

EFFECTS OF MERCURY MINING REGIONS FROM NW DINARIDES ON QUALITY OF STREAM SEDIMENTS

Stanislav Frančišković-Bilinski¹, Halka Bilinski¹, Darko Tibljaš² and Gerd Rantitsch³

¹"Ruder Bošković" Institute, POB 180, HR-10002 Zagreb, Croatia ²Division of Mineralogy and Petrology, Faculty of Science, Horvatovac bb, 10000 Zagreb, Croatia ³Institut für Geowissenschaften, Montanuniversität Leoben, Peter Tunner Strasse 5, 8700 Leoben, Austria

SUMMARY

Two mercury mining regions from the NW Dinarides are compared with respect to their impact on related drainage basins (of Soča and Kupa Rivers). Stream sediments of the rivers Idrijca, Bača and Soča, which drain the area around world-class mercury ore deposit in Idrija (Slovenia), as well as those from the Čabranka and Kupa Rivers, that drain the area around a smaller Hg-only deposit at Tršće near Čabar (Croatia) have been studied, by detailed mineralogical, chemical and geostatistical studies.

According to the results, the Idrijca River is highly contaminated with several toxic elements in the town of Idrija. Concentrations (in ppm = mg/kg) were determined in fractions <63 μ m and 63 – 500 μ m respectively: Hg (9000 and 65000), As (16 and 19.5), Cr (40 and 91), Cu (380 and 113), Pb (55 and 2940). Contamination with Hg, As and Pb persists in downstream Idrijca, as well as in Soča downstream from the confluence with Idrijca. Concentrations of some other trace elements (Zn, Ba, Ni, Cr, Co and Cu) increase in seaward direction. In Soča River drainage basin it was found that in the fraction <63 μ m Hg shows significant correlation with S, Zn, As, Cu, Sn, U, Mo, W and Sb. In the fraction 63 – 500 μ m significant correlation of Hg was found with S, Fe, Zn, Ni, Pb, Cr, As, Cu, Sn, Zr, Mo, Cd, Sb, Tl and Bi.

On the contrary, in the Kupa drainage basin, the closed Hg-mine in Tršće had only a minor effect on stream sediments. The highest measured concentration of Hg (206 ppb = μ g/kg) was determined at the confluence of Kupa and Čabranka Rivers. Significant correlation of Hg (in the fraction <63 µm) was found with Zn, Pb, Cu, Au, Li and Cd. The geochemical baseline for Hg in Kupa drainage basin was determined for the first time as 86.1 ± 47.3 ppb = μ g/kg. With respect to Hg, the basin shows characteristics of a very clean system.

KEYWORDS: stream sediments, chemical composition, mercury pollution, mineral composition, geostatistics, NW Dinarides.

INTRODUCTION

In the region of the NW Dinarides there is a worldclass mercury ore deposit in Idrija (Slovenia) and a smaller Hg-only deposit at Tršće near Čabar (Croatia).

Numerous papers have been published on the geology and genesis of the Idrija deposits, while the Tršće region was studied less intensively. From the mineralogical aspect the ore deposit in Idrija can be classified as a monomineral deposit. Most of the mercury appears in the form of cinnabar (HgS ~70%) and only to a relatively small extent in the form of native mercury (Hg 0 ~30%). Native mercury was found in carboniferous schists [1]. Besides from geological aspects, the environmental impact of mercury mining in the Idrija region has been intensively studied [2-19], because the mercury problem is of local, regional and of global concern. Past research at Idrija has included Hgstudies of the mine wastes, including downstream sediments and water [6,13], Hg speciation studies of mine wastes, soils and sediment-methylation/demethylation rate measurements [8-10,16] and there have also been Hgstudies in the Gulf of Trieste [14,15,17]. Despite the fact that the mine in Idrija was closed after 500 years of exploitation in the year 1994, the Soča River with its Slovenian tributaries Idrijca and Bača still transports heavy metal contamination. The roasting process at 600°C, employed to extract mercury from ores, and the subsequent weathering resulted in secondary mercury mineralisation in the waste piles in the area of Idrija. Abandoned roasted mine wastes or calcines, located below the smelter in Idrija remain one of the primary sources for persistent mercury release into the aquatic environment. A significant fraction of the mercury is transported downstream and has the capacity to bioaccumulate in the food chain. Mercury pollution due to ore processing is not only a local problem. A similar problem was described in California by Kim et al. [20] who identified the variety of mercury phases in the calcines. They concluded that the relative proportions of soluble mercury phases present must be known in order to determine the mobility of Hg from the piles into the environment. In addition, mercury pollution which originates from mercury mining and ore processing was studied in Wanshan, province Guizou,

China [21]. They have concluded that population at risk is located in the vicinity of smelting facilities, mining activities and waste disposal sites. Hines *et al.* [16] have concluded that the Idrija mining district continues to emit high levels of Hg into the Idrijca River with extremely high concentrations of Hg and MeHg present throughout the system, which impacted biota for several tens of kilometers downstream from Idrija mine. Biester *et al.* [2] have performed analytical separation and quantification of cinnabar (HgS) and matrix-bound noncinnabar Hg compound in sediments. They concluded that cinnabar predominantly occurs in coarse grained and noncinnabar Hg in fine-grained material.

Faganeli *et al.* [17] reported distribution sources and fate of Hg in the water column of the Gulf of Trieste. They have concluded that the surface waters in front of the Soča/ Isonzo outflow exhibit rather high total Hg concentrations, that the majority of Hg and to a lesser extent of Me Hg is associated with solid particulate matter (SPM). It appears that the Gulf is an efficient trap for total Hg and a net source of Me Hg.

Other trace elements have been studied less intensively. Modern anthropogenic influence on Cu, Pb, Cd and Cr concentrations has been recognized in the Adige River mouth, in the northern Adriatic, by Boldrin et al. [22]. Covelli et al. [15] determined concentrations of Fe, Cr, Cu, Mn, Ni and Zn in the central part of the Gulf of Trieste and have found Hg enrichment up to 25-fold above the proposed natural regional background of 0.17 ppm = mg/kg. Enrichment values for other heavy metals were lower. They assumed that a source similar to Hg exists for Ni and Zn, while for other trace elements the source is still unknown. According to Covelli et al. [15] there is no reason to believe that this marine environment can be naturally decontaminated in the near future. These are the only data of trace elements in this region of Adriatic, which cannot be directly compared with elements in river sediments presented in this study, but can be useful as comparative measurements near the Isonzo River mouth.

