Zn, Cd, Cu, Ag, Sn). The building of hydrotechnical constructions on the Dniester river led to changes in the ratio of dissolved and suspended forms of trace elements and migration of trace elements in the systems: water- suspended matter-sediments-hydrobionts. The aquatic plants and the species of aquatic invertebrates are metal macro-concentrators, and can be used as effective biomonitor organisms in monitoring programs, water filtrators, but also can be secondary sources in water pollution. The maximum concentrations were observed in the aquatic plants, the species of aquatic invertebrates and fish from Cuciurgan reservoir, the minimum were observed in Dubasari reservoir. Water sediments are the most stable compounds of freshwater ecosystems. The concentration of Zn, Cu, Pb, Ni, Mo and V in water sediments was 2-7 times higher than in the soil. The maximum concentration of trace elements in water sediments were found in Cuciurgan reservoir, while the minimal - in Dniester River. A direct dependence of the content of trace elements in silt on clay particles with a diameter smaller than 0.01 mm was found (r=0.86-0.97).*

Keywords: *trace elements, biomonitors, Dniester River, Moldova*

1. INTRODUCTION

The research on trace elements migration is considered to be today one of the topical interest in modern hydrobiology, ecology and hydrochemistry and has a great theoretical and practical significance. The development of the theory on freshwater ecosystem functioning is impossible without a proper understanding of the processes of chemical element migration.

Trace elements play an important biochemical role in functioning of freshwater ecosystems, their role being compared to that of catalyses in chemical reactions. The environmental pollution in the last years has stimulated a lot of ecotoxicological research directed to establish the biological role of trace elements for hydrobionts and assess the mankind impact of the dynamics of trace element content in freshwater ecosystems. Of special importance is research carried out on biological monitoring - a complex system of investigation, estimation and prediction of freshwater ecosystem status and on the evaluation of the hydrobionts role in migration and circulation of chemical elements.

The above mentioned directions of study are very important for Moldova, where there is a scarcity in good quality water and a continuous increase in mankind impact on the environment. Besides this, the main aquatic artery - Dniester River - has a transboundary position, flowing from Ukraine and passing along Ukraine and Moldova.

On Dniester river dams were built and the main industrial centers of the above-mentioned countries were concentrated here and thus water quality depends on human impact in these regions as well as on applying the environmental protective methods. The elaboration of regulations and protective methods for improving water quality should be based on scientific achievements and knowledge on processes of migration and distribution of chemical elements occurring in freshwater ecosystems.

2. MATERIALS AND METHODS

The research was carried out during 1996-2009. Samples of water, suspended materials, wares sediments, plants, invertebrates and fish were taken from Dniester river as well as from Dubasari reservoir. Trace elements were extracted according to Zolotov and Kuzmin [6]. Trace elements contents of the digest were determined by atomic absorption spectrophotometer AAS Analyst-400, flame atomic absorption spectrophotometer AA-S3 and X-rays fluorescence scanning spectrophotometer Spectroscan-5. Minerals were quantified on the basis of peak areas and comparison with a calibration curve obtained with the corresponding standards [2-4, 6, 10].

3. RESULTS AND DISCUSSION

Among the main factors which determine the distribution and migration of trace elements within the system "water-suspended matter-sediments" of the surface waters of Moldova are the dismemberment of relief, the amount of rainfall, the physico-chemical characteristics of rocks, soil and water as well as the hydrology and status of aquatic fauna and the chemical characteristics of trace elements themselves. Significant effects have also the human activities such as hydrotechnical constructions, the chemization and irrigation of agricultural lands and wastewater discharge. The level of Ti and Pb, as well as that of Cu, Zn, Mn, Ni, Mo and Ag in bed rocks of Moldova, is lower than the Clark value. The soils are enhanced in Cu, Zn, Pb, Mo and Ag [1].

