

Granulometric and Chemical Composition of the Danube River Sediments, Batina Village, Croatia

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Abstract

The size-fractionated recent sediments of the Danube river, from Batina, were assayed for the total concentrations of 15 elements: Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, V, Y, Zn and Zr. It was found that trace metals increased with decreasing particle size, whereas the highest levels of organic matter from loss on ignition tests were found in the 0.5–1 mm fraction. The exchangeable phase accounted for a very minor proportion of the total heavy metal concentrations. Seasonal patterns of exchangeable Pb, Zn, Cu, Ni, Mn and Fe were more irregular than those of total metal levels, both generally reflecting a decrease in concentrations during spring. Rubidium normalization of the Pb, Cu, Zn, Ni, Cr, Mn and Fe concentrations was applied on the <0.063 mm fraction. A certain amount of the Cu and Ni concentrations may be related to anthropogenic rather than natural processes upstream of the study area and around one of the localities.

1. INTRODUCTION

During the last decade special research has focused on an assessment of the environmental state of the river Danube and its delta (LITERATHY & LASZLO, 1995, 1999; WINKELS et al., 1998; GRUIZ et al., 1998; RICKING & TERYTZE, 1999; GUNDAKER, 2000; DINESCU & DULIU, 2001; SECRIERU & SECRIERU, 2002; WEHLAND et al., 2002; MACKLIN et al., 2003; WOITKE et al., 2003). Such attention on the Danube is understandable as it is Europe's second-longest river (after the Volga), and receives various pollutants released from 10 countries before it eventually enters the Black Sea.

To our knowledge, there are no published papers dealing with such environmental problems regarding the Croatian stretch of the Danube. This paper reports the concentrations of Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, V, Y, Zn and Zr determined in three types of recent sediment, taken from the river channel, which are defined as follows: (1) bulk samples collected in August, (2) their grain size fractions, and (3) the size fraction <0.5 mm of samples collected in March, August, September and October to determine temporal patterns of variables. These three types of sedimentary material were subsequently assayed for Cr, Cu, Fe, Mn, Ni, Pb and Zn levels in an exchangeable phase. From the various sediment constituents which are free of human interference (e.g., Al, Sc, Rb, Li, TOC, Ti), rubidium was chosen here as a normalizing factor, used to locate an area of anthropogenic pollution (HANSON et al., 1993; DASKALAKIS & O'CONNOR, 1995; PROHIĆ et al., 1995). Seasonal variations of selected variables are presented graphically.

2. STUDY AREA

The Danube river sediments, at the city of Mohács on the Hungarian stretch of the River and at the village of Batina on the Croatian stretch of the River, are collected in turn, four times a year for the purpose of radiometric measurements. It is a part of the Danube River water management under the Boundary Waters Treaty between Croatia and Hungary. The village of Batina, situated 5 km away from the Croatian–Hungarian border (Fig. 1), also represented one of sampling stations along the river Danube under the Joint Danube Survey (Croatia, River–km 1424) belonging to geo-morphological reach number 5 which was characterized by significant emissions of untreated wastewater in Budapest (VOGEL & PALL, 2001; WOITKE et al., 2003). The river Danube forms a 150 km long border between Croatia and Serbia and Monte Negro (Fig. 1). The Holocene deposits are represented by three alluvial terraces ranging from 10–15 metres in thickness and are composed of clayey, silty and sandy sediments (MAGAŠ, 1987). The fluvial history of the terrain dates back to the Lower Pleistocene, whereas the largest sediment loading in the Lower Holocene resulted from excessive melting of Alpine glaciers due to marked climate change.

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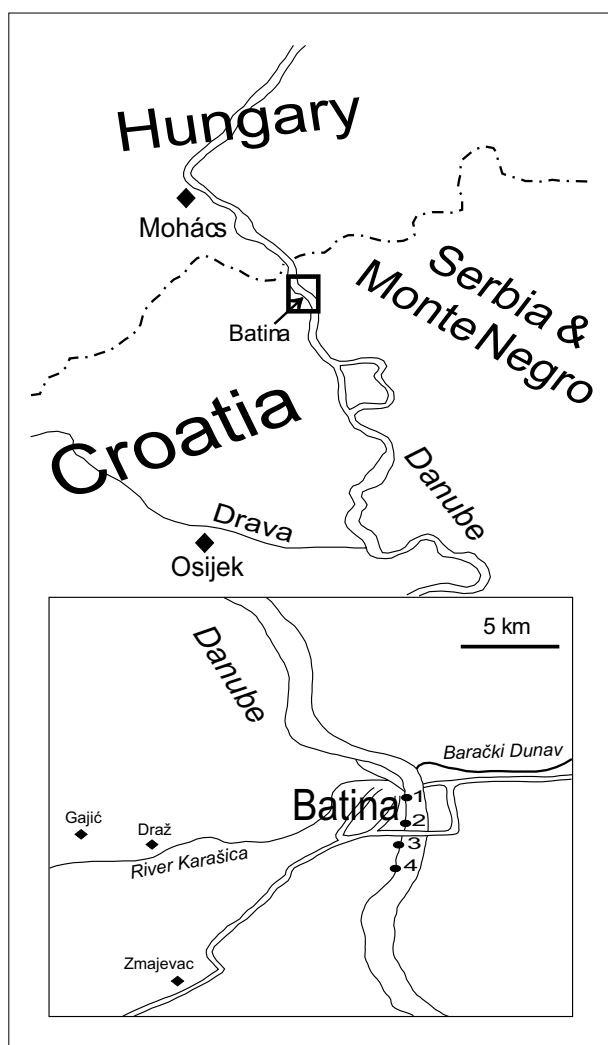


