Environmental geochemistry of the polymetallic ore deposits: Case studies from the Rude and the Sv. Jakob historical mining sites, NW Croatia

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ABSTRACT

This paper presents the results of sampling surveys carried out in order to evaluate the environmental impact of the Rude and the Sv. Jakob historical mining sites, NW Croatia. The studied polymetallic ore deposits differ in their mineralogical and geochemical features as well as in the host rock lithology. The Rude Fe-Cu-Pb-Zn-Ba deposit is hosted by Permian siliciclastic sediments. Siderite, haematite, galena, sphalerite, chalcopyrite, pyrite, barite and gypsum are the major ore minerals. The Sv. Jakob Pb-Zn deposit occurs in the Middle Triassic dolostone. The most abundant ore minerals are galena, sphalerite and pyrite. Although the deposits represent potential sources of numerous toxic metals, no pollution of the drainage streams and associated stream sediments was recorded. The studied mining sites are characterized by high carbonate/sulfide ratios responsible for the alkaline character of the drainage streams (pH=7.3–8.7). Consequently, the mining sites have very low potential for both generation of acid mine drainage and for leaching of heavy metals into the drainage systems. Furthermore, the study revealed that the populated areas (stream waters with decreased redox potential, increased organic matter content, high NO_3^-, NH_4^+ and PO_4^{3-} concentrations; stream sediments enriched in exchangeable Pb and Zn) and the Sava river alluvium (overflowing streams enriched in Hg) represent a greater environmental threat than the investigated polymetallic ore deposits.

Keywords: polymetallic ore deposits, exchangeable metals, stream water, stream sediments, Samoborska Gora Mts., Medvednica Mts., NW Croatia.

1. INTRODUCTION

The polymetallic ore deposits represent the geochemical anomalies of numerous potentially toxic metals such as lead, copper, cadmium, mercury, arsenic and barium. Although the primary minerals of these elements (mostly sulfides) do not represent a significant environmental threat, their weathering under surface conditions may mobilize heavy metals making them biologically available. The environmental be-

haviour of the polymetallic ore deposits varies according to the ore and gangue mineralogy, major and trace element geochemistry and the host rock lithology (e.g. MASCARO et al., 2001; FOLEY, 2002; HUANG et al., 2010; KIRSCHBAUM et al., 2012).

The presented study focused on the two polymetallic ore deposits, at Rude, in the Samoborska Gora Mts., and Sv. Jakob, (Medvednica Mts.), in the vicinity of Zagreb, NW Croatia. The deposits differ in their mineralogical and geo-

chemical features as well as in the host rock lithology. The Rude Fe-Cu-Pb-Zn-Ba deposit is hosted by Permian silici-clastic sediments. Siderite, haematite, galena, sphalerite, chalcopyrite, pyrite, barite and gypsum are the principal ore minerals (PALINKAŠ et al., 2010). The Sv. Jakob Pb-Zn deposit occurs in the Middle Triassic dolostone. The most abundant ore minerals are galena, sphalerite and pyrite (ŠINKOVEC et al., 1988). Both deposits are drained by sur-face streams which could transport potentially toxic metals downstream.

The Rude deposit is drained by the Rudarska Gradna creek. The geochemical and mineralogical study undertaken by ČOVIĆ (2003) to evaluate heavy metal levels in overbank sediments of the Žumberak and Samoborsko Gorje Mts., re-vealed an increased content of numerous metals (Hg, Cu, Pb, Ba, As, Cr and Fe) in samples from the Rudarska Gradna catchment.

Soils developed above the Sv. Jakob historic mining site were found to contain increased concentrations of Pb, Zn and Cd, related to the oxidation of primary sulfides in the near-surface weathering environment (DURN et al., 1998). The deposit is located only 300 m north from the Veliki po-tok creek headwater, and there is a strong possibility that the

creek might transport significant concentrations of heavy metals downstream.

The primary objective of this study was to determine the environmental impact of the historical mining sites on the surrounding ecosystems, including the streams that drain them. Stream water chemistry and stream sediment compo-sition are discussed, as well as the geochemical behaviour of metals during the weathering processes in the two differ-ent types of polymetallic ore deposits.

2. GEOLOGICAL SETTING

The Rude, Samoborska Gora Mts., and the Sv. Jakob, Med-vednica Mts., polymetallic ore deposits are located within the westernmost part of the Zagorje Mid-Transdanubian zone (ZMTZ); PAMIĆ, & TOMLJENOVIĆ, 1998; TOM-LJENOVIĆ, 2002).

The Samoborska Gora and Medvednica Mts. consist of Palaeozoic, Mesozoic-Palaeogene and Neogene formations (Fig. 1). The Autochthon of Samoborska Gora Mts. com-prises: 1) Palaeozoic unit, composed of Late Carboniferous dark gray schists, shales and sandstones. Shallowing of the sedimentary basin evolved into a dry-land phase, followed
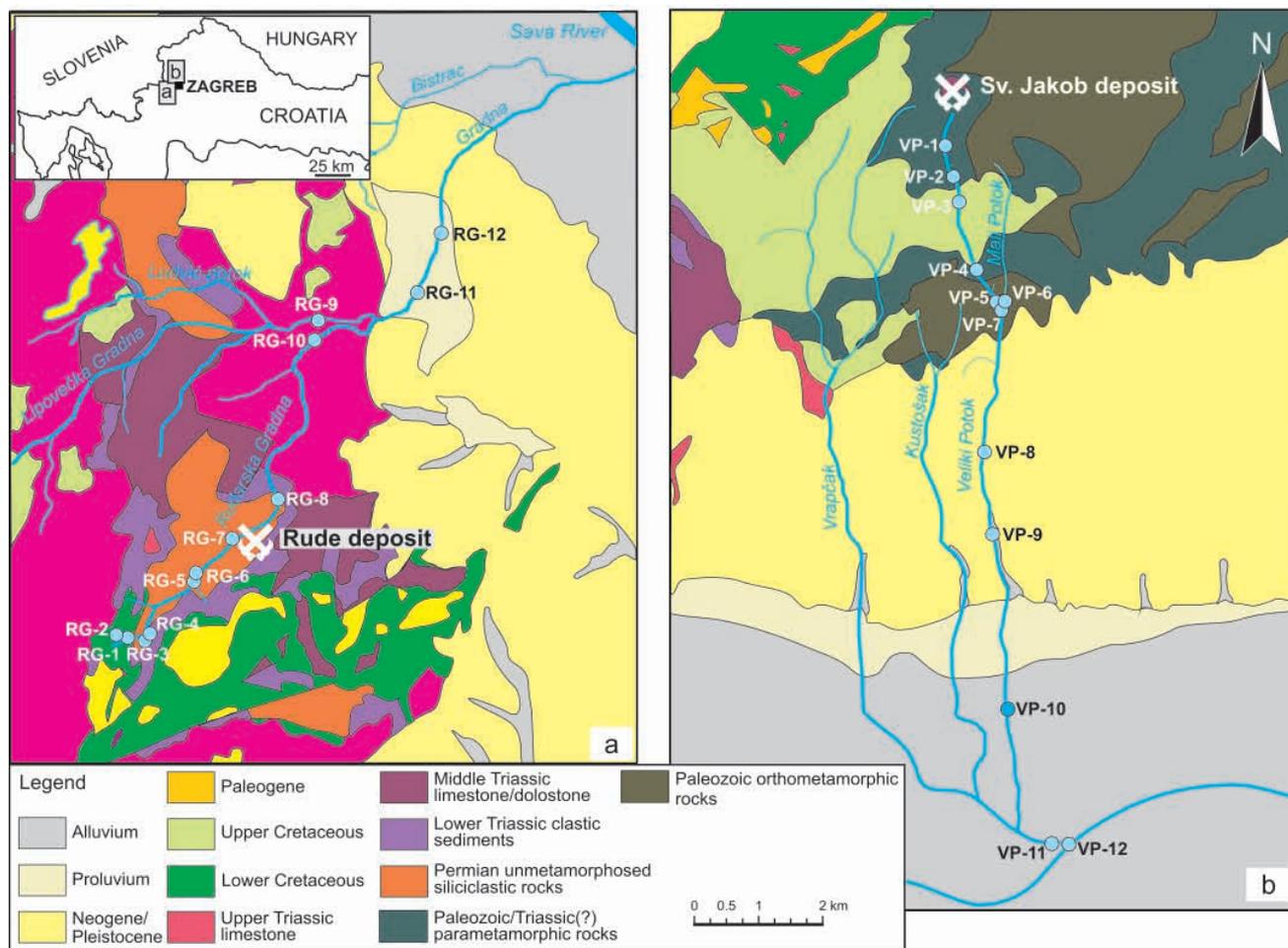

Figure 1: Simplified geological setting of the investigated areas with marked sampling sites along a) the Rude ore deposit and marked sampling sites along the Rudarska Gradna creek (RG-1 – RG-12); b) the Sv. Jakob ore and marked sampling sites along the Veliki Potok creek (VP-1 – VP-12).

