METAL ACCUMULATION IN AQUATIC PLANTS OF DUBĂSARI AND CUCIURGAN RESERVOIRS

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Abstract. Aquatic plants are one of the main components of biota of water bodies and streams, which holds an important role in the migration process and circuit of the chemical elements. Aquatic plants are able to accumulate enough large quantities of metals, which allow their use as biomonitor. The contents of many metals in aquatic plants are highly correlated with their contents in reservoir water and silt: r = 0.87-0.91. The dynamics of trace element accumulation depends on seasonal factors. From the beginning of spring to the end of summer and beginning of autumn, the concentrations of trace elements increased by large increments, while in autumn, with the decrease of water temperature below 10^{o}C, an opposite effect was observed. After plant death, a significant part of accumulated trace elements are released into the water, in most cases this being associated with organic compounds. More than one half of the amount of trace elements is deposited in the bottom sediments.

Keywords: heavy metals, aquatic plants, biomonitor, migration, accumulation.

Rezumat. Acumularea metalelor în plantele acvatice din lacurile de acumulare Dubăsari şi Cuciurgan. Plantele acvatice constituie unul dintre componentele de bază ale biotei bazinelor şi cursurilor de apă, care deţin un rol important în procesul migraţiei şi circuitul elementelor chimice. Plantele acvatice sunt capabile de a acumula cantităţi destul de mari de metale, ceea ce permite întrebuinţarea lor în calitate de organisme-monitoare. Conţinutul multor metale în plantele acvatice se corelează evident cu conţinutul de metale în apele şi mâlurile lacurilor de acumulare investigate: r = 0,87-0,91. Dinamica acumulării microelementelor poartă un caracter sezonier. Din primăvară până la sfârşit de vară - început de toamnă concentraţiile microelementelor cresc în salturi mari, pe când toamna, la scăderea temperaturii apei sub 10°C, este observat fenomenul invers. După pieirea plantelor, o parte semnificativă a microelementelor acumulate pătrund în apă, de cele mai multe ori ele fiind asociate cu compuşii organici. Peste jumătate din întreaga cantitate a microelementelor este depozitată în depunerile subacvatice.

Cuvinte cheie: metale grele, plante acvatice, organism - biomonitor, migraţie, acumulare.

INTRODUCTION

In the development of the fundamental principles of the trace element migration in aquatic ecosystems and, in general, of the theory of chemical composition of natural waters, a particular importance belongs to detailed researches of their accumulation in aquatic plants and animals in dependence of the physical-geographical, biological and anthropogenic factors. The accumulation of metals in plants is one of the most important indices in the biomonitoring of metals in aquatic ecosystems. Aquatic plants are of great importance in the production balance of the water bodies. They form the main part of the primary organic matter-material and energetic basis for the existence of aquatic and semi-aquatic animals, have a strong significance in the environment establishment, change the regime of gases and pH of water, define the local hydrodynamic environment, are engaged in the exchange of macro- and trace elements and transformation of bottom sediments, etc.

In connection with the fact that they possess a high resistance to toxic concentrations of metals (BURDIN & ZOLOTUHINA, 1998) and have an intense growth, they serve as biofilters in the water self-purification processes (CARDWELL et al., 2002; KAMAL et al., 2004). At the same time, aquatic plants may be a source of secondary contamination of water bodies and streams, thus they play a huge role in the migration process and circuit of chemical elements in aquatic ecosystems (BASILE et al., 2012; SLOBODANKA et al., 2008; STANKOVIĆ et al., 2000). Dubăsari reservoir was built on the Dniester River aiming to ensure the operation of Dubăsari Hydropower Plant, which was commissioned in 1954. Cuciurgan reservoir refers to the highly thermophicated cooling reservoirs of thermal power plants, which started to be exploited in 1964 by using fossil fuel. The modification of water temperature led to the changes in hydrochemical regime of water body and determined the peculiarities of its biota. The comparison between metal accumulation in biota components from these two reservoirs are of highly scientific interest, due to the different human impact on their ecosystems.

