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Macrophytes as indicators of bioavailable Cd, Pb and Zn flow in the river Przemsza, Katowice Region

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Abstract—A 5 km stretch of the river Przemsza, in southern Poland, was investigated with the aim of finding out if a gradient of metal pollution was present along the river and to determine the bioavailable flow of Cd, Pb and Zn between water, sediment and submerged macrophytes. *In situ* experiments in pots as well as experiments in sealed jars were performed by using *Potamogeton pectinatus* and *Myriophyllum verticillatum*. These were planted in polluted sediment from 3 localities along the river and in unpolluted sediment in order to find out if metals were taken up by the shoots or roots. After 6 weeks exposure, plants, sediment and water were analysed for their metal contents. The unpolluted sediment accumulated heavy metals, indicating addition of metals from the water, while the polluted sediment instead released metals to the water. The plants accumulated heavy metals, but the absence of differences in metal content in plants grown in unpolluted and polluted sediment indicated that the metals were accumulated mainly by the leaves from the water. Increasing concentrations of Pb in plants indicated an increasing down-stream gradient of Pb. There were also higher concentrations of Cd and Zn in shoots of both plant species downstreams compared with upstreams. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The southern part of Poland is strongly polluted by heavy metals. Mining and metallurgical industries cause heavy metal contamination of soil, water and biota (Grodzinski *et al.*, 1990). Heavy metals mainly originate from unpurified industrial waste water and leakage from mine dumps. The Przemsza is a tributary of the river Vistula, one of the largest rivers in Poland with its outflow in the Baltic Sea. Decreasing heavy metal concentrations down stream have been shown to occur in the Vistula river (Helios-Rybicka and Kyziol, 1991). The water of the river Przemsza, flowing through the heavily industrialized Katowice region, has been classified as highly polluted (Ochrona Srodowiska, 1992). The Cd content of river sediment from the Przemsza has been shown to be up to 154 μg (g dry wt)$^{-1}$ (near the village of Gorzów close to the mouth of the river) approaching some of the highest levels recorded in Europe (Macklin and Klimek, 1992). Zinc and Pb pollution were also severe in the river (Macklin and Klimek, 1992).

Animal and plant life in the polluted river Przemsza is very poor. Naturally growing *Potamogeton pectinatus* only occurs at a few locations along the river in the vicinity of the village Gorzów. That this species and other macrophytes are able to take up heavy metals both by their roots and shoots illustrates that they are suitable for monitoring of bioavailable heavy metals (Agami and Waisel, 1986; Greger and Kautsky, 1990, 1993a,b). The plants give an integrated indication of the available amount of metals both in the water and in the bottom sediment.

The aim of the study was to investigate heavy metal flow in the water–sediment–plant system using 2 submerged macrophytes, *Potamogeton pectinatus* and *Myriophyllum verticillatum*, planted in polluted and unpolluted sediment. An additional aim was to determine if a decreasing pollution gradient occurred along a 5 km strech of the river Przemsza. In order to ascertain if metals were taken up by leaves from the water or by roots from the sediment, plants were planted in both clean sediment from the Goczalkowice reservoir and polluted sediment from the river Przemsza. Plants in polluted sediment were expected to show uptake both from the water and the sediment, while the uptake in plants in the unpolluted sediment would mainly reflect the metals in the water.

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MATERIALS AND METHODS

Potamogeton pectinatus was collected from the fresh water reservoir of Goczalkowice and *Myriophyllum verticillatum* from the river Vistula next to the reservoir. The length of the shoots of *P. pectinatus* was about 10 cm and those of *M. verticillatum* about 25 cm. Plants were planted in unpolluted sediment from the Goczalkowice Reservoir and in heavily polluted sediment sampled from 3 different localities of the river Przemsza (Fig. 1). The experiment was carried out *in situ* at the 3 localities (Fig. 1) to record a likely pollution gradient, and also in plastic jars sealed with lids and placed in the shade outdoors at the Goczalkowice field station in order to additionally determine the heavy metal flow in the water–plant–sediment system. The experiment was carried out during 6 weeks, from 19 June to 2 August 1993.

