

Heavy metals in the sediment of Sava River, Slovenia

Težke kovine v sedimentih reke Save, Slovenija

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Abstract

The Sava River is the longest river in Slovenia and it has been a subject of heavy pollution in the past (Stern & Förstner 1976). In order to determine the anthropogenic contribution of selected metals (Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb and Zn) to background levels, concentrations of these metals were measured in sediments at several downstream locations. An extracting procedure using 25% (v/v) acetic acid was applied for estimation of the extent of contamination with heavy metals originating from anthropogenic activities. In addition, a normalization technique was used to determine background, naturally enriched and contamination levels. Aluminum was found to be good normalizer for most of the measured elements. The results suggest that an anthropogenic contamination of certain metal is not necessarily connected to easily extractable fraction in 25% acetic acid. As a consequence of anthropogenic activities the elevated levels of all measured elements were found near Acroni Jesenice steelworks and at some locations downflow from biggest cities.

Kratka vsebina

Reka Sava je najdaljša slovenska reka in kot taka je bila v preteklosti podvržena onesnaževanju s težkimi kovinami (Stern & Förstner 1976). Da bi določili človekov doprinos določenih kovin (Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb in Zn) k naravnemu ozadju so bile izmerjene vsebnosti teh kovin v sedimentu na nekaterih lokacijah dolvodno po reki Savi. Za oceno človekovega doprinsa teh kovin smo uporabili metodo ekstrakcije s 25% očetno kislino. Za določitev naravnega ozadja, naravnega in antropogenega doprinsa smo uporabili metodo normalizacije. Za večino merjenih kovin smo izbrali kot normalizator aluminij. Rezultati so pokazali, da antropogen doprinos določene kovine ni nujno povezan z lahkotopno frakcijo v 25% očetni kislini. Dolvodno od Acroni Jesenice in še na nekaterih dolvodnih lokacijah ob večjih mestih so povišane vsebnosti skoraj vseh merjenih kovin.

Introduction

River sediments can be used as an indicator of anthropogenic, as well as natural contaminants that enter river ecosystem at upstream locations. Metal concentration in

sediment can therefore also result from their geological background (White & Tittlebaum, 1985; Murray 1996). Several studies used the normalization approach to quantify the degree of anthropogenic pollution in different water environments (White &

