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THE STATE OF ACCUMULATION AND SOURCE RELATIONS OF Co, Ni, Cr, Be AND Zn IN SILT-CLAY SEDIMENTS OF THE ELBE RIVER

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Abstract: Samples of surface sediments were collected along the Czech part of the Elbe River. The average contents of 19.5 mg/kg Co, 55.1 mg/kg Ni and 3.57 mg/kg Be in the silt-clay fractions ($\leq 63\ \mu$m) are close to the background values and are a consequence of natural enrichment through rock denudation. Locally higher values were found only exceptionally. The elevated contents of Cr (191.2 mg/kg) and especially Zn (866 mg/kg) are apparently derived from anthropogenic sources. It was found by six-step sequential analysis that Co, Cr, Ni and Be are concentrated in all the geochemical phases except for exchangeable forms. Zn is primarily present in the exchangeable form and in the adsorbed, largely on clay minerals.

Key words: contamination, stream sediments, Elbe River, sequential analysis, cobalt, nickel, chromium, beryllium, zinc.

Introduction

The contamination of the bottom sediments of Czech rivers has received little attention in the past, although these rivers drain a region with highly developed chemical and machine industries, with a rich history of mining of metallic ores, and with dense residential areas and high surface contamination. Information has been available on the major element contents of the Elbe River water since 1892 (Hanamann 1899) and its composition is monitored. However, it was not until recently that the mineral composition of the bottom sediments (Konta 1990; Borovec & Mráz 1992) and their enrichment with major elements and heavy metals derived from industrial waste and weathering of the rocks was studied in a number of rivers (Pačes 1982; Hátle & Čihalík 1985; Veselý et al. 1989; Beneš et al. 1992; Borovec 1993; Borovec et al. 1993; Skřivan & Vach 1993).

The goal of this work, carried out in the framework of Research State Project Elbe No.EÚ 03.02.07, financed by the Ministry of the Environment of the Czech Republic, was to map and obtain more information on the distribution of Co, Ni, Cr, Be and Zn in the surface sediments of the ecologically affected region of the Czech part of the Elbe River.

Location

The Elbe River drains the largest part of the Bohemian Massif, which is the basic geological unit in Central Europe. Of its total drainage area of 148 541 km^2, 51 393 km^2 lies in Bohemia, i.e. 97.4 % of the total area of Bohemia. For a short distance, the Elbe River flows through the Krkonoše - Jizera crystalline complex, Permian - Carboniferous sediments and melaphyre. The longest part of the water course runs through Cretaceous sediments. In the vicinity of the German border, the river cuts through alkaline volcanic rocks. It then flows through Germany and empties into the North Sea in the estuary at Cuxhaven near Hamburg.

The average temperature in the region of the source of the Elbe is below 5 °C and the annual rainfall is 800 - 1600 mm. The longest part of the water course lies in a temperate and slightly dry to dry area with an average temperature of 8 °C and rainfall of 500 - 600 mm.

In addition to pollution of the Elbe by industrial, agricultural and communal waste, heavy metals also enter the surface waters from the air. The average concentrations of these metals in the air in the Czech Republic are: Pb 20 - 40 ng/m^3 (90 - 150 ng/m^3 in the impact region), Cu 20 - 100 ng/m^3 (600 - 700 ng/m^3), Mn 12 - 20 ng/m^3 (30 - 40), Cd 1 ng/m^3 (9 - 10), Zn 300 - 400 ng/m^3 (600 -1000), Ni 5 - 10 ng/m^3 (100 - 150) (Moldán 1990). In the source region of the Elbe River, the foggy fallout with a pH of 4.5 - 5.0 was found to contain about 8.5 - 8.7 kg Cu/km^2/annum, 25 kg Pb/km^2/annum and 20 - 40 kg Zn/km^2/annum (Jiřele 1989).