The grey–yellowish unpolluted sediments were dense and contained some clay. The polluted sediments were black, probably due to C particles. In location 1 the sediment was fine grained sand, in location 2 it was more unconsolidated and at location 3 it was like black yoghurt.

In situ *experiment*

Four pot systems consisting of 6 2 l pots each filled with 1.8 l of sediment (Greger and Kautsky, 1991) were placed at each of the 3 localities in the river (Fig. 1). Two systems contained unpolluted sediment and the other 2 sediment from the locality. In each pot 3 plants were planted, each species in every other pot. The pots were covered by tissue to prevent sediment and plants from being flushed out. The pot systems were placed about 30 cm apart, at a depth of about 10–15 cm, and fixed to the river bottom by a hook to prevent them from being dislodged.

Outdoor experiment in sealed jars

In this experiment transparent jars of 1.5 l, sealed with white lids and containing unpolluted and polluted sediment from the 3 different locations (Fig. 1), respectively, were used. Sediment depth in the jars was 6 cm. Two to 3 shoots were planted in each jar. Water from the 3 localities was carefully poured into the jars up to 1 cm from the edge so that as little as possible of the sediment was stirred up.

Preparation of samples and analyses of heavy metals and organic content

Sediment, water and plant samples were taken prior to and after the experiments. Plants were washed thoroughly in distilled water until no sediment was left, shoots and roots were separated, and dried in 100°C for 6 h. The plant material was wet digested in HNO_3:$HClO_4$ (7:3, v/v). Sediment samples were dried at 100°C for 24 h, weighed and digested for 2 h in 7 M HNO_3 to obtain the sum of the firmly bound and the plant-available fraction of heavy metals. The concentrations of Cd, Pb and Zn were then analysed by flame atomic absorption spectrophotometry (Varian AA-1275). The water samples were analysed by AAS using a graphite oven. The organic content of the sediment was measured by combustion at 480°C for 2 h.

Statistics have been calculated using the *t*-test. The majority of the mean values were calculated on 5 samples or more. In a few cases, however, 3 values were considered sufficient for these calculations. In the *in situ* experiment, very few plant replicates could be examined and here the statistical calculations could only be made in very few locations, which is why most of these results are not shown.

RESULTS

The content of organic material was about 5% in the unpolluted sediment (Fig. 2). The Przemsza sediment contained an increasing amount of organic

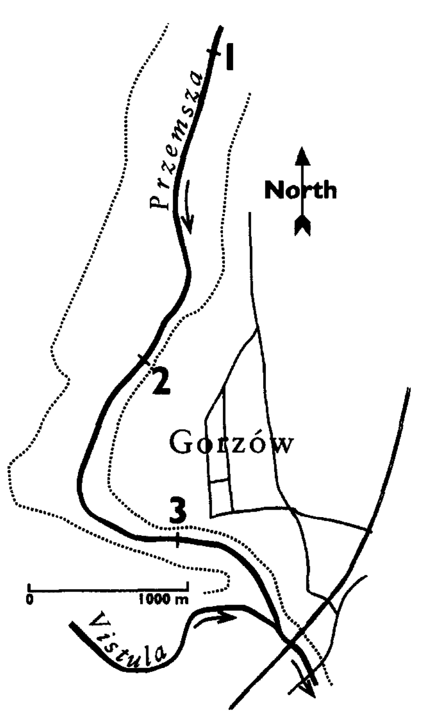

Fig. 1. Map of the Gorzów area showing the 3 locations used in the *in situ* experiment.