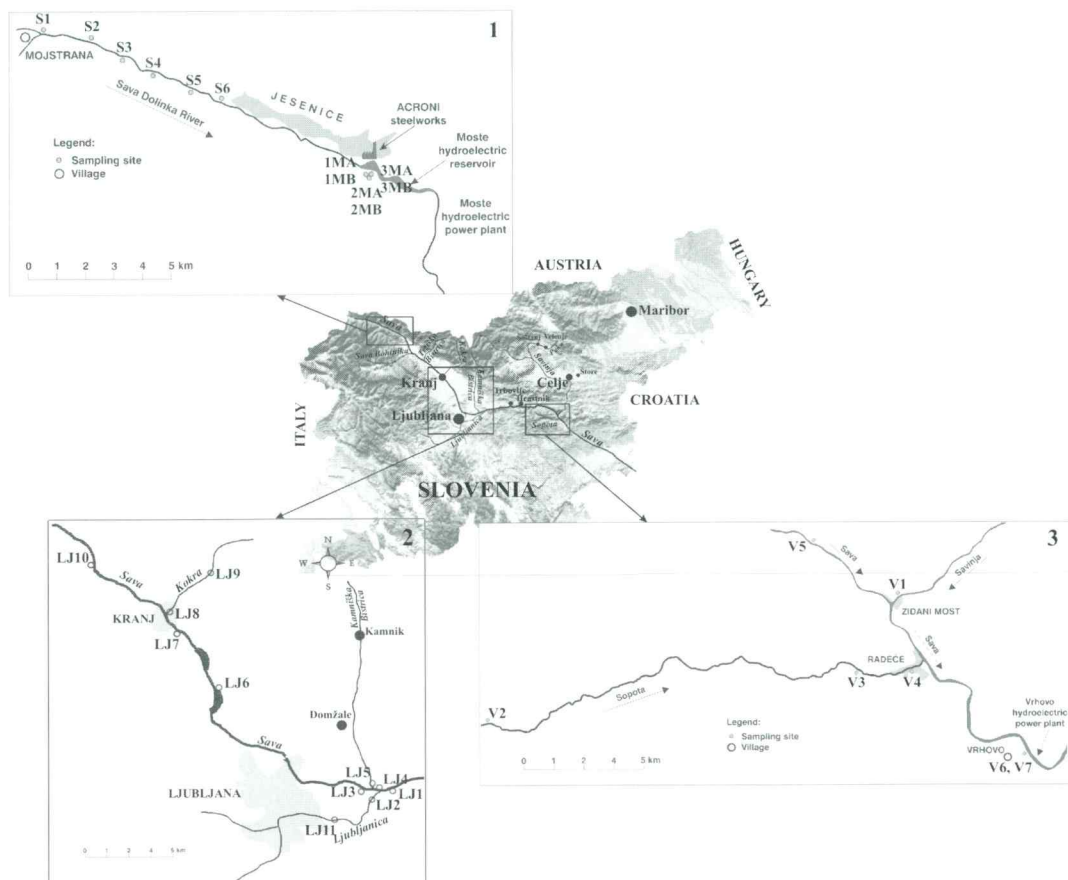


Figure 1. Sampling locations in Sava River and its inflows.

Tittlebaum, 1985; Schropp et al., 1990; Seidemann, 1991; Din, 1992; Parude et al. 1992; Covelli & Fontolan, 1997; Tam & Yao, 1998). This involves dividing the heavy metal concentration by that of a reference element, which is geochemically inactive and abundant in the fine-grained material (Balls et al. 1997). Usually the Al as a major constituent of aluminosilicates (Din, 1992; Tam & Yao, 1998) and Fe as a clay mineral indicator element (Morse et al., 1993; Kennicutt et al., 1994; Tam and Yao, 1998) have been used. In addition to Al and Fe, some other conservative elements such as Li (Loring, 1990), Cs (Ackerman, 1980) and Sc (Ackerman, 1980; Grousset et al., 1995) have been suggested. As an alternative organic carbon has also been used (Daskalakis & O'Connor, 1995; Shine et al. 1995; Tam

& Yao, 1998). However, the use of Al or Fe as a normalizer would be a problem if the contaminant sources introduce a large quantity of Al or Fe into examined environment (Morse et al. 1993).

As total metal concentration in sediment does not give adequate data about metal origin it also does not provide any data about metal solubility, mobility and potential bio-availability in sediment. To study the bio-availability of the metals in sediment several extraction techniques with different chemical extractants in single step and/or in sequence have been developed (Houba et al., 1996; Tack & Verloo, 1996; McGrath, 1996; Quevauviller 1997; Mainz et al., 1997; Ščančar et al., 2000). Chemical partition of sediments is used also to deduce the source and pathways by which natural and anthropogenic heavy metals have entered the envi-

ronment. For marine sediments a method based on the comparison of data for total metal concentration and the portion extractable in acetic acid was suggested to assess the extent of heavy metal contamination originating from anthropogenic activities (Loring & Rantala, 1992; UNEP/IOC/IAEA, 1995).

The present study therefore aims: first to normalize heavy metal concentrations in river sediments with Al and Fe for anthropogenic impact evaluation, and secondly to evaluate extent of anthropogenic pollution of heavy metals by using acetic acid extraction to assess the mobility of the metal.

Experimental

Site description

The largest and longest Slovenian river, the Sava River collects water from an area, which is larger than one half of Slovenia (10.838 km²). Water quality in the Sava River is influenced by several industrial and municipal releases and also by inflows of waters that contribute naturally enriched sediments. In its upper flow (Sava Dolinka River; Figure 1) it passes through typical alpine valley with clastic (claystones, sandstones, conglomerates etc.) and carbonate (i.e. limestone and dolomite) rocks. The main source of pollution in this area are the Acroni Jesenice steelworks, which in the past smelted iron ore and deposited byproducts on landfill near HPP (Hydroelectric Power Plant) Moste water reservoir. Few kilometers downstream from Moste HPP is town Kranj (population: 73.000) with strong industry. Nearby Ljubljana (population: 330.000) the Sava River receives two tributaries, the Ljubljanica River and the Kamniška Bistrica River, which are both heavily polluted with industrial and municipal releases that originate from Ljubljana, Domžale and Kamnik industry. Most industrial and municipal waste water from Ljubljana is cleaned in waste water treatment plant. The water from the plant is released to the Ljubljanica River few hundred meters upstream before it reaches the Sava River. Downstream the Sava River passes across the Zasavje region with strong chemical industry (Hrastnik), coal mining (Trbovlje, Hrastnik) and thermal power plant Trbovlje. Further in

Zidani Most, the Savinja River flows into the Sava River with industrial and municipal releases from Velenje (coal mining), Šoštanj (thermal power plant), Celje (very strong chemical industry) and Štore (steelworks).

