Heavy Metals Environment Accumulation in Somova – Parcheş Aquatic Complex from the Danube Delta Area

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Heavy metals are released into environment from natural and anthropogenic sources. We measured cadmium, chromium, nickel, lead, manganese and zinc in four wetlands species (Phragmites australis, Typha angustifolia, Potamogeton pectinatus and Stratiotes aloides) collected during 6 years (2007-2012) from Somova Parches aquatic complex belonging to Danube Delta (one of the largest Biosphere reservation in Europe), and also in water and sediment samples from the same area. It is for the first time when these actions and monitoring activities are developed on these sites. We determined the metals concentrations in leaves, rhizomes, water and sediments from two sampling sites situated on two lakes (Somova and Rotundu), near a farmland (West) and a dump slam (East) situated in the vicinity of the aquatic complex. High concentrations of Cd, Pb and Ni were found in plants, water and sediments exceeding the permissible maxim values for water and sediment samples. Therefore, the study revealed that Phragmites australis and Typha angustifolia may have a high bioaccumulation potential of heavy metals and Stratiotes aloides is less suitable to be used as bio accumulator in heavy metals retention. Also it was observed that macrophytes accumulate zinc and nickel at high level of concentrations.

Keywords: heavy metals, macrophytes, water, sediment

Present study was carried out in Somova Parcheş aquatic complex, situated upstream the entry of Danube Delta, the most important and protected biodiversity area from Romania and one of the most important in Europe (surface 91.7 km^2). The complex receives important volume of water from the Danube, especially in spring season. Main sources of pollution affecting the complex come from industrial area (mainly aluminium industry) of the Tulcea city, from the slam dump, and from the Danube (practically is the end area after 9 countries and many industrial and agricultural pollution sources). Defining and determining the chemical stressors in this predeltaic area it is very important because they have direct consequences on sensitive and protected species in the Danube Delta, this pollutants mainly originating from human and industrial activities. [1]

Generally, the wetlands are considered a natural filter for the retention of natural and anthropogenic pollution [2]. This fact is given by the retention capacity of the aquatic plants and those from swamps, as well as their accumulation in the sediments. Heavy metals are considered one of the most hazardous categories of pollutants for the aquatic ecosystems, due to their environmental persistence and tendency to be retained in aquatic organisms including plankton, macrophytes, invertebrates and vertebrates as well in sediments [3]. The main problem caused by heavy metals in the environment, living organisms, human health is their tendency of accumulation in different tissue types (plant, animal or human) and their toxicity, even at low concentrations [4]. Over 90% of Cd, Pb, Mn, Ni and Zn content present in freshwater and sediments originates from human activities [5], they associate with suspended particulate matter which settle and are accumulated in the bottom sediment. Rooted aquatic macrophytes, such as common red (*Phragmites australis)* and common cattail (*Typha angustifolia),* are adapted species to survive in fresh water ecosystems and can be used to remove the heavy metals from contaminated water bodies in natural conditions [6,7].

Cadmium occurs naturally in rocks and soils; usually in concentrations of less than 0.001 mg/kg. In freshwater, the presence of soluble form of cadmium ion is connected with anthropogenic sources. In aboveground plant organs the cadmium range is usually from 0.05 to 0.22 mg/kg [8]. The most important anthropogenic sources of chromium in surface water and groundwater are wastewater from electrolytic coatings, leather tanning and textile industries [9].

In addition, deposition of chromium found in suspension in the air is also an important source of chromium in surface waters [10].

Manganese usually occurs in water at a concentration of less than 20 mg/L. Lakes waters that have suffer inversion phenomenon (turn-over seasonal) can reach over 150 mg/L. At concentrations above 0.2 mg/L, in the presence of oxygen it precipitates causing sediment deposits. In plants maximum manganese concentrations considered toxic are situated between 50-500 μ/g [11].

In surface waters, nickel comes from meteoric waters containing solid particles resulted from different emissions (fossil fuel combustion, industrial wastewater etc.), also being found in the sludge generated by water treatment plants [10].

Significant quantities of lead are found in water from municipal discharges and from the sludge generated by wastewater treatment. Released in water, the metallic lead is adsorbed by sediment and it is considered highly toxic [12]. This element is bio accumulated by plants, mainly in roots and a small amount goes into aboveground parts of plants, toxic Pb concentrations found in plant tissue being between 30-300 μ/g [8].

