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Heavy Metal Concentrations in Freshwater Macrophytes from the Aldomirovsko Swamp in the Sofia District, Bulgaria

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Man's impact on the environment has become global and presents an international problem (Martin and Coughtrey 1982). The selective ionic absorption by hydrophytes in littoral ecosystems may be used for indicating the chemistry of water medium and submersed soils (Hejny et al. 1986). The purpose of this investigation was to determine the concentrations of heavy metals in the main species of aquatic macrophytes distributed in the Aldomirovsko swamp in the Sofia District, Bulgaria. An evaluation of the anthropogenic contamination of this area will be made before the area is declared a protected locality.

Aldomirovsko is one of the few inland swamps which is well preserved in Bulgaria. The swamp is situated to the northwest of Slivnica town, at the foot of the Tri Uši hills, around 650 m above sea level (Fig.1). It is of Karst origin. The area is about 2.5 km^2. The water capacity of the swamp varies throughout the year. Its depth decreases down to 1.10 m and is maintained by rainfall. The pH varies from 7.5 to 8.0. There is a considerable layer of silt at the bottom, with a pH of about 8.5. Thus far the swamp has been mainly a study area for floristic, faunistic, phytocoenological and ecological investigations (Kocev and Jordanov 1981; Kocev and Micev 1984; Kocev and Jurukova 1984).

MATERIALS AND METHODS

This study was carried out during the growing seasons of 1988 and 1989. The emergent plants (above-ground biomass) were sampled from 5 sites in the swamp every month. The floating and submerged species (whole biomass) were collected at the peak of their vegetation cycle (n=5)· Plant samples were not treated with organic dissolving agents or distilled water, but any attached periphytic material was carefully scraped off. About 1 g of the dried (at 80°C for 48 hr) and powdered samples was ashed in a muffle furnace overnight at 500° C. The ash was dissolved in 10 mL 20 % hydrochloric acid and heated on a sand bath to about 120°C nearly to dryness, according to the procedure given by Jackson (1962). The filtrate was diluted with double distilled water to 50 mL.The sediment and water samples were collected from 5 sites monthly. The sediments were ground to pass a 1 mm stainless steel sieve, dried (at 90°C for

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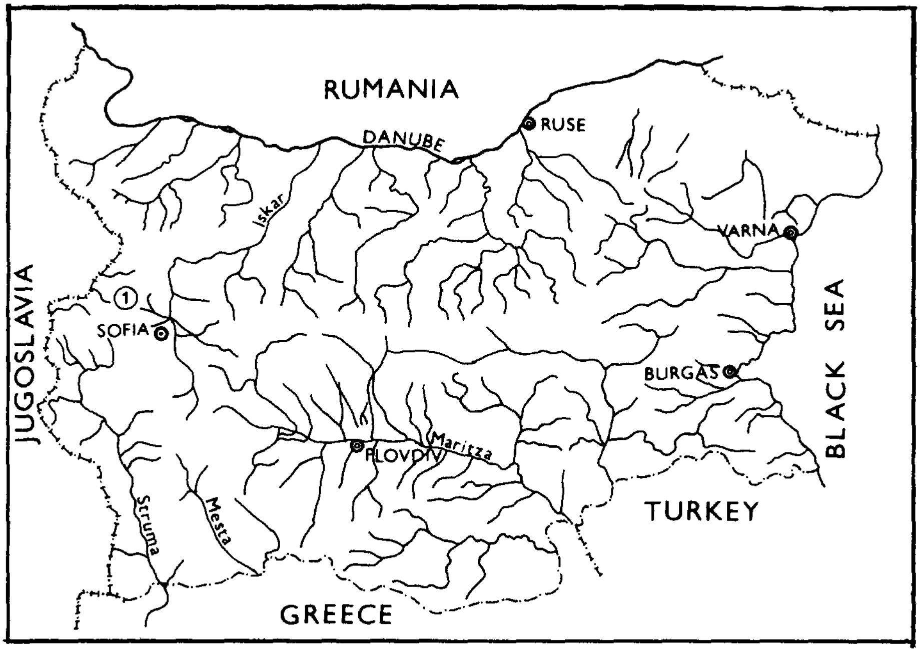

Figure 1. Location of the Aldomirovsko swamp (1) in Bulgaria (latitude 42° 52'24" N, longitude 23°1'45" E).

48 hr) and treated (about 1 g) with a 3:1 mixture of perchloric and nitric acid (10 mL).The mixture was heated on a sand bath nearly to dryness. This procedure was repeated with 10 mL hydrochloric acid. The digested sediment sample was finally filtered and the filtrate made up to 50 mL. Water samples were concentrated 20x (200 mL were heated in a steam bath, evaporated to dryness and then soluted to 10 mL volume in 1 *M* nitric acid and filtered). Analyses for the metals Fe, Co, Ni, Cu, Zn, Cd and Pb were made by flame atomic-absorption spectrophotometry (Perkin Elmer 303) with background correction and acetylene as fuel. Cadmium and lead were determined with a HGA 70 graphite furnace. Analytical precision was checked by replicating; deviation between the duplicates was <5 % in all cases.The results are expressed in mg kg^{-1} dry wt and mg L^{-1}. Each value is the mean of 5 values (plant samples) or 25 values (water and sediment samples). The significance of the seasonal variations for emergent plants was made using *t*-test.