Sample collection

Bottom sediments were collected to study the distribution of Be, Co, Ni, Cr and Zn at 16 sites along the Elbe River (Fig. 1), 3 m from the shore at a depth of

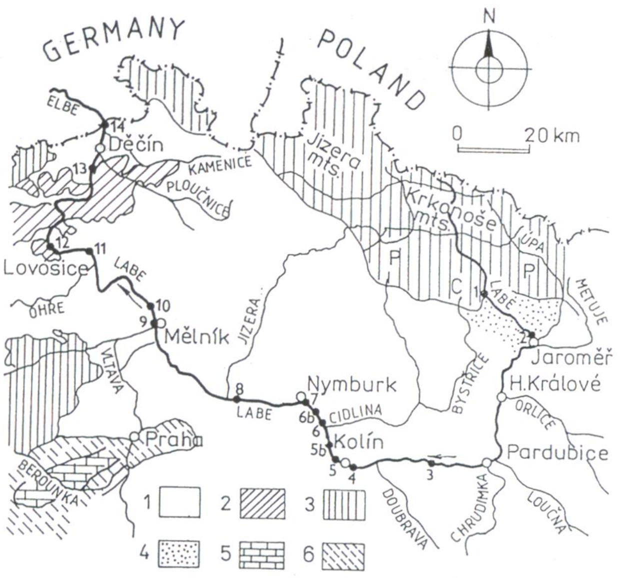

Fig.1. Location of study Elbe River and sampling sites for stream sediments. Explanation to the map: **1** - Cretaceous sediments, mostly marlstones; **2** - Volcanic rocks (basalts up to phonolites); **3** - Crystalline igneous and metamorphic rocks; **4** - Cretaceous sediments poor in calcite; **5** - Palaeozoic sediments rich in calcite or dolomite; **6** - Palaeozoic sediments rich in silicates. **P** - Permian, mostly continental sediments; **C** - Carboniferous sediments.

1.0-1.5 m and 0 - 10 cm from the water-sediment interface. The samples were transported in dark bottles after removal of the air with N_2 gas and were stored at a temperature of ± 2 °C. The $\leq 63\,\mu m$ grain-size fraction was obtained by passing through nylon sieves in a dark room.

Average composition of stream sediments

Phase analysis by X-ray diffraction in the silt-clay fraction ($\leq 63\,\mu m$) of the stream sediments shows that muscovite/illite (29 % by wt.), kaolinite (26 % by wt.), quartz (21 % by wt.) are the major minerals, while chlorite±smectite±vermiculite (7 % by wt.), Na-rich plagioclase (6 % by wt.), calcite (6 % by wt.), K-feldspar (3 % by wt.), amphibole (1.1 % by wt.), gypsum (0.8 % by wt.) and pyrite (0.5 % by wt.) occur in lesser amounts.

An important component of the sediments, that increases their bonding capacity for trace and common elements is amorphous inorganic matter, present in the silt-clay fraction in amounts 19.6 % by wt. In this phase is dominating amorphous Si-oxyhydroxides (24.2 % by wt. as SiO_2), amorphous Al-oxyhydroxides (11.0 % by wt. as Al_2O_3), amorphous Fe- and Mn-oxyhydroxides (8.8 % by wt.).

The content of labile organics (extracted by 30 % H_2O_2) was 6.4 % by wt., stable organics (e.g. humic and fulvic material) extracted by 0.1 M NaOH, was 2.6 % by wt. and the amounts of the "sedimentary chlorophyl" (extracted by acetone) was 1.4 % by wt.

A detailed description of the stream sediments and the methods of their determination are given in Borovec & Mráz (1992).

Chemical extraction of metals

In order to determine the bonding of the metal to the geochemical phase of the bottom sediments, sequential extraction was carried out of the wet, silt-clay fraction ($\leq 63\,\mu m$) using the following procedure:

1 - 1M CH_3COONH_4 (pH 8.3, solid/liquid 1:20, 8 hours shaking) in order to obtain the concentrations

Table 1: Minimum, maximum and average heavy metal content and index of geoaccumulation I_{geo} in the stream sediments (grain-size fraction $\leq 63\,\mu m$) of Elbe River, Czech Republic.

Element	Minimum	Maximum	Average value	Standard deviation	Enrichment	I_{geo}	Sediment contamination
Be	1.8[a]	9.1	3.57	2.31	1.2	–0.3	uncontamined
	11[b]	6					
Co	12.8	29.6	19.5	5.9	1.0	–0.5	uncontamined
	2	13					
Cr	26.6	517.5	191.2	156.6	2.1	0.5	uncontamined to moderately contam.
	1	7					
Ni	31.3	88.3	55.1	17.8	0.8	–0.9	uncontamined
	4	13					
Zn	169	1738	866	413	9.1	2.6	moderately to strongly contamined
	4	8					

a - metal content in mg/kg; b - sample numbers.

of metals bonded in cation exchange sites, largely on clay minerals.