The dynamics of ***aluminum, titan and cobalt*** in surface waters of Moldova is highly influenced by natural factors. The major of Al, Ti, Co input in aquatic ecosystems originates from mountainous rocks and soils. Over 95% of Ti and Al migrate into the waters in suspended forms. In less than 5% -10% of samples Ti and Al exceeded 5 μg/l. During the high flooding period Al and Ti content was higher than during low water period. The dependence of Al and Ti levels on water debit (Q) and the amount of suspended matter in the water (S) was described by the equations for Dniester river:

$$Al=0.012*Q + 0.023*S - 0.8, \quad R=0.84;$$

$$Ti = 0.029*Q + 0.018*S - 1.1, \quad R=0.89.$$

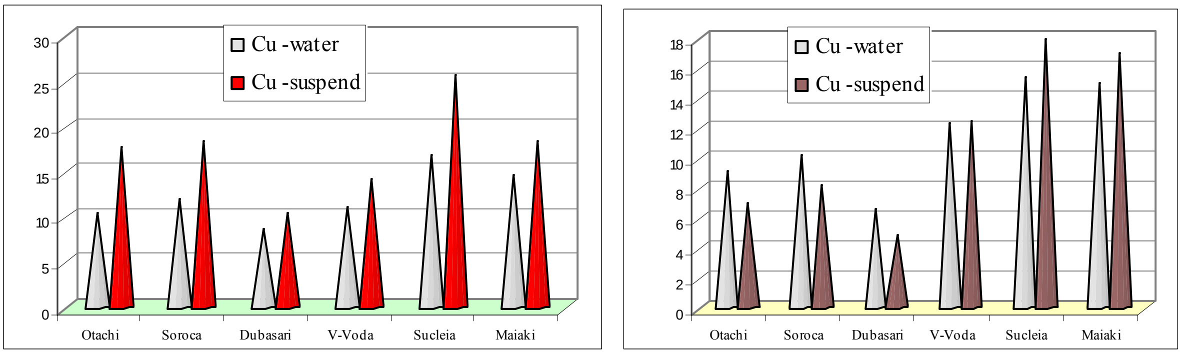
Zinc and ***copper*** content in water varies respectively greatly between 5-165 μg/l and 0.2 to 28.6 μg/l , and in suspended matter - between 11 and 220 μg/l and 2,0 to 270 μg/l. During high flooding period (spring) Zn and Cu content is higher than during low water period (summer-autumn). The dependence of Zn, Cu in water on the amount pesticides used in agriculture (Z, V tone), the volume of wastewater discharged in hydrographic network (R, mln m^3/yr) and water debit (Q) were described by the following regression equations:

$$Zn= 0.0897*Z + 0.007*R + 0.370*Q, \quad R=0.99;$$

$$Cu=0.00210*V+ 0.02*Q + 0.068*W - 28.9, \quad R=0.98.$$

The contribution of anthropogenic factors in the dynamics of Zn and Cu in water ecosystems of Moldova were 46 -78%. The building of hydrotechnical constructions on the rivers, lead to changes in the ratio of dissolved and suspended forms of trace elements. The concentration of suspended forms decreased with 20-70% downstream to the dams and in storage reservoirs the intensification of sedimentation processes occurred (Fig. 1).

The concentration of ***nickel*** in Moldova's waters varies within wide ranges (Fig.2). The highest Ni content (about 250 μg/l) was registered in river's tributaries, while the lowest (0.5 μg/l) in the storage reservoirs.



1981-1983 *2002-2004*

Fig. 1. The change of Cu in water and suspended of Dniester river before (1981-1983) and after (2002-2004) Dniestrovsk hydropower construction.