The present study aims to assess the heavy metals pollution in water, sediment and aquatic plants in two important lakes (Somova and Rotundu) from the predeltaic

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area focusing on the degree of retention capacity of aquatic ecosystems depending on geographic location related to pollution sources. The study also aims to determine heavy metal binding capacity in four aquatic macrophytes species in order to highlight which plant species are more suitable as bio accumulator for the selected chemical elements.

Experimental part

The study has been conducted on Somova- Parches aquatic complex (lat. N 45°12'10.52"/ long. E 28°47'25.58") between Tulcea and Isaccea city) in predeltaic area of Biosphere Reservation of Danube Delta nearby the border between Romania and Ukraine. Total area of the complex is 91.7 km^2 and its landscape mainly consisting of floodplain lakes (Rotundu, Telincea, Parches, Somova), Danube river borders, streams vegetation of reeds and rushes and river grind with willow associations [13]. The investigations were carried out during a period of 6 years, from 2007 until autumn 2012.

Two lakes (Somova and Rotundu) selected were considered representative because of various pollution sources with direct influences on complex. Danube has a direct influence on Rotundu (lat. N 45° 14'07.44"/long. E 28° 31'01.74") and Somova (lat. N 45° 10'41.47"/ long. E 28° 44' 41.68") lakes; in addition, Somova lake, receive direct influences from the slum dump located in the vicinity. These lakes could be representative for the synergic influence of large river and an anthropic pollution and for the study of heavy metals distribution in different components of the ecosystems.

A total of six metals (Cd, Cr, Mn, Ni, Pb and Zn) were monitorised in water, sediments and four aquatic plant species (*Phragmite saustralis, Typha angustifolia*, *Potamogeton pectinatus* and *Stratiotes aloides*). The observations were done seasonally (spring, summer, fall), three time per year in each lake in the same station in the period 2007 – 2012. Average values were taken into consideration for statistical analysis in all systems (water, sediment and macrophytes). In winter, sampling was avoided because the water freezes and plants vegetation cycle is inexistent. Concentrations of heavy metals in aquatic vegetation samples were expressed in mg/kg (ppm) dry matter, sediment samples were expressed in mg/kg and water samples were expressed in μg/L. Microwave digestion, necessary for heavy metals determination, was made using the microwave oven Anton Paar, Multiwave 3000. The heavy metals contents were analysed using the ICP-MS Elan DRC-e which is applicable to the determination of small concentrations of a large number of elements. Chemical species originating from a liquid are nebulized and the resulting aerosols are transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, through an interface, into a mass spectrometer, according to standard SR EN ISO 17294-2, 2005 [14].

Sampling and preservation of water, sediment and aquatic plants

The water samples were collected according to standard SR ISO 5667/1998 [26]. To determine the metal content, 500 mL water was collected and preserved with 2.5 mL of concentrated nitric acid in nonfiltered form. The sediment samples were collected according to standard SRISO 5667-12/1998 [26]. Sediment samples were dried at room temperature to avoid loss of the organic and inorganic micro pollutants. To obtain a subsample of approximately 20 g, a dry sample was ground and sieved through a sieve of 150 μm. All aquatic plants samples (*Phragmites australis, Thypha angustifolia, Stratiotes aloides, Potamogeton pectinatus*) were weighed, dried at 80°C until, constant mass. Drying the samples is important because protects microbial decomposition of a plant material and also provides a constant reference value by determining dry, because wet substance is difficult to quantify [15].

Phragmites australis and *Typha angustifolia* samples, were collected with a sickle, producing a mixed sample.

Sample preparation and instruments

The mineralization stage was made differently depending on the type of sample in Anton Paar oven.

For water: 25 mL of sample and 5 mL HNO_3 were introduced in quartz vessels of Anton Paar oven. After a short pre-reaction time (10 min), the vessels were hermetically sealed using a special device which is inserted into a protective sheath, covered and then placed properly in the rotor. The energy rises to 1200 W in 5.5 min and is maintained at this power for 4.5 min.The total mineralization process lasts 10 min and the total cooling time is 30-35 min. After completing the program and the cooling time, vessels are opened and the content is removed in balloons of 50 mL and brought to the mark with bidistilled water.