2 - 1M CH_3COONH_4 (pH 4.8 with HOAc, solid/liquid 1:20, 5 hours) to determine metals adsorbed/bonded on carbonates.

3 - 1M $NH_2OH.HCl$ (pH 2 with HOAc, solid/liquid 1:100, 12 hours in the dark) to release metals from Mn-oxides/hydrous oxides.

4 - 0.1M oxalate buffer (pH 3, solid/liquid 1:100, 24 hours) for metals bonded in Fe-oxides/hydrous oxides.

5 - 30 % H_2O_2 (pH 2 with 0.02 M HNO_3, solid/liquid 1:100, 2 hours, 80 °C) for metals bonded in sulphides/organics.

6 - Hot 14.5 M HNO_3 (concentrated) to release metals bonded in lithogenic material.

Except for the extraction steps (5) and (6), the extraction was carried out at 18 °C in air-tight closed vessels filled with N_2. Prior to contact with the solid phase, the extractants were bubbled with N_2. Collection of samples, their preparation and sequential extraction were carried out by a slight modification of the method described by Kersten & Förstner (1987) and are described in the work of Borovec et al. (1993).

Analytical determination

The extracted Co, Cr, Ni and Zn metals were determined by flame AAS using an AAS 1N instrument (Carl Zeiss, Jena). Beryllium was determined in a graphite atomizer in an argon atmosphere using a Varian SpectrAA-300Z instrument. Standards were prepared from solutions with compositions as close as possible to those in which the test metals were dissolved after the sequential extraction. Blanks were also determined in all cases.

Results and discussion

The distribution of the metals in the surface sediments of the ≤ 63 μm grain-size fraction exhibited similar trends in some characteristics. However, after separation of the metals from various geochemical phases, the distribution patterns differed in some cases. The results for the average, minimum and maximum concentrations, together with the standard deviation of the samples are given in Tab. 1. The index of geoaccumulation I_{geo} after Müller (1981) was used to express the contamination of the sediments. The distribution of the metals in the geochemical phases of the stream sediments are summarized in Tab. 2 and the changes in their concentrations along the whole Elbe water course are depicted in Fig. 2. The mean contents and standard deviations of the metal concentrations and the percent of the metals in the geochemical phases are also given.

The contents of Co, Be and Zn in the grain-size categories increased with decreasing grain size. This can probably be explained in terms of the presence of surface-dependent bonded forms (e.g. Fe and Mn hydrated oxides, clay minerals and organics) whose surface area increases with decreasing grain size. For Ni and Cr, a tendency to collect on the medium grain-size particles in the silt-clay category was found (Borovec et al. 1993).

