Partitioning of trace metals between particulate, colloidal and truly dissolved fractions in a polluted river: the Upper Vistula River (Poland)

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Abstract

Metal partitioning depends on the physical–chemical conditions of a system and can be affected by anthropogenic inputs. In this study, the authors report the results of trace metal partitioning between particulate (>1.2 μm), colloidal (1.2 μm–1 kDa) and truly dissolved (<1 kDa) fractions in the polluted section of the Upper Vistula River compared with the non-polluted headwaters. It was found that the salt input in the Vistula River induced a decrease of colloid concentration and the increase of suspended particulate matter. Compared with upstream from the polluted section, the metal concentrations (Co, Cu, Cr, Mn and Zn) in the colloidal fraction were lower. It was mainly due to the rapid colloid coagulation at increased salinity, the competition with ligands and major ions (Ca and Mg) and the weak mobility of metals associated with particles at the pollution sources. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Knowledge of the chemical forms of metals is essential to understand their interaction with living organisms, as a metal speciation controls its mobility, bioavailability and toxicity (Buffle, 1988; Tessier and Turner, 1995). Metals in surface water have traditionally been subdivided into two fractions: "dissolved" and "particulate" according to an operationally defined limit (usually 0.45 μm) and separated by filtration. The filter passing "dissolved" fraction clearly does not represent the truly dissolved metal ions, but is composed of free metals, complex ions, metals bound to a variety of ligands, forming molecules of various dimensions and chemical characteristics, which may further be bound to larger entities of colloidal size, both organic and inorganic.

Association of metals with carriers of different dimensions determines their transport (diffusion–advection–coagulation–sedimentation) and their bioavailability. The metals bound to particles are quickly incorporated into the sediments whereas free-metals and metals bound to dissolved ligands have a longer residence time in water and may be transported over long distances. Metals associated with colloids (1.2μm–1 kDa) have an intermediate behaviour since they cannot settle themselves but may eventually aggregate into settling particles.

Although much progress has been made in the last decades to determine the partitioning of metals between these different forms, trace metal speciation in natural water remains a serious challenge. The role of colloids in estuarine and marine systems has been recently extensively studied (e.g. Kraepiel et al., 1997; Guo et al., 2000; Sanudo-Wilhelmy et al., 1996; Wells et al., 1998, 2000; Wen et al., 1997) whereas less is known about

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freshwater systems (Douglas et al., 1993; Ross and Sherrel, 1999), particularly those influenced by anthropogenic inputs (e.g. Guéguen et al., 2000; Sigg et al., 2000).

Partitioning of metals in a polluted river is of particular interest because at a high, potentially toxic concentration, they may, to different degrees, impact on aquatic life. The partitioning in polluted water is difficult to predict, as it depends on a variety of additional factors associated with anthropogenic metal input, such as pollution origin, concentration and characteristics of suspension, colloidal and dissolved ligands and changes in physico chemical parameters of water. The principal goal of this study was to evaluate the modifications of metal partitioning in the polluted section of the river, as compared with the quasi-natural, non-polluted headwaters. The authors examined the role of colloids and found that in the polluted section colloidal metal concentration was low due to coagulation that increased with salinity and because of a weak mobility of some particle associated metals. Thus, despite a high concentration of metals in water, their direct bioavailability is probably limited. The related toxicity assessment is reported elsewhere (Guéguen et al., in prep.).

The Vistula River, one of the biggest European rivers (length 1047 km, watershed area 194 700 km^2, mean discharge 1054.6 m^3 s^{-1} for 1900–1987), is the source of water for 24×10^6 inhabitants. The water quality of the Vistula River deteriorated between 1950 and 1990 (Dojlido, 1997), and although some improvements have been observed in the last decade, it remains heavily polluted especially in its upper course. The high density of industries in the river basin and insufficient number of treatment plants make the Vistula River one of the most significant sources of pollutants (salts, nutrients organics and metals) transported into the Baltic Sea. In this study, the impact of increasing contaminant inputs in the Upper Vistula River on the concentrations, on the size distribution and size speciation of some trace metals (Cd, Co, Cr, Cu, Mn, Pb, Zn) was investigated.

2. Setting and sampling stations

The environmental situation in the upper Vistula River basin has recently been reviewed by Grodzienska (1999). The present study covers a part of the upper Vistula River from the headwaters to Cracow, a section of about 150 km length. Sampling was carried out in November 1998 at 5 stations on the Vistula River and at 1 station on the Przemsza River (Fig. 1) at a moderate to low river flow. The positions of the sampling points are given as a distance in km from the confluence of the Vistula River and the Przemsza River with (+) sign

downstream and (−) upstream (Table 1). Mean annual flow and mean daily flow on the day of sampling measured at the nearest gauging station are also given.

The section from the sources in the Carpathian Mountains to the Goczalkowice reservoir, considered as relatively natural, with no local sources of metal pollution, is represented by the reference sampling station 1-Lipowiec. The headwaters were characterised by a relatively low dissolved ion contents and low Ca level, as the watershed rocks are composed mostly of siliceous sandstones, shales and conglomerates of the flysch formation (Pasternak, 1962). Headwater streams have pH varying between 6.4 and 7.5 (Wrobel, 1966).