RESULTS AND DISCUSSION

Data for the heavy metal concentrations in 16 species of macrophytic aquatic vegetation at the peak of their growth are shown in Table 1. These results are similar to those reported by Dikijova and Petrova (1983) and Dykyjova (1979). These authors noted, however, that any comparison between concentrations of the same plant species from different habitats must consider the specific conditions in the environment. All elements (except Zn and Cu, sometimes Ni) were higher in the submerged plants. The maximum Zn content was found in

Table 1. Heavy metal concentrations (mg kg^{-1} dry wt) in aquatic macrophytes collected from the Aldomirovsko swamp at the peak of their development during 1988 (n=5).

Species	Sampling date	Fe	Co	Ni	Cu	Zn	Cd	Pb
Emergent plants								
Typha latifolia L.	August	43±11	5.9±1.5	10±2	3.4±0.8	9.4±1.1	0.65±0.16	11±3
T. angustifolia L.	August	111±30	4.6±1.2	11±3	4.0±0.9	9.5±2.3	0.64±0.12	6.6±2.0
T. laxmanni Lepechin	August	102±24	2.3±0.8	15±4	4.1±0.8	11±2	0.58±0.15	5.3±1.7
Sparganium erectum L.	July	116±31	6.9±1.9	12±3	3.3±0.6	13±4	0.53±0.14	11±4
Phragmites australis (Cav.) Trin. ex Steud.	September	170±41	6.5±1.5	12±4	4.0±0.8	25±5	0.68±0.15	5.5±1.7
Schoenoplectus lacustris (L.) Palla	July	174±45	5.8±1.6	6.4±2.5	2.6±0.5	8.6±1.9	0.46±0.14	8.4±2.6
Heleocharis palustris (L.) R. Br.	July	147±37	3.9±1.0	10±3	4.0±1.1	11±3	0.42±0.12	6.6±2.0
Carex gracilis Curt.	July	76±18	3.9±1.1	8.9±3.1	10±2	22±4	0.54±0.14	3.6±1.1
C. riparia Curt.	August	188±49	8.4±2.2	9.9±3.0	5.6±1.1	13±3	0.75±0.16	5.6±1.9
Iris pseudacorus L.	June	74±20	4.5±1.1	17±5	6.8±1.7	21±5	1.0±0.3	9.7±3.1
Lythrum salicaria L.	August	244±62	4.7±1.4	12±3	10±2	51±10	1.0±0.2	17±5
Lycopus europaeus L.	August	322±84	9.4±2.7	11±3	16±3	45±9	0.76±0.21	10±3
Floating and submerged plants								
Potamogeton natans L.	July	2154±533	14±3	12±4	7.7±1.9	29±7	0.95±0.19	16±4
P. fluitans Roth.	July	3841±877	13±4	15±6	8.9±2.2	27±5	0.89±0.22	15±4
P. pusillus L.	August	6730±1346	14±3	16±4	9.3±3.1	33±5	1.1±0.2	33±8
Elodea canadensis Rich.	July	8631±1704	12±4	20±4	12±2	29±6	1.2±0.3	28±6

Lythrum salicaria and *Lycopus europaeus* (51 and 45 mg kg^{-1}, respectively). Species of the genera *Lycopus* and *Lythrum* that occurred in the inundation area of the Tisza were noted as zinc-accumulating plants (Tölgyesi and Kozma 1983). A higher Cu concentration (16 mg kg^{-1}) was observed in the species of Labiatae *Lycopus europaeus*. The high Cu content (12 mg kg^{-1}) of *Elodea canadensis* is to be mentioned, as well as the high Ni content (17 and 15 mg kg^{-1}, respectively) of *Iris pseudacorus* and *Typha laxmanni*. The macroelement concentrations are generally a specific feature of higher aquatic plants,however, the uptake of microelements (including heavy metals) depends on the natural environment (Dietz 1972). The widest range of metal levels was that of Fe - from 43 (*Typha latifolia*) to 8631 mg kg^{-1} (*Elodea canadensis*), i.e. 200 times. Increased accumulation of Fe in some species showed Kabata-Pendias and Pendias (1984). The Fe and Zn concentrations of *Phragmites australis* (=*P.communis*) were a little higher than those of the species of the Srebârna biosphere reserve (Nedjalkov et al. 1987), but the Cu content (30x), Fe content (3x) and Zn content (2x) were lower than that of the samples collected from Mandra and Vaja Lakes (Damjanova 1980) in Bulgaria.