Sampling and sample preparation

Samples were taken at all locations where the Sava River is influenced by strong industry or larger municipal releases. The most upstream sampling locations were on the Sava Dolinka River, which is not influenced by municipal and industrial releases. Further the samples were taken just few hundred meters downstream from Acroni Jesenice steelworks, few kilometers upstream of Kranj, between Kranj and Ljubljana, downstream from Ljubljana, upstream of Zidani most, and finally in accumulation basin of Vrhovo hydroelectric power plant (HPP Vrhovo). The sediment samples were also collected on main the Sava's effluents such as the Kokra River, the Kamniška Bistrica River, the Ljubljanica River, the Sopotna River and the Savinja River. The sampling locations are shown in Figure 1. Sediment samples were taken by polyethylene corer (diameter 5 cm) up to depth of 5 cm, either from boat or in shallower waters by hand. At every location at least three separate samples were taken. Samples were transported and stored frozen at -20 °C. Further samples were removed from corers and cut into sections that corresponded to the top layer of 0 to 5 cm of sediment. Then the samples were wet sieved with deionized Milli-Q water on a polyethylene sieve with 0.2 mm pore size, lyophilized for 72 h to constant weight, and then ground and homogenized in agate mortar. The results were calculated to dry weight basis, determined by heating a separate aliquote of the sample at 105 °C until it reaches constant weight.

Determination of total element concentrations

For the determination of total element concentration of Al, Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn wet digestion method was used (Ščančar, 2000). About 0.3 g of lyophilized

zed sample was weighted into a platinum beaker. After 2 ml of nitric acid (1:1, v/v) was added and left for 8 h. Then 12 ml of a mixture of perchloric and nitric acid (1:3, v/v) was added and evaporated on a sand bath. After that 10 ml of hydrofluoric acid was added and evaporated to dryness. The procedure was repeated twice. The residue was dissolved in 3 ml of nitric acid (1:1, v/v), transferred into a 25 ml volumetric flask and filled up to volume with double distilled water. Ni and Cd were determined by flame atomic absorption spectrometry (F AAS) on a Varian Spectra AA 110 atomic absorption spectrophotometer in a dinitrogen oxide-acetylene flame, while Cu, Zn, Cd and Pb were determined on the same instrument in an air-acetylene flame. The Co was determined by electro thermal atomic absorption spectrometry (ETAAS) on a Hitachi Z-8270 polarized Zeeman atomic absorption spectrophotometer, using the standard addition calibration method. Instrumental methods used are shown in Table 1. Reproducibility of methods was 0.5 to 5%. For determination of total Hg about 0.2 g of sample was weighted in a Teflon digestion vessel. After addition of 4 ml of concentrated HNO_3 and 2 ml of concentrated H_2SO_4 , the vessel was closed and left to react at room temperature during night and then heated at 70 °C for 12 h. The digest was diluted with Milli-Q water to 26.8 ml. An aliquot of the digest was added to the reduction vessel and after reduction with SnCl_2 , mercury was swept from the solution by aeration and concentrated on a gold trap. Mercury was then released from the gold trap by heating and measured on an LCD Milton Roy instrument by cold vapor atomic absorption spectrophotometry (CV AAS) (Horvat et al., 1991; Horvat and Lupšina, 1991; Horvat, 1996). Reproducibility of the method is 5 to 10%.

Data quality was checked with the Certified Reference Material, CRM 320, Trace Elements in River Sediment.

Table 1. Analytical methods used for determination of metals in Sava River sediments.

Method	Total elements concentrations	Extraction by 25 % acetic acid
ICP-AES	Al, Fe	Al, Fe
FAAS	Cr, Cu, Pb, Zn	Cr, Cu, Pb, Zn
ET-AAS	Cd, Co, Ni	Cd, Co, Ni
AAS- HP	Hg	

Acetic acid extraction

The acetic acid extractable metal concentration was determined according to the United Nations Environment Program (UNEP) procedure (Loring & Rantala, 1992; UNEP/IOC/IAEA, 1995). About 2 g of air-dried sample was weighed into a 100 ml Erlenmeyer flask. Then 25 ml of 25% v/v acetic acid was added. The flask was capped and slowly shaken for 6 h. After that the content was transferred in a polyethylene centrifuge tube and centrifuged at 2500 RPM for 10 min. The supernatant was decanted into 50 ml volumetric flask. The residual sediment was washed with 10 ml of double distilled water, shaken and centrifuged again. The supernatant was added to the volumetric flask and made up with acetic acid solution to a volume of 50 ml. Extractable metal concentrations were determined as described for determination of total metal concentrations. Metal concentrations in residue sediment were determined next. The decomposition and determination was performed as described in previous section.

