Granulometric and chemical composition of the Sava River sediments upstream and downstream of the Krsko nuclear power plant

Visnja Orescanin · Stipe Lulic · Gordana Pavlovic · Luka Mikelic

Abstract Total concentrations of 13 elements (K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Y, Zr, Pb) in the size-fractionated Sava River sediments upstream and downstream of the Krsko nuclear power plant together with metal speciation within bulk sediment have been investigated. Trace metals generally increase with decreasing particle size, however, because of entrapment of organic matter in the 0.63–1 mm fraction, concentrations in the coarser sediment fraction are higher than expected. Exchangeable Pb, Zn, Cu, Mn, Cr and Fe are generally found to represent a negligible fraction of the total metal concentration of the bulk sediment. Seasonal variations of the Pb, Zn and Cu concentrations in the <0.5 mm fraction reflect decreased values during the spring period. Heavy metal concentrations in the 2003 waste water discharges from the Krsko nuclear power plant released into the Sava River were much lower than their maximum allowed values. Combined rubidium and organic matter normalization of the Zn, Pb and Cu concentrations, which was applied on the minus 0.063 mm fraction, indicated three potential sources of contaminants.

Keywords River sediments · Waste water · Heavy metals · EDXRF · Organic matter · Normalization · Sequential extraction · River Sava

V. Orescanin (✉) · S. Lulic · L. Mikelic
Laboratory for radioecology, Institute R. Boskovic,
Bijenicka 54, POB 180, 10000 Zagreb, Croatia
E-mail: vobescan@rudjer.irb.hr
Tel.: +385-1-4560932
Fax: +385-1-4680205

G. Pavlovic
Faculty of Science, Institute for mineralogy and petrography,
Horvatovac bb, 10000 Zagreb, Croatia

Introduction

During the last decades regular studies have been carried out to estimate the heavy metal content in the Sava River sediments in Slovenia, and data are mostly available in internal reports from the Slovenian ministries and environmental institutions. To our knowledge, there is only one published paper which highlights the problem of metal pollution of these sediments resulting from human activity (Stern and Förstner 1975–76). Anthropogenic contributions to sediments were assessed by comparison with three samples taken from the uppermost part of the river Sava, which was regarded as a relatively unpolluted area. It was found that the zinc and lead contents of sediments sampled from the reservoir of the Moste water power plant, situated near the city of Jesenice in the northwest part of Slovenia, were elevated up to fifty times, and those of cadmium and mercury nearly twenty times (Stern and Förstner 1975–76). Another pollution centre was the metal-manufacturing and chemical industry of the Celje area situated in the central part of Slovenia. Sampling was carried out in the Voglajna River which empties at Celje into the Savinja River which further inflows into the river Sava upstream of Krsko. The chromium and zinc contents of the Voglajna sediment were enriched more than a hundred times whereas copper, lead and cadmium were increased up to 25–50 times regarding the geochemical background (Stern and Förstner 1975–76). The aim of this work is to examine the role of particle size and organic matter in transport of selected elements by river sediment, and the chemical speciation of Pb, Zn, Cu, Fe, Mn and Cr in this system. Sediment contamination is determined using normalization based on Rb and organic matter.

Study area

One of the major Croatian rivers, the Sava River flows in a southeasterly direction into Croatia from Slovenia, drains a series composed predominantly of Mesozoic limestones and dolomites and subordinately of Paleozoic and Paleogene clastites before crossing the border near the Jesenice site (Buser and others 1989). It heads east as a large lowland river displaying a meandering pattern

and forms a well-developed floodplain (Fig. 1). The carbonate bedrock underlies the majority of the Krka drainage basin whereas small outcrops of clastic rocks occur in the middle course of the river Krka. Its lower reaches are characterized by thick Quaternary alluvial sediments (Buser and others 1989). Lithology pertaining the eastern part of the study area comprises various types of non-carbonate rocks ranging from Devonian to Quaternary ages (Sikic and others 1979). A major portion of surficial cover of the Sava plain is composed of Tertiary rocks including limestones and marls of the Lower Pliocene formed in a lacustrine-marshy environment. The Upper Pliocene clay with thin intercalations of fine-grained sand underlies Quaternary deposits. Pleistocene lacustrine-marshy sediments had been sporadically influenced by the fluviatile clastites originating from the nearby Medvednica Mt. and the Samobor Mt. The Holocene is represented by alluvial sediments of the river Sava and its tributaries (Simunic and Basch 1975). Deposits are composed of sand, silt and clay with rare occurrences of gravels. The upper part of the Krapina alluvium consists of clay, clayey silt and fine-grained sand, whereas its lower part is built of gravel mixed with clay or sand (Sikic and others 1979). One part of its catchment area belongs to the Medvednica Mt., which is built of ortho- and parametamorphic rocks, carbonate and clastic sedimentary rocks and igneous rocks (Halamic and others 2001). As a result of tectonic activity at the beginning of the Middle Pleistocene, the river Sava cut its way through the basin downstream of Brezice and filled it with a large amount of coarse grained carbonate material which resulted from the melting of glaciers (Velic and Saftic 1991). During the end of the Middle and at the beginning of the Upper Pleistocene, tectonic activity had gradually ceased and the shallowest part of the Quaternary sand and gravel complex, the thickness of which increases in a downstream direction, had been deposited. Channel migration has been caused by tectonic movements in the Sava plain which sinks and inclines in a southward direction (Sikic and others 1979).