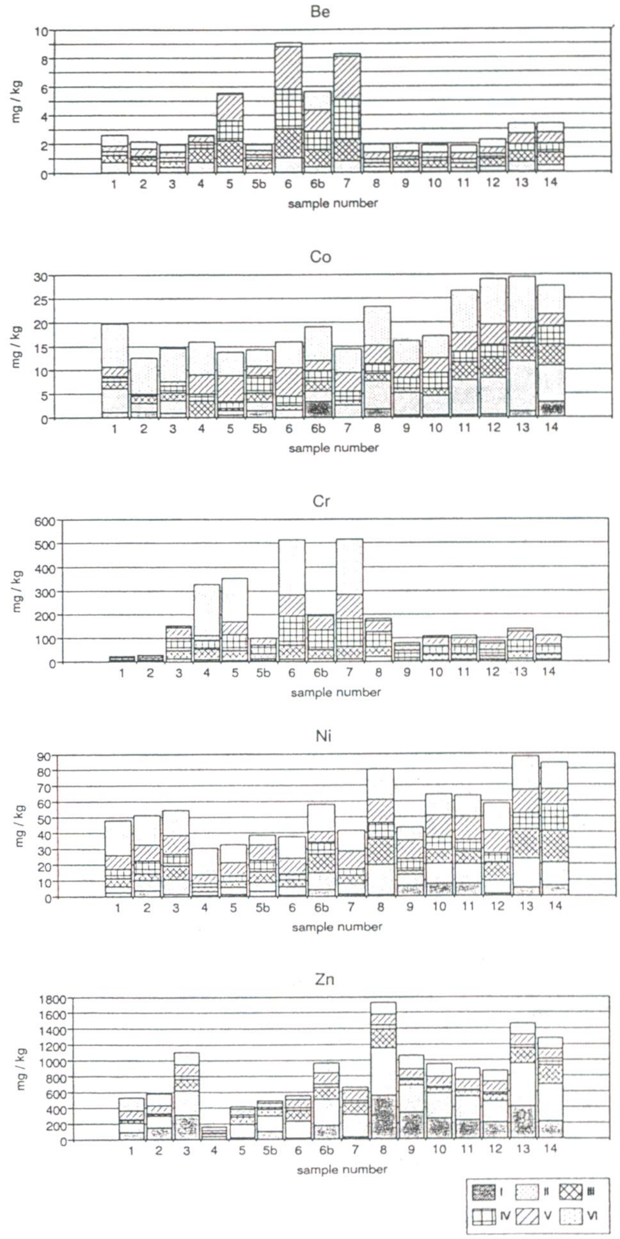

Fig. 2. Geochemical partitioning of Co, Ni, Cr, Be and Zn in the Elbe River sediments (≤63 μm grain-size fractions). Concentration of metals in: **I** - ion exchangeable form; **II** - adsorbed/carbonates phase; **III** - easily reducible components (Mn-oxides); **IV** - moderately reducible phases (amorphous Fe-oxides); **V** - oxidizable sulphidic/organic matter; **VI** - lithogenic material (remnant).

Cobalt and nickel in the sediments reflect changes in the concentrations in the denuded rocks, with minor deviations (the standard deviation for Co was 5.9 and for Ni 17.8). The sediments were enriched during the flow

Table 2: Average metal content (mg/kg) in geochemical phases of stream sediments of Elbe River, Czech Republic.

Geochemical phase		Be	Co	Cr	Ni	Zn
1.	Exchangeable	0.01±0.01[a]	1.03±0.21	0.41±0.07	3.39±0.37	195.5±12.20
	cations	0[b]	1.01	0.92	2.58	156.6
		0.28[c]	5.29	0.21	6.15	22.57
2.	Adsorbed ions/	0.49±0.03	4.21±0.66	8.21±0.56	9.23±1.02	293.6±18.6
	carbonates	0.22	3.02	4.54	4.98	151.5
		13.73	21.61	4.29	16.74	33.89
3.	Mn-oxides/	0.83±0.04	2.17±0.22	29.44±3.11	8.74±1.43	114.0±12.65
	hydrous oxides	0.53	1.41	16.05	5.52	68.9
		23.25	11.14	15.40	15.85	13.16
4.	Fe-oxides/	0.79±0.05	2.14±0.25	52.06±4.32	7.33±0.84	33.9±2.83
	hydrous oxides	0.86	0.97	34.46	3.34	18.9
		22.13	10.98	27.23	13.30	3.91
5.	Sulfides/	0.94±0.06	3.13±0.28	40.76±5.52	11.06±1.41	114.0±14.2
	organics	0.91	1.56	26.23	2.88	33.4
		26.33	16.07	21.32	20.06	13.16
6.	Remnant	0.51±0.03	6.80±0.54	60.31±6.43	15.38±1.04	115.2±5.2
		0.29	1.91	93.53	4.33	54.5
		14.28	34.91	31.55	27.90	13.31

a - metal content (mg/kg) ± relative error value reffering to the precision of the analytical method
b - the standard deviation of the sample
c - percent of metal in geochemical phases

Table 3: Sample numbers with significantly and anomalously high metal values (minimally twice in excess of the mean) in the geochemical phases of Elbe River, Czech Republic.

	Geochemical phase	Be	Co	Cr	Ni	Zn
1.	Exchangeable cations	-	14, 6b	5b+	10, 11	8, 13
2.	Adsorbed ions/carbonates	6	13	8	8, 13	8
3.	Mn-oxides/hydrous oxides	5	12, 14	-	13, 14	-
4.	Fe-oxides/hydrous oxides	6, 7	-	6, 7	14	14
5.	Sulfides/organics	5, 6	-	6, 7	-	-
6.	Remnant	6b	-	4, 5, 6, 7	-	-

[+] Sample numbers with metal values in excess of mean plus 3 standard deviations

of the river water through volcanic rocks and especially by the confluence with the Ploučnice River (Sample 14), whose sediments prior to the confluence with the Elbe River were found to contain 124 mg/kg Ni and 36 mg/kg Co. The elevated metal contents in the lithogenic material corresponded to a nonanthropogenic origin with high correlation (r = 0.812). Part of the Co and Ni is present in the adsorbed/carbonate phase and the remainder is evenly distributed among the remaining geochemical phases except for exchangeable forms (Tab. 2).