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by deposition of fine to coarse-grained sandstones, interlayered with conglomerates, dolostones and evaporites (HERAK, 1956). These deposits are unconformably overlain by an Early Triassic clastic-carbonate unit, followed by Middle and Late Triassic carbonate-marl sediments, with occasional appearances of cherts, and 2) Cretaceous mélange predominantly composed of basalts and diabases within shales, graywackes, conglomerates, radiolarites and limestones of different Mesozoic ages, covered by Neogene sediments. The volcanics, often as basalt-spilite pillow lavas, are probably products of a Triassic rifting stage. The Allochthon is represented by Mesozoic carbonate platform lithotypes (ŠIKIĆ et al., 1979; TOMLJENOVIĆ, 2000; PALINKAŠ et al., 2010).

Tectonostratigraphic units of the Medvednica Mts. are grouped into four main units (Fig. 1). Autochthon: 1) Tectonized ophiolite mélange, including all lithological members, from sediments, to mafic and ultramafic igneous components, 2) Palaeozoic-Triassic magmatic-sedimentary complex overprinted by Early Cretaceous metamorphism, 3) Late Cretaceous-Paleocene flysch, and Allochthon: 4) Triassic and younger sequences belonging mainly to carbonate platform facies (ŠIKIĆ et al., 1978; ŠIKIĆ et al., 1979; ŠIKIĆ, 1995; PALINKAŠ et al., 2010).

3. MINERALIZATION

The Rude Fe-Cu-Pb-Zn-Ba deposit consists of two ore types, an epigenetic, hydrothermal vein-type beneath a stratiform, SEDEX type. Epigenetic, epi-mesothermal, quartz-siderite veins with chalcopyrite, galena, sphalerite and barite, crosscut the Middle-Upper Permian clastic rocks. The epigenetic part of the deposit represents a feeder zone of the SEDEX, stratiform ore lenses formed in an evaporitic pond-lagoon by sedimentation of gypsum-anhydrite, haematite, siderite and barite. Laterally, epigenetic, epithermal barite-galena veins intersect Upper Permian coarse-grained sandstones. The deposit is covered by Lower Triassic variegated clastics (PALINKAŠ et al., 2008; ŠINKOVEC, 1971). Mining activities in the area began in the early 13th century with the exploitation of copper. The production of iron ore from siderite started in 1850 and lasted less than 10 years. According to PALINKAŠ et al. (2010) the Rude deposit is declared as a prototype of the Permian siderite-polysulphide-barite deposits produced during the early stage of intracontinental rifting.

The deposit is drained by the Rudarska Gradna creek (Fig. 1), which originates approximately 1.8 km southwest of the deposit. Generally, it runs southwest-northeastwards for about 16 km. In the upper part of the course, the creek flows through a rural area and it is fed by several small streams. After its confluence with the Lipovečka Gradna creek, it flows through the town of Samobor. The Gradna creek joins the Sava River in the vicinity of Gradna village.

After its headwater in the Middle Triassic carbonates, the Rudarska Gradna creek flows over the Permian unmetamorphosed siliciclastic complex, the Lower Triassic clastic rocks, Middle to Upper Triassic carbonates, Cretaceous limestones, proluvial and alluvial sediments (Fig. 1; ŠIKIĆ et al., 1978; ŠIKIĆ et al., 1979).

The Sv. Jakob Pb-Zn deposit is hosted by non-metamorphosed Middle Triassic dolostone (PALINKAŠ et al., 2008), with the ore occurring in the form of veinlets and lenses. Galena is the principal ore mineral, and it is coarse grained. The vein-type mineralization, beside galena, comprises minor sphalerite, pyrite, quartz and calcite (ŠINKOVEC et al., 1988), and was actively mined during the 17th century. According to the epigenetic character of the ore mineralization, a simple ore paragenesis without copper minerals, and the fluid inclusions and sulfur isotope data, the deposit is classified as a Mississippi Valley type of Pb-Zn deposits formed during the stage of advanced intracontinental rifting in the Middle Triassic (PALINKAŠ et al., 2008; ŠINKOVEC et al., 1988; DURN et al., 1999; BOROJEVIĆ ŠOŠTARIĆ, 2004).

The deposit is located at 830 m above sea level, approximately 300 m north of the Veliki Potok creek headwater. The Veliki Potok creek runs north-south for about 12 km, and is fed in its upper part by the Mali Potok creek and several small streams. The central and lower part of the creek flows through the urban area of Zagreb. In the lowermost part of the course, about 500 m upstream from its entry point into the Sava River; the Veliki Potok has its confluence with the Vrapčak creek (Fig. 1). The Veliki Potok originates in the Palaeozoic parametamorphic complex (Fig. 1) composed of greywackes, siltstones, limestones, dolostones, muscovite-chlorite and muscovite-quartz schists (ŠIKIĆ et al., 1978; ŠIKIĆ et al., 1979). According to several authors (ĐURĐANOVIĆ, 1973; BELAK et al., 1995) some protoliths from the parametamorphic complex are of Triassic age. Continuing downstream, the creek is entrenched in the Cretaceous sedimentary rocks predominantly represented by fine-grained clastics. The orthometamorphic complex, predominantly composed of greenschist and metamorphosed gabbro and diabase, is referred to as being of Devonian-Carboniferous age. Further, the creek flows through the Neogene sediments represented mostly by sandstones, marls and limestones. The lowermost part of the creek dissects the Sava river alluvial sediments (ŠIKIĆ et al., 1978; ŠIKIĆ et al., 1979).

4. SAMPLES AND METHODS

Stream water and sediment samples were simultaneously collected from the Rudarska Gradna creek (n=12), the Veliki potok creek (n=11) and the Sava River (n=1) during the sampling campaign in October 2010. The sampling sites are shown on Figure 1 and listed in Table 1.

Collection and sample handling were conducted in accordance to the standard methodology for the analysis of the selected parameters. Water samples were collected using two half-litre polyethylene (PET) bottles, one for the analysis of anions (SO_4^{2-}, PO_4^{3-}, Cl^-, NO_3^-) and ammonia, and other, which was pre-acid washed (10%, v/v, nitric acid 65%), for trace metal analysis. The bottles were rinsed three times with stream water prior to filling with the water sample. In the

Table 1: Description and location of the sample sites.