Materials and methods

Sediment samples were taken at seven locations upstream and downstream of the Krsko nuclear power plant (NPP) (Fig. 1). At each location about 1 kg of sample was taken with a grab sampler, put into plastic box and transported to the laboratory. Each sample was mixed thoroughly and approximately 100 g of sub-sample was dried at 105 °C in a drying oven, disaggregated in an agate mortar and prepared for the determination of the total elemental composition, the organic mater and carbonate content as well as for sequential extraction analysis. The remainder was wet sieved to six size fractions (<0.063, 0.063–0.250, 0.25–0.63, 0.63–1, 1–2, >2 mm) and then each fraction was dried at 105 °C in a drying oven and weighted. The first four fractions were assayed by XRF analysis and subjected to the determination of the organic matter and carbonate content.

The organic matter content was measured by loss on ignition at 375 °C whereas the carbonate content was determined from the second weight loss at 900 °C. Concentrations of K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Y, Zr and Pb in these four size fractions as well as in bulk samples were determined using energy dispersive X-ray fluorescence, EDXRF method (Orescanin and others 2002). Approximately 2 g of powdered sample was pressed into pellet and irradiated for 7,000 s.
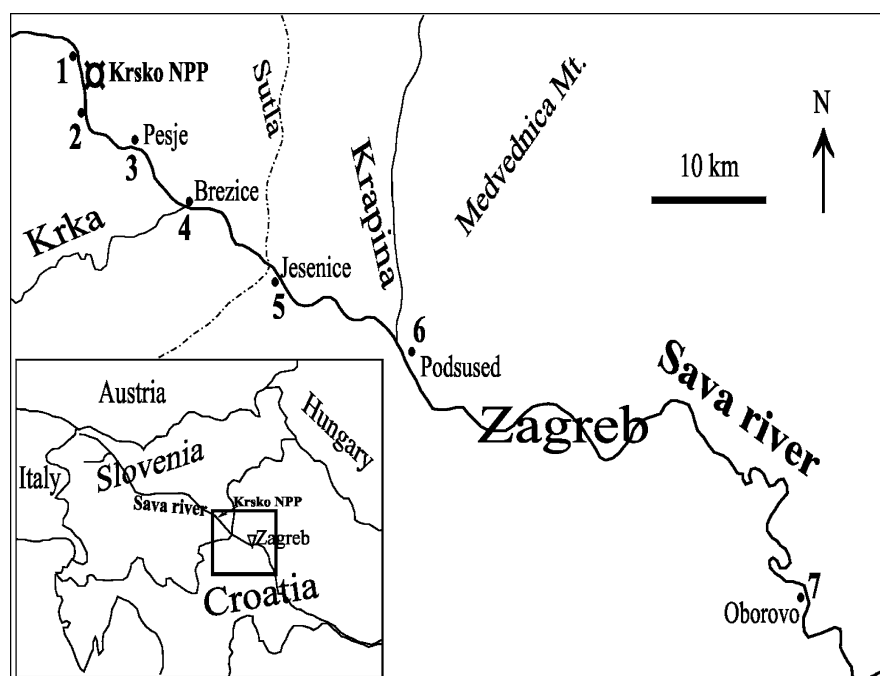

Fig. 1
Geographical location of the study area (*framed part*) and sampling localities (1 - upstream of Krsko NPP, 2 - downstream of Krsko NPP, 3 - Pesje, 4 - Brezice, 5 - Jesenice, 6 - Podsused, 7 - Oborovo). The Sutla River, tributary of the Sava River, comprises part of the Croatian-Slovenian borderline. The site Oborovo marks the downstream direction

1 g of powdered sample (dry weight) was subjected to a sequential extraction procedure which included the following five steps: (1) 1 M NH_4OAc-pH 7 (exchangeable fraction); (2) 1 M NaOAc/HOAc-pH 5 (bound to carbonates); (3) 0.25 M NH_2OHHCl at 90 °C (bound to iron and manganese oxides); (4) 30% $H_2O_2 + HNO_3$ at 86 °C, extraction with NaOAc/HOAc-pH 5 (bound to organic matter); (5) residual fraction was calculated from the difference between the total composition and the sum of all other fractions. The extracts were diluted to 100 mL with double distilled water and adjusted to the pH 3 by the addition of concentrated HNO_3/NH_4OH (same procedure was applied to 100 mL of waste water discharged from the Krsko NPP). After the pH adjustment, samples (the extracts and waste water) were preconcentrated by 2 mL of freshly prepared 1% w/v solution of ammonium-pyroloidinedithiocarbamate (APDC). After the complexation lasted 20 min, the suspension was filtered through a Millipore filter (0.45 μm) and irradiated for 10,000 s. All targets were analyzed by EDXRF. Samples were irradiated by X-rays generated from the [109]Cd annular source. The angle between the sample and the source was 89°. The detection of the characteristic X-ray radiation from the sample was conducted with a Si (Li) detector (Canberra) cooled with liquid nitrogen with the following characteristics: detector size=30 mm^2, Si thickness=3 mm, Be window=25 μm, FWHM for 5.9 KeV [55]Fe 165 eV. The angle between the sample and the detector was 1° and the distance was 1.5 cm. Spectrums were collected by Genie—2000 software (Canberra). Collecting time was 10,000 s for thin targets and 7,000 s for thick targets. Spectral data were analyzed by WinAxil software (Canberra). The calibration file for the thin targets (water samples) was created on the basis of the measurement of the standard solutions (Merck) prepared and analyzed in the