For sediments: In quartz vessels are weighed 0.25 – 0.5 g of sediment, than added 10 mL nitric acids. After 15 min of pre-reaction time, the vessels are hermetically sealed with the protective caps and placed into the rotor of microwave oven. The energy slowly rises at 600 W in 5.5 min and maintains this power for 4.5 min, then rises to 1200 W and held the power for 20 min. After finish program and the cooling time (25 – 30 min), the rotor is taken out, the quartz vessels are opened and the content is removed in balloons of 50 mL and brought to the mark with bidistilled water.

For aquatic vegetation: In quartz vessels was weighed 1– 2 g of aquatic vegetation, and then was added 5 mL HNO_3 and 2 mL H_2O_2. After a short time of pre-reaction (15 min.) the vessels are closed with special lids, place in the sheath with secured protective cap, and then place the rotor properly. The energy slowly rises at 600 W in 5.5 min and maintained at this power for 4.5 min, then rises to 1000 W and maintained this power for 10 min. The total mineralization time is 20 min and the total cooling time is 20 – 25 min . After completing the program and the cooling time, the quartz vessels are opened and the content is removed in balloons of 50 mL and brought to the mark with acidified water.

Results and discussions

Water analysis

In accordance with the Water Framework Directive (no.2000/60/C.E.) [16], transposed into Romanian legislation by Order no.161/2006 [17], the concentrations of heavy metals in the two lakes studied Somova and Rotundu, have been reported to class quality II (good ecological status). In each lake were registered exceedances of heavy metals concentrations (fig. 1-6) depending on the nature influences: natural (Danube debt, season) and anthropic (dump slam).

Analyzing Cd concentration values, in the range of 3.5 μg/L (Rotundu in 2008) and 10.5 μg/L (Somova 2009) it was found that all concentrations value exceed the corresponding values for quality class II of 1 μg/L, having corresponding values for quality class IV and V. By comparison, cadmium concentrations determined in Lake

Somova had registered high exceeding comparing with Lake Rotundu.

For total Cr the measured concentrations ranged between 22.6 μg/L (Lake Rotundu in 2008) and 76.2 μg/L (Somova in 2010). Except 2008, 2009, were observed exceedings of maximum admitted concentrations values of Cr for class quality II of 50 μg/L, in all years studied in Lake Somova. For Rotundu Lake, the exceeding the maximum permissible of chromium concentration were recorded within 2011-2012.

The concentration values of Mn have been situated between 72.8 μg/L (Rotudu 2009) and 178.2 μg/L (Somova 2007). On Lake Rotundu the corresponding value of the good ecological status up to 100μg/L is exceeded in all the analyzed period, with the exception of 2008 - 2010. The lowest concentrations of Mn were recorded in 2008 and 2009 in both lakes studied. The concentrations value of Ni had ranged from 27.8 μg/L (Rotundu 2009) and 76.4 μg/L (Somova 2007). In both lakes studied they exceed the maximum permissible concentration of 25 μg/L, but the lower values were recorded in Lake Rotundu in 2008 and 2009. Pb and Zn concentrations did not exceed the maximum allowable concentrations for class quality II of 10 μg/L (Pb) and 200 μg/L (Zn) for none of the monitored lakes.

Analysing graph representation of heavy metals concentration in water samples from the two lakes studied (fig. 1-6), can be noticed a decrease in Cr, Mn and Ni concentrations in 2008 to 2009, most likely due to lower levels of rainfall, which reduced the amount of water pollutants trained by the effluent from the soil surface. Moreover, was observed a descendant trend in the concentrations of Pb and Zn, possibly due to reducing emissions from the surrounding industrial activity. Cd shows significant variations throughout the period studied, most likely caused by significant contribution of the Danube water (source of water supply of the complex).

Seasonal monitoring reveals (table 1), that in spring season, for Somova Lake it was observed an increase of all heavy metals concentrations in water. This increase in concentrations is most likely influenced by the correlation between the water volume of the Lake Somova and phreatic level (influenced by dump slam). Thus, the underground connection between Somova Lake (water surface) and phreatic water could lead to two possibilities:

- in the spring, when water volume is increasing due to effective rainfall, melted snow and a high water input of the Danube, phreatic coat is fed by runoff containing pollutants from dump slum located near Lake Somova, influencing in this way water quality status;
- during the summer when the water level is low, the influence of phreatic coat is reduced or inexistent.

Melting snows and spring rains determine also important changes, both quantitative and qualitative because they flow and wash the soil surface, involving different pollutants types and carry them into water.