Fig. 1 Geographical location of the study area (framed part) and sampling localities (1, 2, 3, and 4). Site 4 marks the downstream direction.

3. MATERIALS AND METHODS

Sediment samples were collected at four locations upstream and downstream of a bridge crossing the river Danube in the village of Batina (Fig. 1). Sampling was carried out in March, August, September and October of 2002. At each location in the river channel, a composite sample of up to 1 kg was collected from at least three points within a perimeter of 50 m. The samples were taken manually with a plastic scraper and spatula, which were washed and cleaned with stream water between samples. Sediments were put into plastic boxes and transported to the laboratory. Each August sample was mixed thoroughly and approximately 100 g of sub-sample was dried at 105°C in a drying oven to eliminate any water, disaggregated in an agate mortar and prepared for determination of the total elemental composition (Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, V, Y, Zn and Zr), loss on ignition (LOI), and Cr, Cu, Fe, Mn, Ni, Pb and Zn levels in exchangeable phase. The remainder was wet sieved to four size fractions (<0.063 mm,

0.063–0.250 mm, 0.25–0.5 mm and 0.5–1 mm), each fraction being subsequently dried at 105°C and reweighed. The fractions were assayed by XRF analysis for the total elemental composition as well as for heavy metal levels in an exchangeable phase and subjected to determination by LOI. The total elemental composition together with LOI, and heavy metal levels in exchangeable phase were determined in the <0.5 mm fraction of March, August, September and October samples.

Although organic carbon contents are frequently determined by loss on ignition, it is generally held that the results may not be very accurate (TUCKER, 1988), principally due to the presence of water or constituent OH⁻ groups which are tightly bound in minerals and can be driven off at temperatures higher than 105°C. Therefore, loss on ignition determined at 375°C, used as an indicator of organic matter in this investigation, can be considered as an approximation.

Concentrations of Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Ti, V, Y, Zn and Zr in different size fractions as well as in bulk samples were determined using the energy dispersive X-ray fluorescence, EDXRF method (OREŠČANIN et al., 2002). Approximately 2 g of powdered sample was pressed into a pellet and irradiated for 7000 s.

1 g of powdered sample (dry weight) was subjected to a single step sequential extraction procedure. Ammonium acetate/acetic acid (pH 7.0) was employed to liberate exchangeable metals (OREŠČANIN et al., 2003). The extract was diluted to 100 mL with double distilled water and adjusted to pH 3 by the addition of concentrated HNO₃/NH₄OH. After the pH adjustment, samples were precipitated by adding 2 ml of freshly prepared 1% w/v solution of ammonium-pyrrolidinedithiocarbamate (APDC). After the complexation which lasted 20 min, the suspension was filtered through a Millipore filter (0.45 µm) and irradiated.

All targets were analysed by EDXRF. Samples were irradiated by X-rays generated from the ¹⁰⁹Cd 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 mm², Si thickness – 3 mm, Be window – 25 µm, FWHM for 5.9 KeV ⁵⁵Fe 165 eV. The angle between the sample and the detector was 1° and the distance was 1.5 cm. Spectra were collected by Genie-2000 software (Canberra). Collecting time was 10000 s for the thin targets (filters) and 7000 s for the thick targets (pressed pellets). Spectral data were analysed by WinAxil software (Canberra). A calibration file for thin targets was created on the basis of measurement of standard solutions (Merck) prepared and analysed in the same way as unknown samples. Elemental concentrations in the thick targets were calculated using the “Fundamental parameters” method from the WinFund package using IAEA SRM SL-1 and SOIL 7 as standards.