MATERIALS AND METHODS

Systematic researches on the metal dynamics (Mn, Pb, Al, Ti Ni, Mo, V, Cu, Zn) in aquatic plants from the water bodies of Moldova have been carried out during the last 20 years. Plant samples (*Phragmites australis*, *Typha latifolia*, *Potamogeton pectinatus*, *P. perfoliatus*, *P. crispus*, *Ceratophyllum demersum*, *Myriophyllum spicatum*, *Lemna minor*, *Hydrocharis morsus-ranae*, *Cladofora* sp., *Enteromorpha* sp., *Najada marina)* have been collected mainly during the vegetation period, but in some cases also in winter. Concentrations of metals were determined by direct absorption in air–acetylene flame using an atomic absorption spectrophotometer (AAS-3 "Carl Zeiss", Germany) as described elsewhere (SAPOZHNIKOVA et al., 2005). Last three years metals were determined by using a Perkin-Elmer atomic absorption spectrophotometer AAnalist 400 with the HGA 900 graphite furnace (ZUBCOV et al., 2012).

RESULTS AND DISCUSSION

Using aquatic plants in order to assess the level of pollution of the water bodies with heavy metals (according to their content in plant tissues) has a range of advantages in comparison with metal direct determination in water. The plant ability to concentrate metals offer the possibility to reduce considerably the volume of analysed samples, to get an integral picture of the average content of trace elements in a specific period of time, during which the amount of metals in the water can highly oscillate. The analysis of trace element accumulation in plants, also, allows solving the problem of their availability in water environment for living organisms, in general.

An intense coverage with aquatic plants both of Dubăsari and Cuciurgan reservoirs and the Dniester River, especially with filamentous algae, has been registered during last years, this phenomenon being previously seen only at small depths in reservoirs and some river sectors. Currently, they practically cover compactly the main part of the bottom of the reservoir and river. Correspondingly, the knowledge on the accumulation of trace metals in aquatic plants is of great scientific and practical value. The researches on the dynamics of trace metal contents (Mn, Pb, Al, Ti Ni, Mo, V, Cu, Zn, Ag, Co, Cd) in aquatic plants in water bodies and streams of Moldova have been carried out during tens of years by Moldovan researchers. The diapason of oscillations of metal concentration in the investigated aquatic plants from Dubăsari and Cuciurgan reservoirs is quite large (Table 1) and it is determined by plant taxonomic peculiarities, the metal content in water and bottom sediments, chemical properties and biological role of trace elements and, also, by season.

Table. 1. Range of variation of metal concentrations in aquatic plants from Dubăsari (D) and Cuciurgan (C) reservoirs, (min-max µg/g abs. dry mass).