Downstream from the Goczalkowice reservoir the river enters the Upper Silesia mining and industrial district. Groundwaters originating from coal mines are highly saline, with residual waters from some mines containing up to 250 g l^{-1} of dissolved salts, mainly Na$^+$, Cl$^-$ and SO$_4^{2-}$ (Baradziej, 1998). It was estimated that about 11 000 tonnes/day of Cl$^-$ and SO$_4^{2-}$ were drained from the coal mines in 1990, of which about 5000 tonnes/day were released to the Vistula, locally raising the Cl$^-$ concentration in the river to a maximum of 7 g/l (Helios-Rybicka, 1996a; Baradziej, 1998). During the low flow period the contribution of water pumped from the coal mines to the total Vistula discharge was as high as 14–35% (Gajowiec and Rozkowski, 1988). Mine water is enriched in some trace (Zn, Co, Ni, Mn, Cu, Ba) and radioactive (Ra) elements, but during the transfer via a complex system of channels, ponds and streams, the variations in redox conditions, precipitation, dissolution and settling may influence the concentration of trace elements in the water finally entering the Vistula River. (Jasinska et al., 1998; Pluta and Trembaczowski, 2001). The sampling stations 2–4 were selected to reflect the impact of the coal mining area. It should be, however, noted that air and soil in this area are also highly contaminated with metals originating from smelting, coal-based power generation, steelworks, and chemical industry (Helios-Rybicka, 1996b). Further, the Przemsza River, a major tributary of the Vistula, drains an area of historical and present mining of Zn–Pb ores. The whole region suffers from heavy pollution with Zn, Pb, and Cd, originating from mine effluents, smelters and mining wastes. Elevated concentrations of these metals have been observed in soils (Verner et al., 1996; Ullrich et al., 1999), rivers (Jop, 1980; Suschka et al., 1994; Labus, 1999a; Pistelok and Galas, 1999), sediments (Pasternak, 1974; Helios-Rybicka, 1986; Bojakowska and Sokolowska, 1996; Ciszewski, 1998; Labus, 1999b) and, to a certain degree, in aquatic vegetation (Lewander et al., 1996). The sampling stations 3-Chelmek (on the Przemsza River) and 4-Bobrek (on the Vistula, downstream from the confluence with Przemsza) were chosen to examine the effect of these sources. Finally, the stations 5-Metkow
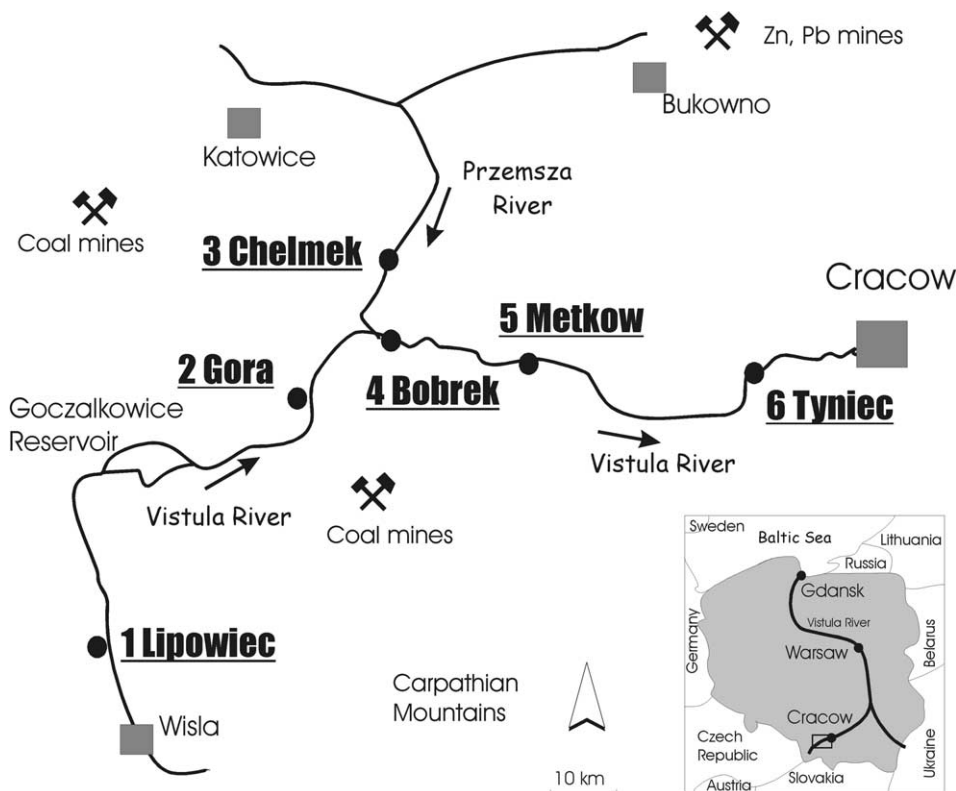
Fig. 1. Location of sampling stations.

and 6-Tyniec were selected to observe the fate of pollutant transported downstream, where the Vistula River is joined by a number of less polluted tributaries (Sola, Skawa and others). Here, previous works have demonstrated a gradual decrease in salinity and an increasing proportion of carbonate ions (Bombowna and Wrobel, 1966), and also a decrease in metal content in suspended matter and sediments (Helios-Rybicka, 1986). Downstream from the station 6-Tyniec an additional loading of metals, particles and colloids from municipal sewage and industrial sites in Cracow (Helios-Rybicka, 1983; Wardas et al., 1996; Guéguen et al., 2000) may contribute to changes in metal partitioning, and thus this section has not been examined in this study.

3. Sample handling and analysis

Surface water (∼10 l) was collected with a polypropylene (PP) drum and thin layer of bottom sediment collected by hand and sieved at 63 μm. Ultra clean conditions were maintained during all stages of sample collection, transport, handling, processing and analysis. Raw water samples were immediately filtered in the field through a 1.2 μm PP cartridge filter (Calyx, MSI). The tangential flow ultrafiltration was performed with a 1

kDa regenerated cellulose cartridge (PrepScale, Millipore) in the laboratory within 4 h after water collection. More details on tangential flow filtration (TFF) separation procedure are given in Guéguen et al. (2002). The factors of concentration (fc) applied for TFF were between 2 and 4. An aliquot of the retentate was separately frozen for the determination of the colloid concentration by weight.

In the total dissolved (< 1.2 μm), colloidal (1 kDa–1.2 μm) and truly dissolved (< 1 kDa) fractions, the concentrations of major elements (Ca, Fe, Mg, Na and Si) and, trace metals (Cd, Co, Cr, Cu, Mn, Pb and Zn) were determined with ICP-AES (Plasma1000, Perkin Elmer) and ICP–MS (HP 4500, Agilent) respectively. Water samples were analysed in 5 replicates and the mean values reported. Certified standard reference material (SRM 1643d from NIST) was run to check the performance of the ICP–MS and ICP–AES during the sample analysis. In addition, standard solutions were run in each series of analyses to ensure data quality. The mass balance of the fractionation process was good for major and trace metals (91–106%).

Total dissolved (DOC), colloidal (COC) and truly dissolved (ultrafiltered UOC) organic C contents were determined with a Shimadzu TOC 5000A analyser. The concentration of COC and UOC in the frozen and fresh

samples was the same. Alkalinity, NH_4, Cl, NO_3 and PO_4 were determined by colorimetric measurements (Bartram and Ballance, 1996).

Metal contents in the bottom sediment were measured by X-ray Fluorescence spectrometry (Philips PW 2400). A certified standard reference material (SRM 1645 from NIST) was analysed to check the accuracy of metal determinations.