4. RESULTS AND DISCUSSION

Particle-size analysis shows that all four locations have rather similar granulometric composition (Fig. 2) which could be defined as muddy, fine to medium sand. This enables the comparison of elemental concentrations between the locations since the textural characteristics of sediments largely govern storage of sediment-associated heavy metals in river systems (FÖRSTNER & WITTMANN, 1979; SALOMONS & FÖRSTNER, 1984; BROOK & MOORE, 1988; GRAF et al., 1991; MACKLIN, 1996; LADD et al., 1998; OREŠČANIN et al., 2002; WALLING et al., 2003). It is generally accepted that the silt and clay fractions of sediments have a strong ability to scavenge trace elements, and this is attributed to the large surface area of fine particles as well as to their varied shape and charge (GIBBS, 1977; ROSE et al., 1979; SALOMONS & FÖRSTNER, 1984; WILLIAMSON et al., 1994). Due to adsorption onto surfaces of particles, the highest concentrations of Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, Sr, Y, Zn and Zr were found in the finest fraction (<0.063 mm), steadily decreasing towards the coarser fractions (Table 1). Loss on ignition at 375°C, as an approximate indicator of organic matter (OM), was also grain size dependent. The coarse sand fraction (0.5–1 mm) of locations 2, 3 and 4 contained the greatest amount of OM, with values declining to the <0.063 mm fraction, whereas the opposite trend was found for location 1 (Table 1). Although total Pb, Rb, Sr, Ca, Mn, Fe, Cu and Zn concentrations are positively correlated with OM, chemical characterization of each size fraction suggests that organic matter does not exert overall control over the levels of the analysed elements compared to the granulometric characteristics of sediments (Table 1).

The exchangeable phase is generally assumed to be the most mobile fraction of elements which is introduced by anthropogenic activities and bound to sediment in the adsorbed form (GIBBS, 1977; FÖRSTNER & WITTMANN, 1979; SALOMONS & FÖRSTNER, 1984; CHAO, 1984; BROOK & MOORE, 1988; HALL, 1998). This phase, as a chemically active and biologically available form, does not pose a threat for the investigated sediments since it forms a negligible proportion of sediment associated metals the patterns of which are almost identical at all four locations (Fig. 3). It can be seen that only copper exhibited slightly higher levels in an exchangeable phase compared to Pb, Zn and Ni at localities 2, 3 and 4. Moreover, exchangeable Cu values were found to be considerably enhanced in the grain size fractions <0.063 mm and 0.5–1 mm (Table 2), thereby positively correlating with organic matter content which showed a marked rise in these two fractions (Table 1). This feature is probably due to the fact that Cu forms stable organo-copper complexes (SALOMONS & FÖRSTNER, 1984; ADRIANO, 1986). It is also in accordance with findings of HALL (1998) about non-specific adsorption due to the negative charges on humus polymers and specific adsorption through surface chelation of metals with various functional groups on organic substances.

Seasonal variation in the elemental content of sediments was determined by analysing the <0.5 mm grain size fraction. This particle size is otherwise routinely used for radiometric measurements, while its chemical composition is first documented in this research. Results for March, August, September and October are presented in Table 3, and selected variables are graphically presented in Fig. 4. From this, it can be inferred that variation in concentrations significantly depends on seasonal

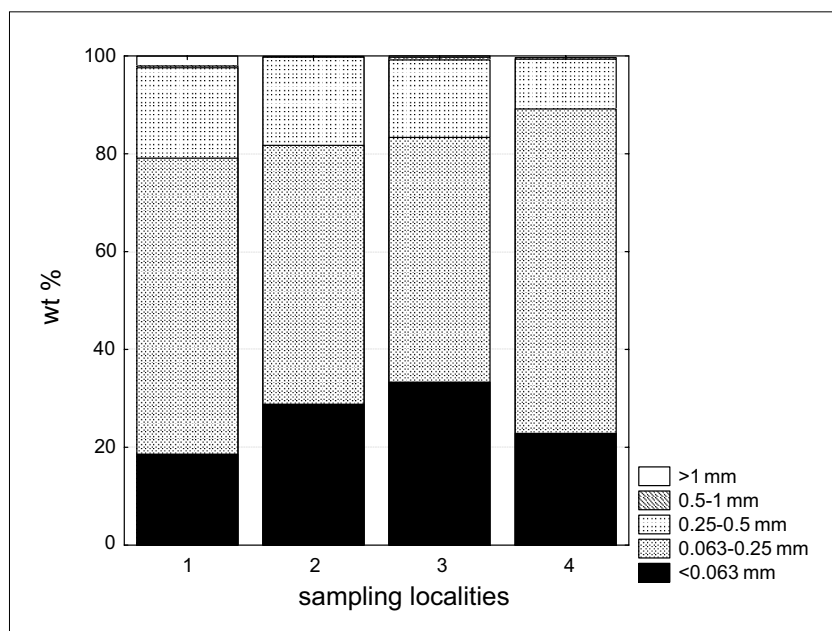


Fig. 2 Grain size distribution of sediment samples collected in August at the four sampling localities (<0.063 mm – clay and silt (mud); 0.063–0.25 mm – very fine and fine sand; 0.25–0.5 mm – medium sand; 0.5–1 mm – coarse sand; >1 mm – very coarse sand).