	Mn	Pb	Al	Ti	Ni	Mo	V	Cu	Zn
				Phragmites australis					
D	82.2-280	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
C	78.2-580	0.7-15.8	23.0-288	2.7-23.2	6.2-27.2	1.0-12.7	1.7-17.9	3.7-28.1	7.9-87.6
				Typha latifolia					
D	160-220	1.7-9.9	3.4-87.9	1.8-12.4	3.2-18.1	1.0-7.1	1.1-8.9	2.4-22.7	8.1-18.2
C	155-420	2.8-17.2	21.2-299	7.9-23.4	5.4-25.7	2.0-9.9	2.7-16.7	4.8-34.1	11.9-78.9
				Potamogeton pectinatus					
D	140-342	3.0-8.9	5,4-112	3.0-18.5	4.3-22.9	0.3-4.3	0.6-6.6	4.9-23.1	12.2-34.5
C	220-402	4.7-18.7	38,9-321	11.3-26.9	7.3-39.4	2.1-21.8	3.8-18.7	14.7-38.1	22.9-163
				P. perfoliatus					
D	132-352	1.9-6.8	4.4-88.8	2,4-13,4	3.5-19.2	0.7-5.7	0.8-7.9	3.3-26.9	17.0-41.1
C	122-382	3.2-14.8	47.7-203	23,7-25,2	6.6-26.7	1.9-17.8	6.4-14.9	17.4-38.9	38.8-141
				P. crispus					
D	155-320	2,0-9,9	2.3-67.4	2.0-11.1	3,2-17,8	0.3-1.9	0.6-5.8	2.9-18.0	7.9-28.7
C	175-438	3,2-14,8	47.7-203	9.7-25.2	6,6-26,7	1.9-17.8	6.4-14.9	17.4-36.7	38.8-134
				Ceratophyllum demersum					
D	122-456	1.8-9.4	1.9-93.9	2.2-21.2	3.2-26.7	0.4-2.2	0.5-4.4	3.7-28.4	9.2-31.5
C	284-565	3.9-17.2	82.9-234	9.8-21.6	7.8-37.9	2.8-14.9	5.6-15.7	15.9-38.3	47.8-109
				Myriophyllum spicatum					
D	100-231	1.8-8.7	1.9-32.9	1.9-12.9	3,3-18,3	0.3-4.2	0.8-6.1	4.4-22..9	6.9-22.7
C	166-421	2.8-9.9	49.9-99.9	22.2-41.3	34,2-86,7	3.4-12.2	5.4-9.5	38.2-66.7	87-315
				Lemna minor					
D	180-560	1.2-8.7	3.9-29.9	2.8-21.6	4.8-23.6	0.6-34	0.7-9.2	5.2-42.9	7.8-39.1
C	240-588	2.3-13.2	23.9-43.7	12.7-41.4	17.8-68.3	2.4-18.5	4.9-11.3	18.9-62.5	41.5-193
				Hydrocharis morsus-ranae					
D	100-340	1.5-7.7	2.2-43.2	1.7-13.9	3.4-14.9	0.3-2.1	0.4-4.3	3.1-21.1	7.2-18.8
C	155-434	2.9-14.2	33.9-86.9	8.8-26.2	34.8-59.6	9.6-23.7	30.1-39.9	25.7-54.6	49.8-178
				C*ladofora, Enteromopha*					
D	190-544	2.8-12.6	10.2-233	12.9-24.9	8.4-32.2	1.9-7.8	1.1-7.7	9.9-33.8	10.454.6
C	290-844	3.2-22.2	39.2-250	22.2-59.7	22.4-63.7	3.9-33.8	2.9-37.2	24.3-60.4	48.4-189
				Najada marina					
D	14-227	1.2-9.9	11.2-23.7	3.5-9.2	8.3-24.3	1.2-4.9	1.6-5.7	8.2-88	25.2-127
C	149-497	2.9-13.7	28.9-47.9	11.7-21.9	23.8-34.9	4.9-8.9	5.0-10.3	28.2-124	87.2-173

The content of investigated trace elements is the lowest in the plants of Dubăsari reservoir and the highest- of Cuciurgan cooling lake, and there is an evident correlation with the dynamics of metal content in water, suspended matters and bottom sediments.

The comparison of the dynamics of metal accumulation in aquatic plants of Dubăsari reservoir in recent years with that until 1991 testifies the content of certain metals, such as zinc, copper, manganese, lead and nickel, in over 80% of cases is 15-60% lower than that of previous years. This phenomenon is related to the decline of industry in the country and as a consequence, the reduction in the volume of waste waters discharged from the urbanized territories and agricultural lands.

Multiannual dynamics of metal accumulation in aquatic plants of Cuciurgan cooling lake revealed that, as a normal rule, it is a reflection of the dynamics of metal content in water and bottom sediments and largely determined by the operation of power plant. Thus, the content of lead, molybdenum, vanadium, zinc and other metals in the plants from the reservoir grew continuously, concomitant with the enhancement of the power plant capacity, and reached the highest values in 1986-1990, when the influence of the thermal power plant operation on the reservoir ecosystem was the highest. Concentrations of most metals in aquatic plants and, in particular, in submerse vegetation have decreased obviously during 1991-1997. At the same time, the level of nickel accumulation had in time a trend of permanent increase, this being characteristic also for the nickel concentration in the reservoir water (Fig. 1).