The Tršće region (in Kupa River drainage basin) was studied less intensively, although a Hg-deposit was recognized 150 years ago. Šinkovec and Jović [23] have concluded that Hg-mineralization has no economical value, because the amount of mercury is relatively small (<0.02%) and the mineralization decreases with depth. According to Šinkovec [24] cinnabarite in Tršće can be found in Permian clastics, sandstones, conglomerates and shales, and also in Lower Triassic dolostones. Savić and Dozet [25] reported that cinnabarite is hosted by Permian conglomerates, Carnian clastics and by Upper Triassic dolomites.

The aim of the present work

The aim of the work is to demonstrate the differences in environmental status of two drainage basins. The Idrija mine within the Soča River drainage basin can be considered as a site of historical mining. The Tršće mine within the Kupa River drainage basin is a site of possible natural mercury pollution by outcropping of an ore deposit. The Soča (Isonzo) River collects and transports, both natural weathering products and those from calcines, towards the Gulf of Trieste (Adriatic Sea). Kupa River transports weathering products to the Sava River, a tributary of the Danube River, which flows into the Black Sea. There are no systematic studies on the mineral and chemical composition of river sediments of the Soča drainage basin. Therefore, this paper aims to describe the downstream variation of the mineral and elemental composition, including also Hg, in two grain size fractions (fractions $<63 \mu m$ and fractions 63-500 µm) of the Soča, Idrijca and Bača stream sediments and find the best possible correlation, using different statistical methods. According to Chandraith et al. [26] some elements are important constituents of sand sediment fraction, while anthropogenic trace elements are important constituents of silt+clay fraction (<63 µm). Results from the Soča River drainage basin will be compared with some results from the Kupa River drainage basin, where Hg-ore processing was not taking place and an anthropogenic factor for contamination was therefore absent.

STUDY AREA

The Soča River drainage basin is located in the western part of Slovenia. A sketch map showing the region and the 12 sampling locations is presented in Figure 1.



FIGURE 1 - A sketch map of Soča (S), Idrijca (I) and Bača (BA) region, with 12 sampling locations: 331 (Podroteja); 371 (under smelter, town Idrija); 351 (Spodnja Idrija); 361 (Travnik); 281 (before Bača inflow); 29BA (before confluence with Idrijca); 32S (Vas Soča); 31S (Kamno); 30S (Modrejce); 27S (Avče); 26S (Morsko); 25S (Plave).

FEB

The upstream part is mountainous (Julian Alps), whereas the middle part is mostly hilly. It further flows over low fertile plains to the Gulf of Trieste (Northern Adriatic Sea). Three hydroelectric power plants at Avče, Plave and Solkan dam the Soča River. The Idrijca River with its tributary Bača joins the Soča approximately in its middle segment. These rivers have a very variable discharge over time. Upstream to Solkan (near the Italian-Slovenian boarder) the catchment area of these rivers is 1533 km². The mean annual discharge is 94 m³/s, with monthly variations from 60-70 m³/s in February and August to 110–120 m³/s in May and June and even 140 m³/s in November [11]. There are typically two annual flow extremes: the longer spring maximum from March till June (snowmelt) and the shorter autumn maximum in October and November. Sampling was performed on August 30 and 31, 2001, between these flow extremes. Because the surrounding mountains prevent air circulation, the annual precipitation varies locally from 2400 and 5200 mm. More details about ecological impact and geology of this region can be found in Palinkaš et al. [5, 27], Rajar et al. [28] and Pirc [29].

The sketch map showing the Kupa River drainage basin with sampling locations is presented in Figure 2. For more details we refer to Frančišković-Bilinski et al. [30]. Tršće with the closed Hg-mine is at sampling point 55 (45°33'32"N, 14°37'05"E, 768 m) in the NW region of the Kupa River drainage basin. Sampling was performed in two campaigns: Ten samples in the upper flow of Kupa River were first collected in November 2002 at high water level, while in summer of 2003 (June to August), 61 samples from the whole Kupa River drainage basin were sampled at low water level. Kupa River itself is 296 km long, from its source under Risnjak Mountain in Gorski Kotar, till its inflow to Sava River in Sisak. Kupa River drainage basin covers 10.052 km².

EXPERIMENTAL

Stream sediment samples from the Soča River drainage basin (taken in 2001) and the samples from the upper flow of Kupa River (collected in 2002) were wet sieved and then dried at 80°C. This temperature was chosen according to Loska and Wiechula [31]. There are authors (Mirlean et al. [32]) who use 60°C. Sediments sampled in 2003 from Kupa River drainage basin were air-dried in the shadow and then sieved using standard sieves of diameter 2000, 500 and 63 μ m (Fritsch, Germany).

The mineral composition of sediments (fraction <63 μ m) from the Soča River drainage basin was determined by using a Philips PW 1050 X-ray diffractometer. The mineral composition of sediments from the Kupa River drainage basin (fraction <63 μ m) was determined by using a Philips 3040/60 X-Pert MPD. The program XPert High Score, Philips, 2002 was used for the interpretation



FIGURE 2 - A sketch map of Kupa River drainage basin with numbers of sampling locations. The Hg mine in Tršće is at location 55.

sampling	M i n e r a l								
station	quartz	dolomite	calcite	muscovite	feldspar	chlorite			
	(46-1045)	(36-426)	(47-1743)	(7-25)	(41-1480)	(46-1324)			
33 I	+ + +	+ + +	+ +	+	+	+			
37 I	+ + +	+ + +	+ +	+	-	-			
35 I	+ + +	+ + +	+ +	+	-	-			
36 I	+ + +	+ + +	+ + +	+	(+)	(+)			
28 I	+ + +	+ + +	+ + +	+	+	+			
29 BA	+ + +	++	+ + +	+	+	+			
32 S	(+)	+ + +	+ + +	-	-	-			
31 S	++	+ + +	+ +	(+)	-	-			
30 S	++	+ + +	+ + +	(+)	(+)	+			
27 S	+ + +	+ + +	+ + +	(+)	(+)	+			
26 S	+ + +	+ + +	+ + +	(+)	(+)	(+)			
25 S	+ + +	+ + +	+ + +	(+)	++	+			

TABLE 1 - Mineralogical composition of sediment fraction <63 μm, estimated according to Boldrin et al. [33] from X-ray diffraction patterns.