same way as unknown samples. Elemental concentrations in the thick targets were calculated with the "Fundamental parameters" method from the WinFund package using IAEA SRM SL-1 and SOIL 7 as standards.

Results and discussion

Granulometric composition of the Sava River sediments upstream and downstream of the Krsko NPP is presented in Fig. 2. Since the fraction >2 mm was composed of only a few carbonate pebbles and some organic detritus whereas the fraction 1–2 mm mostly consisted of organic material, these two fractions were not further characterized. Particle-size analysis shows that most of these locations have rather different granulometric composition (Fig. 2). Therefore the comparison of elemental concentrations among the locations would be fraught with difficulty because textural characteristics of sediments are one of the most important factors controlling storage of sediment-associated heavy metals in river systems (Förstner and Wittmann 1979; Salomons and Förstner 1984; Brook and Moore 1988; Graf and others 1991; Macklin 1996; Ladd and others 1998; Orescanin and others 2002; Walling and others 2003). It is generally accepted that the silt and clay fractions of sediments are probably the most important scavengers of trace metals what is attributed to large surface area of fine particles as well as to their varied shape and charge (Gibbs 1977; Rose and others 1979; Salomons and Förstner 1984; Williamson and others 1994). The sand fraction (0.25–0.63 mm) prevails at the locations 2, 3, 4 and 6 (Fig. 2). Location 5 mostly consists of pellitic material while location 7 is composed of a large amount of fine sand (0.063–0.25 mm). Sediment from location 1 was
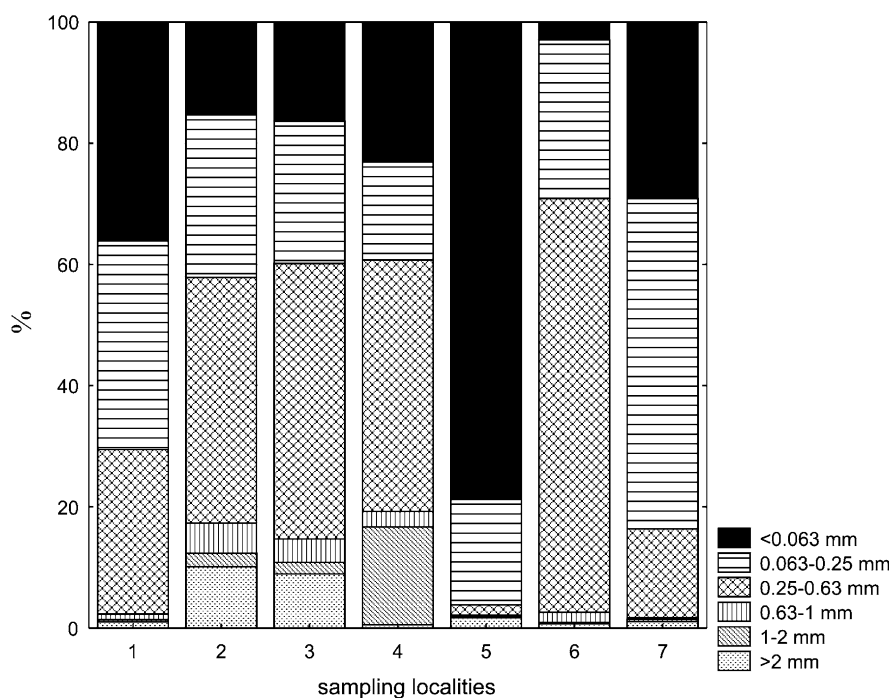

Fig. 2
Sediment grain size distribution at the seven sampling localities

Legend:
- ■ <0.063 mm
- ▤ 0.063-0.25 mm
- ▨ 0.25-0.63 mm
- ▥ 0.63-1 mm
- ▧ 1-2 mm
- ▦ >2 mm

found to be more evenly distributed over the three fractions (<0.063, 0.063–0.25 and 0.25–0.63 mm).