	1			2			3			4										
	A	B	T	A	B	T	A	B	T	A	B	T								
Pb (ppm)	40	14	15	10	22	47	14	15	10	30	45	16	29	19	31	41	16	15	10	27
Rb (ppm)	96.0	46.1	54.0	27.4	61.7	102.0	46.2	47.5	24.3	71	99.6	46.6	48.0	26.2	76.8	92.0	50.9	53.9	20.1	71.7
Sr (ppm)	257	169	106	60	183	222	168	90	49	193	253	161	92	49	199	235	172	91	44	196
Y (ppm)	58	41	17	13	41	56	32	13	12	42	57	31	14	11	42.0	55	43	17	12	46.3
Zr (ppm)	347	279	80	69	226	286	175	53	47	227	352	208	60	50	271	322	284	59	41	353
K (%)	2.11	1.02	1.27	0.70	1.35	1.90	1.11	1.19	0.68	1.6	2.00	1.20	1.12	0.88	1.69	1.90	1.19	1.35	0.68	1.72
Ca (%)	9.9	6.2	2.6	1.8	7.0	7.4	6.4	2.0	1.8	7.5	9.3	6.0	2.1	1.5	7.8	8.7	6.1	1.9	1.7	7.6
Ti (%)	0.318	0.330	0.113	0.096	0.283	0.340	0.252	0.066	0.039	0.30	0.333	0.312	0.089	0.057	0.289	0.32	0.357	0.099	0.031	0.299
V (ppm)	70	70	30	40	60	80	36	21	27	80	80	70	60	34	50	80	60	50	27	50
Cr (ppm)	90	80	52	27	70	90	50	43	26	70	80	100	60	37	66	100	61	60	26	63
Mn (ppm)	630	410	153	134	430	650	325	88	67	520	674	320	130	89	533	560	381	150	67	518
Fe (%)	2.541	1.201	0.770	0.601	1.582	2.808	1.082	0.5459	0.497	1.907	2.739	1.096	0.686	0.574	2.045	2.439	1.311	0.906	0.497	1.968
Ni (ppm)	28	24	23	24	24	50	32	28	30	38	40	27	28	29	30	30	26	27	27	29
Cu (ppm)	150	20	19	14	26	77	19	17	13	26	68	18	17	13	29	60	20	16	12	26
Zn (ppm)	286	55	56	54	110	302	54	43.0	40	156	299	58	55	50	172	261	68	69	57	146
LOI at 375°C (%)	4.47	0.3	0.39	3.38	1.71	5.49	0.37	0.4	13.44	2.64	5.79	0.451	0.50	12.32	2.84	5.69	0.44	0.72	15.99	2.33

Table 1 Loss on ignition (LOI, in %) and total-metal analysis of size-fractionated sediments collected in August (numbers 1–4 mark sampling sites). Capital letters indicate size fractions as follows: A: <0.063 mm, B: 0.063–0.25 mm, C: 0.25–0.5 mm, D: 0.5–1 mm, T: bulk sediment.

	1			2			3			4										
	A	B	T	A	B	T	A	B	T	A	B	T								
Cr	0.9	0.6	0.9	0.6	0.7	1.0	0.9	0.9	1.0	1.0	0.9	1.2	0.6	0.9	0.8	0.9	0.8	0.6	0.8	0.8
Mn	0.9	1.0	2.5	0.8	0.9	1.1	1.5	3.2	1.2	3.0	1.0	1.9	1.3	0.9	1.5	1.2	2.0	3.2	1.3	1.9
Fe	3.3	3.9	8.5	9.1	3.3	4.4	4.9	12.3	4.2	10.7	3.0	6.8	4.7	3.3	5.7	6.2	8.7	14.1	5.9	8.5
Ni	0.8	0.5	0.5	0.8	0.5	0.7	0.6	0.3	0.7	0.4	0.6	0.4	0.3	0.6	0.8	0.5	0.3	0.2	0.5	0.8
Cu	13.1	1.5	1.1	1.1	1.2	3.4	1.3	1.0	2.9	1.4	3.9	1.1	0.9	3.4	1.5	3.7	1.0	0.9	3.5	1.8
Zn	2.8	6.1	4.4	2.3	5.6	6.3	1.7	2.4	5.8	3.8	1.1	4.0	1.9	1.0	6.0	0.5	5.1	2.8	1.2	3.2
Pb	1.3	1.3	0.9	1.1	1.1	1.4	1.3	1.1	1.3	0.9	1.3	1.0	1.2	1.1	1.4	1.4	1.2	0.9	1.3	1.2

Table 2 Exchangeable phase (in ppm) of size-fractionated sediments collected in August (numbers 1–4 mark sampling sites). Capital letters indicate size fractions as follows: A: <0.063 mm, B: 0.063–0.25 mm, C: 0.25–0.5 mm, D: 0.5–1 mm, T: bulk sediment.