(JCPDF #); + + + (>30%); + + (10-30%); + (5-10%); (+) (<5%); - not detected

I-Idrijca; BA-Bača; S-Soča

of XRD patterns. By comparing relative intensities of the strongest peak for each mineral found, the mineralogical composition of the samples was determined semiquantitatively, as described in Boldrin *et al.* [33].

Elemental content was determined by inductive coupled plasma – mass spectrometry (ICP-MS) carried out by Actlabs laboratory (Ontario, Canada) in aqua regia extracts, using Ultratrace 2 program. Although this digestion is not total, its use is justified because the international standard methods for determining action limits are based on aqua regia leach, not on total natural baselines [34]. Total mercury was determined from the same extracts at 90°C, using 1G program, atomic absorption spectrometry and flow injection techniques. Control materials used by Actlabs were USGS standards GXR-6, GXR-2, GXR-1, GXR-4 and SO-2. Standards were measured before and after each series of measurements. Detection limit for Hg is 5 ppb = μ g/kg.

RESULTS

X-ray diffraction

The semiguantitative mineral composition of sediment fraction <63 µm from the Soča River drainage basin is presented in Table 1. Quartz, dolomite and some calcite are identified as major components of the Idrijca River sediments. The Bača River sediments contain quartz, calcite, and less dolomite. In the Soča River sediments upstream to the confluence with Idrijca dolomite and calcite are major mineral components. Further downstream in Soča the amount of quartz increases, so that quartz also becomes an additional major mineral component. Muscovite, feldspar and chlorite are present as trace components in most samples. The only exception is feldspar, which is present as a minor component in the lowermost location (sample 25). In sample 37I several minerals have been identified microscopically in the fraction $63 - 500 \mu m$: carbonates, hematite, pyrite, cinnabar, magnetite, limonite, wüstite, chalcopyrite and slag particles.

The mineral composition of sediments from the whole Kupa River drainage basin was investigated. But only four of them, those in vicinity of the mercury mine in Tršće, will be discussed here, namely samples 55, 54, 56 and 53.

In 55, Sokolica-Tršće: dolomite (36-0426) +++; calcite (05-0586) and silica (33-1161) ++;

In 54, Čabranka-Osilnica: quartz (46-1045) +++; dolomite (36-0426) and muscovite (01-1098) ++; clinochlore (46-1323) +; sanidine (10-0357) (+);

In 56, Kupa at inflow of Čabranka: quartz, low (05-0490) +++; dolomite (11-0078), muscovite (07-0032) and clinochlore, ferroan (07-0078) ++; anorthite (41-1486) and albite (20-0554) +;

In 53, Kupa-Hrvatsko: quartz (46-1045) +++; calcite (05-0586) ++; dolomite (05-0622), phlogopite (16-0344) and anorthite (41-1486) +; olivine (03-0195) and clinochlore, manganoan (45-1321) (+).

It should be emphasized that it is possible to determine minerals present at amount <5% (+), but due to limitation of the XRD method they cannot be determined with certainty.

Elemental analysis of sediments from the Soča River drainage basin

Tables 2 and 3 show elemental analysis (50 elements) of sediments from Idrijca and Bača Rivers in two grain size fractions (f <63 μ m and f 63-500 μ m). Ca, Mg, Fe, K and Al are the most abundant elements in all samples. Among them Ca and Mg are more abundant in coarse-grained sediment, while Fe, Al and K are more abundant in the fine fraction. In all locations most of the trace elements are more abundant in fine fraction. The only exception is location 37I, where concentrations of S, Hg, Pb, Mo, Sn, Sb, B, Au and Re are significantly higher in the coarse fraction. Tables 4 and 5 show elemental concentrations in sediments of the Soča River. Ca and Mg are the most abundant elements in all samples. Fe, Al and K are more abundant in fine fraction, but comparatively of smaller



Element	33 I	37 I	35 I	36 I	28 I	29BA
Ca	65300.0	112000.0	121000.0	126000.0	123000.0	122000.0
Mg	30100.0	50200.0	41300.0	47400.0	32600.0	19800.0
Fe	27600.0	31700.0	22200.0	26100.0	18500.0	23900.0
Al	18300.0	9400.0	9800.0	9100.0	9100.0	10100.0
K	1900.0	1300.0	1200.0	1300.0	900.0	1200.0
Mn	781.0	517.0	436.0	510.0	332.0	801.0
S	600.0	4090.0	2440.0	1930.0	1600.0	480.0
Р	440.0	450.0	720.0	430.0	480.0	300.0
Na	240.0	200.0	240.0	220.0	220.0	150.0
Zn	67.2	112.0	124.0	81.0	68.6	59.0
Sr	57.5	120.0	137.0	250.0	147.0	198.0
V	48.0	28.0	27.0	21.0	24.0	17.0
Ni	40.7	31.9	28.0	26.1	20.1	50.8
Cr	31.9	40.0	26.9	22.3	16.7	27.5
Li	23.2	12.2	10.5	16.7	12.1	25.9
Ba	112.0	97.5	77.4	81.8	81.3	81.8
Cu	17.7	380.0	75.1	44.3	27.4	30.8
Rb	17.4	9.4	9.0	8.5	5.7	8.7
Hg	17.1	9000.0	322.96	348.98	132.38	2.6
As	15.2	16.4	12.8	14.4	11.2	9.1
Y	15.0	9.1	8.9	9.1	8.7	12.5
Со	12.2	10.4	9.2	9.2	6.9	11.9
Ce	54.4	21.8	21.6	20.8	19.3	18.5
Pb	42.1	55.4	68.1	69.0	47.0	30.4
La	25.7	10.4	10.2	9.4	9.2	10.0
Nd	25.5	11.2	10.5	10.6	9.4	11.6
Ga	4.67	2.24	2.18	2.17	2.03	2.73
Mo	2.37	4.27	2.11	1.97	1.19	0.58
Zr	1.9	1.2	1.0	1.1	2.7	1.0
Be	1.9	1.0	0.9	0.9	0.7	0.8
Th	2.4	1.8	0.5	1.8	0.4	1.9
Sm	5.3	2.6	2.6	2.6	2.3	3.0
U	1.4	2.0	1.3	1.6	1.4	0.4
Se	1.1	1.4	1.8	1.1	0.9	0.6
Cd	1.0	0.5	0.6	0.4	0.5	0.3
Nb	0.6	0.3	0.4	0.3	0.2	0.1
Cs	1.7	1.0	0.9	0.8	0.6	1.6
Sn	1.60	15.01	4.91	13.88	4.42	1.41
W	0.5	4.8	5.0	0.9	0.6	0.4
TI VI	-	0.32	0.29	0.24	0.17	0.14
Yb	1.1	0.7	0.7	0.7	0.6	0.8
Sb	0.70	2.65	0.81	0.59	0.50	1.41
Eu	0.8	0.5	0.4	0.5	0.4	0.6
10 D:	0.6	0.4	0.4	0.3	0.3	0.4
B1	0.40	0.44	0.36	0.30	0.30	0.30
Ag T-	0.08	0.78	2.34	0.30	0.21	0.07
I e	0.12	0.09	0.10	0.08	0.12	0.15
<u>В</u> А.::	-	4	0.0250	1	2	-
Re	-	0.0127	0.0239	0.001	0.000	-

