Heavy metals content in aquatic plant species from some aquatic biotopes in Slovakia

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Introduction

Heavy metals are accumulated in different components of the environment in different ways being controlled by various mechanisms. Aquatic plants absorb heavy metals from the water, those rooted ones also from the bed material. Generally, aquatic plants can accumulate high amounts of heavy metals. In such a way, they reflect the toxicity of the water environment, and may serve as a tool for the biomonitoring of contaminated waters (e.g. Wang 1991, Sawidis et al. 1995, Ravera 2001, Zurayk et al. 2001, Cardwell et al. 2002). Heavy metals occurrence in aquatic plants in Europe has already been studied by numerous authors (e.g. Atri 1983, Sawidis et al. 1995, Samecka-Cymerman & Kempers 1996, Szymanowska et al. 1999, Stanković et al. 2000, Pajević et al. 2003). In Slovakia, however, almost no published data exist on this topic, with a single exception of a brief report on the occurrence of mercury in two aquatic plants, the alga *Spirogyra* and *Zannichellia palustris*, in the sedimentation basin of Poproč (deposit area of Rudňany) published by Banásová & Holub (1994). Therefore, the objectives of this paper are: i) to give a pilot screening of heavy metals content in aquatic plants from various sites in Slovakia, and ii) to provide a preliminary insight into the bioaccumulation patterns.

Material and Methods

In total, 53 samples of 21 aquatic plants (see Table 3) from 17 sites in Western and Central Slovakia (Table 1) were collected. The study focused primarily on rivers (11 sites), and less on other aquatic biotopes (e.g. reservoirs or oxbows). Waterbodies affected by industrial and mining activities were preferred, where the occurrence of heavy metals was assumed. The two localities were selected as control sites, where little antrophogenic influence was supposed (bold in Table 1).

Table 1 Study sites and their brief characteristics
Legend: Con_type – conectivity type, Cond. – water conductivity (20 ° C), Num. – the sample number

Locatity_L	L_number	Con_type	Altitude	Cond	pH	Num.	Samples = Species
Slatina_Zvolenská Slatina	1	River	335	253	7.87	3	Ba, Fa, Ms
Ipeľ_Kalinovo	2	River	203	179	7.50	1	Ba
Turiec_Socovce	3	River	440	522	8.17	4	Ba, Fa, Ms, Pc
Váh_Vrútky	4	River	380	510	8.55	3	Ba, Fa, Ms
Váh_Sereď	5	River	125	430	8.49	8	Af, Cd, Cg, En, Nm, Pn, Pp, Ppe
Hron_Heľpa	6	River	640	307	8.42	1	Bp
Hron_Žiar nad Hronom	7	River	226	487	7.97	2	Fa, Ms
Malina_Zohor	8	River	144	571	7.60	2	Cd, Pn
Malina_Malacky	9	River	159	491	7.97	2	Pc, Pp
Myjava_Kúty	10	River	152	981	8.45	2	Ms, Pp
Danube_Chorvátske arm_Bratislava	11	Oxbow	133	992	7.67	2	Mv, Se
Danube_Bratislava – Pálenisko	12	Oxbow	133	450	7.25	4	Cd, Ms, Pp, Ppe
Danube_Reservoir_Hamuliakovo	13	Reservoir	129	437	8.42	3	Ag, Nm, Ppe
Danube_Seepage canal_Hamuliakovo	14	Seepage canal	129	453	7.82	8	Bt, Cc, Cg, En, Lm, Mv, Pc, Pp

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Malý Dunaj_ Dunajský Klátov	15	River	114	720	8.03	3	Ms, Ppe, Se
Muránska Lehota	16	Reservoir	373	528	8.10	2	Cv, Pp
Bratislava – Štrkovec	17	Reservoir	130	919	8.45	3	Ms, Nm, Ppu

Only aboveground plant parts were sampled. Five individuals per plant species (one sample per plant) growing at the sample site were collected randomly. In the laboratory, the sampled material was washed with distilled water, air-dried at the temperature of 85°C during 48 hours (Dykyjová et al. 1989), homogenized using the Fritsch laboratory mill (Pulverisette 7) and the amount of 0,5 g of dry matter from each sample was decomposed in 5 ml of highly pure nitric acid using microwave digestion. Metals contents (cadmium, lead, zinc and copper) were determined through Galvanostatic Stripping Chronopotentiometry (GSC) on the ECA Flow 150 GLP device made by ISTRAN Ltd., Bratislava, the Slovak Republic (http//www.istran.sk). A sample of water was collected from each study site. Samples of water were analyzed using the same GSC method, without a previous sample-adjustment.

Results

Mean values of heavy metals content in aquatic plants referring to respective study sites as well as the values of heavy metals content in the water are presented in Table 2.

Table 2. Mean values of some heavy metals contents in aquatic plants and in the water as per study site, in ppm. Legend: a locality number and the number of samples in the locality are presented according to Table 1.