Geochemical normalization

The geochemical normalization uses metal data from non-contaminated sediments of the study area to calculate the regression line of the metal on the normalizer at other sampling location. To produce such plot it is necessary to remove outlier values and to delineate a confidence band of 95% of the regression line of the metal on the normalizer. After that the data points from possibly contaminated areas should be projected on diagram. All points which are found inside the 95% confidence band can be characterized as natural non contaminated sediments, while all points above this area should be considered as contaminated sediments. The procedure is described in Loring (1990) and Loring & Rantala (1992).

In this study the Al and Fe were used as normalizers. Because of the steel industry in the Sava River upper flow and possible contamination of sediment by Fe, the Al was finally chosen as a normalizer. The dataset used for normalization included 29 samples collected at locations along the Sava River.

Results and discussion

Analyses of Certified Reference Material CRM 320 show a good agreement between certified and determined values. The total metal concentrations (Al, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb and Zn) are shown in Table 2. In general, the highest total metal concentrations in sediments were found at Moste hydro power plant reservoir, which is influenced by effluents from Acroni Jesenice steelworks. Concentrations of metals from the Sava River upstream (sampling sites S1 to S6) are low and represent their geochemical background with exception of Cd. Cd is higher in upper flow and at HPP Moste and it is probably a consequence of uncontrolled anthropogenic source in upstream region. The highest Hg concentrations (0.7 – 1.5 mg/kg) were found downstream at sampling locations V5, V6 and V7, due to effluents from Hrastnik chlor-alkali plant (TKI Hrastnik), which used "mercury cell" until year 1997 and has since changed to membrane technology.

Regarding to Slovenian legislation (Table 4) some metals in sediments exceed limit,

warning and critical concentrations that are proposed for dangerous substances in soils (Official Gazette of Republic of Slovenia, No. 68/96). Co exceeds the limit concentration (20 mg/kg) only at location LJ2 (20.2 mg/kg) (immediately downstream of Ljubljana) waste water treatment plant as a consequence of plant effluent to the Ljubljanica River. Critical concentration of Cr (380 mg/kg) is exceeded in two samples collected in Moste reservoir (2MA and 3MA), warning concentration (150 mg/kg) is exceeded at locations 1MA and 3MB and limit concentration of Cr (100 mg/kg) is exceeded at locations 1MB and 2MB. In three samples from Moste reservoir the concentration of Cu exceed limit value (60 mg/kg) and in one sample it exceeds warning concentration (100 mg/kg). Mercury exceeded limit concentration (0.8 mg/kg) at two locations (V5 and V7) downstream from Hrastnik Chlor-Alkali plant. Nickel exceeded warning concentration (70 mg/kg) in four samples from Moste and critical concentration (210 mg/kg) at two locations in Moste reservoir. Pb is higher than warning value (100 mg/kg) at two locations as well as Zn (warning conc. 300 mg/kg),

Table 2. Total metal concentrations in sediments collected in Sava River and its inflows.