TABLE 2 - Concentrations (in ppm) of 50 elements in decreasing order in sediments (fraction < 63 µm) of Idrijca River (Slovenia).

- not detected

Element	33 I	37 I	35 I	36 I	28 I	29 BA
Ca	94700	142000	148000	146000	152000	172000
Mg	46500	62800	78400	77200	71700	26300
Fe	11400	33400	9000	11800	12400	13000
Al	5500	2100	2100	2700	5200	4400
K	800	400	300	300	500	300
Mn	272	223	129	200	240	719
S	560	9720	510	340	360	210

TABLE 3 - Concentrations (in ppm) of 50 elements in approximately decreasing order in sediments (fraction 63 – 500 μ m) of Idrijca River (Slovenia).



Element	33 I	37 I	35 I	36 I	28 I	29 BA
Р	80	80	60	100	130	110
Na	230	170	180	200	200	130
Zn	20.5	48.1	23.3	26.6	29.8	30.5
Sr	59.1	99.7	92.1	141.0	148.0	330.0
V	16.0	17.0	16.0	15.0	14.0	8.0
Ni	9.3	59.4	9.4	12.1	11.9	29.0
Cr	12.6	91.0	3.9	5.4	6.3	10.2
Li	6.0	1.8	1.7	2.4	6.0	8.9
Ba	37.7	17.0	17.2	26.4	24.3	43.4
Cu	4.7	113.0	7.8	78.8	6.3	15.2
Rb	6.8	2.2	1.8	2.0	2.8	1.9
Hg	1.004	65000	172	172	51	0.309
As	6.2	19.5	10.2	10.7	6.5	5.4
Y	5.5	3.2	3.2	3.4	5.0	8.5
Со	4.3	4.7	2.1	2.9	2.9	5.2
Ce	35.1	8.82	14.9	13.7	12.4	10.3
Pb	15.0	2940.0	9.84	11.1	9.82	7.81
La	16.4	4.4	7.6	6.7	6.5	7.0
Nd	16.5	4.8	7.4	7.2	6.5	8.1
Ga	1.44	1.36	0.45	0.63	1.19	1.06
Mo	1.18	8.38	0.78	0.97	0.90	0.30
Zr	1.8	2.2	1.0	1.5	1.1	0.7
Be	0.4	0.3	0.1	0.2	0.2	0.2
Th	3.2	1.6	1.3	1.5	1.8	1.1
Sm	3.2	1.0	1.5	1.6	1.6	2.1
U	1.3	2.2	1.5	1.5	1.7	0.3
Se	-(<0.1)	4.1	-	-	-	-
Cd	0.3	0.6	0.2	0.2	0.2	0.2
Nb	0.1	0.2	-	-	-	-
Cs	1.1	0.3	0.3	0.3	0.3	0.2
Sn	0.51	172.0	0.35	0.31	2.25	0.10
W	-(<0.2)	0.5	-	-	-	-
Tl	0.13	0.37	0.05	0.06	0.08	0.03
Yb	0.5	0.3	0.3	0.3	0.4	0.6
Sb	0.70	30.6	0.23	0.31	0.16	0.12
Eu	0.5	0.2	0.2	0.3	0.3	0.4
Tb	0.3	0.1	0.2	0.2	0.2	0.3
Bi	0.08	0.96	0.05	0.07	0.08	0.08
Ag	-(<0.05)	0.72	-	-	-	-
Te	-(<0.02)	0.05	-	-	-	0.12
В	6	2	2	2	2	2
Au	-(<0.0002)	0.11	-	-	-	-
Re	0.001	0.007	-	0.002	-	0.02

TABLE 3 – continued.

TABLE 4 - Concentrations (in ppm) of 50 elements in approximately decreasing order in sediments (fraction < 63 μ m) of Soča River (Slovenia).

Element	32 S	31 S	30 S	27 S	26 S	25 S
Ca	337000.0	282000.0	279000.0	248000.0	245000.0	221000.0
Mg	78800.0	91200.0	60300.0	53800.0	55600.0	50500.0
Fe	5100.0	8500.0	10500.0	19200.0	17800.0	14000.0
Al	1700.0	4000.0	5100.0	7500.0	6700.0	5500.0
K	500.0	900.0	800.0	700.0	700.0	700.0
Na	490.0	220.0	210.0	190.0	160.0	180.0
S	270.0	250.0	250.0	630.0	280.0	600.0
Р	250.0	170.0	230.0	310.0	290.0	290.0
Sr	106.0	142.0	155.0	173.0	163.0	190.0
Mn	72.0	170.0	421.0	637.0	628.0	402.0
Ba	19.7	18.7	32.3	49.9	42.8	43.8
Zn	17.4	52.3	55.3	74.7	60.3	60.7
Ni	22.1	23.5	33.5	43.6	39.4	30.0
Pb	22.9	9.74	13.9	34.4	31.7	15.3