Sample	Gauss-Krüger coordinates		Lithology	Sample site description
	x	y		
RG-1	5551315	5068279	Middle Triassic limestone	The Rudarska Gradna headwater
RG-2	5551349	5068151	Middle Triassic limestone	The Rudarska Gradna creek, upstream from the Rude deposit
RG-3	5551311	5068284	Middle Triassic limestone	The Rudarska Gradna creek, upstream from the Rude deposit
RG-4	5551315	5068279	Middle Triassic limestone	The Rudarska Gradna creek, upstream from the Rude deposit
RG-5	5551823	5068293	Permian unmetamorphosed siliciclastic rocks	Right confluent of the Rudarska Gradna creek
RG-6	5551820	5068295	Permian unmetamorphosed siliciclastic rocks	The Rudarska Gradna creek, upstream from the Rude deposit
RG-7	5552531	5069116	Permian unmetamorphosed siliciclastic rocks	Right confluent of the Rudarska Gradna creek, abandoned waste-rock dump
RG-8	5553843	5070412	Lower Triassic clastic sediments	The Rudarska Gradna creek, downstream from the Rude deposit
RG-9	5554470	5073216	Upper Triassic limestones	The Lipovečka Gradna creek
RG-10	5554409	5072907	Upper Triassic limestones	The Rudarska Gradna creek, downstream from the Rude deposit
RG-11	5556019	5073652	Proluvium	The Gradna creek, Samobor center
RG-12	5556384	5074588	Proluvium	The Gradna creek
VP-1	5572129	5082230	Paleozoic/Triassic(?) parametamorphic rocks	The Veliki Potok creek
VP-2	5572251	5081745	Paleozoic/Triassic(?) parametamorphic rocks	The Veliki Potok creek
VP-3	5572316	5081344	Cretaceous clastic sediments	The Veliki Potok creek
VP-4	5572617	5080280	Paleozoic/Triassic(?) parametamorphic rocks	The Veliki Potok creek
VP-5	5572958	5079768	Paleozoic orthometamorphic rocks	The Veliki Potok creek
VP-6	5573059	5079758	Paleozoic orthometamorphic rocks	The Mali Potok creek
VP-7	5572994	5079604	Paleozoic orthometamorphic rocks	The Veliki Potok creek
VP-8	5572763	5077404	Pliocene clastic sediments	The Veliki Potok creek, urban area
VP-9	5572867	5076130	Pliocene clastic sediments	The Veliki Potok creek, urban area
VP-10	5573103	5073379	Alluvium	The Veliki Potok creek, urban area
VP-11	5573816	5071199	Alluvium	The Veliki Potok creek, urban area
VP-12	5574057	5071255	Alluvium	The Sava River

laboratory, samples for trace metal analysis were filtered through 0.45 μm pore cellulose syringe filters, acidified with HNO_3 to pH<2 and stored at 4°C. Another bottle was frozen at –18°C for subsequent analyses of anions and ammonia.

Stream sediment samples were collected and stored in double polyethylene bags. At the laboratory, samples were air dried, disaggregated in an agate mortar, homogenized, and finally dry-sieved through stainless-steel screens to the fraction of <125 μm.

Water temperature, pH, redox potential, electrical conductivity and dissolved oxygen (DO) measurements were conducted *in situ* on unfiltered water using a portable Hach Lange HQ40d Multimeasure Device.

Nitrate was electrochemically measured using a low-level calibrated nitrate-sensitive electrode (Hach Platinum Series combination electrode, model 51920), connected to a volt meter (Hach SensIon 2). To avoid the interference effects of bicarbonate ions, the pH of samples was adjusted to 3 by the addition of an acidic buffer (H_2SO_4).

Ammonia content was determined using Hach Intelli-CAL™ ISENH3181 gas-sensing ammonia ion selective el-ectrode (ISE) with a replaceable membrane module, refill-able outer body, double junction reference and built-in temperature sensor. The measuring range is in the interval between 0.007 mg/L and 14,000 mg/L NH_3–N. The sample preparation procedure required the addition of an alkaline buffer (LiOH) to ensure that the ammonia was essentially de-ionised prior to analysis.

The chloride ion concentration was determined using a selective Radiometer Analytical chloride electrode ISE25Cl.

Sulphate was determined by a titrimetric method. A 0.1 ml volume of methyl orange was added to 100 ml of each water sample. The sample was titrated against 0.1 M HCl to a permanent orange colour. An additional 1 ml of 0.1 M HCl and 25 ml of $BaCl_2$ solution were then added. Samples were heated to boiling and cooled in tap water. After 30 minutes, 25 ml volume of potassium chromate, 1 drop of aluminum chloride and 1.6 ml 0.1 M KOH solutions were added. After 1 hour, any precipitate was removed by filtration and 100 ml of each filtrate was titrated against 10 ml 10% potassium io-dide solution and sodium thiosulphate using starch indicator.

Total phosphates were analyzed by the ascorbic acid method (APHA Standard Method 4500-P; APHA, AWWA,

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Table 2: Stream water analytical data for the Rudarska Gradna and Veliki Potok creeks.

Sample	pH	Eh (mV)	DO (mg/l)	Conductivity (µS/cm)	N-NO$_3^-$ (mg/l)	N-NH$_4^+$ (mg/l)	Cl$^-$ (mg/l)	SO$_4^{2-}$ (mg/l)	P-PO$_4^{3-}$ (mg/l)	Fe (mg/l)	Mn (mg/l)	Pb (mg/l)	Zn (mg/l)	Cu (mg/l)	Hg (µg/l)	Cd (µg/l)
RG-1	7.39	306.7	9.75	520	1.10	0.05	1.74	3.1	<d.l.	0.012	<d.l.	0.045	0.006	<d.l.	0.043	<d.l.
RG-2	8.45	257.8	10.77	527	1.41	0.04	1.91	4.4	<d.l.	0.016	<d.l.	0.038	0.013	<d.l.	0.040	<d.l.
RG-3	8.47	258.6	10.29	506	1.65	0.04	3.44	4.4	0.005	0.037	<d.l.	0.039	0.030	<d.l.	0.049	<d.l.
RG-4	8.52	239.4	10.10	538	1.94	0.07	13.96	4.2	0.013	0.259	0.004	0.031	0.014	<d.l.	0.043	<d.l.
RG-5	8.12	202.4	10.18	518	1.67	0.12	11.62	6.6	0.021	0.183	<d.l.	0.022	0.028	<d.l.	0.041	<d.l.
RG-6	8.45	225.9	10.36	605	2.26	0.08	16.14	5.3	0.023	0.163	0.006	0.015	0.006	0.002	0.056	<d.l.
RG-7	8.34	252.0	10.58	666	1.77	0.03	12.54	8.1	<d.l.	1.107	0.119	0.012	0.040	0.009	0.099	<d.l.
RG-8	8.43	222.3	10.20	631	3.02	0.20	16.68	7.6	0.021	0.166	<d.l.	0.038	0.029	0.004	0.033	<d.l.
RG-9	8.62	232.5	10.94	512	2.26	0.05	9.38	3.2	0.008	0.101	<d.l.	0.071	0.033	0.005	0.037	<d.l.
RG-10	8.44	212.0	10.51	627	2.31	0.14	14.36	6.1	0.023	0.428	<d.l.	0.065	0.015	0.009	0.178	<d.l.
RG-11	8.68	229.5	10.84	547	2.35	0.04	10.90	4.5	0.044	0.130	<d.l.	0.087	0.009	0.003	0.078	<d.l.
RG-12	8.69	223.9	10.70	545	2.25	0.04	11.84	4.7	0.016	0.110	<d.l.	0.076	0.010	<d.l.	0.747	0.092
VP-1	7.60	200.1	11.14	427	2.03	0.03	23.80	5.8	0.005	0.173	<d.l.	0.049	0.009	0.008	0.375	<d.l.
VP-2	7.33	201.1	11.20	418	1.82	0.04	22.30	3.8	0.010	0.822	0.071	0.046	0.025	0.009	0.335	<d.l.
VP-3	8.00	201.5	11.90	422	1.64	0.08	22.00	4.7	0.007	0.905	0.096	0.054	0.035	0.008	0.025	<d.l.
VP-4	7.79	201.6	11.68	387	1.71	0.03	15.00	4.4	0.002	0.209	<d.l.	0.027	0.020	0.008	0.005	<d.l.
VP-5	8.23	194.8	11.91	381	1.77	0.04	14.00	4.5	0.006	0.619	0.011	0.055	0.022	0.007	0.043	<d.l.
VP-6	8.03	196.4	11.81	350	1.27	0.03	12.80	4.9	0.005	0.220	<d.l.	0.050	0.018	0.007	0.081	<d.l.
VP-7	7.96	179.8	11.87	376	1.70	0.05	13.88	4.9	0.004	0.121	<d.l.	0.049	0.028	0.009	0.058	<d.l.
VP-8	7.87	178.9	11.29	551	3.35	0.23	17.78	4.2	0.013	0.267	<d.l.	0.074	0.022	0.010	0.078	<d.l.
VP-9	8.41	168.9	11.75	552	3.41	0.18	18.28	5.0	0.031	0.213	<d.l.	0.028	0.021	0.010	0.806	<d.l.
VP-10	8.45	166.3	11.37	563	3.78	0.25	18.75	5.8	0.021	0.509	<d.l.	0.072	0.034	0.010	1.282	<d.l.
VP-11	8.38	168.6	11.64	535	3.18	0.20	11.14	5.7	0.013	0.882	0.003	0.053	0.029	0.012	0.864	<d.l.
VP-12	8.02	170.9	10.92	420	2.35	0.12	5.55	4.5	0.007	0.159	<d.l.	0.046	0.071	0.010	0.848	<d.l.