The bulk sediment composition and chemical characterization of each size fraction of the Sava River sediments are presented in Tables 1 and 2 respectively. It can be inferred that loss on ignition at 375 °C and 900 °C, corresponding to the organic mater (OM) and carbonate (CC) content respectively, was grain size dependent (Table 2). The coarse sand fraction (0.63–1 mm) comprised the greatest amount of OM whereas its smallest values were found in the fine sand (0.063–0.25 mm) fraction. Quite opposite trends were found for the carbonate content (Table 2). Due to adsorption onto surfaces of particles the highest concentrations of Zn, Fe, Mn, Cr, Cu, Ti, Pb and Sr were found in the finest fraction (<0.063 mm) followed by the coarse sand fraction where the metals are bound by organic material. In comparison to the finest fraction of sediment from the most downstream location (Oborovo), even higher concentrations of Zn, Fe, Mn and Cr were found in the coarse sand fraction, which could be interpreted as resulting from the highest abundance of organic matter (Table 2). Taking into account that this site is located downstream of the city of Zagreb (Fig. 1) it certainly bears some imprint of urban activities. It is also affected by local extensive agriculture and therefore it could be assumed that the organic material was derived from the input of agricultural and domestic wastes (Adriano 1986). For example, Zn concentration in the silt fraction of the Oborovo sample was almost twice as high as that found in the Jesenice sample where almost all analyzed elements reached their lowest values (Table 2). Mutually similar downstream trends of OM, Zn, Cu and Pb in the fine, medium and coarse sand fractions are consistent with the bulk sample analysis demonstrating sediment metal level dependence on the organic matter content (Fig. 3). It is generally known that organic matter can form water-soluble and insoluble complexes and chelates with metal ions (Chao 1984; Adriano 1986; Hall 1998). As regards K, Zr, Y and Rb, these elements were mostly grain size dependent, whereas Ca was only dependant on the CC content (Table 2).

Sequential extraction analysis of bulk river-sediment samples (Fig. 4) showed that residual, 'reducible' (bound to iron and manganese oxides) and 'oxidisable' (bound to organic matter) phases accounted for a major proportion of total Fe and Cr concentrations. Although Cr had somewhat larger contributions from carbonate-related and exchangeable phases than Fe, these forms were both found to be negligible. Pb, Zn, Cu and Mn are fractionated approximately equally in residual, 'reducible', 'oxidisable' and carbonate-related phases, while exchangeable forms were of greater importance compared with Fe and Cr (Fig. 4). The exchangeable phase is generally assumed to be the most mobile fraction of elements which is introduced by anthropogenic activities and bound to the sediment in adsorbed form (Tessier and others 1979; Salomons and Förstner 1984). Since it forms only a tiny proportion of analyzed sediment-associated metals it can be inferred that investigated sediments pose a low risk of potential metal bioavailability.

Seasonal variation in Pb, Zn and Cu content of sediments was determined by analyzing the minus 0.5 mm grain size fraction. This particle size is otherwise routinely used for radiometric measurements, while its chemical composition is hereby documented for the first time. Results for the February, May and October of the year 2003 are graphically presented. From there it can be inferred that concentration variability significantly depends on seasonal dilution with snow melt. Therefore concentrations were lowest in the late winter/early spring (February) and then rose in the late spring/early summer (May) and reached the highest values in the autumn (October). The most notable feature is heavy metal decline at the Podsused site, which is also present on Fig. 3. This may be attributed to the influence of weathering of the SW part of the Medvednica Mt., which is chiefly built of limestones and dolomites (Sikic and others 1979). When considering the months separately it can be seen that metal patterns are mutually quite similar, whereas each metal exhibits somewhat different downstream trends when comparing the three months in question (Fig. 5).

Table 1
Loss on ignition (LOI, in %) and total-metal analysis of size-fractionated sediments (numbers 1–7 mark sampling sites)

Variable	1	2	3	4	5	6	7
Zn (ppm)	219	110	82	160	249	55	227
Cu (ppm)	27	22	26	36	57	20	46
Fe (%)	1.839	1.09	0.922	2.175	1.440	1.034	1.942
Mn (ppm)	350	124	120	260	200	169	370
Cr (ppm)	90	122	60	90	90	58	110
Ti (%)	0.235	0.12	0.123	0.24	0.196	0.100	0.25
Ca (%)	12.4	30	14.1	14.7	13.6	15.0	15.6
K (%)	1.54	1.1	1.47	1.5	1.09	0.84	1.6
Zr (ppm)	206.9	93	114.6	155	221	102.7	214
Y (ppm)	43	25.4	25	40	50	27.3	46
Sr (ppm)	117.4	82.8	108.0	162	121.7	133.6	157
Rb (ppm)	64.7	33.4	39.9	59.3	69.4	34.3	67
Pb (ppm)	33	22.2	15	31	30	15	54
LOI (375 °C)	7.46	7.33	6.4	8.38	12.97	7.33	6.40
LOI (900 °C)	13.56	16.27	15.40	15.57	14.10	16.27	17.15

Table 2

Loss on ignition (LOI, in %) and total-metal analysis of size-fractionated sediments (numbers 1–7 mark sampling sites). Capital letters indicate size fractions as following: A: <0.063, B: 0.063–0.25, C: 0.25–0.63, D: 0.63–1 mm. Chemical analysis was not carried out for the fraction 0.63–1 mm in the sample from the Jesenice site