Mean values ppm	**Aquatic Plants**				**Water**			
Locality_number	**Zn**	**Cu**	**Pb**	**Cd**	**Zn**	**Cu**	**Pb**	**Cd**
1	92.743	8.410	19.717	0.737	643.00	2.80	14.60	14.10
2	22.100	11.160	72.260	0.050	390.20	2.10	2.70	0.40
3	26.815	4.250	8.980	0.253	204.10	2.90	5.90	1.50
4	17.227	8.463	18.407	0.086	454.70	4.30	4.20	1.50
5	27.114	8.015	10.294	0.396	543.75	2.65	12.90	11.99
6	89.950	10.090	11.750	0.250	461.80	4.50	6.00	0.60
7	90.575	17.830	8.585	0.165	1181.00	5.01	26.27	29.05
8	30.505	7.970	4.465	0.030	873.50	3.90	7.40	1.50
9	17.355	3.960	15.615	0.790	931.00	4.30	11.30	1.00
10	171.660	8.600	20.275	1.700	707.40	4.90	7.80	1.03
11	12.210	4.220	12.290	0.110	708.80	4.65	7.70	1.15
12	20.268	7.435	15.100	0.275	506.25	3.50	14.50	11.70
13	10.023	5.730	10.690	0.167	931.00	4.01	9.10	1.07
14	12.883	4.308	3.126	0.243	923.00	4.03	8.80	0.60
15	29.900	3.030	11.187	0.267	887.80	4.60	9.00	0.50
16	40.700	2.480	14.460	0.790	476.14	3.70	5.90	1.20
17	35.033	4.453	6.223	0.577	801.50	4.75	7.40	1.02

The highest values of heavy metals in the water were detected in the Hron river below Žiar nad Hronom, evidently due to the largely developed industry in this town, and also the water flowing from abandoned mines of the Štiavnické vrchy Mts. The highest mean values of the Cu content were found in aquatic plants from this site, whereas Zn, Cd and Pb contents were the highest in plants from the Malina stream (the factory in Malacky upstream the sample site) and the Ipeľ River (the glass factory with plumbeous fint glass production in Poltár upstream the sample site), respectively. The concentrations of zinc, lead, and copper in the water and in aquatic plants from the control sites, the Turiec-Socovce locality (3) and the Muránska Lehota locality (16), were rather low compared to other localities. Cadmium content in water samples from these control sites was slightly higher than the average value from other studied localities. At the Muránska Lehota locality, a surprisingly high cadmium content in *Potamogeton pectinatus* was recorded.

The mean, maximum and minimum contents of heavy metals in aquatic plants are listed in Table 3. The highest mean values of Zn, Cu, Pb and Cd were registered in submersed aquatic plants *Batrachium penicillatum* (Zn and Cu), *Fontinalis antipyretica* and *Potamogeton pusillus*, respectively. In species analysed in more than 3 samples, the highest mean values of heavy metals content (Zn, Cu, Pb and Cd) were detected in *Myriophyllum spicatum*, *Fontinalis antipyretica*, *B. aquatile* and *Potamogeton pectinatus* (following the order). Out of all analysed macrophytes, the absolutely highest values of heavy metals were found in the above mentioned species.

Table 3. Mean, Maximum and Minimum values of some heavy metals in aquatic plants.
Legend: The values of heavy metals in aquatic plants are presented in ppm.

			Mean value and its range (min – max) , ppm			
Species		**No. Samples**	**Zn**	**Cu**	**Pb**	**Cd**
Alisma gramineum	Ag	1	9.48	6.41	13.75	0.08
Azolla filiculoides	Af	1	45.58	5.13	16.10	0.20
Batrachium aquatile	Ba	4	43.56 (19.19-105.64)	10.22 (6.38 - 12.05)	25.16 (4.09 – 72.26)	0.38 (0.05 – 1.03)
Batrachium penicillatum	Bp	1	89.95	10.09	11.75	0.25
Batrachium trichophyllum	Bt	1	5.36	5.21	1.35	0.26
Callitriche cophocarpa	Cc	1	5.00	6.80	0.30	0.12
Ceratophyllum demersum	Cd	3	37.48 (17.95 – 55.47)	7.45 (7.19 – 7.93)	9.48	0.22
Cladophora glomerata	Cg	2	31.06 (10.24 – 51.88)	9.81 (4.40 – 15.21)	6.85 (0.50 – 13.20)	0.43 (0.12 – 0.73)
Elodea nuttallii	En	2	8.72 (2.40 – 15.03)	5.04 (3.79 – 6.28)	4.13 (3.34 – 4.91)	0.18 (0.13 – 0.23)
Fontinalis antipyretica	Fa	4	37.92 (6.70 – 76.19)	10.96 (3.92 – 20.98)	21.43 (10.66 – 35.44)	0.09 (0.06 – 0.12)
Chara vulgaris	Cv	1	4.10	0.96	14.58	0.13
Lemna minor	Lm	1	14.68	3.59	2.71	0.17
Myriophyllum spicatum	Ms	8	61.80 (3.63 – 61.8)	6.10 (1.59 – 14.68)	10.81 (1.22 – 24.15)	0.43 (0.02 – 1.75)
Myriophyllum verticillatum	Mv	2	27.37 (10.43 – 44.30)	3.13 (0.73 – 4.0)	6.21 (5.16 – 7.25)	0.47 (0.20 - 0.73)
Najas marina	Nm	3	24.02 (3.10 – 60.11)	6.61 (3.61 – 11.42)	4.75 (10.61 – 1.40)	0.70 (0.11 – 1.69)
Potamogeton crispus	Pc	3	33.01 (2.38 – 61.07)	3.06 (2.34 – 3.10)	12.05 (3.87 – 17.10)	0.36 (0.08 – 0.50)
Potamogeton nodosus	Pn	2	4.43 (3.32 – 5.54)	7.63 (7.25 – 8.01)	5.95 (5.66 - 6.24)	0.03 (0.02 - 0.03)
Potamogeton pectinatus	Pp	6	47.98 (3.05 – 148.68)	5.25 (3.56 – 7.64)	14.82 (3.09 - 27.36)	0.86 (0.09 – 0.11)
Potamogeton perfoliatus	Ppe	4	46.46 (17.49 – 72.92)	6.22 (4.35 – 8.08)	12.32 (9.69 – 16.92)	0.38 (0.12 – 0.62)
Potamogeton pusillus	Ppu	1	64.65	6.65	12.63	1.60
Sparganium emersum	Se	2	13.57 (13.15 – 13.99)	4.67 (3.15 – 6.19)	15.03 (12.73 – 17.33)	0.07 (0.02 –0.11)