Location	Al g/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Fe g/kg	Hg mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
S1	16.0	1.73	2.35	12.1	7.30	4.72	n.d.	9.56	4.65	17.9
S2	12.2	1.59	1.90	12.8	8.10	5.45	n.d.	12.6	5.15	24.3
S3	14.0	2.38	2.04	9.1	5.20	3.76	n.d.	10.1	4.60	13.4
S4	21.0	2.25	1.95	5.3	5.00	4.39	n.d.	9.70	4.48	14.5
S5	12.6	2.34	2.03	4.6	5.67	5.67	n.d.	11.8	6.47	17.1
S6	19.1	1.83	4.89	21.6	12.5	8.10	n.d.	19.2	10.1	34.7
1MA	35.0	2.56	12.3	325	52.6	22.4	0.10	183	37.4	106
1MB	38.2	2.35	6.90	110	36.1	18.0	0.02	107	37.4	108
2MA	36.6	3.30	13.10	805	110	26.7	0.08	351	72.5	195
2MB	33.3	4.17	8.40	166	77.3	36.6	0.15	147	220	800
3MA	29.5	3.60	10.5	1846	91.6	20.6	0.03	385	81.0	303
3MB	43.6	3.45	8.70	223	60.6	29.8	0.09	162	119	502
V1	33.8	0.78	8.10	17.6	13.3	19.5	0.05	20.8	13.9	92.5
V2	52.5	1.48	14.5	41.0	19.4	28.8	0.04	29.6	18.5	83.5
V3	60.6	1.57	16.5	56.4	24.6	31.4	0.09	34.7	23.8	100
V4	66.4	1.57	16.1	57.4	22.2	37.3	0.07	36.6	21.7	99.6
V5	33.6	0.90	7.31	27.3	20.7	20.6	1.26	23.9	25.7	79.3
V6	58.8	1.14	13.7	40.8	38.1	28.9	0.76	43.8	44.2	178
V7	56.0	1.09	12.0	34.8	30.3	27.2	1.51	37.2	41.0	142
LJ1	38.3	0.65	13.8	66.1	33.6	22.6	0.267	25.2	38.9	117
LJ2	44.6	0.78	20.2	98.3	43.9	22.9	0.540	29.9	63.7	182
LJ3	47.4	0.40	13.9	50.2	38.5	26.5	0.126	31.7	50.3	89.0
LJ4	56.0	0.77	14.7	51.7	39.4	31.4	0.257	27.3	38.3	127
LJ5	43.9	0.37	12.3	41.4	22.3	27.1	0.278	22.4	24.6	112
LJ7	41.7	0.38	10.9	57.8	17.1	22.4	0.154	23.5	30.0	85.0
LJ8	33.6	0.33	7.90	28.1	12.5	18.9	0.079	12.2	25.7	72.0
LJ9	46.5	0.29	11.6	41.8	16.5	27.5	0.348	17.4	25.2	77.0
LJ10	26.4	0.38	9.60	149	32.0	17.1	0.128	45.0	45.7	130
LJ11	27.0	0.52	13.0	52.8	19.9	19.2	0.241	16.2	43.3	109

n.d. = not determined

which also exceeded critical value (720 mg/kg) in one sample in Moste reservoir. We can conclude that legislative concentrations are exceeded mostly in sediments in Moste HPP reservoir for Cr, Cu, Ni and Zn, while at three other locations only Co and Hg were slightly higher than limit values.

their natural background (Co) almost all data points are located within the limits of the 95% confidence band of the regression line, except LJ11 and LJ2, which represent sampling locations on the Ljubljana upstream and downstream Ljubljana waste water treatment plant. The metals that show the ant-

Table 3. Metal concentrations soluble in 25% (v/v) acetic acid in sediments collected in Sava river.

Location	Fe g/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg	Ni mg/kg
S1	n.d.	0.14	0.54	1.21	1.10	6.80	0.79	0.86
S2	n.d.	0.11	0.67	1.02	1.38	7.53	0.82	0.63
S3	n.d.	0.12	0.24	1.09	1.04	4.96	0.69	0.61
S4	n.d.	0.18	0.33	1.10	0.95	4.93	0.45	0.68
S5	n.d.	0.12	0.41	0.82	1.19	4.79	0.58	0.71
S6	n.d.	0.15	0.29	1.51	2.25	10.1	2.22	1.34
1MA	n.d.	0.14	4.20	17.3	7.30	47.4	33.4	86.0
2MA	n.d.	0.09	2.30	43.1	9.30	94.2	57.2	145
3MA	n.d.	0.17	3.60	85.5	3.20	114	81.0	152
LJ3	6.6	u.l.d.	1.90	1.44	u.l.d.	16.8	n.d.	n.d.
LJ4	12.6	u.l.d.	2.74	1.95	u.l.d.	31.1	n.d.	n.d.
LJ7	13.1	0.19	1.93	2.20	u.l.d.	19.3	n.d.	n.d.
LJ10	14.5	0.29	2.27	8.87	9.08	57.3	n.d.	n.d.
LJ11	8.6	0.27	2.10	9.02	u.l.d.	39.4	n.d.	n.d.
V5	4.50	0.24	1.24	1.71	1.63	13.6	3.00	1.82
V6	19.9	0.47	3.74	6.98	1.39	67.2	3.60	8.10
V7	23.6	u.l.d.	2.95	5.35	1.22	45.1	3.60	7.10

n.d. = not determined
u.l.d. = fraction soluble in acetic acid was under the limit of detection