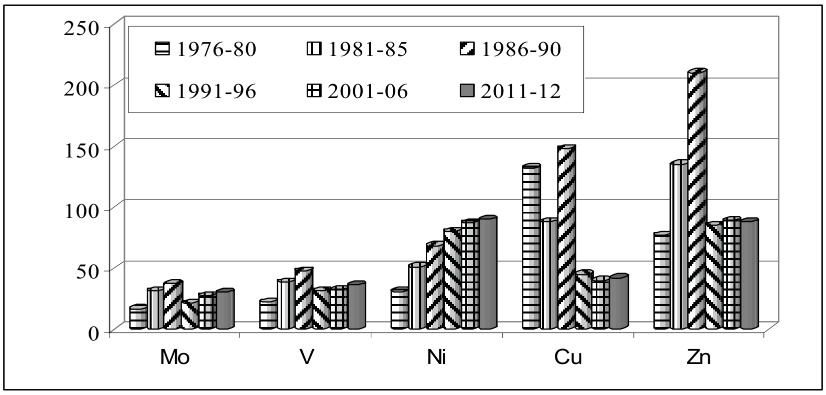

Figure 1. Dynamics of trace element content in filamentous algae (*Cladofora* sp., *Enteromorpha* sp.) in Cuciurgan reservoir in 1976-2012, µg/g abs. dry mass.

High concentrations of copper, which were revealed in 1976-1980, can be explained by the fact that until 1980, as a method of fighting the algae blooming, the introduction of blue vitriol (pentahydrate copper sulphate) and other copper preparatus in the water body was used. In 1986-1990 in the agriculture of Moldova there were applied enough large amounts of agrochemicals with copper and zinc, this being one of the main sources of penetration of these metals both in water and aquatic organisms, including aquatic plants of Cuciurgan reservoir.

The analysis of the results of multiannual investigations allowed establishing the dependence of content of a range of trace elements in aquatic plants of Cuciurgan reservoir on their concentrations in the water. This correlation is described by the equations of linear regression and the correlation coefficient ranges between 0.87-0.92 (ZUBCOV et al., 2013). Such dependence was established for helophyte plants (*Phragmites australis*, *Typha latifolia*) and metal content in bottom sediments for all investigated aquatic ecosystems ($r = 0.86$-0.97). With rare exceptions, the dynamics of the accumulation of Zn, Mn, Cu, Mo, V, Al, and Co has a seasonal character. Thus, the analysis of the dynamics of the accumulation of metals in leaves and stem (submerged and aerial parts) of the reed (*Phragmites australis*) showed the metal concentrations increase by large increments from spring to the end of the summer-beginning of autumn (Fig. 2).

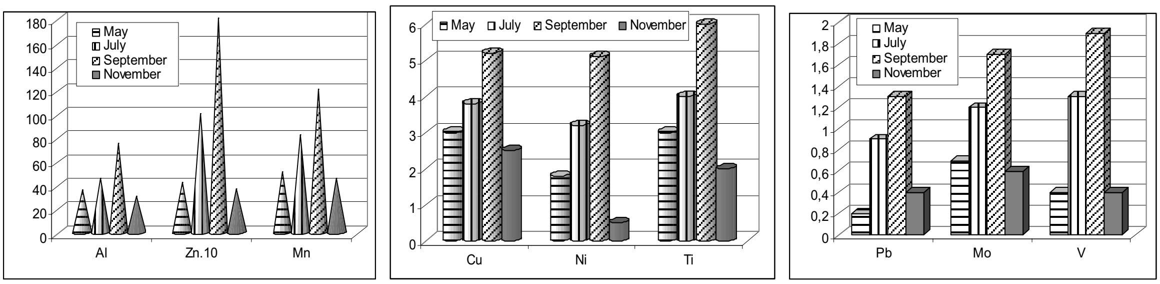

Figure 2. Seasonal features of Pb, Mo, V, Cu, Ni, Ti, Al, Mn, Zn accumulation in leaves and aerial stem of *Phragmites australis* (vertical axis- µg/g abs. dry mass) from Dubăsari reservoir.