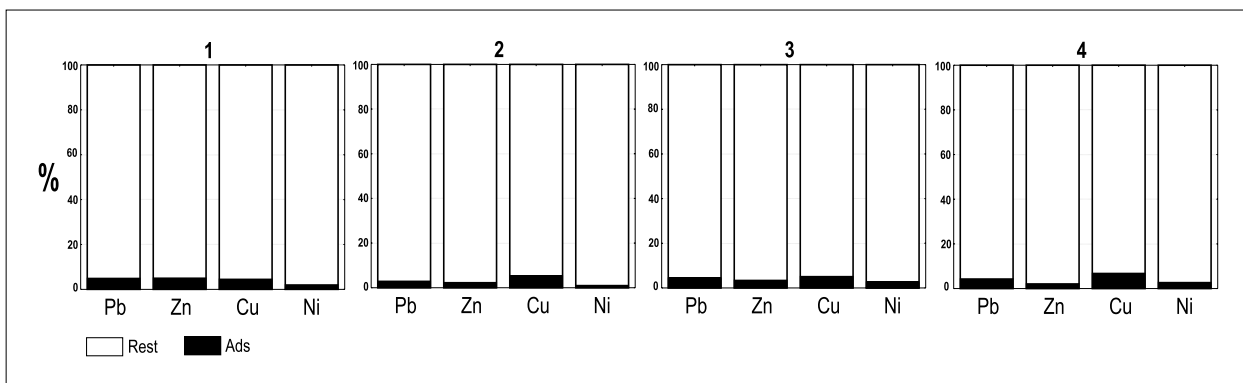


Fig. 3 Exchangeable phase (Ads) vs. total metal levels in August sediment samples. The remainder represents other phases that were not analysed.

dilution with snow melt. Therefore concentrations are low in spring (March) and they gradually rise in summer and early autumn (August, September). While the majority of variables show concordant patterns for March, August and September, this cannot be said for October (Fig. 4). Patterns obtained for March generally decrease towards location 3 and increase slightly again at location 4, whereas August and September are characterized by concentration peaks at locality 2 and a gradual decrease in the downstream direction. Patterns observed for October show that all the presented variables (Fig. 4), except Pb, increase in a downstream direction, which is unexpected because there are no tributaries of the Danube which could feed the lower stretch of the study area (Fig. 1).

Table 4 shows the temporal variability of heavy metals in exchangeable phase within the <0.5 mm grain size fraction. Figure 5 demonstrates that the concen-

trations of all the analysed variables decrease during spring snowmelt due to dilution. Element patterns for March are mutually quite concordant showing an enhanced peak at locality 2, which has already been observed for August and September on Fig. 4, and a steep decline in a downstream direction. The other three months are characterized by generally higher concentrations of Fe, Zn, Mn and Pb, whereas Cu and Ni values are either lower or similar to those found for March (Fig. 5). When considering mutual comparison of the summer and autumnal element patterns separately for each month (Fig. 5), it is obvious that they are rather irregular which is in contrast to the patterns depicted on Fig. 4. Only the patterns for Fe and Mn are fairly similar when observing individual months (Fig. 5).

Although the sampling sites were all rather similar in granulometric composition, Fe and Zn vary by a wide range during summer and autumn, which is in

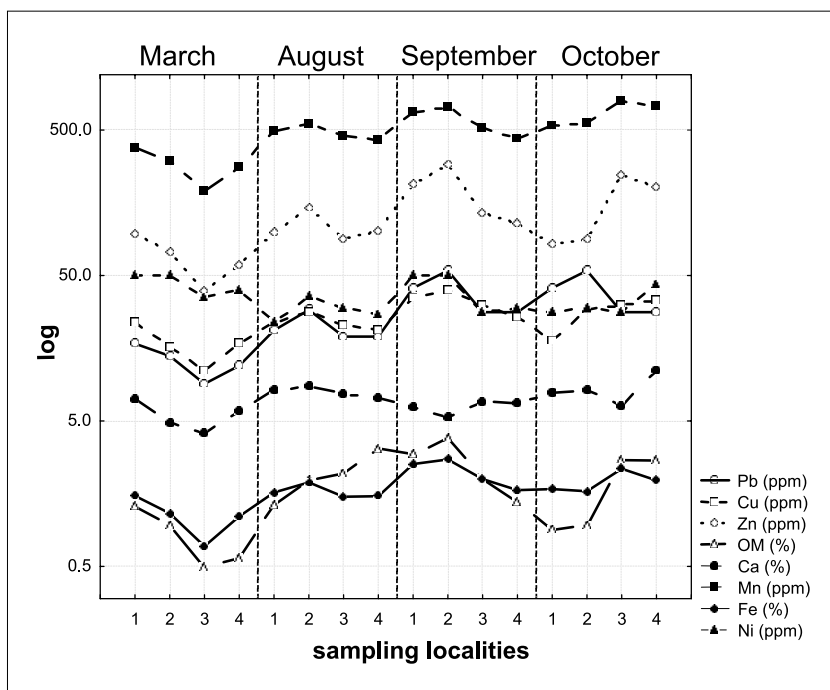


Fig. 4 Seasonal variation in the elemental content of the <0.5 mm grain size fraction.