It is apparent from Fig. 3a that the Co:Ni ratio in the bulk samples (total ≤ 63 μm fraction) appears to be quite constant (1 : 2.8), similar to the lithogenic material (1 : 2.3). However, the Ni : Cr ratio fluctuated in the bulk samples between 1 : 14.3 and 1.8 : 1 with an average value of 1 : 3.4 (standard deviation 0.11); in the li-

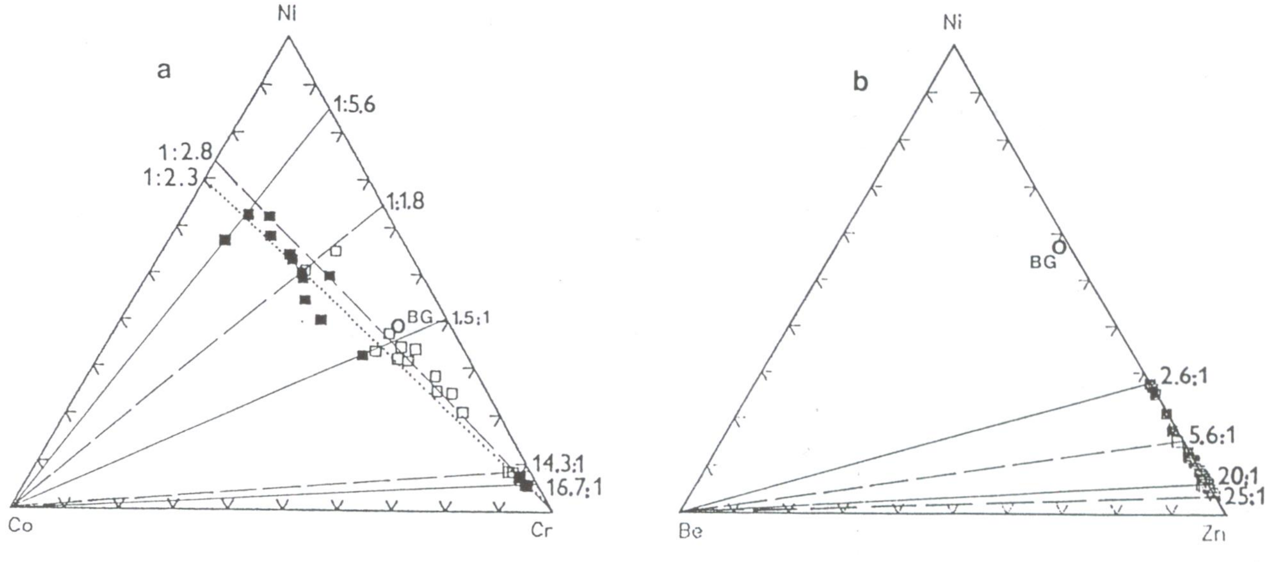

Fig. 3. Percent partitioning of **(a)** - Co, Ni and Cr and **(b)** - Ni, Be and Zn in the bulk samples (□) and in the lithogenic material (■). BG is background value.

thogenic material it fluctuated between 1 : 16.7 and 5.6 : 1, with an average value of 1 : 4.0 (standard deviation 0.05). Similarly, the Cr : (Ni/Co) value exhibited high scatter in the bulk samples between 7.4 : 1 and 217.2 : 1 (average 67.8 : 1, standard deviation 51.7), as did the lithogenic material, where this value was between 1 : 1.6 and 91.4 : 1 (average 26.5 : 1, standard deviation 40.3), which does not correspond to the ratios in the denudated rocks (from data Čadková & Mrázek 1987). In the anthropogenically unaffected sediments, the ratio is Co : Ni = 1 : 3.6, close to the values found for the Elbe River, while the Ni : Cr = 1 : 1.3 and Cr : (Ni/Co) = 25.1 : 1 ratios were very different from the Elbe sediments, probably as a consequence of mixing of anthropogenic Cr with non-anthropogenic Cr. It seems that part of the Cr in the Elbe sediments was of anthropogenic origin, while the Co and Ni are entirely terrestrially derived.