Table 4. Slovenian legislative concentrations for soils (Official Gazette of Republic of Slovenia. No. 68/96)

Element	Limit value (mg/kg)	Warning value (mg/kg)	Critical value (mg/kg)
Cd	1	2	12
Co	20	50	240
Cr	100	150	380
Cu	60	100	300
Ni	50	70	210
Pb	85	100	530
Zn	200	300	720
Hg	0.8	2	10

The total metal concentrations are not sufficient to evaluate the level of contamination by certain metals in river sediment. To quantify level of anthropogenic contamination in sediment normalization of data to conservative element has been considered. The regression of each metal on Al in the Sava River sediments was calculated using 29 stations along the river. The diagrams are presented in Figure 2 where solid lines represent regression line of certain metal while dashed lines represent the 95% confidence band. Basically two patterns were distinguished on those scatter plots. Among metals where the concentration represents

hropogenic contribution (Cd, Cr, Cu, Fe, Ni, Pb, Zn) have elevated Me/Al ratio at same locations. The data points at contaminated locations lie above the 95% confidence band. Concentration of Cd shows natural background at locations downstream from HPP Moste while the levels in sediments at upper flow and in HPP Moste reservoir show anthropogenic contribution most probably due to local input from Acroni Jesenice steelworks. The normalization of the data showed higher Me/Al ratios for Cu and Fe only in sediments collected in HPP Moste reservoir while the Me/Al ratios for Cr, Ni, Pb and Zn show anthropogenic contribution in sediments from HPP Moste reservoir and at certain locations around Ljubljana, especially at sampling locations LJ2 and LJ10. Elevated metal levels in HPP Moste reservoir and at location LJ10 (first sampling location downstream from Moste HPP) have its origin in over 100 years of steelwork tradition in Jesenice. Elevated ratios at location LJ2 are consequence of releases from Ljubljana waste water treatment plant.

Acetic acid extraction efficiently removes the weakly bound fraction of heavy metals held at ion-exchange positions, easily solu-