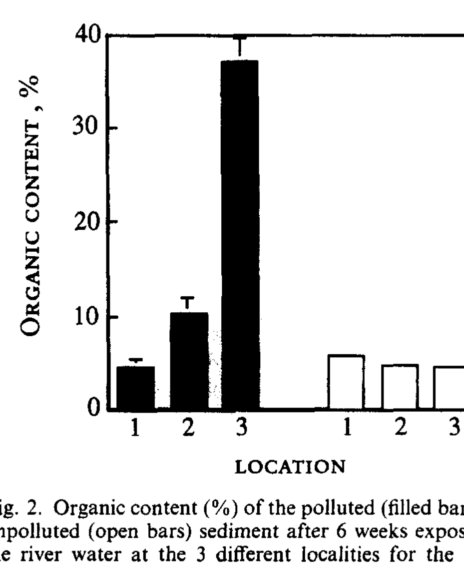

Fig. 2. Organic content (%) of the polluted (filled bars) and unpolluted (open bars) sediment after 6 weeks exposure to the river water at the 3 different localities for the *in situ* experiment and the corresponding jars of the sealed pot experiment. Values are means of 5 replicates, ±SE are indicated in all bars.

Table 1. Concentrations of Cd, Pb and Zn [μg (g dry wt)$^{-1}$] in polluted and unpolluted sediment (HNO_3-fraction) before and after exposure to river water

Metal	Location	Unpolluted sediment			Polluted sediment		
		Before	After		Before	After	
			In situ	Sealed jars		*In situ*	Sealed jars
Cd	1	3.0	25.8	2.9	224	167	159
	2	3.0	n.d.	3.4	350	—	96
	3	3.0	20.3†	4.0	361	—	263
Pb	1	12.6	38.1*	19.2	295	213	155
	2	12.6	12.3	22.5	263	—	135
	3	12.6	29.7†	16.7	429	—	771
Zn	1	33.8	611	149	15433	5513	1640
	2	33.8	467	166	6679	—	596
	3	33.8	466	164	6373	—	1481

Values are means of 5–6 replicates. $\pm$SE $\leq$ 13% except *20% and †30%. n.d. = not detectable.

material from location 1 to location 3, the latter with a content of 37.2%. There was no significant difference between the organic content before and after the experiment (not shown).

At the start of the experiment the Cd content of the polluted sediment was 100 times higher, Pb 2–3 and Zn 190–470 times higher than in the unpolluted sediment (Table 1). During the 6 weeks of exposure to the river water the unpolluted sediment increased its concentration of all 3 investigated metals, while the opposite was found for the polluted sediment, except for Pb at location 3 (Table 1). However, the increase in the Cd concentration of the unpolluted sediment was not found in the sealed pots. Addition of heavy metals from the water to the unpolluted sediment was highest at location 1 and declined at locations 2 and 3 (Table 1; *in situ* experiment).

The concentration of heavy metals in the water was only analysed in the sealed pot experiment (Table 2). Generally, during the 6 weeks of exposure the concentration of heavy metals had declined in all cases, except for Pb in the jars containing polluted sediment from location 1, here a slight increase was found. The Pb content decreased in the water from locations 1 to 3, while no significant difference was found in Cd concentration in the water between the 3 locations. In the unpolluted sediment series, the Zn level of the water was highest at location 1 while the opposite was found in water from the jars with polluted sediment.

Table 3 shows the concentration of Pb, Cd and Zn in roots and shoots of the macrophytes after 6 weeks of exposure. The lower background concentration of metals in plants showed that metals had been taken up during the experiments. In the *in situ* experiment with unpolluted sediment, the shoots of both plant species had considerably higher concentrations of all 3 metals at location 3 than at location 1 after exposure to the polluted running water. The concentrations of metals in the roots and shoots of the 2 macrophytes were not generally higher if they had grown in polluted sediment than if they had grown in unpolluted sediment (Table 1; sealed pot experiment). The 2 macrophyte species differed in their uptake of heavy metals. In the sealed pot experiment, *Myriophyllum verticillatum* generally contained higher levels of Zn