The determination of colloid concentrations in mg/l was performed after ultracentrifugation (Centrikon T-1080) of the retentate fraction isolated by the TFF process. Stokes' law was used to calculate the duration of ultracentrifugation. The density of the colloidal components was taken at 1.1 g cm^{-2}, the rotation velocity was set at 26 000 rpm and the temperature at 5 °C. After 14 h of ultracentrifugation the supernatant, supposed to contain the smaller colloids (20 nm–1 kDa), was carefully pipetted, into a pre-cleaned plastic bottle. A new aliquot of the TFF retentate was added and ultracentrifuged. This procedure was repeated 7–8 times. The concentration of larger colloids (>20 nm) was determined after freeze-drying of the cake and correction for salt content.

Experimental results of size speciation were compared with those obtained by computational simulation of chemical equilibrium based on stability constants (MINTEQA2 version 3.11; Allison et al., 1991).

4. Results and discussion

4.1. General physicochemical characteristics of water

As the sampling was performed in late autumn, water temperature (Table 2) was low (from 0.0 to 4.9 °C). The values of pH were comparable for all stations (7.2–7.7). Varying in a narrow range, these two parameters did not account for the modification of the metal partitioning discussed later.

The total DOC contents varied within a factor of two (4.3–8.2 mg l^{-1}) between the six stations. By contrast, strong differences were observed in conductivity (and salinity) and concentrations of Cl, NH_4 and suspended particulate matter (SPM), with the lowest values at station 1 and the highest at stations 2 or 4. In the mining district, the Przemsza River (station 3) had lower salinity, Cl and SPM concentrations but higher alkalinity and content of nutrients, which reflects the more carbonate character of the watershed rocks and a higher urban sewage input. Although the Przemsza River receives groundwater from many coal mines, water is less saline as the mines are not as deep in this area as in the south (Gajowiec and Rozkowski, 1988). Major element contents in colloidal and truly dissolved fractions are shown in Table 3 and the concentrations of some ions presented in Fig. 2. At station 1, the concentrations

Table 1
Location of sampling points and water flow data

Station no./river	Station name	Location (km)[a]	Date of sampling	Gauging station	Mean flow at the date of sampling (m^3 s^{-1})	Mean annual flow (m^3 s^{-1})
1 Vistula	Lipowiec	−83.0	23 November 1998	Ustron	2.21	2.64[b]
2 Vistula	Gora	−21.0	23 November 1998	Jaszowice	5.12	12.3[b]
3 Przemsza	Chelmek	−6.0	25 November 1998	Jelen	19.2	19.3[b]
4 Vistula	Bobrek	+0.5	25 November 1998	Pustynia	25.7	43.8[c]
5 Vistula	Metkow	+15.0	25 November 1998	Smolice	57.2	76.4[d]
6 Vistula	Tyniec	+63.5	21 November 1998	Czernichow	50.2	89.7[e]

[a] Distance from the confluence of the Vistula and Przemsza Rivers: (−) upstream, (+) downstream.
[b] Data from the IMGW Katowice (1956–1999).
[c] Data from IMGW Krakow: 1961–1999.
[d] Data from IMGW Krakow: 1951–1999.
[e] Data from IMGW Krakow: 1997–2000.

Table 2
General water quality in the Upper Vistula River

Station	T (°C)	Cond. (µS/cm)	Salinity	pH	SPM (mg/l)	Alk (mM)	NH_4^+ (mg/l)	P–PO$_4$ (mg/l)	NO$_3$ (mg/l)	Cl$^-$ (mg/l)
1 Lipowiec	0.0	463	0.3	7.7	5.3	0.5	0.6	<0.25	8	5.61
2 Gora	1.4	2702	2.4	7.2	45.6	1.9	4.6	0.45	3	1321
3 Chelmek	4.9	1574	1.3	7.8	13.9	4.2	3.8	0.67	10	491
4 Bobrek	3.7	3862	3.5	7.5	99.5	3.5	4.0	0.29	5	2500
5 Metkow	3.1	1788	1.5	7.6	39.3	2.8	2.0	0.51	10	724
6 Tyniec	2.1	1134	0.9	7.5	5.4	2.0	0.9	0.29	12	590

Table 3
Concentrations in mg/l of dissolved organic carbon (DOC) and major element (Fe, Si, Ca, Na and Mg) in the colloidal and the truly dissolved fractions

Station	DOC		Fe		Si		Ca		Na		Mg	
	COC	UOC	Colloidal	Truly dissolved	Colloidal	Truly dissolved	Colloidal	Truly dissolved	Colloidal	Truly dissolved	Colloidal	Truly dissolved
1	4.93±0.10	0.89±0.01	0.018±0.001	n.d.	n.d.	6.80±0.09	2.49±0.13	15.17±0.19	0.52±0.04	3.32±0.10	0.32±0.02	1.56±0.02
2	6.92±0.43	1.30±0.03	0.347±0.003	n.d.	n.d.	11.34±0.01	2.93±0.45	127.61±0.74	n.d.	621.61±0.63	n.d.	44.97±0.90
3	5.82±0.10	0.97±0.19	0.070±0.001	n.d.	n.d.	11.01±0.39	3.71±0.43	122.02±1.05	n.d.	248.35±0.74	0.64±0.15	49.07±0.32
4	2.35±0.05	4.11±0.05	0.158±0.001	n.d.	n.d.	11.26±0.07	1.51±0.64	130.45±2.04	26.14±4.51	960.88±11.68	n.d.	89.44±1.46
5	5.63±0.19	2.28±0.04	0.069±0.001	n.d.	n.d.	9.61±0.17	2.65±0.53	89.35±1.51	n.d.	347.38±2.90	n.d.	42.97±0.64
6	1.83±0.18	2.45±0.03	0.222±0.003	n.d.	n.d.	8.55±0.13	3.41±0.48	72.35±0.82	5.10±1.55	286.66±0.61	n.d.	30.53±0.59

COC and UOC mean colloidal and truly dissolved (ultrafiltered) organic carbon, respectively. n.d. (not detected) means that the measured concentrations were below the limit of detection (0.004 mg/l Fe, 0.020 mg/l Si, 0.013 mg/l Ca, 0.027 mg/l Na and 0.003 mg/l Mg).

of major elements were one or two orders of magnitude lower than at other locations, except for DOC and Si. The predominance of flysch formation (sandstones, shales) in the watershed (Pasternak, 1962) may explain relatively high silica and low Ca concentrations in headwaters. At station 2 the increase of dissolved salts, with Na and Cl concentrations rising by more than two orders of magnitudes was striking. As expected, the input of highly saline waters originating from deep coal mines was clearly seen at this point. Chloride concentration at station 4 was higher than the maximum concentrations observed on 1985 (Gajowiec and Rozkowski, 1988), but nearly 3 times lower than the maximum reported by Baradziej (1998) from 1996 for the same station. Downstream from the mining district, the concentrations of salts decreased; thus at station 6 the concentration of Na was 3 times lower than at station 4 due to the dilution by low-salt water discharged by tributaries draining the Carpathians. A similar decrease was observed by Bombowna and Wrobel (1966) at low water flow conditions, although the maximum the salt concentrations in the 1960s were roughly half of these observed in 1998.