<d.l. – below detection limit

EFA, 1998). Absorbance was measured at 880 nm using a Hach DR4000 spectrophotometer.

Acidified sample solutions were used for heavy metal concentration measurements, using the flame atomic absorption method for Fe, Mn, Pb, Cu, and Zn and the graphite furnace technique for Hg and Cd measurements (Perkin-Elmer AAnalyst 800).

Exchangeable metals were extracted from the stream sediments (m = 10 g) using 250 ml of 1 M NH$_4$OAc solution at pH =7.00. The sediment-solution slurry was shaken for 2 h, and the solution separated from the solid by filtration. The addition of NH$_4^+$ in excess to the soil displaces the rapid exchangeable alkali and alkaline cations from the exchange sites of the soil particles. The concentrations of metals in the solution were measured with a Perkin-Elmer AAnalyst 800 Atomic Absorption Spectrometer.

Bulk stream sediment composition was estimated using energy dispersive X-ray fluorescence (EDXRF). Measurements were made with a W anode and Mo secondary target in orthogonal geometry, with measurement parameters of 40 kV and 35 mA. The irradiation time was 1000 s. X-ray spec-

tra were collected with a Si(Li) detector (FWHM=170 eV at 5.9 keV) and were analyzed using QXAS program package-direct comparison method. IAEA "Lake Sediment" was used as a reference material.

Highly oriented samples of the <2 µm fraction of selected stream sediment samples were prepared for clay mineral identification on air-dried, ethylene-glycol saturated, and heated (at 400 and 550 °C, respectively) samples according to the procedure described by Starkey *et al*. (1984). Instrumental conditions were 40 kV, 40 mA and constant time 5 s, with step scanning (0.02°2θ).

5. RESULTS

The chemical characteristics of the water samples from the Rudarska Gradna and Veliki Potok creeks are listed in Table 2. According to the Croatian water quality guidelines (OG 77/98), analyzed samples are classified within Classes I and II, concerning the general physicochemical parameters (pH, conductivity and dissolved oxygen; Fig. 2). According to nitrate and ammonium concentrations, the water samples belong to Classes II and III and Classes I and II, respectively
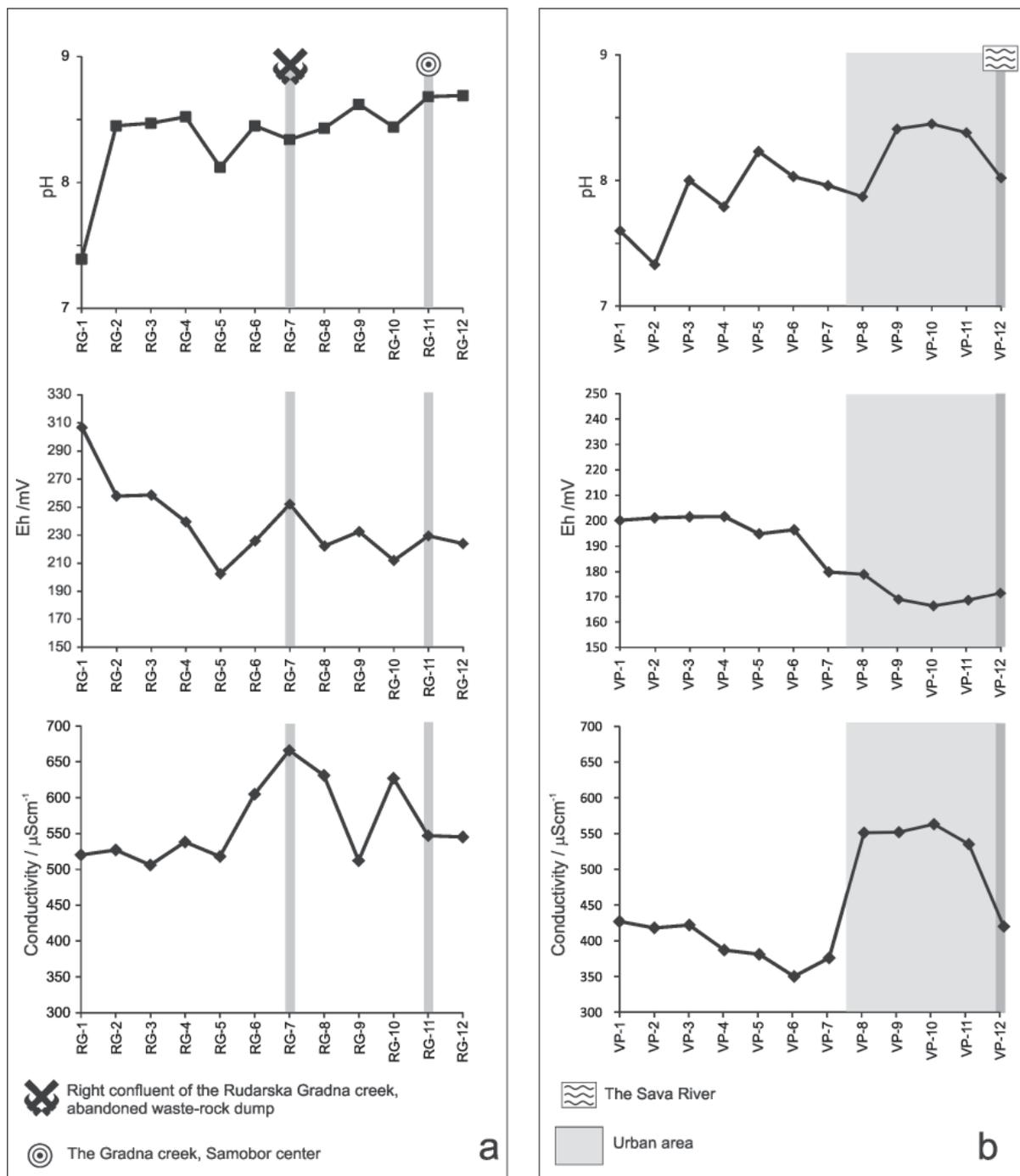
Figure 2: The physico-chemical parameters of a) the Rudarska Gradna creek, b) the Veliki Potok creek.

(Fig. 3). Increased concentrations of various forms of nitrogen in rural and urban areas indicate the influence of domestic wastewaters, mostly attributed to the discharge of sewage into the creeks or to the drainage from septic tanks. The results for total phosphorus classify all samples within Class I (Fig. 2). Measured concentrations of sulfates and chlorides were considerably lower than the maximum allowable concentrations (MAC) allowed by the Croatian regulations for drinking waters (OG 47/08).

Iron and manganese concentrations in water samples mostly exceed the MAC for drinking waters (Fig. 4). Ele-

vated lead content classifies the analysed samples within Classes IV and V. Lead had its highest water content in urban areas (sampling sites RG-11 and VP-10; Fig. 4) reflecting an anthropogenic origin. According to their mercury concentrations, the water samples mostly belong to Class IV (Fig. 4). The copper level varies from Class I to Class III. Low concentrations of zinc and cadmium are within the ranges proposed for Class I.