Table 2. Concentrations of Cd, Pb and Zn ($\mu g\ l^{-1}$) of water from 3 locations of the river Przemsza before and after 6 weeks in sealed pots placed outdoors

Metal	Location	Before	After	
			Unpolluted sediment	Polluted sediment
Cd	1	16.8	9.7	8.1
	2	16.7	9.7	8.2
	3	14.8	9.7	10.6
Pb	1	18.7	14.5	26.2
	2	20.8	12.3	11.6
	3	25.5	9.0	11.4
Zn	1	618	121	28.2*
	2	480	37	45.1
	3	444	37†	104.0

Values are means of 5–6 replicates. $\pm$SE < 20% except *29% and †34%.

Table 3. Concentrations of Cd, Pb and Zn [μg (g dry wt)$^{-1}$] in roots and shoots of *Myriophyllum verticillatum* and *Potamogaton pectinatus* after being grown in pots for 6 weeks in unpolluted or polluted sediment from the 3 locations in the river

Metal	Location	*In situ* experiment				Sealed jar experiment			
Sediment		*P. pectinatus*		*M. verticillatum*		*P. pectinatus*		*M. verticillatum*	
		Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots
Cd									
Unpolluted	1	14.3	10.3	3.2	1284	9.9^{a}	36.0^{b}	13.7^{b}	8.0^{a}
	2	—	—	—	—	28.7^{a}	49.8^{a}	17.6^{a}	29.0
	3	29.9^{a}	23.4^{b}	26.6	—	0.8	n.d.	4.6	18.8^{a}
Polluted	1	—	—	—	—	13.0	33.5^{a}	4.6	18.3
	2	—	—	—	—	15.5^{a}	12.6	6.4^{a}	20.4^{a}
	3	—	—	—	—	—	—	34.3	—
Pb									
Unpolluted	1	26	158	26	4257	126	n.d.	22.2	n.d.
	2	—	—	—	—	79	783^{c}	25.2^{a}	116
	3	92^{a}	154^{b}	287	—	761^{b}	1482^{b}	29.5^{a}	346^{a}
Polluted	1	—	—	—	—	n.d.	3	8	155^{b}
	2	—	—	—	—	250^{b}	420	24^{b}	87^{c}
	3	—	—	—	—	—	—	288	—
Zn									
Unpolluted	1	4946^{b}	6564	3009	3295	481^{a}	511^{c}	1248^{b}	907^{a}
	2	—	—	—	—	604	315^{a}	1203^{a}	527
	3	18,269^{a}	8547^{b}	7689	—	391^{a}	782^{a}	730^{a}	529
Polluted	1	—	—	—	—	2020^{b}	1470^{b}	1684	1751^{a}
	2	—	—	—	—	356^{a}	293^{a}	1648	690
	3	—	—	—	—	—	—	4126	—

Prior to the experiments, the concentrations of Cd, Pb and Zn in *P. pectinatus* were 6.7, 15.9 and 234 in shoots and 21, 21.4 and 166 in roots, respectively, and in *M. verticillatum* were n.d., n.d. and 23.9 in shoots and n.d., n.d. and 12 in roots, respectively. Values are means of 5–6 replicates. $\pm$SE $<$ 15% except ^{a}16–35%, ^{b}36–45% and ^{c}46–55%. n.d. = not detectable.

than *Potamogeton pectinatus*, while *P. pectinatus* contained higher levels of Pb and Cd.

DISCUSSION

The running water causes a continuous exposure of the sediment and plants to high levels of dissolved and particulate metals transported along the river. This is suggested as one of the reasons for a higher concentration of heavy metals in both the unpolluted sediment and the plant shoots after 6 weeks of exposure to metal-polluted water in the *in situ* experiment in comparison with the sealed jar experiment (Tables 1 and 3).