4.2. Characteristics of colloids

Major elements (Fe, Si, Ca, Na, Mg) and DOC were measured in the colloidal and truly dissolved fractions (Table 3). All of total dissolved Fe was found in the colloidal fraction, still iron was only a minor constituent of colloids that were mainly composed of COC and Ca. Only a small part of the total dissolved Ca was in colloidal form, but it makes by weight about half of the concentration of COC, except at station 6, where COC was less abundant. It has been previously shown that aquatic colloids can contain significant amounts of Ca
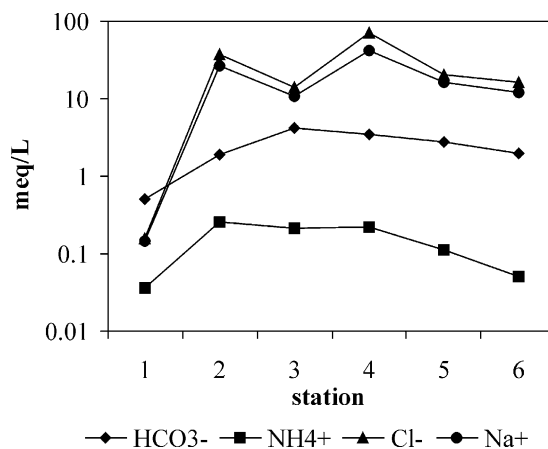

Fig. 2. Concentration of dissolved ions in the Vistula River.

which is supposed to be adsorbed to organic matter (Ran et al., 2000). However, as the colloidal Ca/COC ratio in the Vistula River was high, we believe that colloidal Ca was present in the form of carbonates.

Surprisingly, no colloidal silica was detected. Aluminium could not be accurately measured, but its concentration in the colloidal fraction was only a few µg l^{-1}. This suggests that clays were only a minor constituent of colloids and the detection limit for Si of about 20 µg l^{-1} is too high to measure clay-bound silica in the colloidal fraction.

The concentration of colloids (C_c) was determined by two methods:

1. by calculation (Sanudo-Wilhelmy et al., 1996; Guo et al., 2000; Baskaran et al., 1992) using a conversion factor of 2.5 between organic C and organic matter (Buffle, 1988):

$$C_c(mg/l) = 2.5 * COC$$

   It was assumed that the colloidal fraction is composed entirely of organic matter.
2. by weighing: the large colloids were isolated by ultracentrifugation and weighed ($C_{c\ large}$), the smaller colloids (<20 nm, $C_{c\ small}$) remained in the supernatant. Organic C was analysed in the supernatant and the weight of small colloids calculated, under the more realistic assumption that they are mainly organic

$$C_{c\ small}(mg/l) = ((OC_{supernant} - OC_{permeate})/fc) * 2.5$$

$$C_c^*(mg/l) = C_{c\ large} + C_{c\ small}$$

As expected, the colloid concentrations measured by weight were higher (Fig. 3). The difference was due to the inorganic fraction of the colloids which represented up to 65% of the total. Assuming that Ca was in the CaCO$_3$ form, it can explain partially the difference at stations 1 (48%) and 2 (65%), and totally at other stations.

Although the colloid concentration was lowest for the highest salinity, there is no correlation between the two variables. However, when the ratio between colloid and SPM concentrations is plotted against salinity on a semi-logarithmic scale (Fig. 4), a clear inverse correlation appears ($r^2 = 0.93$). It seems thus that the proportion of colloidal fraction decreases with salinity suggesting an increasing coagulation effect. This effect can be attributed to the suppression of the double electric layer at colloid surfaces and the increase of the sticking factor at a higher electrolyte concentration (Stumm and Morgan, 1970).

4.3. Metal content in bulk and filtered water

At station 1 the concentrations of Cr, Co, Cu and Mn in the total dissolved fraction (<1.2 µm) (Table 4) were of the same order of magnitude as these found in unpolluted rivers (Meybeck, 1979). Although Cd, Pb and Zn contents were slightly higher, probably due to regional atmospheric pollution, they were well below international norms compatible with aquatic life (Chapman and Kimstach, 1992). Station 1 can thus be considered as the reference station on the Vistula River in this study.

The concentration pattern of trace elements in bulk and filtered water (Table 4) distinguishs 3 groups of metals.

• A sharp increase of Cu and Mn occurred at station 2, coinciding with the increase in salinity and SPM (see Table 2). The highest metal contents in bulk water were measured at station 4, where the concentrations of Cu and Mn were 43 and 111 times higher than at the reference station 1, respectively. Both metals increased greatly in the total dissolved fraction, while in the particulate fraction the increase was moderate. The concurrent increase of salinity suggests that both elements were delivered in dissolved form along with coal mine drainage water, however other sources, such as mining
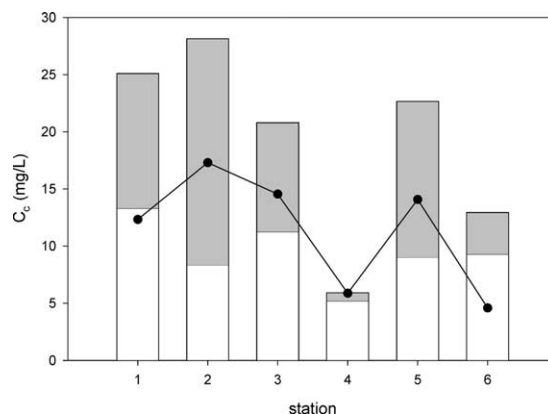

Fig. 3. Concentration of colloids, C_c, determined by two methods (see text for details): calculation method (line) and weighting method (bars: white, $C_{c\ large}$; grey, $C_{c\ small}$).