It is possible to observe that maximum levels of heavy metals in spring for Rotundu are lower comparing with Somova, due to the exclusive influence of the Danube River in this season.

Sediment analysis

All six heavy metals analysed in sediments are increasing in sequence of Cd< Pb< Ni< Cr< Zn< Mn, results in accordance with studies realized by Fawzy et al. 2012 [18] and Van den Berg 1998 [19]. Minimum and maximum seasonal concentrations of elements in sediments (in both Somova and Rotundu lakes) are presented in table 2.

In sediment, all Cd concentrations analyzed within 2007-2012 have exceeded the maximum allowable concentration for class quality II of 0.8 mg/kg. Cadmium concentrations showed variations between 2.69 mg/kg

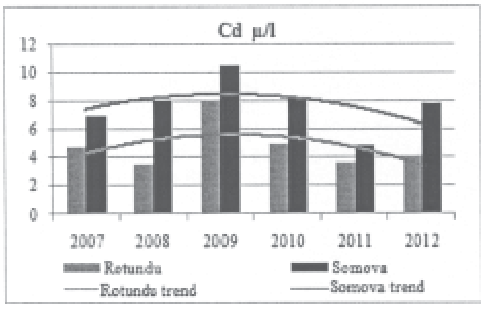

Fig. 1. Multi-annual dynamics and trend of cadmium average concentrations in water samples

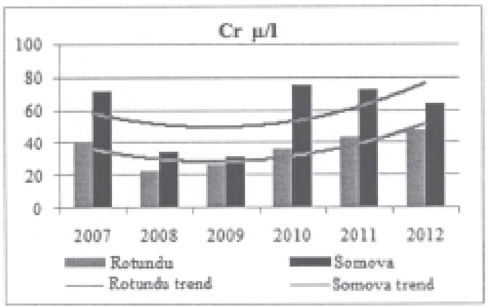

Fig. 2. Multi-annual dynamics and trend of chromium average concentrations in water samples

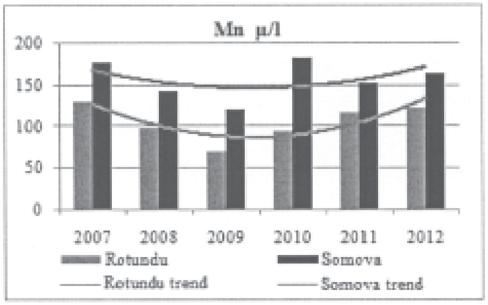

Fig. 3. Multi-annual dynamics and trend of manganese average concentrations in water samples

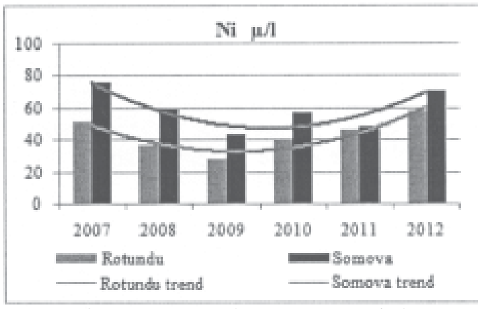

Fig. 4. Multi-annual dynamics and trend of nickel average concentrations in water samples

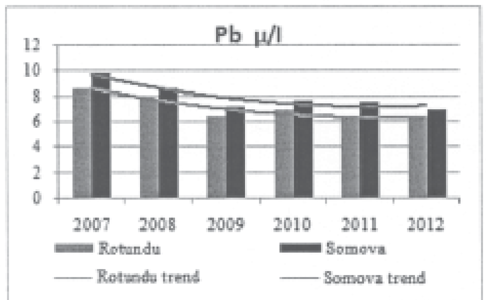

Fig. 5. Multi-annual dynamics and trend of lead average concentrations in water samples