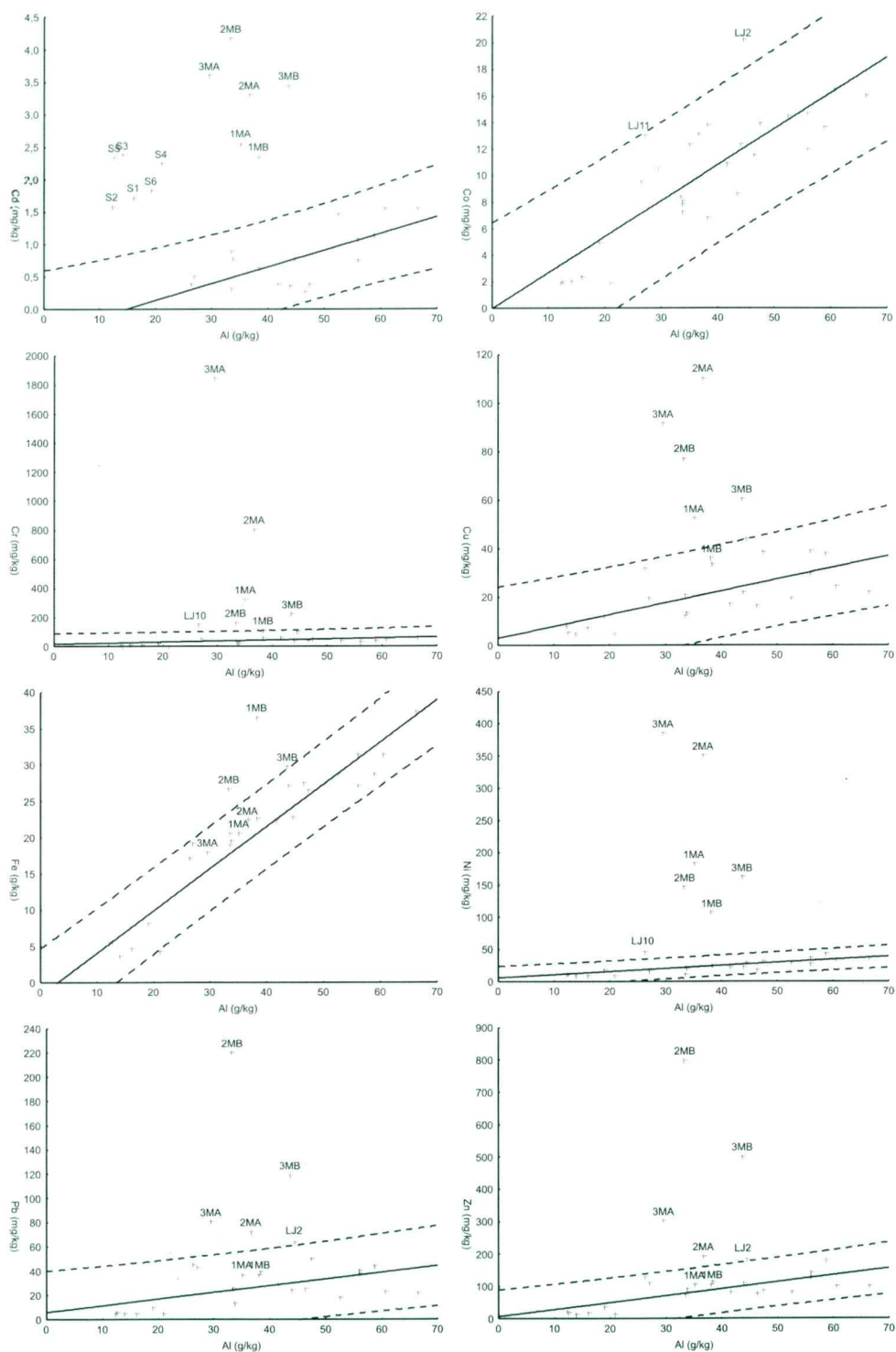


Figure 2. Scatter plots Me/Al for surface sediments in Sava River. Solid lines represents regression line and dashed lines represent the 95% confidence band.

ble amorphous compounds of iron and manganese, carbonates and metals weakly bound to organic matter (UNEP/IOC/IAEA, 1995). Mercury was not measured in these extracts. The extractant does not disturb silicate lattices, resistant iron and manganese

minerals or organic compounds. The method is intended to estimate the extent of heavy metals contamination from anthropogenic sources (Loring and Rantala, 1992; UNEP/IOC/IAEA, 1995). However, we believe that this method is of limited use, and that the