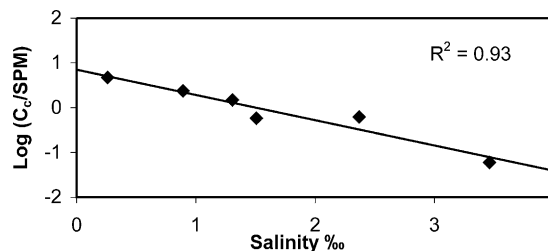Fig. 4. Plot of colloid to SPM weight ratio against the salinity.

Table 4
Trace metal concentration (µg/l) in the bulk and filtered water samples

Station	Cd		Co		Cr		Cu		Mn		Pb		Zn	
	Bulk	Filtered	Bulk	Filtered	Bulk	Filtered	Bulk	Filtered	Bulk	Filtered	Bulk	Filtered	Bulk	Filtered
1	0.63±0.01	0.60±0.01	0.25±0.01	0.25±0.01	0.49±0.01	0.61±0.01	2.2±0.1	0.9±0.1	5.4±0.1	5.3±0.1	0.8±0.01	0.27±0.01	25.7±0.1	16.2±0.1
2	0.70±0.05	0.63±0.01	1.68±0.01	1.34±0.01	7.83±0.18	1.62±0.04	65.8±1.9	46.3±0.2	493.9±4.9	482.0±5.7	5.0±0.1	0.24±0.01	31.8±0.1	17.3±0.1
3	5.57±0.07	0.73±0.01	2.93±0.01	2.24±0.01	9.62±0.05	0.98±0.01	27.5±0.1	17.8±0.5	422.6±1.5	385.8±4.0	80.7±0.8	0.26±0.01	717.8±1.2	145.5±0.4
4	4.11±0.07	0.51±0.05	4.01±0.06	3.03±0.03	15.33±0.64	2.44±0.09	92.9±1.4	90.0±2.3	603.5±4.4	583.8±9.6	75.1±0.5	0.29±0.01	563.4±1.3	129.2±0.9
5	2.65±0.02	0.59±0.01	1.83±0.02	1.41±0.01	5.99±0.09	0.97±0.01	31.7±0.6	25.6±0.2	346.1±2.8	303.2±3.2	55.1±0.4	0.39±0.01	566.2±5.7	168.7±1.1
6	3.34±0.06	0.70±0.01	1.90±0.03	1.19±0.01	13.18±0.68	2.11±0.02	25.8±0.3	18.3±0.1	339.6±3.7	329.4±4.3	28.4±0.01	0.30±0.01	254.8±2.7	99.9±0.3

spoils, cannot be excluded. Pluta and Trembaczowski (2001) reported a Mn concentration in coal mine effluents of 2–7 mg l^{-1}. The occurrence of Mn essentially in the filtered fraction and thus reduced form suggests its origin from the coal mines, where a reducing environment prevails. It seems that oxidation kinetics in the Vistula River are slow, as the dissolved form of Mn remains dominant downstream to station 4.

• The second group includes Zn, Pb and Cd, which showed a sharp concentration increase in bulk water at station 4, downstream of the confluence with the Przemsza River and even higher concentrations at station 3 on the Przemsza itself. Clearly, these metals were derived from the Przemsza watershed, a region of Zn–Pb mining and smelting. The major minerals of the local Pb–Zn deposits are galena (PbS) and sphalerite (ZnS). The latter may contain up 4% Cd (Bolewski and Manecki, 1993). The main sources of metal contamination are mine wastewater. Just one of the still operating mines (Bukowno) discharges to the river some 384, 62 and 1.9 kg/day of Zn, Pb and Cd, respectively (Ciszewski, 1998). Concentrations in mine effluents may be as high as 5 mg/l for Zn and 2 mg/l for Pb. The elevated concentrations of Pb and Cd in the Przemsza and the Vistula were only observed in bulk water (Table 4), while the concentrations in filtered water remained similar to these in the upstream stations 1 and 2. This may suggest that these metals are transported in particulate, more or less inert form. This is also true for Zn, although increased concentration in filtered water implies an enhanced chemical mobility of this metal as compared to Pb. This can be illustrated by comparing the Zn/Pb and Zn/Cd ratios in bulk and filtered water at station 3 and 4 (Table 5). The ratios in bulk water are similar to these found in sediments while the ratios in filtered water are distinctly higher, especially for Zn/Pb. This ratio in water from mines is about 6 (Ciszewski, 1998) and in soils it varies from 3 to 4 (Verner et al., 1996; Ulrich et al., 1999). These values confirm a preferential mobility of Zn as compared to Pb.

• The third group of metals includes Co and Cr. Their concentrations increase moderately in the polluted section (stations 2–6) above the reference value (station 1), but the sources of contamination seem to be more diffuse. Chromium concentrations increase mainly in the bulk water and the sources may include tanneries and the plating industry.

Compared with other polluted rivers, the total dissolved contents of trace metals in the Upper Vistula River were higher than in the Pô River, downstream of its most polluted tributary, the Lambro River (Pettine et al., 1996). The total dissolved metal contents were between one and three orders of magnitude higher than in the 'world average' river (Meybeck, 1988; Meybeck and Helmer, 1989). This section of the Upper Vistula

Table 5
Zn/Pb and Zn/Cd ratios in water and sediments at stations located close to the mining and smelting region of non-ferrous metals

	Zn/Pb	Zn/Cd
Station 3 (Przemsza)		
Sediment	11	169
Bulk	9	129
Filtered	560	199
Station 4 (Vistula)		
Sediment	9	123
Bulk	7	137
Filtered	445	253

has been classified as very polluted based on water quality monitoring performed in 1992 (Dojlido, 1997).

Total dissolved concentrations of metals were on the same order of magnitude as those reported from samples collected in 1982/1983 by Helios-Rybicka (1986) at stations 3, 5 and 6, although the mean values seems to be somewhat lower for Cr, Cd and especially Pb. The concentrations in bulk water are lower by about a factor of 2 than the mean values reported by Pistelok and Galas (1999) from 1994 for stations 3 and 4, even if the water flow during the present sampling was close to or below the mean annual water discharge. As the instantaneous concentration in water may be extremely variable no temporal trend can be inferred from this comparison. It shows, however, that measured concentrations at the same stations but years apart are still on the same order of magnitude.