Higher mean content of heavy metals (in ppm) was found in submersed aquatic plants rather than in floating leaves species (49 and 4 samples, respectively): Zn 37.39 and 17.28, Cu 6.59 and 5.99, Pb 12.39 and 7.68, Cd 0.40 and 0.10). Similar results were obtained in terms of broad-leaved and small-linear-leaved species. Mean values in the first group were lower than in the second one (39 and 14 samples, respectively): Zn 40.92 and 21.79, Cu 6.99 and 2.29, Pb 12.29 and 11.31 and Cd 0.45 and 0.17.

Comparing the heavy metal concentrations in all studied plants, we found the highest variability for the lead, with the maximum value exceeding 144 times the minimum observed. For Zn, Cu, and Cd it was almost 82 times, more than 13 times, and 87 times, respectively.

Comparing heavy metals concentrations in three aquatic plant species (*Batrachium aquatile*, *Fontinalis antipyretica* and *Myriophyllum spicatum*) growing in three identical localities, we detected the highest content of Zn, Cu and Cd in *Batrachium aquatile*. The highest mean values of Pb were observed in *Fontinalis antipyretica*.

Discussion

Large range of the heavy metals concentration in studied aquatic plants apparently indicates different extent of pollution of studied aquatic biotopes. This high variability is associated with site selection. The recorded values of heavy metals concentration in the aboveground biomass of aquatic plants are more or less in accordance with the values obtained at similar biotopes, or they are somewhat lower (Kárpáti et al. 1980; Atri 1983; Sawidis et al. 1995; Samecka-Cymerman & Kempers 1996; Stanković et al. 2000; Szymanowska et al. 1999; Pajević et al. 2003; Klink 2004).

As we selected localities rich in species composition, we did not dispose of sufficient data for a deeper statistic comparison of heavy elements content in individual aquatic plants. Though, it is evident that submersed dissected and small-linear-leaved species with larger leaf area accumulate higher average heavy metal contents than broadleaved and natant species. From the three analysed hydrophytes, the highest contents of the four studied heavy metals were found in *Batrachium aquatile*. Different accumulation abilities of species more or less depend on individual plants; nevertheless, some studies exist pointing out differences between the groups, e.g. submerged and emergent species (Szymanowska et al. 1999, Al-Saadi et al. 2002, Cardwell et al. 2002). On the other hand, some authors do not confirm this differences (Demirezen & Aksoy 2004).

Our findings provide a preliminary result; the discussed topic requires involving a wider spectrum of localities, hydrophytes, and the data on heavy metals occurrence in the water and the sediments, along with focusing on the relationships between the heavy metals contents in the water, sediments, and macrophytes.

Summary

The content of heavy metals – Zn, Cu, Pb and Cd in the phytomass of 21 aquatic plants growing mostly in runnig waters of Western and Central Slovakia was studied. The highest values of heavy metals content were observed in submersed dissected and small linear-leaved species, e.g. *Batrachium penicillatum*, *Fontinalis antipyretica*, *B. aquatile* and *Potamogeton pusillus*. In submersed aquatic plants, a higher heavy metals content was recorded than in floating leaf species. Out of 3 aquatic plants (*Batrachium aquatile*, *Fontinalis antipyretica*, and *Myriophyllum spicatum*) growing in three identical localities, *B. aquatile* displayed the highest mean values of Zn, Cu and Cd, and *Fontinalis antipyretica* showed the highest average content of Pb.

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