20
Ш
L 🕖

Element	32 S	31 S	30 S	27 S	26 S	25 S
Cr	10.5	11.8	15.7	22.8	21.5	15.4
Ce	4.30	11.0	9.62	11.6	11.2	11.2
As	7.9	10.1	10.3	11.0	10.1	9.5
Cu	6.9	7.9	14.7	22.8	22.1	14.7
Nd	1.9	5.3	5.4	6.6	6.4	6.5
V	5.0	13.0	16.0	21.0	20.0	16.0
La	2.3	5.5	4.9	6.0	5.8	5.9
Y	2.7	5.1	5.7	7.2	6.8	6.9
Rb	2.4	5.2	4.7	5.0	4.7	4.7
Со	2.3	4.4	6.5	10.4	9.5	6.6
Li	1.8	5.9	9.6	14.4	13.1	9.8
Sm	0.4	1.2	1.3	1.7	1.6	1.6
Sn	5.76	0.43	1.22	4.66	9.06	0.67
Zr	1.1	1.4	1.1	2.0	1.1	1.2
Hg	0.93	1.47	7.09	21.09	27.60	26.04
Th	0.2	1.2	0.8	0.7	0.9	0.8
U	0.5	1.1	0.7	1.0	1.1	0.9
Мо	0.61	0.82	0.38	0.87	1.03	0.44
Cd	0.5	0.3	0.4	0.3	0.3	0.3
W	0.5	0.4	0.5	0.5	0.4	0.5
Cs	0.3	0.5	0.4	0.5	0.5	0.5
Yb	0.2	0.3	0.4	0.5	0.4	0.4
Ga	0.35	1.06	1.36	2.07	1.85	1.47
Eu	-	0.2	0.3	0.4	0.4	0.3
Sb	0.13	0.22	0.25	0.32	0.35	0.24
Tl	0.07	0.31	0.22	0.23	0.20	0.29
Se	0.20	0.30	0.50	0.60	0.60	0.50
Tb	-	0.20	0.20	0.20	0.20	0.20
Bi	0.07	0.09	0.13	0.15	0.17	0.15
Те	0.05	0.07	0.10	0.14	0.13	0.12
Nb	0.1	-	0.1	0.1	0.1	0.1
В	-	3	3	-	-	-
Be	-	0.2	0.3	0.4	0.4	0.4
Ag	-	-	-	0.08	0.05	0.05
Au	0.0019	-	-	-	-	-
Re	-	0.003	-	-	-	-

TABLE 4 – continued.

TABLE 5 - Concentrations (in ppm) of 50 elements in approximately decreasing order in sediment fraction 63 – 500 μm of Soča River (Slovenia).

Element	32 S	31 S	30 S	27 S	26 S	25 S
Ca	195000	214000	245000	223000	213000	222000
Mg	79300	69200	53700	67300	57600	60000
Fe	1600	2900	3400	6300	6600	8800
Al	200	800	800	1600	2500	3000
K	-	200	200	300	300	400
Na	210	200	160	170	160	170
S	140	160	210	250	290	260
Р	20	50	40	80	110	90
Sr	77.4	137	172	184	209	193
Mn	38	155	220	240	374	303
Ba	5.8	7.2	9.5	13.2	16.6	21.8
Zn	3.0	9.3	14.9	14.0	16.6	26.0
Ni	8.9	10.8	12.8	11.9	14.7	19.2
Pb	0.46	1.15	1.95	2.91	4.15	4.53
Cr	1.9	3.4	3.9	4.5	5.9	8.5
Ce	1.6	2.95	3.24	5.15	7.07	7.08
As	9.4	7.6	6.9	9.7	10.7	8.0
Cu	1.2	1.9	4.1	3.8	5.3	7.1
Nd	0.8	1.6	2.0	3.0	3.9	4.1
V	7	8	7	17	18	16

FEB

Element	32 S	31 8	30 S	278	26 S	25 8
La	0.9	1.7	2.1	3.0	4.1	4.0
Y	1.4	1.8	2.3	3.6	4.3	4.4
Rb	0.3	0.8	0.8	1.1	1.4	2.3
Со	0.6	0.9	1.2	1.5	2.0	2.9
Li	0.5	0.9	1.2	2.2	3.7	6.6
Sm	0.2	0.3	0.4	0.7	1.0	1.0
Sn	-	-	-	0.05	0.17	0.09
Zr	0.9	0.7	0.7	0.9	1.0	1.1
Hg	0.042	0.014	0.349	20	20	11
Th	0.1	0.2	0.2	0.6	0.7	0.8
U	0.4	0.7	0.6	1.0	1.0	0.9
Mo	0.10	0.18	0.12	0.32	0.25	0.61
Cd	0.40	0.3	0.3	0.2	0.4	0.2
W	-	-	-	-	-	-
Cs	-	-	-	0.1	0.1	0.2
Yb	-	0.1	0.2	0.2	0.3	0.3
Ga	0.05	0.17	0.19	0.38	0.52	0.88
Eu	-	-	-	0.2	0.2	0.2
Sb	0.05	0.05	0.03	0.05	0.08	0.09
Tl	-	0.04	0.02	0.04	0.06	0.08
Se	-	-	-	0.1	0.5	1.2
Tb	-	-	-	-	0.1	0.1
Bi	-	-	-	0.04	0.04	0.04
Те	0.03	0.04	0.03	0.03	0.07	-
Nb	-	-	-	-	-	-
В	-	1	1	2	4	2
Be	-	-	-	0.1	0.1	0.2
Ag	-	-	-	-	-	-
Au	-	-	-	-	-	-
Re	0.003		0.001		_	0.001

TABLE 5 – continued.

- not detected





FEB



FIGURE 4 - Shale-normalized element patterns for coarse ($63 - 500 \ \mu m$) and fine (f < $63 \ \mu m$) fraction of sediments from Soča River. Data, which were normalized, are taken from Tables 5 and 4.



FIGURE 5 - Concentrations of 8 elements (Zn, Pb, Cr, As, Cu, Hg, Cd, Ni) vs. flow direction in km for f (63-500 µm) and f <63 µm.



concentrations than in Idrijca River. Almost all trace elements are more abundant in fine fraction. Shale normalized [35] element patterns for sediments from Idrijca and Soča rivers (f 63-500 μ m and f <63 μ m) are presented in Figures 3 and 4, respectively. In order to visualize background levels of eight selected elements, location of contamination source and downstream dilution, results are plotted (Figure 5) in a conventional manner [36], as concentration vs. flow direction in km for the two studied fractions of sediments from Idrijca and Soča Rivers.

Mercury analysis of sediments (f <63 $\mu\text{m})$ from the Kupa River drainage basin

Repeated analysis of total mercury samples collected in two campaigns has shown that the Kupa River drainage basin is not contaminated with Hg. It is clearly illustrated in Figure 6 where the Hg results of all 61 sampling locations are presented. The lowest concentrations (<50 ppb) were observed in the middle and south part of the drainage basin. The highest concentration (206 ppb) was determined in sample 56, which is close to the Tršće Hgmine. The concentrations of Hg in sediments in all locations are comparable to those found in clean estuaries of Öre River (Sweden) and of Krka River (Croatia), by Kwokal et al. [37] and lower than found in the Dragonja River at Slovenian-Croatian border by Frančišković-Bilinski et al. [38].