4.4. Trace metal in sediments

Concentrations of trace metals measured in sediments (Table 6) confirm the spatial trends in the Vistula river pollution based on measurements in water samples. The largest increase of Cu and Cr was noted at station 2, while a dramatic increase in Zn, Pb and Cd was observed downstream from the confluence with the Przemsza River (station 4) and in sediments of the Przemsza itself (station 3). Concentrations of Zn, Pb,

Cd, Cu, and Cr in sediments were similar to these reported by Helios-Rybicka (1986) and Bojakowska and Sokolowska (1996). As the century flood in 1997 probably removed a large portion of bed sediments, sediments collected in November 1998 are almost certainly deposited after the flood. Metal concentrations in these sediments are at the same level as those collected in 1982/1983 (Helios-Rybicka, 1986), suggesting no notable decrease of the pollution in the last 15 a. It should be however noted that the sediments at station 6 show a considerable concentration decrease in Cd, Pb, and Zn by factors from 3 to 5, as compared to the most polluted section (stations 3 and 4).

4.5. Effects of the pollution on metal partitioning

Anthropogenic input clearly influenced the metal repartitioning between particle/colloid/truly dissolved. Three situations are examined for Cu, Cd and Zn: (1) low salinity and no pollution, station 1; (2) high salinity and high Cu pollution, station 2; (3) maximum salinity and high Cd and Zn pollution, station 4 (Fig. 5).

With a massive input of Cu between stations 1 and 2, a part of the total dissolved fraction, and in particular, the truly dissolved fraction increased. Between stations 2 and 4, the relative contribution of the colloidal and particulate fraction of Cu is further reduced, possibly due to desorption and complexation with the increasing amount of UOC. For Zn, a concurrent decrease of colloidal and an increase of particulate fractions between stations 1 and 2 may be due to colloid coagulation and aggregation, while an increase of Cd in the truly dissolved fraction may result from desorption and the formation of Cd–chloro complexes due to the increase in salinity (Thouvenin et al., 1997; Zwolsman et al., 1997). Cd and Zn partitioning at station 4 is clearly influenced by the pollution load from mines, which apparently occurs mainly in particulate form. Although the percentage of the truly dissolved fraction of Zn decreases, the absolute concentration notably increases between station 2 and 4, indicating a certain mobility of Zn. The massive increase of particulate Cd is not accompanied by any increase in the dissolved fraction, suggesting a weaker mobility of Cd than Zn, which is rather unex-

Table 6
Concentrations of major and trace elements in the bottom sediments

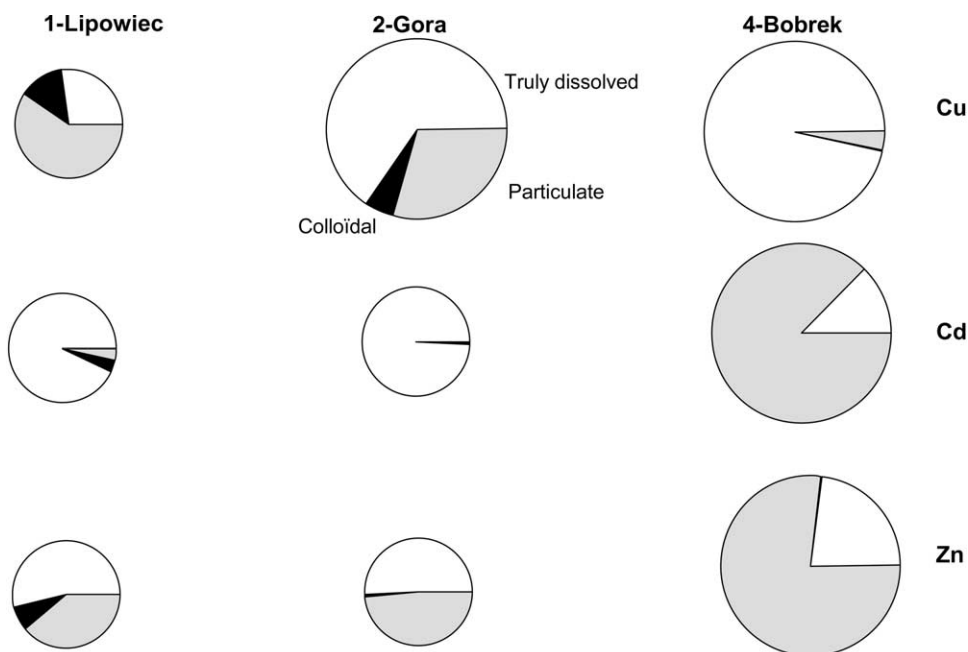| Station	Si (mg/g)	Al (mg/g)	Fe (mg/g)	Mg (mg/g)	Ca (mg/g)	POC (mg/g)	Cd (µg/g)	Co µg/g	Cr (µg/g)	Cu (µg/g)	Mn (µg/g)	Pb (µg/g)	Zn (µg/g)
1	281	73	28	8	7	148	4	72	87	71	610	64	460
2	264	73	44	8	9	146	5	27	387	220	462	154	656
3	177	73	39	11	42	283	60	117	747	197	620	886	10 179
4	215	76	42	10	22	224	42	23	456	199	491	570	5170
5	254	60	38	13	26	164	93	60	240	38	736	1340	7422
6	273	76	36	11	13	125	23	27	216	97	662	223	1972

Fig. 5. Repartition (%) of Cu, Cd and Zn between the particulate (grey), colloidal (black) and truly dissolved (white) stations 1, 2 and 4. The size of circles is proportional to the unfiltered metal contents.

pected and contrasts with Cd behaviour in the non-contaminated river section (station 2), but confirmed by observations from stations 5 and 6. Cadmium in soils of the region seems to be more mobile than Zn (Ullrich et al., 1999) and in the Vistula sediments occurs mainly in the easily reducible fraction (Helios-Rybicka, 1986). In contrast, in sediments from the highly polluted Przemsza River, most of the Cd is bound to organic-sulphide and residual phases (Helios-Rybicka, 1986; Suschka et al., 1994).

The metal partitioning between particulate, colloidal and truly dissolved fractions is thus essentially dependent on the chemical species in which the pollutant is delivered to the system, and on water salinity. Clearly, these observations on a very limited number of samples, performed at moderate to low flow conditions are preliminary and the conclusions may not be generally valid. Further work, at different flow conditions is under way.

4.6. Partitioning in the total dissolved fraction: field observations and modelling

The partitioning colloidal/truly dissolved fraction showed notable differences between station 1 and the other stations (Table 7). At the reference station 1, the colloidal fraction of Cu and Cr represented 33 and 56% of total dissolved metal contents, respectively, whereas downstream, they made up only to 7% for Cu and 24% for Cr. For Cd, Co, Mn, Pb and Zn, the colloidal fraction was between 4 and 12% of the total

dissolved metal contents in the unpolluted section. In the polluted section, Co, Mn and Zn were largely found in the truly dissolved fraction whereas for Cd and Pb, the colloidal fraction increased up to 8 and 25% respectively.