Table 1
THE RANGE (MINIMUM – MAXIMUM) OF HEAVY METALS CONCENTRATIONS IN WATER SAMPLES FROM ROTUNDU AND SOMOVA LAKES

Heavy metals	Somova						Rotundu					
	Spring		Summer		Autumn		Spring		Summer		Autumn	
µg/L	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Cd	6.62	10.5	4.26	8.41	6.26	8.41	4.71	8.46	3.5	6.46	3.6	7.32
Cr	43.1	81.2	31.0	64.2	35.2	73.1	30.1	48.2	20.6	37.0	29.4	44.6
Ni	49.6	78.9	41.2	59.1	43.4	71.2	40.0	59.1	27.9	46.6	36.2	52.8
Pb	7.76	11.2	6.11	7.52	6.83	8.91	6.81	8.96	6.24	7.21	6.23	7.81
Mn	126.4	196.1	104.0	164.7	117.4	179.2	99.4	133.2	70.1	119.4	87.2	121.3
Zn	161.2	209.8	138.2	188.7	146.9	179.6	124.5	181.9	100.2	164.0	117.7	179.3

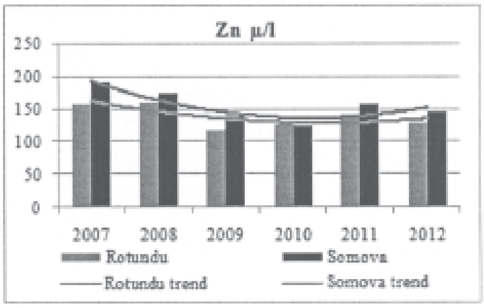

Fig. 6. Multi-annual dynamics and trend of zinc average concentrations in water samples

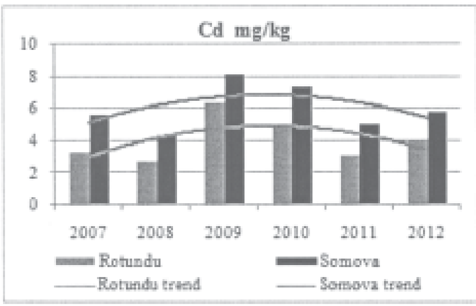

Fig.7. Multi-annual dynamics and trend of cadmium average concentrations in sediment samples

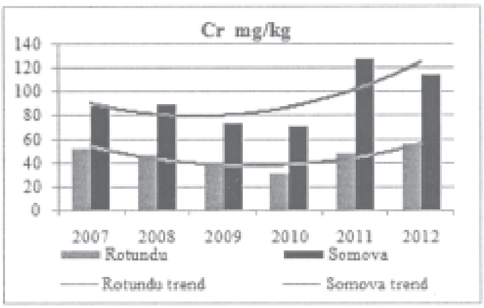

Fig.8. Multi-annual dynamics and trend of chromium average concentrations sediment samples

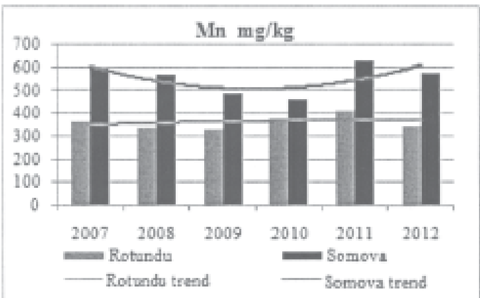

Fig.9. Multi-annual dynamics and trend of manganese average concentrations in sediment samples

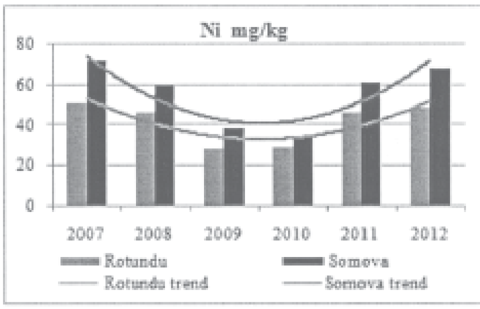

Fig.10. Multi-annual dynamics and trend of nickel average concentrations in sediment samples

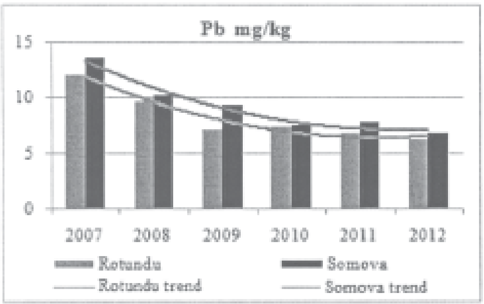

Fig.11. Multi-annual dynamics of lead concentrations average in sediment samples

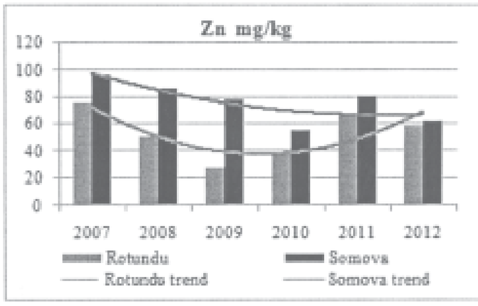

Fig.12. Multi-annual dynamics of zinc concentrations average in sediment samples

(Rotundu 2008) and 8.18 mg/kg (Somova 2009). Lowest Cd concentrations were recorded in Rotundu lake (fig. 7).