	March				August				September				October			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Pb (ppm)	17	14	9	12	21	29	19	19	41	54	28	28	41	54	28	28
Rb (ppm)	65.0	53.5	34.6	52.8	55.5	68.7	53.8	47.2	95	102	77.0	65.0	51.7	46.8	70	70.0
Sr (ppm)	164	131	105	146	192	203	180	142	210	195	203	186	185	177	185	242
Y (ppm)	39	35	24	32	46	43	37	40	53	57	49	43	53	51	56	46
Zr (ppm)	184	144	130	154	277	241	265	302	231	216	258	248	348	279	407	261
K (%)	1.40	1.11	0.78	1.17	1.28	1.63	1.33	1.50	2.20	2.20	1.70	1.46	1.21	1.19	1.70	1.52
Ca (%)	7.1	4.9	4.1	5.9	8.2	8.7	7.6	7.2	6.2	5.3	6.8	6.6	7.9	8.2	6.3	11.0
Ti (%)	0.222	0.159	0.114	0.193	0.340	0.266	0.309	0.290	0.316	0.350	0.302	0.280	0.420	0.450	0.430	0.246
V (ppm)	60	60	50	50	90	70	50	80	140	90	90	70	90	90	110	60
Cr (ppm)	45	40	42	51	50	80	61	60	60	80	80	70	70	80	100	80
Mn (ppm)	380	310	190	280	490	553	457	430	660	710	520	440	540	560	800	730
Fe (%)	1.528	1.159	0.688	1.104	1.611	1.890	1.506	1.520	2.528	2.717	1.993	1.673	1.700	1.644	2.347	1.951
Ni (ppm)	50	50	35	40	24	36	30	27	50	50	28	30	28	30	28	43
Cu (ppm)	24	16	11	17	24	28	23	21	35	40	31	26	18	29	31	34
Zn (ppm)	97	73	39	59	99	147	90	101	214	291	135	114	82	89	244	205
LOI at 375°C (%)	1.29	0.96	0.49	0.57	1.32	1.95	2.18	3.24	2.96	3.82	1.99	1.38	0.89	0.95	2.69	2.70

Table 3 Seasonal variation in elemental content of the grain size fraction <0.5 mm. Numbers 1–4 mark sampling sites.

	March				August				September				October			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Cr	1.7	1.0	1.2	1.0	0.8	0.8	1.0	0.8	0.8	1.1	1.0	0.7	0.8	0.8	1.0	0.8
Mn	0.8	0.7	0.6	0.4	1.0	1.4	1.3	2.0	1.0	1.2	1.1	0.7	2.4	2.3	0.8	0.9
Fe	2.1	3.8	2.5	1.6	2.5	3.7	3.2	6.9	2.8	3.3	4.2	2.9	8.2	7.7	2.8	3.6
Ni	0.3	0.8	0.4	0.2	0.6	0.6	0.4	0.5	0.3	0.8	0.8	0.3	0.7	0.6	0.8	0.6
Cu	1.1	3.6	1.6	1.0	1.2	1.9	1.7	1.4	1.0	1.6	1.1	0.9	1.0	1.2	1.4	1.6
Zn	1.2	4.3	1.5	0.3	4.9	2.7	2.9	1.6	1.1	7.2	1.7	1.4	3.1	1.5	4.9	1.0
Pb	0.2	0.2	0.2	0.2	1.3	1.4	1.1	1.1	1.1	1.3	1.5	0.9	1.3	1.1	1.1	0.9

Table 4 Seasonal va

contrast to their much more uniform spring patterns. This striking feature has yet to be clarified and requires future work. Generally, it can be said that there is no clear trend of exchangeable metal concentrations in a

downstream direction during the summer and autumnal periods (Fig. 5).