A summary of the NH_4OAc extracted contents of Fe, Mn, Pb, Zn, Cu, Hg and Cd in stream sediments is given in Table 3 and Figure 4. Iron contents vary from 0.550–2.075
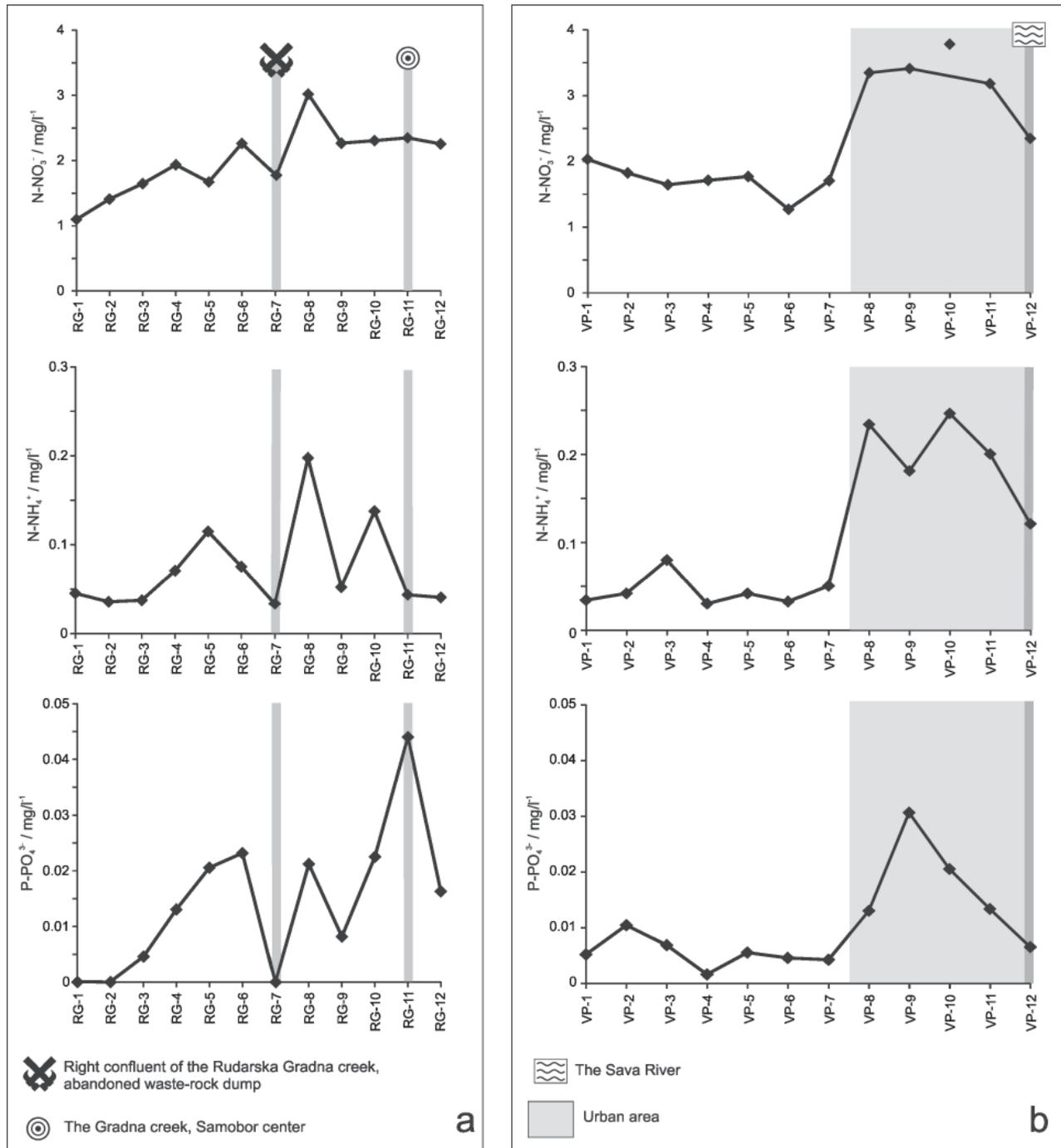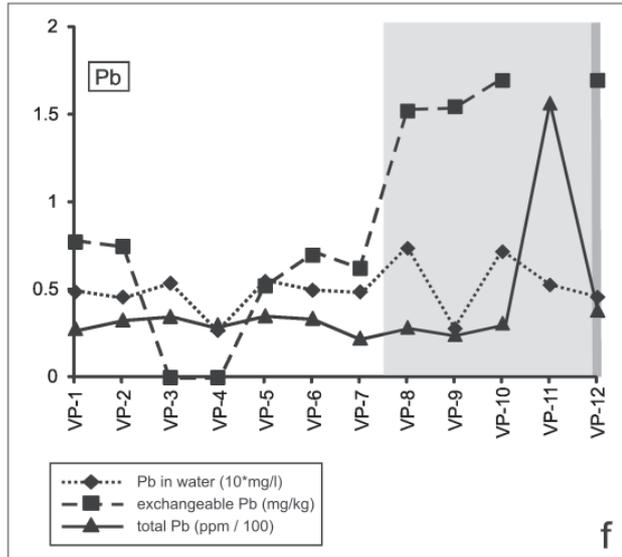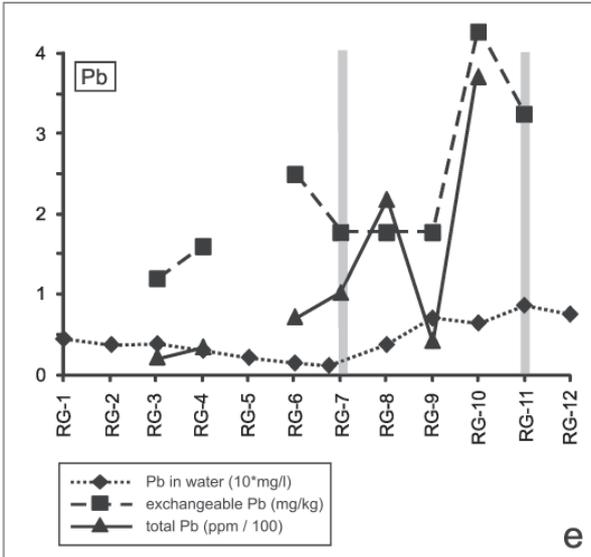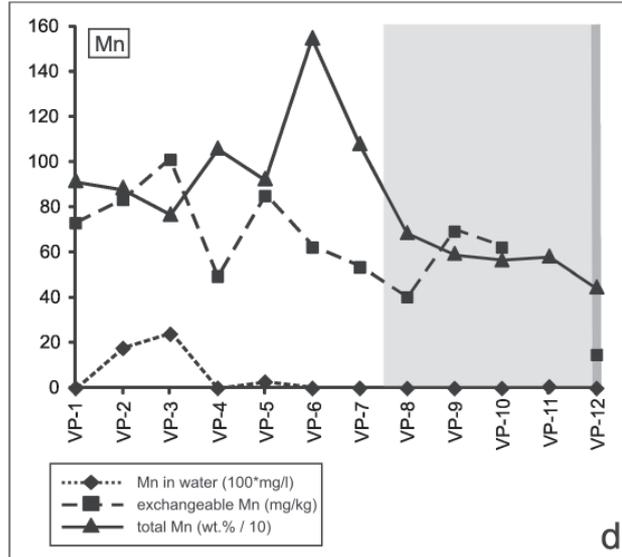
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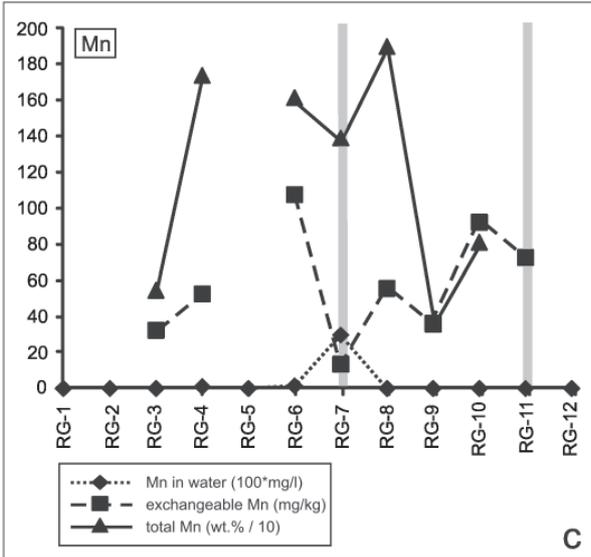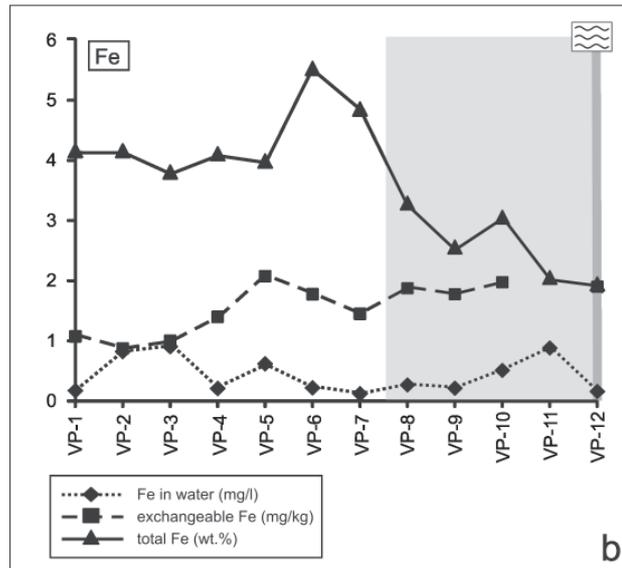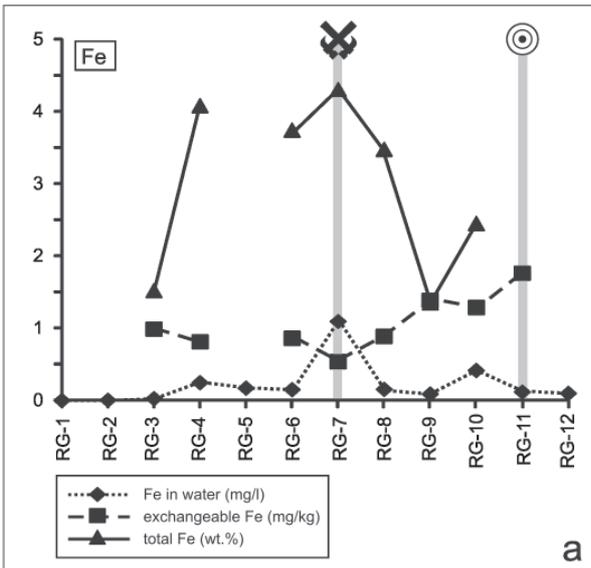
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Figure 3: Variations in nitrate, ammonia and phosphate content along a) the Rudarska Gradna creek, b) the Veliki Potok creek.
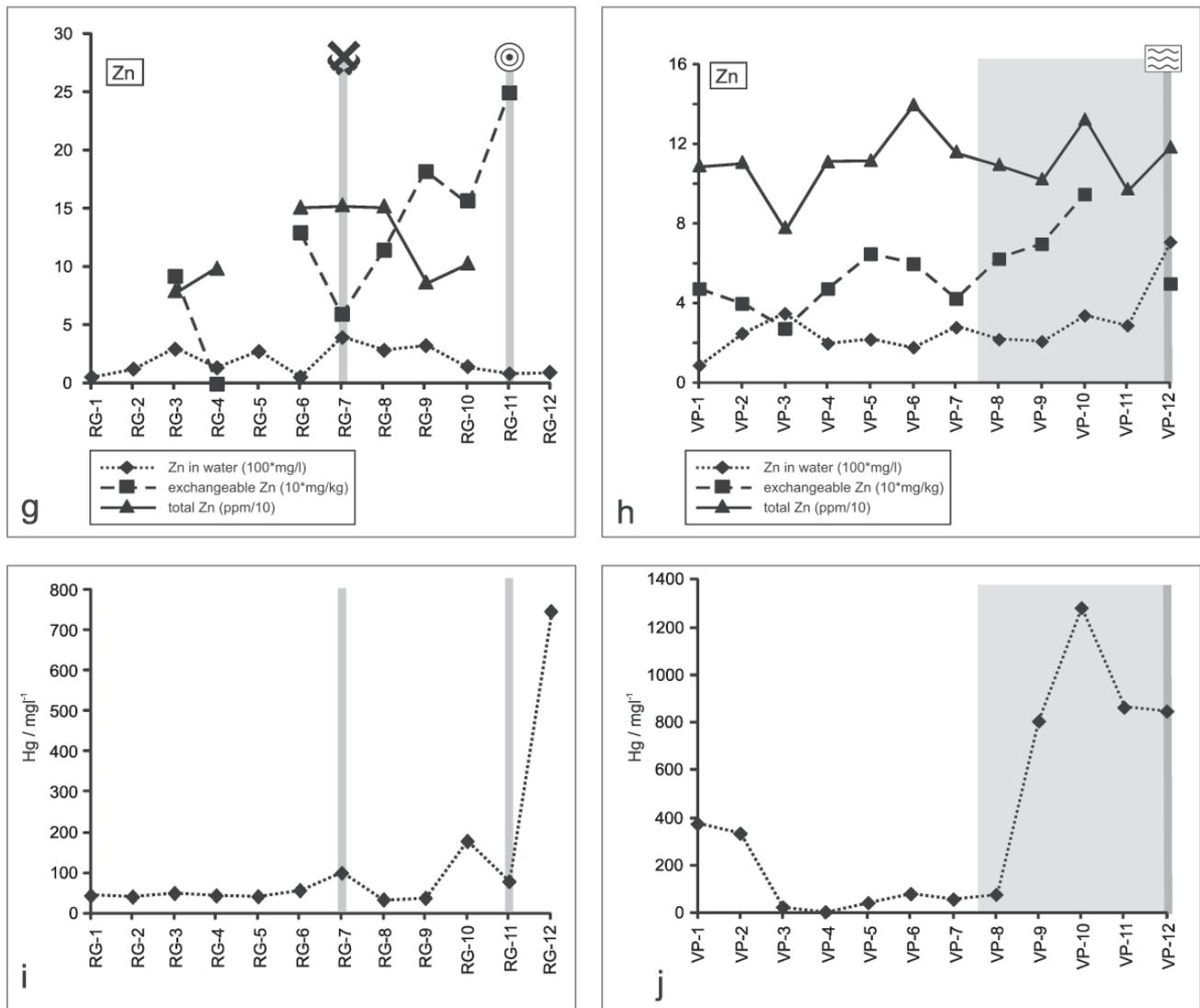
mg/kg, Mn content from 13.550–107.775 mg/kg, Pb up to 4.275 mg/kg, Zn up to 3.425 mg/kg, Cu from 0.275–8.575 mg/kg, and Cd from 6.625–98.250 μg/kg. Mercury is mostly below the detection limit. The exceptions are samples VP-3 and VP-10 with Hg concentrations of 0.900 and 1.650 mg/kg, respectively.