Statistical analysis

Principal component analysis (PCA) tries to explain the covariance structure of the data by means of a small number of components, which represent the hidden data structure. Components are equivalent to the controlling factors in geochemistry. However, geochemical data almost never show normal or lognormal distributions [39]. Therefore, robust statistical methods have to be applied if such data are examined [40]. A requirement for a stable solution from a PCA is that there are sufficient numbers of samples for the number of variables. However, in this case study only twelve samples with 46 analyzed elements are available. Hubert and Vanden Branden [41] introduced an algorithm for a robust PCA (ROBPCA), which can also be used to detect and classify multivariate outliers. As demonstrated in Hubert and Vanden Branden [41] this approach



FIGURE 6 - Distribution of Hg-concentrations (in ppb) in the Kupa River drainage basin.



FIGURE 7 - Application of PCA (ROBPCA) method of Hubert et al. [41] to detect data outliers in the diagram in which the robust score distances are plotted against the orthogonal distances for 12 studied stream sediments from the Soča River drainage basin. 7a (above) – for fraction 63-500 μm; 7b (below) – for fraction <63 μm.

gives reliable results in low-dimensional data bases (number of variables > 5 times the number of samples). Therefore, ROBPCA is used here, to illustrate how useful the method is to detect data outliers. According to the diagnostic plot of Hubert and Vanden Branden [41], which plots for each observation (sample) the robust score distances against the orthogonal distances, all observations can be classified in regular observations, good leverage observations, orthogonal outliers and bad leverage observations. Variables have been transformed to a logarithmic scale to give a better approximation to the normal distribution. The In-transformed variables are first standardized to mean zero and median absolute variance one, in order to put everything to a common scale (see Filzmoser [42]). ROBPCA was applied using the MATLAB® toolbox for robust calibration [43]. Using the concentrations of the coarse fraction, the diagnostic plot of Hubert et al. [44] indicates sample 37I, 33I and 29BA as outliers (Figure 7a). In the fine fraction, the samples 33I, 35I, 36I, 37I and 32S are identified as outliers (Figure 7b). Extremely high Hg accumulation (61500 ppm) in the coarse fraction of sample 37I results in a bad leverage outlier position. This value is so high, that location 37I could be identified as polluted without statistical analysis. All other outliers plot either in the field of orthogonal outliers or good leverage outliers. Apart from the pollution related outlier (37I), the other outliers of the coarse fraction (29BA, 33I) are samples which are unaffected by contamination. Consequently, the "regular observations" can be interpreted as a homogeneous data population. The bad leverage outlier position of sample 37I shifts to an orthogonal outlier position in the fine fraction. Sample 35I and 36I plot here in the same field. Hence, multivariate geochemical signature of those samples is anomalous. The good leverage outliers 33I and 32S are sampled in an upper stream position. They are therefore indicators of an unpolluted data population.

Pearson's correlation coefficients among elements in the two sediment fractions can be considered only as an approximate, due to small number of samples. In fraction <63 μ m Hg is significantly correlated with S, Cu, Mo, W and Sb. In f 63-500 μ m Hg is significantly correlated with Fe, S, Ni, Pb, Cr, As, Cu, Sn, Mo, Sb and Tl.



FIGURE 8 - Frequency histogram distribution of Hg in the Kupa River drainage basin (8a, above); two dimensional scatter/box diagram for Hg in the Kupa River drainage basin, obtained by program STATISTICA 6.0 (8b, below).



FIGURE 9 - Factor loadings of the first three components in the coarse fraction ($63 - 500 \mu m$) and factor loadings of the first three components in the fine fraction (f < $63 \mu m$) of 12 studied stream sediments from the Soča River drainage basin.

In the present work the state of total mercury in sediments of the Kupa River drainage basin was investigated in order to observe possible influence of environment of closed Hg-mine in Tršće. In order to get basic statistical parameters for Hg, all analytical data were presented in Figure 8a, as a frequency histogram distribution. The values (in ppb) are between min. 13.4 and max 206.2, mean 84.9, geomean 69.0, median 86.1 and standard deviation 47.3. Two dimensional scatter/box diagrams in Figure 8b show that there is no Hg-anomaly caused by the Tršće mine. The geochemical baseline, determined for the first time in this region, for Hg is 86.1 ± 47.3 ppb. Frančišković-Bilinski [45] has shown that Hg in fraction <63 µm is significantly correlated with Zn, Pb, Cu, Au, Cr, Li and Cd. More complex multivariate statistical analysis was performed only on sediments from Soča River drainage basin.

DISCUSSION

ROBPCA identifies the polluted sample 37I, samples, which are unpolluted and samples, which are affected by the diluted Hg-contamination. From the "regular observations" a PCA extracts the main elemental associations, which control the multivariate signature of the data base. In Figure 9 factor loadings of the first three components in the two fractions are presented. The data were preprocessed as explained before. In the fraction 63-500 μ m, three PCA components explain 90% of the data variance. The factor loadings of component 1, which account for 68.5 % of the variance, are explained by the detrital proportion of the sediment. Component 2 explains 16 % of the variance and is related to the carbonaceous fraction. Component 3 (5.4% of the variance) assembles some elements (As, S, V, Hg). In the fine fraction (<63 μ m) three component 3 with 11%) explain 91% of the data variance. The difference was observed with fine fraction (<63 μ m), in which Component 2 assembles As, S, V, Hg and some other trace elements.

Summarizing these observations, the geochemical data can be interpreted as a result of weathering of a pollution source, in which series of trace elements are dissipated in the downstream direction. The stream sediment geochemistry can be explained by an antagonistic data structure, consisting of detrital and carbonaceous derived elements. This is clearly related to the bedrock lithology which is eroded by weathering and transport processes.

Regarding possible toxicity of some elements, according to existing criteria issued by the University of Waterlloo, Canada, it is obvious that sample 37I is polluted



with Hg, As, Cr, Cu, Pb, mostly at concentrations that cause significant toxic effects. In Soča after confluence of Idrijca, concentration of Hg which is above significant toxic levels (>2 ppm) persists down to 25S (the last sampling location before Italian-Slovenian boarder). Concentrations of As remain above the value which causes the lowest toxic effects (>6 ppm). Pb is gradually decreasing from concentrations, which cause the lowest toxic effects (>31 ppm) to unpolluted sediments. Concentrations of Cu and Cr are below toxic levels (<28 ppm and <26 ppm, respectively). It should be emphasized that toxicity does not only depend on the total concentration, but more importantly on the availability of the elements in the aquatic environment. Therefore bioavailability of Hg and other toxic elements in the area impacted by past mining activities should be further investigated.