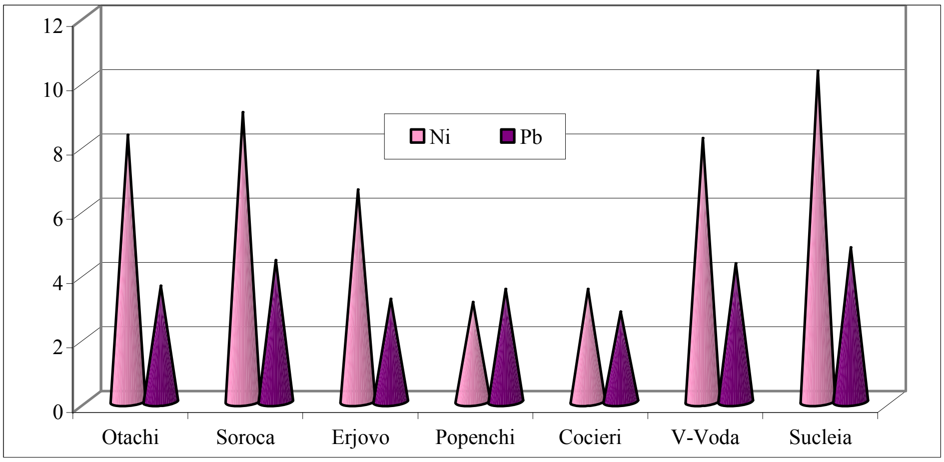


Fig. 2. The dynamics of Ni and Pb in water of Dniester river and Dubasari reservoir (Erjovo-Cocieri), μg/l.

The seasonal dynamics of Ni was not very well expressed, but a difference of this metal during high flooding periods and lower water periods was observed. The dependence of Ni content on water debit (Q), the amount of raw wastewater (R) and the amount of suspended matter (S) were described by the equations:

$$Ni=1.6-0.001 * Q + 0.080 * R + 0.021 * S \qquad R=0.90$$

The concentration of Ni in suspended matter from Dniester rivers was 5-14 times higher than in the soils of its hydrological basin [1, 8].

The concentration of ***lead*** in Dniester River (1.8-5.6 μg/l) is relatively low and only in 15 % of cases exceeds 5 μg/l. In suspended mater the Pb content fluctuates within wider limits: between 0.5 and 17 μg/l. The content of lead in water of Dniester river and Dubasari reservoir decreased (the highest concentrations were estimated after 1986, the increasing in Pb content being assumed to be due to the Chernobyl accident, when high Pb concentrations were found on the entire territory of Moldova [8]. Lead content in rivers, reservoir suspensions was 10-23 times higher than in bed rocks and soils.

The content of ***cadmium*** in water varies between 0.25 and 4.65 μg/l and in suspended matter- between 0.25 and 3.85 μg/l. In Dniester river, the highest Cd concentrations were found near Bender and Tiraspol towns. Very high concentration of Cd – 24.6 μg/l - was found in Byc river (tributary of Dniester river, near Chishinau), this level being 6-8 times higher than outside of the city [7,8]. The content of ***silver*** in 80% of samples varied between 0.1 and 1.0 μg/l. High concentrations of Ag (5 μg/l) were found only in 6 samples collected from Dniester river. The highest Ag concentration was found during low water period. The quota of suspended forms of Ag exceeded those of dissolved forms (57-77).

Thus, it could be pointed out that the dynamics of trace elements in water is a function of climatic and physico-geographical patterns of the basin and the impact of mankind activities. Although the building of hydrotechnical constructions led to significant changes in hydrological regimes of Prut and Dniester rivers, the mobility of trace elements is very much affected by water turbulence and water debit (r=0.77-0.97). Water sediments are the most stable compounds of freshwater ecosystems. The concentration of Zn, Cu, Pb, Ni, Mo and V in water sediments was 2-7 times higher than in the soil. A direct dependence of the content of trace elements in silt on clay particles with a diameter smaller than 0.01 mm was found (r=0.86-0.97) [4, 8].

The range of oscillations in trace element distribution within the granulometric fractions depends on the granulometric composition of subaquatic depositions [7, 8]. A negative correlation between the total amount of the mobile forms of trace elements and the quantity of clay particles and organic matter was found (r>0.7).