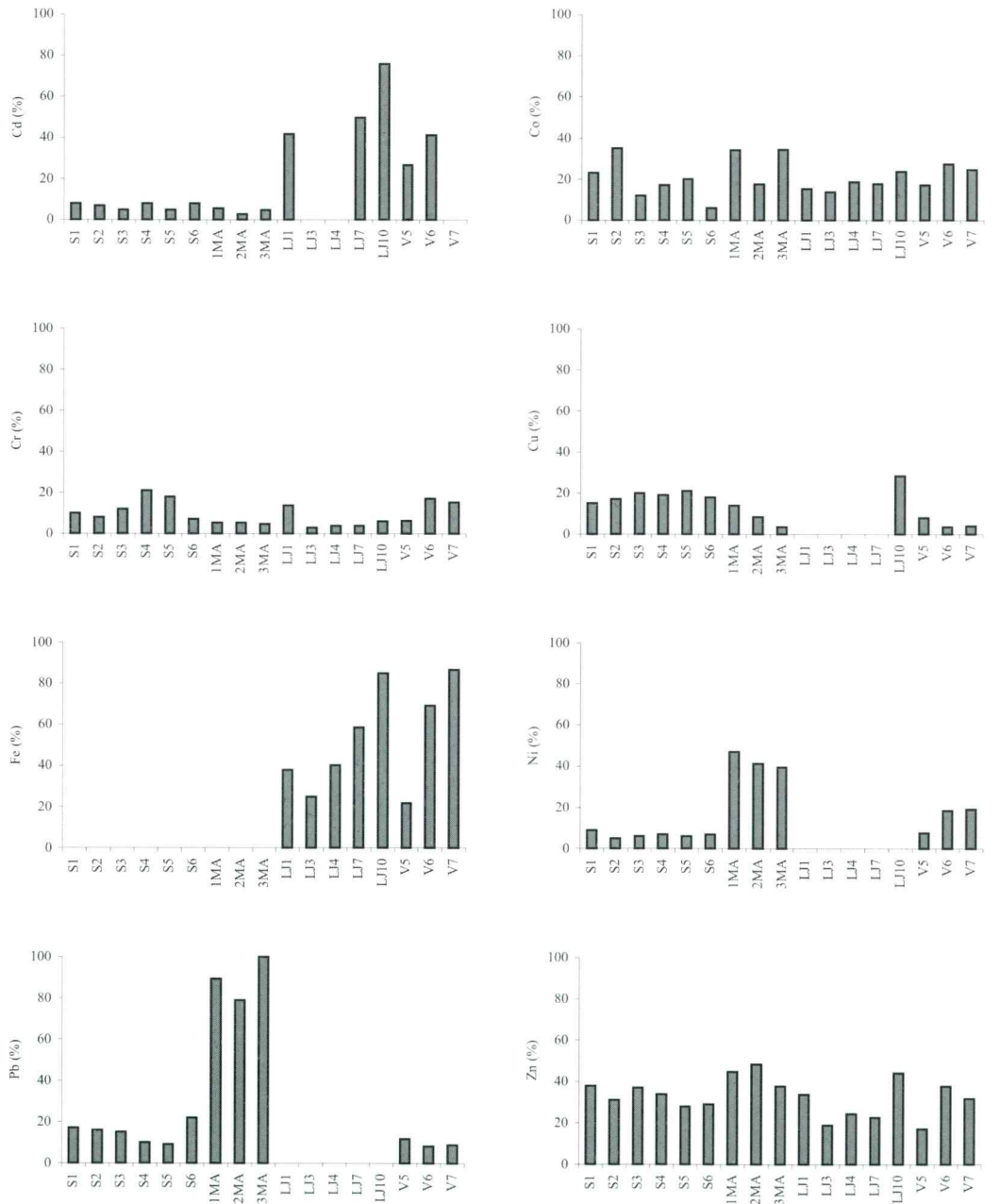


Figure 3. Percentage of metals in the fraction soluble in acetic acid.

obtained information is only suitable to consider the solubility of a metal and its potential bioavailability. The concentration of metal soluble in 25% (v/v) acetic acid is shown in Table 3. The percentage of soluble metal in acetic acid is shown on Figure 3. Cd was most soluble in sediment at downstream locations (LJ and V stations). The percentage of extractable Cd was 26 to 76%, while at upstream locations Cd was strongly bound, with extractable fraction only between 2 and 8%. The geochemical normalization of Cd to Al indicates the anthropogenic source (industrial or municipal) at upstream locations (S and M), while acetic-acid extraction shows that Cd is strongly bound at those locations. At downstream locations lower Cd concentrations were found, indicating weaker bound.

Co, Cr, Cu and Zn showed very uniform distribution of extractable fraction along Sava River. For Ni and Pb the soluble fraction were the highest in sediments collected at HPP Moste (Ni: 40 – 47%; Pb: 79 – 100%) and significantly lower at up- and downstream locations (Ni: 5 – 19%; Pb: 9 – 22%) and show the same distribution pattern as normalization to Al. The lower percentage of extractable metal was found for Cr (2 – 21%) followed by Cu (3 – 28%), Co (6 – 34%) and Zn (17 – 48%). Extractable fraction of Cr, Cu, Co and Zn do not show the same distribution pattern as geochemical normalization. It can therefore be concluded that Ni and Pb in sediments from HPP Moste reservoir originate from anthropogenic activities, while solubility of other metals is not necessary connected to anthropogenic contribution of those metals to their natural background concentrations.

Conclusions

To obtain as much as possible information about elements behavior and origin in sediments the measuring of total element concentration is not enough. The geochemical normalization to element, which is abundant in certain sediment give adequate information on origin of element (i.e. natural or anthropogenic), while acetic acid extraction does not give any information on origin, but it gives some information on mobility and bioavailability of the certain element.

In our case the results obtained from total metal (Al, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb and Zn) concentration, acetic acid extraction (25%, v/v) and normalization to Al indicate that sediment in HPP Moste is the most polluted area in the Sava River flow by Cd, Cr, Cu, Ni, Pb and Zn. Elevated concentrations of Co, Cr, Pb and Zn were also observed at location on the Ljubljana River just downstream Ljubljana waste water treatment plant (LJ2). At other locations the concentrations of those metals represent their natural background. The results obtained by acetic acid extraction agreed well with normalization to Al for Pb and Ni. For other analyzed metals the acetic acid soluble fractions not connected to anthropogenic activities.

To obtain more information on bioavailability and mobility of certain element in sediments some other methods should be applied among which the acetic acid extraction is just one of the options. It would be also helpful to study the influence of sample preparation (i.e. dry vs. wet sieving) on results obtained by acetic acid extraction. This will be the object of future research.

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