Concentrations of Cr ranged between 31.10 mg/kg in Rotundu 2010 and 128.20 mg/kg in Somova 2011). For Cr, maximum value corresponding for class quality II is 100 mg/kg, and was exceeded in 2011 and 2012 in Somova. Throughout the monitoring period, in Rotundu were not reported exceeding of the maximum permissible concentrations.

For Mn are not established the maximum permissible values. In the period studied manganese values range within 301.9 mg/kg (summer) - 452.2 mg/kg (spring) in lake Rotundu and 389.7 mg/kg (summer) – 687.9 mg/kg (spring) in lake Somova (table 2).

For Ni were identified values between 28.60 mg/kg (Rotundu 2009) and 72.31 mg/kg (Somova 2007).

Heavy metals mg/kg	Somova						Rotundu					
	Spring		Summer		Autumn		Spring		Summer		Autumn	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Cd	6.12	8.26	4.16	7.81	4.97	7.88	4.26	6.81	2.12	4.92	3.47	4.99
Cr	88.1	134.2	67.2	93.1	71.5	117.6	44.9	58.6	29.4	47.9	38.5	52.4
Ni	54.6	79.1	31.2	67.1	48.1	69.1	33.3	54.6	27.1	46.0	28.3	49.5
Pb	7.16	13.99	6.22	7.61	6.81	7.89	7.14	12.2	5.18	7.31	6.02	8.99
Mn	451.7	687.9	389.7	578.7	412.7	613.2	339.2	452.2	301.9	376.9	336.1	417.2
Zn	164.2	204.7	131.2	171.2	158.2	187.5	148.2	197.9	122.1	168.3	139.1	178.5

Table 2
THE RANGE (MINIMUM – MAXIMUM) OF HEAVY METAL CONCENTRATIONS IN THE SEDIMENTS SAMPLES OF ROTUNDU AND SOMOVA LAKES

Table 3
HIGHLIGHTING THE CAPACITY OF AQUATIC VEGETATION FOR RETENTION OF HEAVY METALS FROM ENVIRONMENTS WITH DIFFERENT LEVELS OF CONTAMINATION