The lithogenic material contains more Cr than Be (Fig. 2). There is also a negative correlation between the two elements (r = - 0.685).There is a minimum of Cr in the carbonate phase and the exchangeable form. The Cr could be derived from Permian - Carboniferous sediments containing 52.6 mg/kg Cr, claystone and siltstone Cretaceous sediments with 82.9 mg/kg Cr, volcanic rocks with 145 mg/kg Cr and the confluence with a number of rivers (up to 194 mg/kg Cr in Moldau (Vltava) River sediments).

The content of Be in the denudated rocks is low (max. 5 mg/kg in the Permain - Carboniferous sediments) (Čadková & Mrázek 1987). The enrichment of the sediments in Be in the central part of the water course was derived from solutions flowing from the sludge beds of power-plant ash between samples 3 and 4 (Borovec 1993), or the confluence with the Ohře River (samples 13 and 14), whose sediments contain 9.80 mg/kg Be, and from Veselý & Sirotek (1992) filtered water (filter 0.45 µm) 0.02 µg/l and unfiltered water 0.03 µg/l Be. Part of the Be can be derived from the mineral-water springs in the Western Bohemian spa of Karlovy Vary (Carlsbad) (the Vřídlo spring contains 78.3 µg/l Be) and Františkovy Lázně (3.8 - 22.6 µg/l Be)(Macháček et al. 1966). The maximum contents of Be are 3-times and of Cr 6-times higher than the geochemical background value (3 mg/kg Be and 90 mg/kg Cr). However, on an average, the Elbe sediments are not contaminated with Be (I_{geo} = - 0.3) and are only slightly contaminated with Cr (I_{geo} = 0.5).

The Be : (Zn/Ni) ratio was almost constant in the bulk samples (1 : 4.8; standard deviation 0.1). However, the Ni : Zn ratio fluctuated between 1 : 5.6 and 1 : 25, with an average value of 1 : 16.7 (standard deviation 0.04) and the Ni : Be ratio was between 4.2 : 1 and 40.5 : 1, with an average value of 16.5 : 1 (standard deviation 7.72). In the lithogenic material, the Be : (Zn/Ni) ratio was also almost constant (1 : 14.3; standard deviation 0.02) and the Ni : Zn ratio fluctuated in a wide range (Fig. 3b) with an average value of 1 : 7.7 (standard deviation 0.08) and the Ni : Be ratio was 30.2 : 1 (standard deviation 14.9).

In the denudate rocks, the Be : (Zn/Ni), Ni : Zn and Ni : Be ratios differed considerably from the above values, where the values for the Permian-Carboniferous rocks were 3.2 : 1, 1 : 1.6 and 5.4 : 1, respectively, for the claystones and siltstones 3 : 1, 1 : 1 and 8.7 : 1, respectively, and for the volcanic rocks 3.1 : 1, 1 : 1.3 and 20.5 : 1, respectively. For the anthropogenically unaffected sediments, these ratios have the values 2.1 : 1, 1 : 1.4 and 22.7 : 1, respectively. It is thus apparent that only the Ni : Be ratio approaches the values determined for the lithogenic material in the Elbe sediments.

The nine-fold increase in the Zn content in the sediments, with a maximum of 18-fold (sample 8) compared to the content in the uncontaminated sediments (95 mg/kg) is anthropogenic in origin, as the denudated Permian - Carboniferous sediments contain an average of 42.1 mg/kg Zn, claystones and siltstones in the Cretaceous sediments 21.1 mg/kg and basalt rocks 105 mg/kg (Čadková & Mrázek 1987). The largest amounts of Zn were found in the adsorbed/carbonate phase, where there is good correlation between Zn and Ni (0.936) and in the form of exchangeable ions on clay minerals, which is characteristic for the surface oxide sediments (Kersten & Förstner 1987). A relatively small amount was found in the lithogenic material (13 %). These findings correspond to the high concentration of Zn in the filtered Elbe River water (0.45 μm filter), which varied between 20 and 80 μg/l, with a maximum of 612 μg/l between sampling sites 12 and 13 (Veselý et al. 1991).