In this study, the chemical speciation of Cd, Cu and Zn in the total dissolved fraction was modelled with MINTEQA2 (Allison et al., 1991). For the other trace metals, the stability constants with dissolved organic matter (DOM) are not available, precluding the modelling. In the model, it was assumed that the complexation by colloids was related to the association metal–DOM. A good agreement obtained between field results and model calculation (Table 8) suggests that the total dissolved metals were in equilibrium in respect to the colloid/truly dissolved partition and the association with DOM was the main complexation process controlling metal partition in the total dissolved fraction, despite the significant fraction of colloidal carbonates. However, the concept of metal partition is based on the assumption that all or a large fraction of metal is in exchange equilibria between macromolecules and water and that these chemical equilibrium are governed by stability constants. As the calculation and the field data were in good agreement for the distribution in the total dissolved fraction, the influence of the particulate fraction on the repartitioning of colloidal/truly dissolved via sorption processes can possibly be considered as negligible. This may be true when most metals, especially Cd, Pb and partly Zn were quasi-completely locked up in

Table 7
Distribution of trace metals (µg/l) in the colloidal and truly dissolved fractions

Station	Cd Truly dissolved	Cd Colloidal	Co Truly dissolved	Co Colloidal	Cr Truly dissolved	Cr Colloidal	Cu Truly dissolved	Cu Colloidal	Mn Truly dissolved	Mn Colloidal	Zn Truly dissolved	Zn Colloidal	Pb Truly dissolved	Pb Colloidal
1	0.53±0.01	0.021±0.001	0.24±0.01	0.024±0.001	0.26±0.02	0.338±0.009	0.6±0.0	0.30±0.01	5.8±0.1	0.23±0.06	13.2±0.1	1.76±0.26	0.20±0.01	0.018±0.001
2	0.55±0.04	n.d.	1.36±0.01	n.d.	1.48±0.02	0.184±0.025	43.7±1.0	3.43±0.71	513.3±8.8	n.d.	15.1±0.2	0.21±0.12	0.21±0.01	0.029±0.004
3	0.58±0.01	0.048±0.003	2.09±0.02	0.024±0.009	0.82±0.02	0.254±0.015	16.8±0.5	0.67±0.18	399.6±4.7	2.82±1.49	142.2±2.3	3.13±0.71	0.26±0.01	0.019±0.001
4	0.53±0.03	n.d.	2.94±0.02	n.d.	2.46±0.10	n.d.	82.1±2.0	n.d.	600.3±7.7	n.d.	129.8±0.9	1.13±0.38	0.22±0.01	0.028±0.003
5	0.63±0.01	0.019±0.004	1.40±0.01	0.007±0.003	0.92±0.02	0.136±0.006	23.8±0.3	0.65±0.25	308.5±3.5	1.86±1.17	162.0±1.1	3.45±0.29	0.21±0.01	0.068±0.001
6	0.56±0.01	0.024±0.007	1.12±0.01	n.d.	1.87±0.03	0.055±0.018	18.1±0.2	0.90±0.12	321.3±4.7	n.d.	91.2±1.2	1.31±0.72	0.28±0.01	0.051±0.007

Table 8
Percentage of the total dissolved metal in the colloidal fraction determined experimentally and with the model calculation

Station		Cd	Cu	Zn
1	Field	3.8±0.1	32.8±0.1	11.7±0.1
	Model	5.6	32.3	9
2	Field	n.d.	7.3±0.2	1.4±0.6
	Model	<1	8.1	2
3	Field	7.6±0.1	3.8±0.3	2.2±02
	Model	<1	1.8	<1
4	Field	n.d.	n.d.	0.9±0.3
	Model	<1	2.2	1.1
5	Field	2.9±0.2	2.7±0.4	2.1±0.1
	Model	<1	1.9	1.3
6	Field	4.0±0.3	4.7±0.1	1.4±0.6
	Model	<1	7.7	2.1

the lattice of minerals and do not interact with the surrounding water at a given set of environmental conditions (this study; Guéguen et al., 2000). In contrast to the repartitioning between particulate and total dissolved fractions, the metal distributions between colloid and truly dissolved fractions were not related to the source of the metals in the Vistula. However, the decrease of colloid importance in the metal complexation coincides with the salt inputs to the river. Simulations were performed to infer the impact of salts and in particularly the effect of Ca and Mg on metal partitioning at station 4, where the pollution is greatest. The hypothetical decrease of Ca and Mg contents from the concentration measured at station 2 to the level measured in the unpolluted section 1, showed that the association with DOM would increase up to about 2% for Cd, 10% Cu and 5% for Zn (Fig. 6). While the amount of Cu and Zn associated with DOM increased, the decrease of Ca and Mg would only marginally enhance the Cd–DOM binding. The same trends have already been described in experimental studies (e.g. Cabaniss, 1992; Tipping, 1993; Pinheiro et al., 1999). Copper and Zn are A-type cations and consequently have strong preference for ligand atoms such as O and N, whereas the B-type cation, Cd prefers soft ligands such as S. DOM have more O and N than S sites. (Buffle, 1988), thus less Cd is bound to DOM.

4.7. Distribution coefficients of particles and colloids

The partitioning coefficients between the particulate and total dissolved fractions (K_d) have been extensively studied in natural waters (e.g. Balls, 1989; Chiffoleau et al., 1994; Zwolsman and van Eck, 1999). Partitioning between particulate and truly dissolved fractions (K_p) and, between colloidal and truly dissolved fractions (K_c)
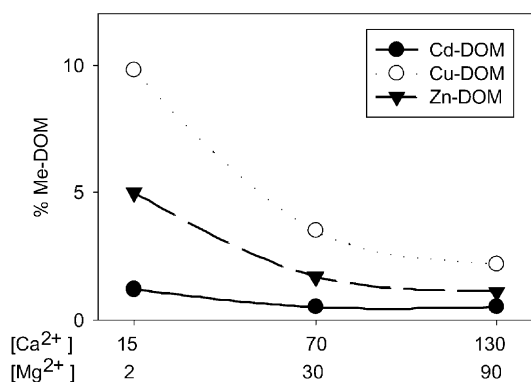
Fig. 6. Evolution of fraction of Cd, Cu and Zn associated with colloids assuming as dissolved organic matter (DOM) vs the concentrations of Ca^{2+} and Mg^{2+}. The major element concentrations are in mg/l.

were only reported in a few cases (Wen et al., 1999; Sanudo-Wilhemy et al., 1996).