The range in concentrations of metals in the three species of *Typha* varied little. A wider range in Fe and Pb concentrations was noted. The Fe and Co content of *Carex riparia* was higher, whereas the Cu and Zn concentrations were high in *C. gracilis*. The three species of *Potamogeton* analyzed concentrated metals differently dependent on their ecology. The Fe, Zn and Cu concentrations were lower than the results reported by Riemer and Toth (1969).

The seasonal differences in heavy metal concentrations in helophytes were not tested statistically (Table 2). Copper, Fe and Pb had a maximum variation up to 3x. The Cu concentration usually decreased from spring to autumn, whereas Zn

Table 2. Seasonal differences in heavy metal concentrations (mg kg^{-1} dry wt) in above-ground biomass of widely distributed emergent plants collected from the Aldomirovsko swamp during 1989 (n=5).

Species	Sampling date	Fe	Co	Ni	Cu	Zn	Cd	Pb
P. australis	May	143	5.2	12	10	29	0.33	3.8
	June	119	3.7	9.8	8.5	27	0.35	4.1
	July	107	5.5	9.0	5.6	18	0.42	9.0
	August	112	9.3	8.7	4.2	20	0.55	5.6
	September	165	6.8	11	4.1	23	0.64	5.5
T. angustifolia	May	120	5.6	12	8.4	24	0.62	2.7
	June	58	3.7	9.8	3.9	10	0.65	8.4
	July	115	4.5	10	4.8	8.8	0.58	6.1
	August	99	4.6	8.9	4.0	9.0	0.77	6.6
	September	91	3.9	11	3.4	5.3	0.44	5.4
T. latifolia	May	102	4.6	9.8	7.0	19	0.81	3.3
	June	74	4.9	14	4.7	9.8	0.78	11
	July	50	6.2	10	3.8	9.2	0.58	11
	August	44	5.3	10	4.0	9.7	0.65	7.0
	September	71	6.4	11	2.9	7.1	0.71	5.9
S. lacustris	May	112	2.5	9.0	5.1	20	0.52	5.0
	June	281	3.7	10	6.0	18	0.48	3.3
	July	202	5.2	8.2	5.8	10	0.72	8.2
	August	170	5.5	7.0	4.2	9.2	0.53	8.3
	September	161	5.0	9.5	4.0	11	0.44	5.1

was highest at the beginning of the vegetation period. Lead was sometimes higher during the summer. Some of these trends confirm the data of Ozimek (1988).

The ranges and mean concentrations in water and sediments are reported in Table 3. They were within the limits reported by Moore and Ramamoorthy

Table 3. Heavy metal concentrations in water and bottom sediments collected monthly during 1989 from the Aldomirovsko swamp (n=25).

Element	Water, mg L^{-1}		Sediment, mg kg^{-1}	
Fe	(0.0117 - 0.0836)	0.0531±0.0202	(3045 - 8040)	6205±1020
Co	(0.0028 - 0.0182)	0.0068±0.0027	(4.6 - 18)	14±4
Ni	(0.0082 - 0.0672)	0.0123±0.0051	(11 - 27)	17±6
Cu	(0.0008 - 0.0460)	0.0176±0.0052	(6.1 - 30)	18±6
Zn	(0.0041 - 0.0902)	0.0336±0.0098	(21 - 76)	41±14
Cd	(0.0007 - 0.0017)	0.0011±0.0003	(1.3 - 2.4)	2±0.4
Pb	(0.0108 - 0.0335)	0.0266±0.0082	(12 - 51)	32±10

(1984). Wide variation in Cu and Zn concentrations were present in water samples. Iron in sediments was 10x higher than that of the other metals. The mean microelement content for the macrophytes, water and sediment samples was in the descending order of: Fe>Zn>Pb>Cu>Ni>Co>Cd.

In accordance with the calculated biological absorption coefficients (concentrations in emergent plants in mg kg^{-1} dry wt - concentrations in sediments in mg kg^{-1} dry wt), there was no biological accumulation in the above-ground biomass. The Ni coefficients were close to 1 for *Iris pseudacorus* and *Typha laxmanni*.

The concentration factors, being a relationship of the concentrations in plant species (mg kg^{-1} dry wt) to the concentrations in the water (mg L^{-1}), were in the range of 10^2 to 10^5 in the submerged plants, the composition of which is determined exclusively by the water environment. Iron was accumulated in the greatest quantity (162,542 for *Elodea canadensis* and 126,742 for *Potamogeton pusillus*). The elements Co, Ni, Pb and Cd followed in the order of 10^3. Zinc and Cu were accumulated to a smaller extent, i.e., 10^2. Similar values for the concentration factors were reported by Kovacs et al. (1985). In the floating species the concentration factor for Fe was 10^4, for Co - 10^3, for Ni - 10^2 - 10^3, while for the other heavy metals it was 10^2. The biological absorption coefficients (with respect to the sediments) in the submerged plants attached to the substrate (*Potamogeton species*) were around 1 for Co in the three species, and for Fe, Pb and Ni in *Potamogeton pusillus*.

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