Anthropogenic sources of Zn (together with Cd) could be fertilizers (superphosphates), waste water from metal surface finishing (sample 8) or from chemical factories (sample 3) and solid fall-out from the atmosphere (300 - 400 ng/m^3, locally as high as 600 - 1000 ng/m^3). The Zn in the river source region could be derived from soggy fall-out (20.40 kg/km^2/annum), appearing as an increased Zn content in filtered Elbe River water (27 μg/l). High contamination of the sediments by Zn was found in side streams of the Elbe, whose upper parts (samples 2 and 3) contained up to 500 mg/kg Zn, where the content at German border after flowing through basic rocks (Ploučnice River) equalled 745 mg/kg Zn. Good correlation was found between Zn and Ni (r =0.880), Zn and Fe (r =0.782) and Zn and Co (r =0.597).

Consideration was given to a statistical method that could distinguish stream sediment samples in the geochemical phases with significantly or anomalously high metal concentrations. The threshold value for each metal population in each geochemical phase of the stream sediments was calculated according to the method of Mantei & Foster (1991) as the mean content plus three times the standard deviation. The results in Tab. 3 demonstrate that significantly elevated metal concentrations indicate a number of sources for all the metals. Only for Be and Cr is sample 6 repeated, for Ni and Co samples 13 and 14, and for Zn sample 8. Thus, there are significant sources emitting Be, Cr and Zn in the central part of the Elbe, while the Ni and Cr were derived from sources close to the German border. However, this method did not yield any point source emitting anomalously high concentrations of the test metals.

Conclusions

Presence in exchangeable forms on clay minerals and bonding of metals in the adsorbed/carbonates phase was limited mainly to Zn (57 %). All the metals (22 % Co, 29 % Ni, 43 % Cr and 45 % Be) are bonded in the reducible phase of Fe- and Mn-oxides/hydrous oxides, with the exception of Zn, which is present primarily in the Mn-phase. Mainly Be (26 %), Cr (21 %) and Ni (20 %) were bonded in the oxidizable sulphide phase and some kinds of organic matter. Elements that are extractable in larger amounts into solution through the action of conc. HNO_3 are derived almost exclusively from detritic silicate materials and from humic material that is resistant to attack by H_2O_2. Thus these amounts of metals are probably terrestrially derived. Under normal conditions in a natural environment, these elements are released into solution only after a prolonged period of time and their concentrations are not hazardous for living organisms.

Comparison of the distribution of the total concentration of metals and the calculated index of geoaccumulation with the concentration values in sediments unaffected by human civilization revealed that the silt-clay fraction (≤ 63 μm) of Elbe River sediments are not, on an average, contaminated with Co, Ni and Be, are moderately contaminated with Cr and moderately-to-strongly contaminated with Zn. The locally determined maxima for Ni and Co reflect their elevated concentrations in the denudated rocks, Be and Cr are derived primarily from the contaminated side streams of the Elbe, and Zn is derived primarily from anthropogenic sources.

Summary

The accumulation of Co, Ni, Cr, Be and Zn in the surface bottom sediments of a stream along the Czech part of the Elbe River was studied. The average contents of 19.5 mg/kg Co, 55.1 mg/kg Ni and 3.57 mg/kg Be in the fine-grained fractions (<63 μm) are close to the background values (19 mg/kg Co, 68 mg/kg Ni and 3 mg/kg Be) and are thought to have resulted from a natural enrichment due to rock denudation. Locally higher values were found only exceptionally.

The elevated contents of Cr (191.2 mg/kg vs. 90 mg/kg for background) and especially Zn (866 mg/kg vs. 95 mg/kg for background) are obviously related to anthropogenic activities. In flux of waste water from factories and sewage system influenced the contents of Cr and Zn.

Quantitative information on metal speciation has been obtained from sequential leaching studies of the bottom sediments. Results of six-step sequential analysis show that Co, Cr, Ni and Be are present predominantly (72 % Be, 64 % Cr, 49 % Ni and 38 % Co) in reducible and oxidizable phases. Zn is primarily concentrated in exchangeable form (23 %) and in the adsorbed and/or carbonate phase (34 %).

Metals in the residual phase (Cr >Zn >Ni >Co >Be) are believed to have come primarily from humic material that is resistant to an attack of H_2O_2, silicates and other resistant minerals.

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