Variable	1 A	1 B	1 C	1 D	2 A	2 B	2 C	2 D	3 A	3 B	3 C	3 D	4 A	4 B	4 C	4 D
Zn (ppm)	470	123	134	34	564	130	43	28	410	164	63	216	483	99	168	133
Cu (ppm)	80	21	26	13	115	29	14	11	80	29	19	44	129	22	28	30
Fe (%)	2.823	1.564	1.927	0.235	2.430	2.170	0.383	0.225	1.792	1.626	0.763	2.053	1.856	1.128	2.013	1.199
Mn (ppm)	480	280	300	124	255	261	63	61	240	290	110	240	230	170	240	130
Cr (ppm)	110	80	80	27	109	87	30	29	80	90	49	100	100	50	70	67
Ti (%)	0.39	0.22	0.15	0.039	0.30	0.28	0.07	0.04	0.20	0.16	0.113	0.16	0.191	0.13	0.22	410
Ca (%)	12.7	14.5	12.4	11.5	13.6	16.8	15.1	11.8	12.7	15.4	16.4	19.9	13.5	18.4	14.4	7.4
K (%)	2.4	1.3	1.2	0.3	2.1	1.3	0.4	0.3	1.7	1.6	0.76	1.2	1.52	0.82	1.61	<0.186
Zr (ppm)	388	148	122	52	275	94	66	41	263	141	92.0	139	184.5	133.6	135.6	104.2
Y (ppm)	63	33	33	14	53	29	12	12	55	35	22.9	46	46.3	23.3	41	45.6
Sr (ppm)	159	112	129	44	131	103	75	41	151	164	80.7	152	139.6	105.0	170.8	136.2
Rb (ppm)	106	48	51	12.3	79.4	39.9	18.6	11.7	81	52	30.9	57	75.3	36.5	58.6	31.3
Pb (ppm)	50	19	26	23	70	20	13	22	45	23	15	38	52	17	23	46
LOI (375 °C)	11.68	3.22	5.17	19.40	7.79	2.64	3.96	18.60	15.74	2.96	3.02	15.00	10.73	1.47	3.44	46.92
LOI (900 °C)	14.08	16.17	13.56	13.31	14.52	18.46	16.62	13.07	13.64	16.58	17.94	11.81	14.04	18.69	15.38	9.50