The bulk chemical composition of the stream sediments is summarized in Table 4. Mean K content for the sediments on metamorphic and siliciclastic terrains is comparatively higher than for the sediments on carbonate terrain, reflecting the lithological contribution of this element. The principal carriers of K are K-feldspars, biotite, micas and clay minerals. As expected, the highest Ca values are recorded for the stream sediments collected on carbonate terrains. The Fe concentrations are mostly lower than the average shale value (Table 4). Sampling site RG-7 near the abandoned waste-rock dump of the Rude deposit is the exception. The mean concentrations of Pb, Zn, Cu and As are significantly higher than the average shale concentrations.

According to the XRD patterns, kaolinite and illite represent the most abundant clay minerals in all the analyzed stream sediments.

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Figure 4: Variations in dissolved, exchangeable and total metals content along the Rudarska Gradna and Veliki Potok creeks. a) Iron, Rudarska Gradna; b) Iron, Veliki Potok; c) Manganese, Rudarska Gradna; d) Manganese, Veliki Potok; e) Lead, Rudarska Gradna; f) Lead, Veliki Potok; g) Zinc, Rudarska Gradna; h) Zinc, Veliki Potok; i) Mercury, Rudarska Gradna; i) Mercury, Veliki Potok.

6. STATISTICAL TREATMENT

The statistical analyses that applied univariate (basic statistic parameters) and bivariate analysis (correlation matrix) were performed on the analytical results obtained from 24 sampling sites. For each sampling site, 42 descriptors consisting of 5 lithological and 37 geochemical variables were observed and included in the statistical treatment. Lithological variables were defined as a percentage of selected lithological units at the sampling site (e.g. ROSE et al., 1970; PEH, 1992; HALAMIĆ et al., 2001). As the bedrock lithologies of the Medvednica and Samoborska Gora Mts. comprise a variety of igneous, sedimentary and metamorphic rocks of different stratigraphic and tectonic settings, a simplified representation of lithology with as little as possible loss of useful information was necessary (HALAMIĆ et al., 2001). For this purpose lithological data were generalized from the geological map of Croatia (scale 1:100.000), Zagreb Sheet (ŠIKIĆ et al., 1978). The study areas comprise only five lithological units which were broadly related to the corresponding stratigraphic nomenclature (Table 1). These units were further utilised as lithological variables which were specified as follows: LIT1 – Triassic carbonate rocks; LIT2 – Permian unmetamorphosed complex, Triassic, Cretaceous and Pliocene clastic sediments; LIT3 – Prolluvium and alluvium; LIT4 – Parametamorphites; and LIT5 – Orthometamorphites. Additionally, the settlement influence variable was estimated for all sampling sites. An environmental impact of the settlements is pronounced in both urban and rural areas with no sewage and sewerage facilities.