		Cd (mg/kg)		Cr (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		Pb (mg/kg)		Zn (mg/kg)	
Year	Plant	Rotundu	Somova	Rotundu	Somova	Rotundu	Somova	Rotundu	Somova	Rotundu	Somova	Rotundu	Somova
2007	*P. australis*	0.777	0.904	2.792	3.476	0.663	0.825	8.451	10.522	0.850	3.068	9.441	11.754
	T. angustifolia	0.990	1.233	2.752	3.426	0.505	0.629	5.169	6.436	1.310	4.205	13.936	17.351
	S. aloides	0.393	0.489	1.722	2.144	0.427	0.532	4.132	5.144	0.160	1.013	5.741	7.148
	P. pectinatus	0.586	0.729	2.507	3.121	0.669	0.833	4.917	6.122	0.320	3.826	8.948	11.140
2008	*P. australis*	0.786	0.992	0.999	1.244	0.553	0.688	7.923	9.864	0.360	3.929	7.924	9.866
	T. angustifolia	0.986	1.228	3.894	4.848	0.336	0.418	7.104	8.844	0.820	3.066	20.308	25.284
	S. aloides	0.447	0.556	1.581	1.968	0.292	0.364	2.451	3.052	0.080	1.206	6.959	8.664
	P. pectinatus	0.800	0.996	3.908	4.866	0.577	0.718	4.526	5.635	0.160	4.613	7.884	9.816
2009	*P. australis*	1.546	1.963	4.102	5.107	0.745	0.928	7.563	9.416	0.300	2.124	11.482	14.295
	T. angustifolia	1.627	2.026	3.428	4.268	0.654	0.814	9.827	12.234	0.960	2.977	15.733	19.587
	S. aloides	0.715	0.890	2.054	2.557	0.355	0.442	3.696	4.601	0.240	0.919	12.609	15.698
	P. pectinatus	1.513	1.884	3.863	4.810	0.545	0.678	5.210	6.486	0.380	2.031	12.146	15.122
2010	*P. australis*	0.929	1.246	2.641	3.288	0.374	0.466	9.547	11.886	1.020	3.682	10.146	12.632
	T. angustifolia	1.088	1.355	3.892	4.846	1.306	2.124	11.287	14.052	1.140	5.792	14.967	18.634
	S. aloides	0.521	0.649	1.722	2.144	0.329	0.451	1.786	2.224	0.110	1.859	6.937	8.637
	P. pectinatus	0.989	1.231	3.353	4.174	0.710	0.884	6.467	8.051	0.420	4.134	10.890	13.558
2011	*P. australis*	0.731	1.232	2.390	2.674	0.770	3.634	10.462	3.228	1.080	2.395	12.364	10.264
	T. angustifolia	1.196	1.580	3.553	2.447	0.966	2.686	8.662	3.196	0.970	4.104	11.668	14.262
	S. aloides	0.612	0.479	1.228	1.624	0.286	1.128	1.630	2.778	0.220	1.926	5.744	8.630
	P. pectinatus	1.300	1.186	3.279	3.903	0.410	1.210	4.643	5.721	0.210	1.979	11.264	10.563
2012	*P. australis*	0.822	1.182	3.256	0.957	1.002	3.889	8.254	2.967	0.980	2.998	12.365	10.339
	T. angustifolia	1.251	1.768	1.665	3.462	1.221	2.456	10.235	2.938	1.180	3.224	11.733	12.634
	S. aloides	0.545	0.882	2.404	2.110	0.401	2.119	2.220	2.967	0.301	2.156	9.875	12.316
	P. pectinatus	1.921	1.475	3.156	3.479	0.669	1.869	4.524	5.266	0.314	4.451	13.865	7.964

Excepting years, 2009 and 2010 in Rotundu and 2010 in Somova, the maximum allowable value for nickel (35 mg/kg) was exceeded in all studied period. For Ni were identified values between 28.60 mg/kg (Rotundu 2009) and 72.31 mg/kg (Somova 2007). Excepting years 2009 and 2010 for Rotundu, and 2010 for Somova, the maximum allowable value for nickel (35 mg/kg) was exceeded in all studied period.

Pb concentrations were situated within the range of 6.31 mg/kg (Rotundu 2012) and 13.76 mg/kg (Somova 2007). During 2007-2009 on Somova and 2007-2008 on Rotundu, the maximum allowable value of 8.5 mg/kg was exceeded.

Zn registered variations between 27.2 mg/kg (Rotundu 2009) and 96.7 mg/kg (Somova 2007). It is observed that the maximum permissible value of 15 mg/kg corresponding for class quality II was exceeded in all studied years.

Analyzing the results (fig. 7-12) of heavy metals accumulation in sediment samples from Somova-Parches aquatic complex, it was observed a decrease in concentrations of chromium, manganese and nickel in 2009 and 2010. Due to the given results, within 2008-2009, the heavy metal concentrations in water had a decrease tendency which explains the lower values in 2009-2010 for heavy metal content in sediment, retaining process being made more slowly. Lead and zinc maintained a decreasing tendency, even if they exceeded the maximum permissible in 2007 on Lake Somova.

In sediment samples, the variations registered between the three sampling seasons are caused by the influence of water and suspended sediment input from the Danube (water supply source of the complex). A very important role in variation of heavy metal content is holded by the existent pollutants in lower layers of sediment, which in flooding time are trained in water, returning in the sediment surface. Different concentrations of heavy metals were registered in sediment of the two lakes due the fact that the influence of the industrial area of Tulcea city is more evident on Somova. Minimum and maximum values shown in table 2 reveals a higher concentration of heavy metals in sediment accumulated in Somova compared with Rotundu.