The most dynamic component of aquatic sediments is the silt solution. The concentration of all trace elements, with the exception of vanadium, was higher in silt solution than in bottom water fractions. The migration of trace elements within the system "bottom water-silt solution" was similar to that within the system "water - water sediments". The range of trace element content in plants widely varies (Table 1), the lowest values being found for samples collected from Dubasari reservoir, while the highest – in those collected from the Dniester river (Bender and Tiraspol stations).

Presently, the level of Zn, Cu, Mn, Pb and Ni content in plants collected from Dniester river and Dubasari reservoir in more than 80% of samples was 15-60% lower than before 1991 period [4,5,8]. Such aquatic plants can be successfully used as biomonitor organisms in assessing the level of trace element pollution of aquatic ecosystems (Fig. 3).

Table 1.The range of oscillations in trace element in plants from Dubasari and Dniester River, μg/g of wet weight

	Mn	Pb	Al	Ti	Ni	Mo	V	Cu	Zn
Phragmites australis									
min-max	36.2-160	0.3-4.2	3.1-180	2.2-9.1	2.2-12.2	0.5-2.7	0.7-7.1	2.7-12.3	6.9-20.4
Potamogeton perfoliatus									
min-max	32-252	2.9-6.8	4.4-88.8	2.4-13.4	5.5-19.2	0.7-5.7	0.8-7.9	3.3-26.9	17.0 41.1
Ceratophyllum demersum									
min-max	22-256	2.8-9.4	1.9-93.9	2.2-21.2	4.2-26.7	0.4-2.2	0.5-4.4	3.7-28.4	9.2-31.5

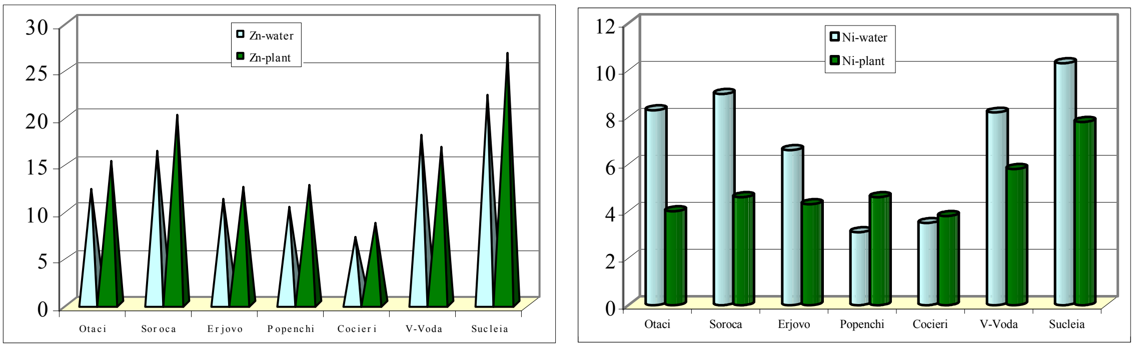


Fig. 3. The dynamics of Zn and Ni content in water (μg/l) and plants (μg/g) in Dniester river and Dubasari reservoir (Erjovo-Cocieri).

Aquatic animals play an important role in freshwater ecosystems because they represent an intermediary step in transferring the trace elements into the food chains and they are more sensible to water pollution than the plants and form many ecological complex links. Besides these, the animals can move within the water system and thus being able to reflect the status of their living environment.