Variable	5 A	5 B	5 C	6 A	6 B	6 C	6 D	7 A	7 B	7 C	7 D
Zn (ppm)	306	137	114	304	67	53	108	610	77	127	660
Cu (ppm)	93	43	48	116	19	17	22	120	22	37	110
Fe (%)	1.538	1.184	1.010	2.123	1.311	0.9798	1.380	3.628	0.645	1.641	4.90
Mn (ppm)	210	200	160	384	320	151	225	770	150	280	100
Cr (ppm)	90	60	80	80	43	54	65	110	80	70	150
Ti (%)	0.199	0.176	0.095	0.25	0.22	0.09	0.07	0.51	0.13	0.18	0.25
Ca (%)	13.6	15.5	12.7	18.8	22.3	18.2	11.2	13.6	19.0	10.9	7.3
K (%)	1.06	1.09	0.89	1.7	1.0	0.83	0.8	2.9	0.8	1.9	1.0
Zr (ppm)	247	124.0	103.9	222	101	86.4	83	334	108	117	113
Y (ppm)	51	30.7	26.5	40	21	18.4	25	66	19	34	42
Sr (ppm)	123.1	121.2	114.8	158	117	142.2	117	228	91	142	183
Rb (ppm)	70.0	48.9	36.8	66.7	26.7	29.5	31.9	118	28.1	51	44
Pb (ppm)	40	22	28	47	22	15.6	20	105	25	32	99
LOI (375 °C)	6.25	10.25	10.69	5.65	0.95	1.24	8.02	10.26	3.05	6.17	52.49
LOI (900 °C)	16.54	13.94	14.63	18.86	24.24	19.87	12.28	14.81	20.64	11.50	8.03
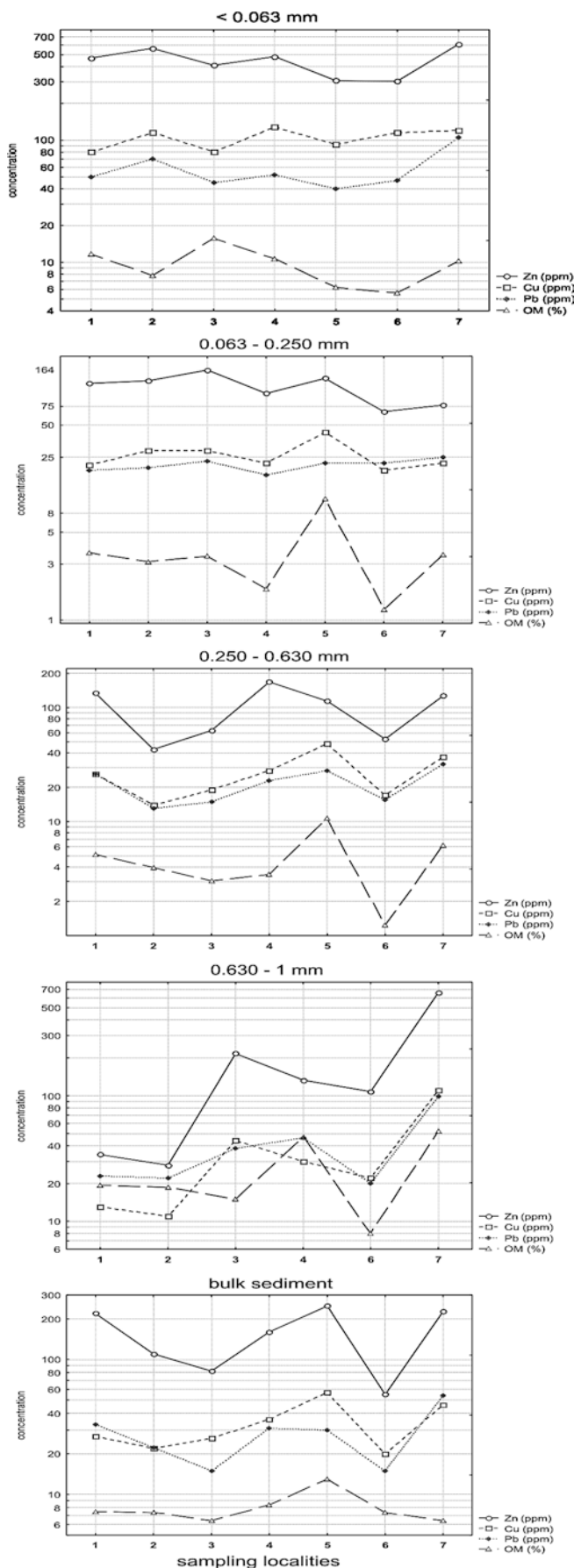
In order to assess the degree to which a sediment had been subjected to possible trace metal pollution from the river water it was necessary to carry out normalization by calculating the ratio of measured concentrations of selected elements to the contents of conservative elements whose concentrations are unaffected by human activity (Salomons and Förstner 1984; Hanson and others 1993; Daskalakis and O'Connor 1995; Orescanin and others 2001). Therefore the concentrations of Zn, Pb and Cu have been plotted after combined normalization to Rb and OM (Fig. 6). Three points, where significant amounts of heavy metals were introduced into the river system, were located, quite expectedly, immediately downstream of the Krsko NPP and downstream of the principal tributaries of the river Sava, i.e. Krka and Krapina. The highest ratio of Zn to Rb and OM was found in the sample taken downstream of the Krsko NPP. It could be linked to the cultivation of numerous orchards in the vicinity of the site since Zn-carrying fertilizers are by far the largest source of Zn (Adriano 1986). This statement is attested by measurements of heavy metal concentrations in the 2003 waste water discharges from the Krsko NPP released into the Sava River (Table 3). Briefly, the listed values were 2–20 times lower than their maximum allowed values (MAV). The total volume of waste water discharged into the Sava River was 1,860 m^3 in the year 2003. This amount was used for the calculation of approximate masses of heavy metals (g/yr) emitted into the river during the year 2003 (Table 4). These data suggest that the Krsko NPP was not the principal source of heavy metal emissions in the Sava River. Figure 6 demonstrates that Zn content decreased in the following order: downstream of the Krsko NPP >Podsused >Brezice >Oborovo >upstream of the Krsko NPP=Jesenice >Pesje. A similar pattern was observed both for Cu and Pb (Fig. 6). The river Krka was identified as a major cause of elevated metal levels at the location Brezice. Although it drains very thick, silicate soils, some anthropogenic input due to the pharmaceutic industry of Novo Mesto, located along its middle course, cannot be excluded. Metal enrichment in sediment of the location Podsused could be interpreted as resulting from the Krapina River inflow. The natural component of metal levels may be attributed to erosion of rather complex lithology consisting of ortho- and parametamorphic rocks, carbonate and clastic sedimentary rocks and igneous rocks (Halamic and others 2001), whereas human influence could have resulted from an industrialized catchment area as well as agriculture. Since positive deviations of the ratio normally increase as concentrations of normalizing factors
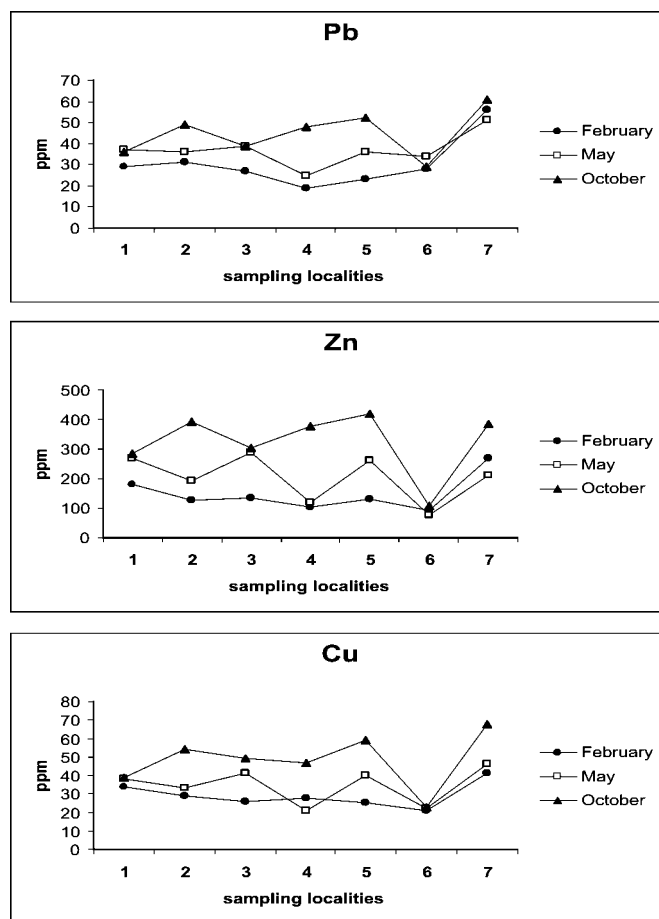
▶