The partitioning coefficients are defined as follows:

$$K_d \, (l/kg) = \frac{\text{mass of particulate metal/mass solids}}{\text{mass of truly dissolved metal/volume of water}}$$

$$K_p \, (l/kg) = \frac{\text{mass of particulate metal/mass solids}}{\text{mass of truly dissolved metal/volume of water}}$$

$$K_c \, (l/kg) = \frac{\text{mass of colloidal metal/mass colloids}}{\text{mass of truly dissolved metal/volume of water}}$$

As expected, there is practically no difference between K_d and K_p for metals examined in the Vistula, as the fraction bound to the colloids makes up only a small part of the total metal content. The K_d values (Fig. 7) show a consistent decrease with increasing particle concentration for Cr, Co and Cu ($r^2 > 0.9$). A similar, but less consistent trend is observed for Zn and Mn. The relationship is not evident for Pb and Cd, because two samples show distribution coefficients one to two orders of magnitude lower than the others. These two samples are taken from stations 1 and 2, located upstream from the major Pb–Zn–Cd input from the metal mine district. The high distribution coefficients for Pb and Cd in the samples from the polluted section reflect again the refractory character of Pb–Cd pollution, concentrated in the particulate fraction that does not readily equilibrate metals with water. The effect is less pronounced for Zn, as this metal has been shown to be more mobile than Pb and Cd, although the two samples from the stations upstream from the confluence of the Vistula and Przemsza Rivers also have slightly lower K_ds than the downstream samples.
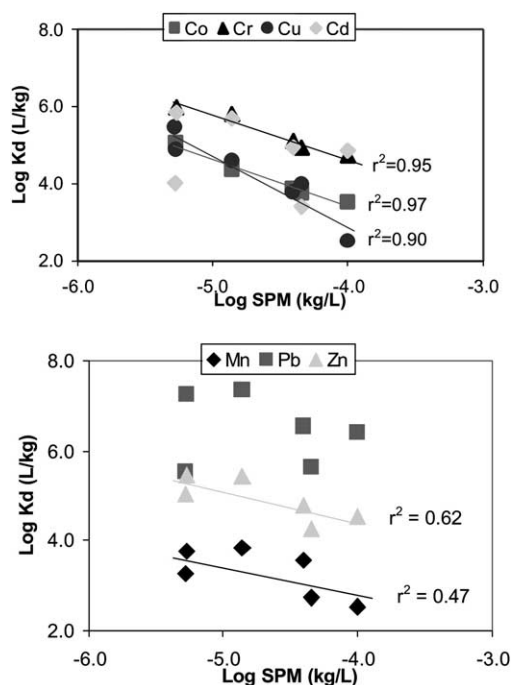

Fig. 7. Partition coefficient of metals (K_d) plotted against suspended particle concentration (SPM) on log–log scale.

The reason for the decrease of K_d with SPM concentrations, so-called "particle concentration effect" is not clear. It has been shown that in the presence of a significant amount of metals in the colloidal fraction this effect occurs and can be considered as an artefact (Honeyman and Santschi, 1989). However, in the Vistula River the K_ps, which are free of this effect, are virtually the same as K_d, as the colloidal fraction of metals is not significant. In the laboratory experiments it has been shown, that the particle concentration effect may arise from some physical interactions between particles, resulting in a "particle induced desorption" (DiToro et al., 1986). Although this possibility cannot be excluded, the authors believe that other factors, such as variations in particles' character or ionic strength of water may be responsible for an observed trend. A strong correlation between particle concentration and salinity ($r^2 = 0.93$) suggests that the relation between K_d of some metals and the SPM could merely be fortuitous. Indeed, one would expect a decrease of K_d with increasing salinity.

Contrary to the K_ds, the K_c values show no relationship with the colloid mass concentration. The variability of colloid mass concentration is too small to reveal such an effect even if it exists. The K_c values, for all metals but Cu, are in general at least one order of magnitude lower than the K_p, which can be seen as unusual, because of a much larger specific surface of colloids. This can be considered as evidence, that an important

portion of particulate metals cannot be exchanged with water, resulting in much higher apparent partition coefficients. This is particularly true for Pb and Cd, and to a lesser extend for Zn and Cr. Probably only Cu and possibly Mn and Co have a larger fraction in particulate form which may equilibrate with water.

The earlier evidence indicates again, that the concept of partition coefficient understood as an indicator of a dynamic equilibrium between particulate and dissolved metals is not valid in many rivers, contaminated or not, as long as only total metal concentration in the particulate phase is determined. The partition coefficient which represents the concept derived from adsorption—desorption isotherms may only be obtained from field work if the labile fraction of particulate metal is considered.

5. Conclusions

Metal concentrations in water and sediments of the Upper Vistula river remain at a very high level and the spatial variability of their concentrations reflects the input from two major sources: the coal and Zn–Pb mines of Upper Silesia. In the polluted section the concentrations of Cd, Co, Cr, Cu, Mn, Pb and Zn in bulk water increase by at least one order of magnitude over the concentrations measured at the reference headwater station. The same is true for concentrations of Cd, Cr, Pb and Zn in bottom sediments, which are as contaminated as a decade ago. Some contaminants such as Pb and Cd are transported mostly in particulate form (K_d in the range 10^6–10^7 and 10^5–10^6, respectively), while others such as Cu and Mn have a very significant truly dissolved component (K_d in the range 10^2–10^4). Zinc shows an intermediate behaviour.

The fraction of metal in the colloidal form is very low in the polluted section of the river probably because of an increased salinity resulting in loss of some metals from this fraction via colloid coagulation or by desorption of others from colloid surfaces. The latter effect is due to a competition of ligands such as Cl^- (especially for Cd), and major cations (Ca, Mg). Finally the low colloidal concentration of some metals is also due to a weak mobility of particle associated metals originating from mining and smelting (Pb, Cd). Further studies at different flow conditions should be carried out to confirm a weak mobility of Cd and to examine the nature of its association with particles, as this metal can be highly toxic if it occurs in a bioavailable form.

The field observations of metal partitioning between colloidal and truly dissolved forms are well explained by a speciation model. It is also shown that the partitioning concept in which K_d is defined in terms of adsorption–desorption equilibrium is not applicable for metal pollutant (in this case Pb and Cd) which are strongly bound to particles and show a very limited chemical mobility.

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