In autumn, with the decrease of water temperature below 10°C, an opposite phenomenon was observed – quite evident decrease of metal contents in aerial parts of plants, accompanied by their slightly increase in root parts. Specifically in this period an increase of metal content in the mud solutions, obtained from the bottom sediments picked up in stands, was registered in both reservoirs. All this conduct to the assumption the partial flow of metals from aquatic plants to the bottom sediments has occurred in autumn through their root systems. In later autumn and in the beginning of winter, when the aerial plant parts perish, the metal content in semi-decayed leaves and stems consists of less that 10-20% of that from the end of the summer. Probably, an important part of metals penetrates into the water layer both in dissolved and suspended forms. As confirmation, an experimental work showed that from dry leaves of *P. australis*, which were placed in an aquarium with river water, up to 50% of nickel, molybdenum, vanadium, lead and zinc, and about 20% of manganese, aluminium and titanium were released into environment. Therefore, aquatic plants may also be sources of secondary pollution of water with metals. At the same time, a significant amount of accumulated metals along with submerged part of stem (especially that covered by dense suspensions) and the root system are preserved in bottom sediments. At the perishment of aquatic plants and their deposit on the bottom of the water body, a considerable amount of metals is adsorbed on their surface. As example, in the stems of *P. australis* covered by a dense layer of suspensions, which were sampled from the bottom in February-March, the metal concentration was 1.8-5.5 times higher than in the same stems after removing the suspensions.

However, in spite of the variation of metal accumulation, for all water bodies and streams some similar regularities of accumulation of one or another metal have been revealed. Thus, in most of the cases and for majority of aquatic plants, the trace metals have formed the following decreasing row, in conformity to their contents: Mn > Al > Zn > Cu > Ni > Ti > Pb > V > Mo. In Cuciurgan reservoir the lead has changed the place with vanadium at *Lemna minor* and filamentous algae (*Cladofora* sp., *Enteromorpha* sp.), and nickel- with copper at *Ceratophyllum demersum, L. minor, Najada marina* and *Myriophyllum spicatum.* In the aquatic plants of Dubăsari reservoir sometimes the copper changes the place with zinc. These differences are caused mainly by the ratio between the given metals in the water.

One of the indices of accumulation role of aquatic plants is the trace element bioaccumulation coefficient, which is calculated as the ratio between the concentration of trace elements in hydrobionts and their concentration in water. The following diapason of the accumulation coefficient values was obtained (by taking in account the lowest and the highest trace element concentrations): for manganese - 2230-50540, lead - 42-6520, aluminium - 170-142900, titanium - 720-49750, nickel - 410-30900, molybdenum - 145-2600, vanadium - 156-8310, copper - 230-30800 and zinc - 620-10090. The figures demonstrate the aquatic plants are important macro-concentrators of trace metals.

CONCLUSION

The metal accumulation in aquatic plants is a function of plant taxonomic features, dynamics of their content in water and bottom sediment of reservoirs and water streams, and season.

Aquatic plants, particularly *Potamogeton pectinatus*, *P. perfoliatus*, *P. crispus, Ceratophyllum demersum*, *Myriophyllum spicatum*, *Lemna minor*, *Hydrocharis morsus-ranae*, *Cladofora* sp., *Enteromorpha* sp., *Najada marina*, can be used as monitoring organisms in the metal biomonitoring of water ecosystems.

Aquatic plants can act as a source of secondary metal pollution of the water layer, but simultaneously, an important amount of metals, accumulated in the submerged part of the stem (especially the part covered by dense suspensions) and root system is preserved in bottom sediments.

Moreover, at the death of aquatic plants and their deposition on the reservoir bottom, a notably quantity of metals is absorbed on their surface.

ACKNOWLEDGEMENTS

We would like to extend our appreciation to SCSTD, Moldova (projects 06.411.012 F, 11.817.08.15A).

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Received: March 29, 2013
Accepted: May 27, 2013