7. DISCUSSION

The primary ore mineralization usually is not stable under surface conditions (low temperature and pressure, high activities of water, oxygen and CO_2). Weathering products could be summarized within 3 principal groups: 1) Residual

Table 3: Exchangeable metals content in the stream sediments from the Rudarska Gradna and Veliki Potok creeks.

Sample	Fe (mg/kg)	Mn (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Cd (∝g/kg)
RG-3	1.000	32.400	1.200	0.925	0.675	*<d.l.*	38.725
RG-4	0.825	52.650	1.600	*<d.l.*	0.600	*<d.l.*	50.250
RG-6	0.875	107.775	2.500	1.300	0.875	*<d.l.*	98.250
RG-7	0.550	13.550	1.775	0.600	1.300	*<d.l.*	60.425
RG-8	0.900	55.675	1.775	1.150	4.250	*<d.l.*	83.875
RG-9	1.400	36.375	1.775	1.825	0.625	*<d.l.*	51.525
RG-10	1.300	92.375	4.275	1.575	8.575	*<d.l.*	76.325
RG-11	1.775	72.775	3.250	2.500	2.300	*<d.l.*	63.850
VP-1	1.075	73.150	0.775	*<d.l.*	0.475	*<d.l.*	11.125
VP-2	0.875	83.475	0.750	0.525	0.400	*<d.l.*	38.575
VP-3	1.000	101.250	*<d.l.*	*<d.l.*	0.275	0.900	25.325
VP-4	1.400	49.575	*<d.l.*	*<d.l.*	0.475	*<d.l.*	15.450
VP-5	2.075	85.125	0.525	*<d.l.*	0.650	*<d.l.*	10.950
VP-6	1.775	62.350	0.700	*<d.l.*	0.600	1.650	28.575
VP-7	1.450	53.575	0.625	*<d.l.*	0.425	*<d.l.*	26.775
VP-8	1.875	40.425	1.525	0.925	0.625	*<d.l.*	22.925
VP-9	1.775	69.400	1.550	2.125	0.700	*<d.l.*	57.475
VP-10	1.975	62.300	1.700	3.425	0.950	*<d.l.*	6.625
VP-12	1.900	14.825	1.700	1.000	0.500	*<d.l.*	40.225

<d.l. – below detection limit

primary minerals, resistant to chemical and physical weathering; 2) Secondary minerals, including clay minerals, hydrous Fe-Al-oxides, sulfates and carbonates; and 3) Soluble (mobile) products. The mobility of metals depends mostly on pH and the redox potential of the solution as well as on the possibility for the formation of complexes. Metals may be adsorbed onto Fe- and Mn-hydroxides (HEM, 1977; TESSIER et al., 1985; FENG et al., 2007), clay minerals (RYBICKA et al., 1985), organic matter (DAVIS, 1982; ÖZKARAOVA GUNGOR et al., 2010) and amorphous silica (JAMES & MACNAUGHTON, 1977). Co-precipitation with ferric and/or manganese oxyhydroxide can also decrease heavy metal content in the stream waters.

The Rude deposit represents a potential source of lead (galena), zinc (sphalerite), iron (siderite, chalcopyrite, haematite), as well as sulfate (gypsum, anhydrite and oxidized sulfide species). The ore mineralization of the Sv. Jakob deposit is simple and comprises only galena, sphalerite and pyrite. Numerous geochemical surveys revealed an increased content of heavy metals in the topsoils of urban and pristine areas of the Zagreb region (NAMJESNIK-DEJANOVIĆ, 1994; ROMIĆ & ROMIĆ, 2003; SOLLITTO et al., 2010) as well as in the overbank sediments of the Sava River (ČOVIĆ, 2003; PAVLOVIĆ et al., 2004). As both deposits are drained by the surface streams there is the possibility that they also contribute to the pollution.

According to the principal geochemical features, the Rudarska Gradna creek is divided into 3 segments: 1) the headwater, 2) the segment upstream from the Rude mining site, and 3) the segment downstream from the Rude mining site.

Although the Rudarska Gradna creek rises within the Middle Triassic carbonate rocks, the headwater is characterized by a slightly decreased pH value (RG-1; Fig. 2), reflecting the strong influence of the underlying siliciclastic sediments, mostly Cretaceous shales, sandstones and cherts (Fig. 1). An increased Eh value suggests low organic matter content. The NO_3^-, NH_4^+ and PO_4^{3-} concentrations, as well as the content of all analyzed metals, with exception of lead, are very low (Fig. 4). An increased Pb concentration is attributed to the remobilization of lead from the Middle Triassic sediments under moderately low pH.

The segment between the headwater and the Rude mining site displays a uniform pH value (pH≈8.5) despite the presence of several small tributary streams with low alkalinity (e.g. RG-5; pH=8.12). The progressive decrease in redox potential coincides with the increase in nitrate, ammonia and phosphate concentrations, suggesting a common source of organic matter, nitrogen and phosphorous. The stream water shows a gradual decrease in lead content mainly due to its alkaline character causing the precipitation and/or adsorption of lead to the stream sediments. The sediment analyses revealed an increase in the exchangeable and total lead content downstream (Fig. 4) indicating that both processes, adsorption and precipitation, should be considered.

Water at the abandoned waste-rock dump of the Rude ore deposit is characterized by a slight decrease in pH and an increase in the Eh value. Nitrates, ammonia and phosphates are significantly lower than in the main stream, indicating the diminished influence of anthropogenic pollution. Increased concentrations of metals in the water are expected due to the weathering of ore minerals. The weathering of sulfide-bearing parageneses usually results in a large decrease in pH value. In the case of the Rude deposit, the observed decrease is minor, indicating that weathering of siderite reduces the acidification effect. Namely, according to reactions (1) and (2), weathering of siderite produces a neutral to slightly acid solution as indicated in the reactions below (SKOUSEN et al., 1997):

$$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3 + H_2CO_3\ (1)$$

$$\text{and } H_2CO_3 \leftrightarrow H_2O + CO_2\ (2).$$
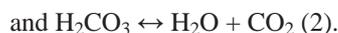
Consequently, the weathering of Fe-minerals under oxidizing conditions results in the precipitation of Fe-hydroxide which represents the predominant phase in the bulk sediment composition (Fig. 4). The decreased content of all exchangeable metals (Fig. 4) suggests pH as a key parameter controlling metal mobility. Under decreased pH, the competition between H^+ and the dissolved metals for ligands is more significant. It decreases the adsorption abilities of metals, and consequently increases their mobility. Sometimes, with only a drop in a few pH units, the fixation percentage of metals on sediment particles may range from almost 100% to 0% (GUNDERSEN & STEINNES, 2003; PENG et al., 2009).

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Table 4: Bulk chemical composition of the stream sediments from the Rudarska Gradna and Veliki Potok creeks.