Fig. 5
Seasonal variation in heavy metal content of the grain size fraction <0.5 mm. Loss on ignition (LOI, in %) and total-metal analysis of bulk sediment. Numbers from 1 to 7 mark sampling localities

decrease, it is emphasized (Daskalakis and O'Connor 1995) that high concentration ratios should not be connected with contamination without examination of the actual numbers that comprise the ratio. Such a pattern is evident for OM in the silt fraction (Fig. 3). Comparison with the average shale and soil composition (Adriano 1986; Thornton 1995), although approximative, suggests certain human influence since heavy metal concentrations are, most notably in the case of zinc, above natural levels.

Conclusions

Normalization based on Rb and organic matter was carried out to estimate the relative enrichment of heavy metals (Zn, Cu, Pb) in the Sava River sediments arising from fertilizing activities downstream of the Krsko NPP as well as from input of sediment load by two tributaries of the river Sava, i.e., the rivers Krka and Krapina. Since a good correlation exists between heavy metals and organic matter in particle size fractions as well as in bulk sediment, sediment metal transport appears to be governed primarily by chemical sorption-desorption processes associated with organic matter. Although two size fractions (<0.063 and 0.63–1 mm) have metal concentrations higher than the other two, they don't make up the bulk of stream sediments. Sequential extractions of bulk sediment samples show that residual, 'reducible' (bound to iron and manganese oxides) and 'oxidisable' (bound to organic matter) phases account for a major proportion of total Pb, Zn, Cu, Mn, Fe and Cr concentrations. The exchangeable phase proved to be the least significant transporter of the heavy metals. Temporal variability of heavy metals showed that their concentrations were lowest during early spring snowmelt due to dilution. Particle-size data, combined with the data for metal speciation, suggest that the investigated Sava River sediments don't constitute an environmental problem. Moreover, heavy metal levels in the 2003 waste water discharges from the Krsko NPP released into the Sava River were 2–20 times lower than their maximum allowed values.
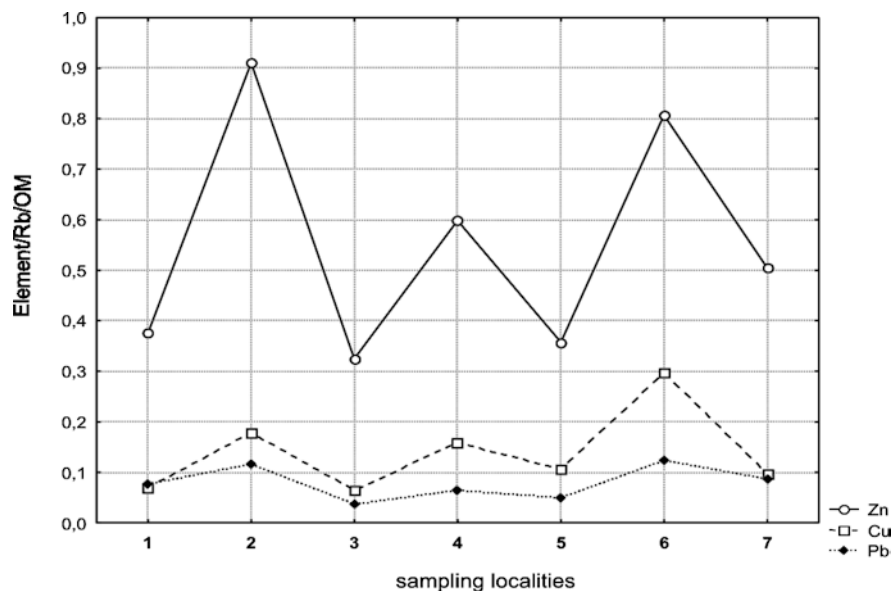

Fig. 6
Heavy metal levels after combined normalization on Rb and organic matter. Chemical analysis wasn't carried out for the fraction 0.63–1 mm in the sample from the Jesenice site

Table 3
Heavy metal concentrations in the 2003 waste water discharges from the Krsko NPP released into the Sava River, together with their maximum allowed values (MAV)