Analysis of aquatic vegetation

The highest accumulation of cadmium was recorded in 2009 in *Typha angustifolia* with 1.627 mg/kg in Lake Rotundu and 2.026 mg/kg in Lake Somova (table 3), results comparable to those reported by Drazewiecka et al., 2010 [8]. Minimal accumulations were identified in 2007 in *Stratiotes aloides* of 0.393 mg/kg in Rotundu and 0.489 mg/kg in Somova. *Phragmites australis* showed a high capacity for chromium retention in 2009, with 4.102 mg/kg in Lake Rotundu and 5.107 mg/kg in Lake Somova. *Stratiotes aloides* retain low concentrations of Cr 1.228 mg/kg in Rotundu and 1.624 mg/kg in Somova in 2011, findings observed in all monitored years, this plant being less suitable for bioaccumulation of heavy metals.

Compared with concentrations of manganese found in sediment (table 2), it was observed that aquatic vegetation has much smaller capacity retention of this metal. Thus, the highest concentration of manganese accumulated was found in *Phragmites australis* with 3.889 mg/kg in 2012 in Lake Somova and 0.374 mg/kg in Lake Rotundu. The minimum Mn values were found in *Stratiotes aloides* 0.286

mg/kg in Lake Rotundu and 1.128 mg/kg in Lake Somova. Also, species *Potamogeton pectinatus* has showed high capacity retention of lead, up to 4.613 mg/kg (table 3) in Somova in 2008, being a plant with high potential for pollution monitoring [20]. These results are comparable to those reported by Samecka-Czmerman and Kempers 2004 [21]. The minimum values of lead were recorded in 2008 in Rotundu 0.08 mg/kg. Comparing the four macrophytes species studied, *Typha angustifolia* presents a great potential for zinc retention. Highest values were recorded in 2008, 25.284 mg/kg in Somova and 20.308 mg/kg in Rotundu. The lowest values of zinc concentration were reported in 2011, 5.744 mg/kg for Rotundu in 2007 and 7.184 mg/kg for Somova.

Conclusions

The study revealed that heavy metal content in water and sediment samples from the two studied lakes (except Zn in water samples) exceeded the maximum permissible concentration for quality class II (regulated by WFD and transposed into Romanian legislation by Order No. 161/2006 [16, 17], and it was especially high in Somova, this lake being affected by anthropogenic load and the slum dump.

Metal concentrations in water, sediment and plants follow a similar ascending trend in order: Cd <Pb <Ni <Cr <Zn <Mn, which is in agreement with studies by Fawzy et al 2012[18] and Mishra et al. 2008 [22]. Increased heavy content was observed in spring season, higher values being reported on Somova, possible caused by interaction between phreatic coat and surface water, also because of trained pollutants from riparian areas, snowmelt and rainfall.

In summer period was observed a decrease of heavy metals concentrations, most likely caused by the fixation of pollutants in sediment and vegetation, followed by a higher increasing tendency on Somova, possibly caused by the input of water and suspended sediment from the Danube.

Based on the results, bioaccumulation capacity of the four aquatic plants studied is very high and, can be arranged according to this pattern: *Typha angustifolia* > *Phragmites australis* > *Potamogeton pectinatus* > *Stratiotes aloides.* This helophytic plants tolerates high concentrations of Cd, Pb, Ni, Zn (except Mn), species *Typha angustifolia* and *Phragmites australis* being important due to high organic production biomass and exploitable due to their potential as building materials [23]. Like the aforementioned aquatic plants, heavy metals concentrations registered in *Potamogeton pectinatus* present significant differences between the two lakes studied, this plant possessing a good capacity to bio accumulate heavy metals, result in accordance with Kejian et al. 2008 [24].

Study revealed that *Stratiotes aloides* stores low concentrations of heavy metals being a less suitable candidate to use as bio accumulator, finding also reported by [25]. Concentrations of all metals studied were higher in Somova comparative to Rotundu. This demonstrates the importance of using these plants in the phytoremediation processes, as well as biological filters for the ecosystems in which they live. It is worth mentioning that all aquatic plants that were studied showed no visible deficiencies in development and growth rate.

Furthermore, after investigations it was concluded that seasonal differences between heavy metal concentrations recorded, are mainly due to the impact of the Danube on Rotundu, with the specification that, on Somova, besides the influence of the Danube, is added the influence of industrial polluter and the dump situated near Tulcea city. The content of heavy metals in the studied plants varies significantly from a lake to another, their retention capacity increases with the concentration of metals in water and sediment.

It is also important to fulfil the important influence of the Danube River (loaded with pollutants from 9 countries situated upstream) and the necessity to have global measures in order to avoid at least the increase of the Danube pollution in the near future.

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