CONCLUSIONS

The geochemical data of sediments from the Soča River drainage basin presented here can be interpreted as a result of weathering of a pollution source (mostly from Hg ore processing and waste disposal), in which trace elements are dissipated in the downstream direction. In coarse fraction (63 - 500 µm), trace elements are associated with the detritus. This is the result of physical weathering process. In contrast, trace elements in the fine fraction ($<63 \mu m$) form a single elemental association. This can be explained by chemical weathering process. The fine fraction is more effective in respect to elemental transport downstream and finally to the Adriatic Sea. Regarding toxicity Idrijca is polluted with Hg, As, Cr, Cu, Pb in the town of Idrija, at concentrations that cause significant toxic effect. Idrijca brings the pollution to the Soča River, which become polluted particularly with Hg, after confluence with Idrijca.

On the contrary, in the Kupa River drainage basin, closed Hg-mine in Tršće shows very small effect on sediments of Čabranka and Kupa Rivers. There was no Hg ore processing in Tršće and HgS remained buried in a closed mine. Concentration of Hg in stream sediments was found to be everywhere far below toxic limit. The highest concentration (206 ppm) was found at the confluence of Čabranka and Kupa Rivers.

As toxicity does not depend only on total concentration, the bioavailability of a series of toxic elements should be further investigated.

ACKNOWLEDGEMENTS

This research was funded by Ministry of Science Education and Sport of the Republic of Croatia, project 0098041 (principal investigator H. Bilinski). Additional support for sampling in Slovenia was obtained from the bilateral project Croatia-Slovenia (principal investigators H. Bilinski and D. Hanžel). Elemental analysis was performed from the rest of the money from project JF-169, USGS-Croatia. The part of the paper regarding Kupa River drainage basin is from the corresponding author's Ph.D Thesis, accepted on 10th December 2004 and defended on 24th March 2005 at Faculty of Science, University of Zagreb, Croatia (supervisors L. Palinkaš and E. Prohić). L. Palinkaš is thanked for his suggestions to study the Tršće region.

REFERENCES

- [1] Dizdarevič, T. (2001). The influence of mercury production in Idrija mine on the environment in the Idrija region and over a broad area. *RMZ-Materials and Geoenvironment* **48**, 56-64.
- [2] Byrne, A.R. and Kosta, L. (1970). Studies on the distribution and uptake of mercury in the area of mercury mine Idrija. *Vestnik slovenskega kemijskoga društva* 17, 5-11.
- [3] Kosta, L., Byrne, A.R., Zelenko, V., Stegnar, P., Dermelj, M. and Ravnik, V. (1974). Studies on the uptake, distribution and transformations of mercury in living organisms in the Idrija region and comparative areas. *Vestnik slovenskega kemijskega društva* 21, 49-76.
- [4] Gosar, M. (1992). Ocena vsebnosti živega srebra v sedimentih Idrijce. Onesnaževanje in varstvo okolja, geologija in tehnika za okolje, 213-217.
- [5] Palinkaš, L.A., Pirc, S., Miko S.F., Durn, G., Namjesnik, K. and Kapelj, S. (1995). Ch.32: The Idrija mercury mine, Slovenia, a semi-millennium of continuous operation: an ecological impact. *Environmental Toxicology Assessment (ed. M.Richardson), Talyor & Francis Ltd.*, 317-339.
- [6] Gosar, M., Pirc, S. and Bidovec, M. (1997). Mercury in the Idrijca River sediments as reflection of mining and smelting activities of the Idrija mercury mine. *Journal of Geochemical Exploration* 58, 125-131.
- [7] Gosar, M., Pirc, S., Šajn, R., Bidovec, M., Mashyanov, N.R. and Sholupov, S. (1997). Distribution of mercury in the atmosphere over Idrija, Slovenia. *Environmental Geochemistry* and Health **19(3)**, 101-110.
- [8] Biester, H., Gosar, M. and Müller, G. (1999). Mercury speciation in tailings of the Idrija mercury mine. *Journal of Geochemical Exploration* 65, 195-204.
- [9] Biester, H., Gosar, M. and Covelli, S. (2000). Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia. *Environmental Science and Technology* 34, 3330-3336.
- [10] Biester, H., Gosar, M., Covelli, S. and Müller, G. (2001). Mercury speciation in tailings, soils and sediments of the Idrija mercury mining area. *RMZ-Materials and Geoenvi*ronment 48, 79-86.
- [11] Širca, A., Rajar, R., Harris, R.C. and Horvat, M. (1999). Mercury transport and fate in the Gulf of Trieste (Northern Adriatic) – a two-dimensional modelling aproach. *Environmental Modelling & Software* 14, 645-655.