The higher concentrations of all analysed metals in plant shoots at location 3 compared with location 1 indicates an increasing pollution gradient of bioavailable heavy metals along the river (Table 3). The differences in metal concentrations of sediments were, however, not that obvious and a difference similar to that in plant shoots was only found for Pb in the sealed pots (Table 1). At shorter distances, as in this case (5 km), local stream conditions may be more important than at longer distances, and may influence the organic content and precipitation of heavy metals to the sediment. A previous study on heavy metal concentrations in sediment at the same localities, but over a greater distance (90 km) than in this study, showed a declining gradient for Zn and Pb along the river (Macklin and Klimek, 1992).

The accumulation of heavy metals from the river water by the unpolluted sediment shows that the concentration of heavy metals of the river water is high (Table 1). However, polluted sediment released metals to the water which indicates that this sediment is saturated with heavy metals (Table 1). This type of metal release from polluted sediment may also occur during periods of high turbulence in the river. The high Zn level in the water at location 3, compared with the other locations, showed that the polluted sediment was unable to hold all metals despite its high organic content (Table 2, Fig. 2).

The metals released from the polluted sediments are likely to be accumulated by the plant shoots since the metal content of the water decreased during the experiment (Tables 1 and 2). The metals in the polluted sediment are also accumulated by the plant roots which seems to be the case when the organic content is low (in location 1), but not at higher organic concentrations (locations 2 and 3; Table 3, Fig. 2). High organic content lowers the mobility of metals (Kuntze, 1985) and is correlated with low plant availability of heavy metals in sediment (Greger and Kautsky, 1990). In the present study, the organic content does not seem, however, to capture Cd and Zn in the sediment but could be the reason for the high Pb content in the sediment from location 3 of the sealed pots (Fig. 1, Table 1). Low levels of Pb in the water and high levels in the polluted sediment are probably due to high organic . ıtent (Table 1 and Table 2). Cadmium and Zn are more mobile than Pb in river sediments, where Pb is sorbed to sediment particles in greatest amounts and Cd in the smallest (Helios-Rybicka and Kyziol, 1991). Cadmium has a higher solubility than other heavy metals (Förstner and Wittmann, 1979).

The highest Pb concentration was found in the roots of the plants and the concentration increased from locations 1 to 3 (Table 3). Since this is also the case in the presence of unpolluted sediment, in which there is no increase in Pb concentration from location 1 to location 3, the uptake of Pb is probably mainly by the shoots with a subsequent transportation to the roots. However, the transport of Pb within plants is shown to be restricted (Peter *et al.*, 1979; Knowlton *et al.*, 1983). Nonetheless, except for Pb, many heavy metal species can be transported from shoots to roots in submerged macrophytes (Greger, unpublished results). It is interesting to note that plants grown in polluted sediment did not show higher metal concentrations after 6 weeks of exposure than plants grown in unpolluted sediment (Table 3). This may be due to metals preferably being taken up by shoots from the water, which was polluted to a similar extent in both cases.

The 2 plant species showed preferences in accumulating different metals. *Myriophyllum verticillatum* accumulated Zn to a higher degree than did *Potamogeton pectinatus*. High Zn accumulation has also been found for other Myriophyllum species, such as *M. spicatum* (Greger and Kautsky, 1992) and *M. heterophyllum* (Cushing and Thomas, 1980).

In conclusion, transportation of metal-contaminated particles and dissolved ions within water, the re-suspension and precipitation patterns, as well as organic matter content of the sediment, seem to be major factors affecting how heavy metals are distributed along the investigated river. There are indications of higher levels of bioavailable heavy metals down stream. The unpolluted sediment accumulated heavy metals and could be a suitable tool for monitoring metal transportation in polluted rivers where little submerged vegetation occurs. The polluted sediment released some of its heavy metals, showing that it was already excessively saturated by these. The plants probably prefer to accumulate the metals through the leaves from the river water.

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