Sample	K (%)	Ca (%)	Fe (%)	Mn (ppm)	Ti (ppm)/	Cr (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)	As (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)
RG-3	1,23	5,60	1,53	547	2365	53	70	23	80	46	10	59	88	43	332
RG-4	2,26	0,97	4,10	1742	4107	113	116	35	100	57	19	123	111	73	312
RG-6	2,39	1,52	3,76	1618	4129	60	79	73	152	61	29	117	137	74	318
RG-7	2,90	0,74	4,32	1394	5075	41	52	103	154	111	51	141	153	89	465
RG-8	2,28	2,72	3,49	1903	3766	61	51	219	153	139	81	99	170	68	389
RG-9	1,43	6,69	1,36	358	2743	44	45	43	88	32	17	53	113	44	315
RG-10	1,67	4,01	2,47	813	3568	29	33	372	104	171	130	79	153	64	447
VP-1	2,98	1,07	4,17	921	5726	87	76	28	110	33	20	129	120	90	423
VP-2	3,19	0,33	4,16	890	6565	103	68	33	111	39	19	142	115	95	424
VP-3	2,98	1,00	3,81	772	5275	52	56	35	79	39	20	140	129	87	368
VP-4	2,77	1,13	4,11	1065	4949	61	71	30	112	41	22	127	147	85	402
VP-5	2,47	1,32	3,99	930	5364	81	61	35	112	45	21	115	159	89	5035
VP-6	3,25	0,40	5,53	1554	5657	117	92	34	140	56	25	148	156	85	345
VP-7	2,34	0,97	4,85	1085	6164	79	58	23	117	39	17	108	145	82	405
VP-8	2,39	3,39	3,29	690	4243	59	49	29	110	33	17	107	197	71	370
VP-9	2,03	3,76	2,56	598	4306	42	42	25	103	31	14	87	169	70	403
VP-10	2,22	2,56	3,06	569	4937	50	56	31	133	40	15	105	168	75	447
VP-11	1,78	4,84	2,06	586	2948	45	42	157	98	96	56	70	131	49	315
VP-12	1,75	7,15	1,95	451	1872	46	44	39	119	26	15	72	220	46	206

The segment downstream from the Rude mining site displays a decrease in redox potential and an increase in nitrogen and phosphorous species, suggesting the enhanced influence of urbanization on the water quality. The concentrations of iron, manganese and zinc in the water gradually decrease downstream, suggesting the diminishing influence of the ore deposit (Fig. 3). The increase in copper concentration is attributed to agricultural activities and the usage of $CuSO_4$-based fungicides in the vineyards (HALAMIĆ et al., 2003). The stream sediments, characterized by the progressive increase in the exchangeable and total metal contents downstream (Fe, Mn, Pb, Zn, Cu), indicate that the mobility of metals is controlled by adsorption and precipitation.

According to the geochemical features, the Veliki Potok creek is divided into 2 segments: 1) the upper course flows through an uninhabited area and 2) the lower course flows through the urban area. The upper segment of the creek is characterized by moderate pH and high redox potential. An increased Eh value suggests low organic matter content. The NO_3^-, NH_4^+ and PO_4^{3-} concentrations, as well as the content of all analyzed metals, with the exception of manganese, are very low (Fig. 3; Fig. 4). An increased Mn concentration might be attributed to the remobilization of manganese from the Middle Triassic sediments. The low heavy metal content in the upper course, as well as a low sulfate concentration, indicates that the Sv. Jakob Pb-Zn-Ag deposit does not represent a potential pollution source for the draining streams.

The lower part of the creek is characterized by an increased pH value especially in the segment which flows over alluvial sediment (VP-10 to VP-12). Increased conductivity of the stream water within the populated area generally points to a higher content of total dissolved solids. The progressive decrease in redox potential coincides with the increase in nitrate, ammonia and phosphate concentrations, suggesting a common source of organic matter, nitrogen and phosphorous, mostly from domestic wastewaters in the urban areas without sewerage facilities. Agricultural activity in the suburbs, including the use of synthetic and organic fertilizers, may also increase the nitrate, ammonia and phosphate contents of the stream waters. The stream sediments display a progressive increase in the exchangeable and total metals contents (Fig. 4).

Statistical analyses applied to the results obtained from both of the study areas allow additional data interpretation. A positive correlation between the measured pH values of the stream water and the presence of Triassic carbonates (variable LIT1; r=0.53) is expected due to the high buffering capacity of carbonate rocks. Whereas the content of several exchangeable metals positively correlates with the pH value (r_{Pb}=0.55, r_{Zn}=0.52, r_{Cd}=0.51), so pH should be considered to be an important factor in the control of metal mobility.

The redox potential (Eh) correlates positively with the variable LIT1 (r=0.59) and negatively with variable LIT3 (r=–0.48). Electrical conductivity of water, the measure for the concentration of total dissolved solids, increases in the siliciclastic terrains (LIT2; r=0.54) and decreases in the orthometamorphites (LIT5; r=–0.58). Conductivity is also increased in the urban/rural areas (r=0.56).

Generally, the concentration of metals in water does not show correlation with the lithological variables. The exceptions are mercury and zinc which correlate positively with alluvial/proluviall sediments (LIT3; $r_{Hg}=0.82$, $r_{Zn}=0.66$). The increased Hg concentrations in the Sava river alluvium were attributed to the urbanization, industrial and mining activities upstream (NAMJESNIK-DEJANOVIĆ, 1994; PALIN-KAŠ et al., 1996; HALAMIĆ et al., 2003; PAVLOVIĆ et al., 2004). Exchangeable zinc also correlates with LIT3 (r=0.52).

The bulk metal concentrations display a strong lithological influence. Triassic carbonates (LIT1) correlate positively with the total Ca content (r=0.46) and negatively with K, Rb, Fe, Zn, Ti, V and Y concentrations. Alluvial/proluviall sediments (LIT3) show a positive correlation with Ca (r=0.39) and Sr (r=0.53). Parametamorphitic rocks (LIT4) correlate with total K (r=0.48), and orthometamorphites (LIT5) display correlations with the group of immobile elements, such as Fe (r=0.54), Cr (r=0.48), Zr (r=0.54), and Ti (r=0.44).

Whereas both of the investigated ore deposits were situated in the vicinity of the settlements, it was important to determine the influence of the urban/rural areas on the quality of stream water and sediments. Increased conductivity of stream waters within populated areas (r=0.56) generally indicates a higher content of total dissolved solids. The populated areas correlate well with the concentrations of nitrate (r=0.91), ammonia (r=0.86) and phosphate (r=0.64) indicating their common source, mostly from domestic wastewaters in the urban and rural areas without sewerage facilities. In the rural area, agricultural activities, including the use of synthetic and organic fertilizers, may also increase the nitrate, ammonia and phosphate contents in the stream waters. Furthermore, the urban/rural areas statistically correlate with the concentration of mercury in stream waters (r=0.60) and with the content of exchangeable lead (r=0.49) and zinc (r=0.82) from the stream sediments. For the appropriate interpretation of the heavy metals origin, it is important to keep in mind that the populated areas are mostly located on the alluvial deposits (LIT3; r=0.43).

As mentioned above, the Hg content in stream waters positively correlates with LIT3 and the urban/rural areas. Furthermore, it displays a negative correlation with the Eh value (r=–0.61) indicating the increased Hg mobility in a reducing, organic rich, environment, probably as a consequence of the Hg complexation with organic ligands. Among the organic ligands, humic substances are the most important compounds naturally occurring in soils, sediments and waters (THURMAN, 1986; GUNGOR, & BEKBOLET, 2010). As humic and fluvic acids are soluble in dilute alkali solutions, and the pH of all water samples collected over LIT3 is above 8, these types of organic molecules could significantly contribute to the mobilization of mercury from the alluvial sediments.

The concentration of copper in the water samples also correlates negatively with measured Eh values (r=–0.75) pointing to the importance of organic complexes in copper mobilization. According to WU *et al.*, (2002) humate and fluvate complexes mobilize Cu (II) ions at pH greater than 8. Negative correlation (r=–0.42) between lead in water and the measured redox potential suggests that formation of the Pb-organic complexes might also mobilize lead.

8. CONCLUSION

Although the Rude and the Sv. Jakob polymetallic ore deposits represent potential sources of numerous heavy metals, pollution of water and stream sediments downstream from the deposits was not recorded. Buffering reactions with the carbonate country rocks (dolostone, limestone), as well as with carbonate ore and gangue minerals (siderite, calcite), are responsible for the alkaline character of the drainage streams. Consequently, the deposits are not considerably weathered and the mobility of metals is significantly reduced.

The present study revealed that the populated areas represent a greater environmental threat than the investigated polymetallic ore deposits. Stream waters in the populated areas, especially in the urban and rural areas without sewerage facilities, are characterized by a decreased redox potential (attributed to the high organic matter content), increased conductivity and increased concentrations of nitrate, ammonia and phosphate. Stream sediments in the urban/rural areas have high contents of exchangeable lead and zinc.

The Sava river alluvium, characterized by its high mercury content, represents an additional environmental threat. The accumulation of Hg within the alluvial deposits is attributed to the urbanization, industrial and mining activities upstream. The overlapping of the populated areas (decreased redox potential, high organic matter content) and the Hg enriched alluvium resulted in the increased Hg mobility probably due to the complexation of mercury with the organic ligands.

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