- [12] Horvat, M., Covelli, S., Faganeli, J., Logar, M., Mandić, V., Rajar, R., Širca, A. and Žagar, D. (1999). Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *The Science of the Total Environment* 237/238, 43-56.
- [13] Horvat, M., Jereb, V., Fajon, V., Logar, M., Bonzongo, J.C., Faganeli, J. and Hines, M.E. (2001). Mercury distribution in water, sediment and soil in Idrijca and Soča river systems. *RMZ-Materials and Geoenvironment* 48(1), 65-78.
- [14] Covelli, S., Faganeli, J., Horvat, M. and Brambati, A. (1999). Pore water distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste (Northern Adriatic Sea). *Estuarine Coastal and Shelf Science* 48, 415-428.
- [15] Covelli, S., Faganeli, J., Horvat, M. and Brambati, A. (2001). Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic Sea). *Applied Geochemistry* 16, 541-558.
- [16] Hines, M.E., Horvat, M., Faganeli, J., Bonzongo, J.-C., Barkay, T. and Major, E.B. (2000). Mercury biogeochemistry in the Idrija River, Slovenia, from above the mine into the Gulf of Trieste. *Environmental Research* 83, 129-139.
- [17] Faganeli, J., Horvat, M., Covelli, S., Fajon, V., Logar, M., Lipej, L. and Cermelj, B. (2003). Mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea). *The Science of the Total Environment* **304**, 315-326.
- [18] Gosar, M. and Šajn, R. (2003). Geochemical soil and attic dust survey in Idrija, Slovenia. *Journal de Physique IV* 107(Part 1), 561-564.
- [19] Falnoga, I., Jereb, V. and Smrkolj, P. (2003). Hg and Se in foodstuffs grown near a Hg-mining area. *Journal de Phy*sique 170, 447-450.
- [20] Kim, C.S., Brown Jr., G.E. and Rytuba, J.J. (2000). Characterization and speciation of mercury-bearing mine wastes using X-ray absorption spectroscopy. *The Science of the Total Environment* 261, 157-168.
- [21] Horvat, M., Nolde, N., Fajon, V., Jereb, V., Logar, M., Lojen, S., Jacimovic, R., Falnoga, I., Liya, Qu, Faganeli, J. and Drobne, D. (2003). Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *The Science of the Total Environment* **304**, 231-256.
- [22] Boldrin, A., Juračić, M., Menegazzo Vitturi, L., Rabitti, L. and Rampazzo, G. (1989). Geochemical considerations on trace element distribution in suspended matter and sediments at the river/sea interface, Adige river mouth, northern Adriatic Sea. *Applied Geochemistry* 4, 409-421.
- [23] Šinkovec, B. and Jović, P. (1959). Rudarskogeološka istraživanja pojava cinabarita kod Tršća (in Croatian). Fond stručne dokumentacije Geološkog Zavoda, Zagreb, quated in: *Basic geological map 1:100000, sheet Delnice, L 33-90.*
- [24] Šinkovec, B. (1977). Istraživanje pojave cinnabarita kod Tršća u Gorskom Kotaru. Fond stručne dokumentacije IGI, 3229, Zagreb.
- [25] Savić, D. and Dozet, S. (1983). Basic geological map of Yugoslavia, M 1:100000, sheet Delnice L 33-90. Geološki zavod, OOUR za geologiju i paleontologiju Zagreb and Geološki Zavod, Ljubljana.

- [26] Chandrajith, R., Dissanayake, C.B. and Tobschall, H.J. (2001). Enrichment of high field strength elements in stream sediments of a granulite terrain in Sri Lanka – evidence for a mineralized belt. *Chemical Geology* **175**, 259-271.
- [27] Palinkaš, L., Strmić, S., Spangenberg, J., Prochaska, W. and Herlec, U. (2003). Ore-forming fluids in the Grübler orebody, Idrija mercury deposit, Slovenia. *Swiss Bulletin of Mineralogy and Petrology*, accepted.
- [28] Rajar, R., Žagar, D., Širca, A. and Horvat, M. (2000). Threedimensional modelling of mercury cycling in the Gulf of Trieste. *Science of the Total Environment* 260, 109-123.
- [29] Pirc, S. (2001). Geology and geochemistry of mercury in Slovenia. *RMZ-Materials and Geoenvironment* 48, 37-48.
- [30] Frančišković-Bilinski, S., Bilinski, H., Širac, S. (2005). Organic pollutants in stream sediments of Kupa river drainage basin. *Fresenius Environmental Bulletin* 14(4), 282-290.
- [31] Loska, K. and Wiechula, D. (2003). Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere* 51, 723-733.
- [32] Mirlean, N., Andrus, V.E. and Baisch, P. (2003). Mercury pollution sources in sediments of Patos Lagoon Estuary, Southern Brazil. *Marine Pollution Bulletin* 46, 331-334.
- [33] Boldrin, A., Juračić, M., Menegazzo Vitturi, L., Rabitti, S. and Rampazzo, G. (1992). Sedimentation of river-borne material in a shallow shelf sea: Adiga River, Adriatic Sea. *Marine Geology* **103**, 473-485.
- [34] Salminen, R. and Tarvainen, T. (1997). The problem of defining geochemical baselines. A case study of selected elements and geological materials in Finland. *Journal of Geochemical Exploration* 60, 91-98.
- [35] Turekian, K.K. and Wedepohl, K.H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin* 72, 175-192.
- [36] Moon, C.J. (1999). Towards a quantitative model of downstream dilution of point source geochemical anomalies. *Jour*nal of Goechemical Exploration 65, 111-132.
- [37] Kwokal, Ž., Frančišković-Bilinski, S., Bilinski, H. and Branica, M. (2002). A comparison of anthropogenic mercury pollution in Kaštela Bay (Croatia) with pristine estuaries in Öre (Sweden) and Krka (Croatia). *Marine Pollution Bulletin* 44, 1152-1169.
- [38] Frančišković-Bilinski, S., Bilinski, H., Tibljaš, D. and Hanžel, D. (2003). Characterization of sediments from Dragonja, river at the boarder line between Croatia and Slovenia. 3rd Croatian Conference on Waters – Croatian waters in the 21st century, Osijek, Croatia, 28-31 May 2003.
- [39] Reimann, C. and Filzmoser, P. (2000). Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. *Environmental Geology* 39, 1001-1014.
- [40] Reimann, C., Filzmoser, P. and Garrett, R.G. (2002). Factor analysis applied to regional geochemical data: problems and possibilities. *Applied Geochemistry* 17, 185-206.

- [41] Hubert, M. and Vanden Branden, K. (2003). Robust methods for Partial Least Squares regression. *Journal of Chemometrics* 17, 438-452.
- [42] Filzmoser, P. (1999). Robust principal component and factor analysis in the geostatistical treatment of environmental data. *Environmetrics* 10, 363-375.
- [43] Verboven, S. and Hubert, M. (2003). A MATLAB toolbox for robust calibration. *International Conference On Robust Statistics*. Abstracts, Antwerp.
- [44] Hubert, M., Rousseeuw, P.J. and Vanden Branden, K. (2004). ROBPCA: a new approach to robust principal component analysis, revised version. [http://www.wis.kuleuven.ac.be/stat/ robust.html].
- [45] Frančišković-Bilinski, S. (2005). Geochemistry of stream sediments in Kupa River drainage basin. Doctoral Thesis, Faculty of Science, University of Zagreb, 197 pp.

Received: May 03, 2005 Accepted: June 22, 2005

CORRESPONDING AUTHOR

Stanislav Frančišković-Bilinski Ruđer Bošković" Institute POB 180 10002 Zagreb - CROATIA

e-mail: francis@irb.hr

FEB/ Vol 14/ No 10/ 2005 - pages 913 - 927