In order to estimate the degree to which a sediment had been subjected to possible heavy metal pol-

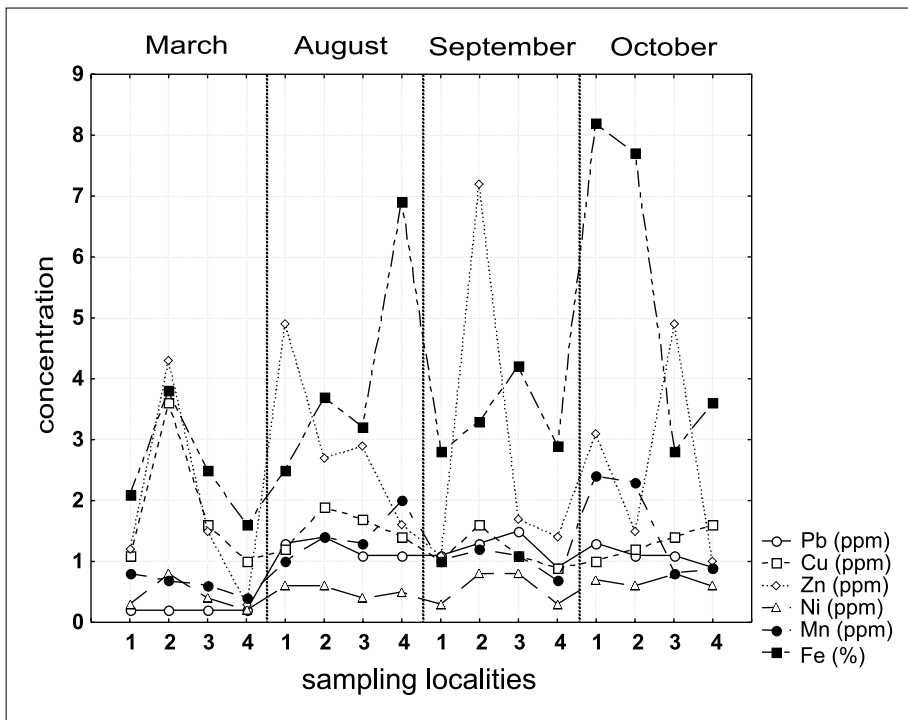


Fig. 5 Seasonal variation in the elemental content of exchangeable phases of the <0.5 mm grain size fraction.

lution from the river water, it was necessary to carry out normalization by calculating the ratio of measured concentrations of selected pollutants to the contents of conservative elements the concentrations of which are unaffected by human activity (SALOMONS & FÖRSTNER, 1984; HANSON et al., 1993; DASKALAKIS & O'CONNOR, 1995; PROHIĆ et al., 1995; OREŠČANIN et al., 2001). Therefore Pb, Cu, Zn, Cr, Mn, Fe and Ni concentrations in the fraction <0.063 mm (Table 1) have been plotted after normalization to Rb.

The results in Fig. 6 show highly elevated levels of Cu and Ni at locations 1 and 2, respectively, and a slightly increased level of Cr at location 4. Because positive deviations of the ratio normally increase as concentrations of normalizing factors decrease, it is suggested that high concentration ratios should not be explained in the pollution context without examination of the actual numbers that comprise the ratio (DASKALAKIS & O'CONNOR, 1995). From an inspection of Fig. 7 it is evident that presumed pollution by Cu and Cr at

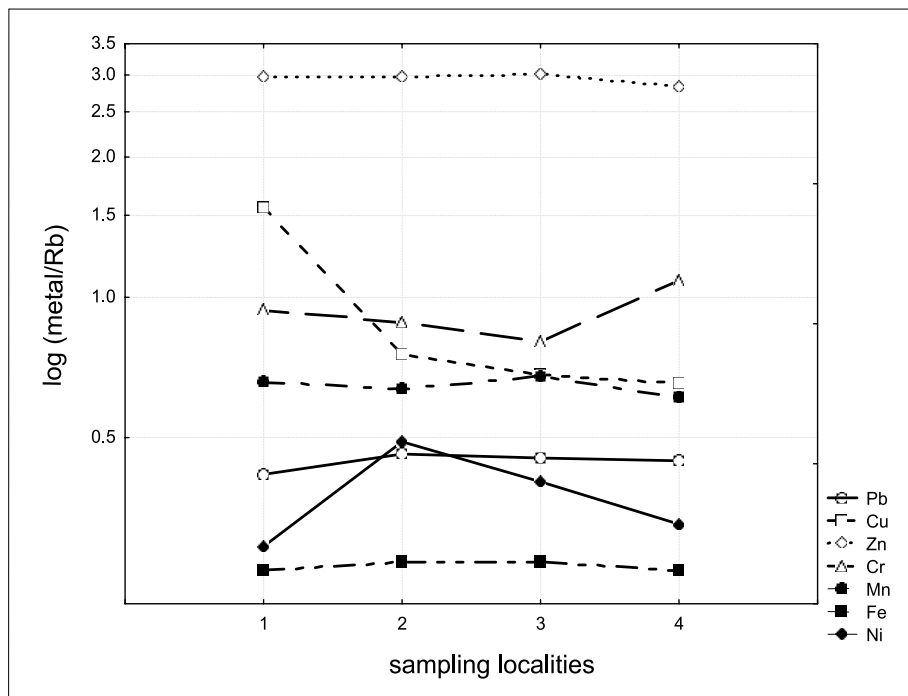


Fig. 6 Heavy metal levels after normalization on Rb.