Month	Concentration (µg/L)					
	Pb	Zn	Cu	Ni	Fe	Cr
January	19.7	69.4	20.8	17.4	197.9	16.2
February	20.0	131.4	22.5	9.7	314.0	17.8
March	23.9	60.4	10.9	25.1	136.8	9.1
April	17.0	51.0	10.8	5.0	49.0	7.0
May	13.8	26.2	12.7	10.0	253.5	0.9
June	22.0	454.0	19.0	50.0	169.0	17.0
July	21.0	397.0	22.0	170	251.0	23.0
August	13.9	309.3	34.9	6.1	74.8	7.6
September	14.1	89.6	27.5	6.1	200.7	4.6
October	23.8	258.0	15.5	17.2	208.9	8.3
November	18.2	50.2	21.7	8.0	73.0	9.1
December	13.5	193.6	8.9	10.0	174.0	5.0
MAV	200	1,000	100	1,000	2,000	100

Table 4
Mean values of heavy metals ($\bar{X}$) in the 2003 waste water discharges from the Krsko NPP and masses of metals (m) emitted into the Sava River during the year 2003

Element	$\bar{X}$ (µg/L)	m (g/yr)
Pb	18.4	34.2
Zn	174.2	323.6
Cu	18.9	35.2
Ni	15.1	28.1
Fe	175.2	325.9
Cr	10.4	19.3

References

Adriano DC (1986) Trace elements in the terrestrial environment. Springer, Berlin Heidelberg New York

Brook EJ, Moore JN (1988) Particle-size and chemical control of As, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in bed sediment from the Clark Fork River, Montana (U.S.A.). Sci Tot Environ 76:247–266

Buser S, Ramovs A, Drovenik M, Plenicar M (1989) Geological setting of Slovenia. In: Encyclopedia of Slovenia, 3rd edn. Mladinska knjiga, Ljubljana, pp 195–203

Chao TT (1984) Use of partial dissolution techniques in geochemical exploration. J Geochem Explor 20:101–135

Daskalakis KD, O'Connor TP (1995) Normalization and elemental sediment contamination in the coastal United States. Environ Sci Technol 29:470–477

Förstner U, Wittmann GTW (1979) Metal pollution in the aquatic environment. Springer, Berlin Heidelberg New York

Gibbs RJ (1977) Transport phases of transition metals in the Amazon and Yukon Rivers. Geol Soc Am Bull 88:829–843

Graf WL, Clark SL, Kammerer MT, Lehman T, Randall K, Schroeder R (1991) Geomorphology of heavy metals in the sediments of Queen Creek, Arizona, USA. Catena 18:567–582

Halamic J, Peh Z, Bukovec D, Miko S, Galovic L (2001) A factor model of the relationship between stream sediment geochemistry and adjacent drainage basin lithology, Medvednica Mt., Croatia. Geol Croat 54:37–51

Hall GEM (1998) Analytical perspective on trace element species of interest in exploration. J Geochem Explor 61:1–19

Hanson PJ, Evans DW, Colby DR, Zdanowicz VS (1993) Assessment of elemental contamination in estuarine and coastal environments based on geochemical and statistical modeling of sediments. Mar Environ Res 36(4):237–266

Ladd SC, Marcus WA, Cherry S (1998) Differences in trace metal concentrations among fluvial morphologic units and implications for sampling. Environ Geol 36:259–270

Macklin MG (1996) Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. In: Anderson MG, Walling DE, Bates PD (eds) Floodplain processes. Wiley, New York, pp 441–460

Orescanin V, Nad K, Valkovic V, Mikulic N, Mestrovic O (2001) Red mud and waste base: Raw materials for Coagulant Production. J Trace Microprobe Tech 19(3):419–428

Orescanin V, Mikulic N, Obhodas J, Nad K, Valkovic V (2002) Distribution of trace elements in the coastal sea sediments: Punat bay in the Northern Adriatic. J Trace Microprobe Tech 20(2):247–260

Rose AW, Hawkes HE, Webb JS (1979) Geochemistry in mineral exploration, 2nd edn. Academic Press, New York

Salomons W, Förstner U (1984) Metals in the hydrocycle. Springer, Berlin Heidelberg New York

Sikic K, Basch O, Simunic A (1979) Geology of Zagreb Sheet. Basic geological map of Yugoslavia, 1:100000. Institute of Geology, Zagreb, Beograd (Federal institute of Geology) (in Croat., Engl. Summary)

Simunic A, Basch O (1975) Stratigraphy of Quaternary sediments of the Sava plain in the Zagreb region. Geol Vjes 28:153–164

Stern J, Förstner U (1975–76) Heavy metals distribution in the sediment of the Sava Basin in Slovenia. Geologija 19:259–274

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851

Thornton I (1995) Metals in the global environment: facts and misconceptions, 1st edn. The International Council on Metals and the Environment, Ottawa

Velic J, Saftic B (1991) Subsurface spreading and facies characteristics of middle Pleistocene deposits between Zapresic and Samobor. Geol Vjes 44:69–82

Walling DE, Owens PN, Carter J, Leeks GJL, Lewis S, Meharg AA, Wright J (2003) Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. Appl Geochem 18:195–220

Williamson RB, Hume TM, Molkrijnen JA (1994) Comparison of the early diagenetic environment in intertidal sands and muds of the Manukau harbor, New Zealand. Environ Geol 24(4):254–266