The range of trace element content in Daphnis sp. (Crustacea, Cladocera) varied widely: for Mn – 99.4- 189 μg/g, Pb- 4.7-22.4 μg/g, Al - 80-980 μg/g, Ti – 12.5-58.8 μg/g, Ni- 28.5-93 μg/g, Mo – 1.3 -7.7 μg/g, V – 2.8-6.5 μg/g, Cu – 8.4-56 μg/g and that of Zn – 8.1-34 μg/g of dry weight. A direct dependence between the metal content in the Daphnis body and that in the water was observed. The range of content oscillation in benthic invertebrates of freshwater ecosystems varies greatly and is conditioned by the variation of natural factors, biological role of trace elements as well as by taxonomical and age characteristics of hydrobionts. The maximal values of trace elements in benthic invertebrates was found in cooling reservoir Cuciurgan, whereas the minimal - in dam reservoirs Dubasari and Costesti-Stinca (Fig. 4).

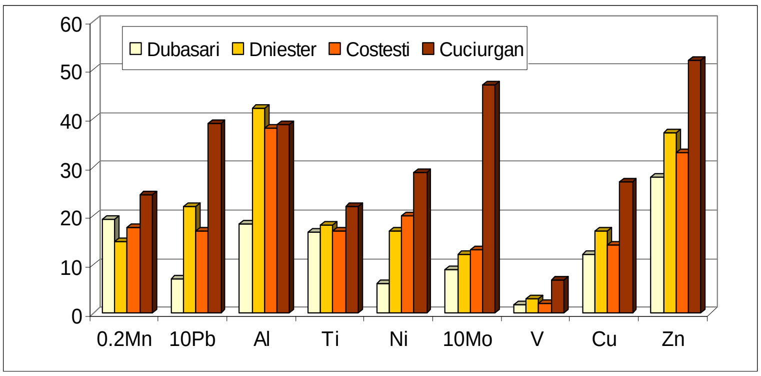


Fig. 4. Trace element content in *Lithoglyphus naticoides* collected in Dniester river and Dubasari, Costesti and Cuciurgan reservoirs of Moldova, μg/g of dry weight.

The level of trace element accumulation in benthic species was quite high in highly polluted environments. The concentration of Pb, Ni, Cu, Zn, Cd and Ag in samples collected from Byc river, within Chisinau was 3-8 and 2-4.5 times higher than in the surroundings, thus reflecting a high level of pollution of trace elements in sediment silt (r>0.87).

Experimental research on *Dreissena polymorpha* showed a functional dependence between metal accumulation and metal content in water. The metal content in shells was highly correlated with that in the water (r>0.98), while for soft tissue, the correlation values were r=0.84-0.98. Most probably that the physico-chemical processes from the shells prevail over biological, while the content of metals in the soft tissue is strictly regulated by the biological needs of the organism and thus reflects a well-developed homeostasis in mollusks [8].

The accumulation patterns of trace elements in tissue and organs of mature fish are very diverse and complex and are influenced by environmental factors and physiological and biochemical status of the organisms themselves. The content of trace elements was significantly high in the organs which have a direct contact with the water (i.e. the skin, the scales, the gills and the fins) and this was influenced by element content in water and sediment silt (r>0.68). High Zn content was found in muscles and those of Pb, Cd, V and Ti – in gonads [9, 10].

A continuous change in trace element content along the whole life cycle of fish was observed. For example, during intense feeding, accumulation of Fe, Cu, Zn and Mn have taken place before spawn period increasing in the content of Fe, Zn, Co, Cu and Mo occurred in gonads, and this was accompanied by decreasing in the content of these elements in muscles. After being incorporated in the fish body, the trace metals undergo a process of distribution among different organs, this depending upon the biological needs of the animals. In the most cases, the highest concentration of Pb, Mo, V, Cu, Ni and Cd was found in the liver, of Mn, Al and Zn – in gonads, whereas the lowest Mn, Al, Ni, Mo, Cu [10].

The level of the majority of metals in fish tissue and organs collected from Byc river was significantly higher than in those collected from Dubasari reservoir and Dniester river. Therefore, there is no doubt that dependence exists between the trace element accumulation level in fish and the content of metals in water, despite the homeostatic mechanisms which are well-developed in fish.

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