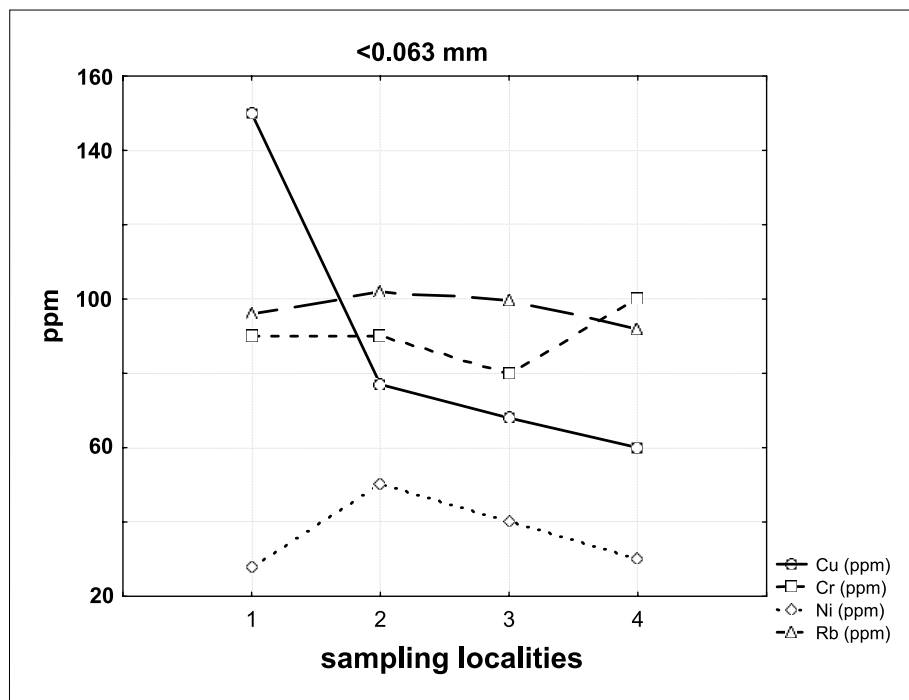


Fig. 7 Heavy metal and Rb concentrations in the <0.063 mm grain size fraction.

the localities 1 and 4, respectively, is arguable since they are not correlated with Rb. On the contrary, a positive excursion of the Ni/Rb ratio at location 2 (Fig. 6) appears to be explained by a factor (anthropogenic?) other than natural processes, according to covariation of Ni with Rb (Fig. 7). It was noted above that the village of Batina, under the auspices of the Joint Danube Survey (Croatia, River–km 1424), belonged to geomorphological reach number 5 which was characterized by significant emissions of untreated wastewater in Budapest (VOGEL & PALL, 2001; WOITKE et al., 2003). This study suggests that these wastewaters presumably have not contributed to heavy metals incorporated in studied sediments to any extent, based on a comparison of the total Pb, Cu, Zn, Cr, Mn, Fe and Ni concentrations (Table 1) with the average shale and soil composition (ADRIANO, 1986; THORNTON, 1995). Future work should target the importance of the organic and carbonate fractions in acting as a reservoir for holding heavy metals, Cu and Ni in particular, as well as detailed mineralogical analysis of sediments.

5. CONCLUSIONS

Recent channel sediments of the Danube river in the village of Batina are mainly composed of muddy, fine to medium sand. It was found that the greatest proportion of the total heavy metal load is contained in the clay and silt fraction, and therefore sediment metal transport appears to be governed primarily by sorption–desorption processes associated with fine-grained particles. Generally, no correlation was found between trace metals and loss on ignition, which served as an indicator

of organic matter content, but this subject has yet to be firmly established in future work.

Sequential extraction of bulk sediment samples showed that negligible concentrations of heavy metals were present in exchangeable phases. Among the exchangeable metals analysed, only Cu correlated with loss on ignition, since both were enriched in the size fractions <0.063 and 0.5–1 mm.

Seasonal variation in the elemental content of the <0.5 mm grain size fraction and its exchangeable phase was found to be considerably dependent on seasonal dilution with snow melt. A number of analysed elements decreased in concentration through the spring period whereas their levels increased during the summer and autumnal periods.

Normalization based on Rb in the <0.063 mm size fraction showed that Cu and Ni exhibited only light enrichments at locations 1 and 2, respectively. A comparison of the total Pb, Cu, Zn, Cr, Mn, Fe and Ni concentrations with the average shale and soil composition suggests that the analysed metals represent mostly natural levels in the investigated sediments.

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