

Distribution of copper and zinc in the soil of an industrial zone in the city of Garešnica, Croatia



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ABSTRACT

Soils from an industrial zone in Garešnica, Croatia have been analysed by EDXRF and XRD. In the area surrounding two adjacent factories named 'Bakrotisak' and 'Croatia Protekt', thirty soil sites (depth 5–15 cm) were sampled in December 2007, together with five soil sites from the forest (control samples) situated 0.5 km away. The locality was selected for its periodic, industrially induced environmental pollution which affects nearby streams and fish ponds, resulting in occasional fish kills in the region. Analysis included the determination of soil mineralogy, total organic matter content, cation exchange capacity, bulk multi-element composition and trace metal levels in leachates (exchangeable fraction). Multi-element concentrations in the control samples constituted natural background levels. The Kruskal-Wallis test showed higher, statistically significant ($p < 0.001$) concentrations of Cu in the soil surrounding 'Bakrotisak' compared to the control samples. Furthermore, leaching analysis confirmed copper contamination of the 'Bakrotisak' soil, as shown by the highly significant positive correlation, (the Kendall's Tau correlation coefficient > 0.99) between its extractable Cu and total Cu levels. Moreover, enrichment factors of Cu based on Al as a reference element are found to be > 2 for approximately 50% samples of the 'Bakrotisak' soil, suggesting moderate anthropogenic contamination.

Keywords: urban soil, anthropogenic impact, trace metal leaching, enrichment factor, 'Bakrotisak' factory, Garešnica, Croatia

1. INTRODUCTION

Garešnica is a small town with approximately 11 600 residents, situated in the central part of Croatia at the foot of the Moslavačka Gora hill. Its industrial zone includes the 'Bakrotisak' (B) and 'Croatia Protekt' (CP) factories, which have been in operation for the last thirty years. B is a chemical factory that produces flexible packaging products for the food, confectionery, pharmaceutical and tobacco industries, whereas the main activity of CP is rubber tyre protection. Although they both currently comply with official environmental policy, in B's beginnings there was an accidental spill

of organic liquid waste which caused one of the numerous fish kills in nearby fish ponds. In addition, the local drainage system is composed of a number of streams, the largest of which is the Ilova River. It drains the upstream area around Grubišno Polje which has a long tradition in the dairy industry. In the past, such a food industry did not have proper purification facilities and pollution fluxes purposely or accidentally released into the Ilova River, obviously affecting the ecosystem downstream.

MACKLIN (1992) describes the metal pollution of soils and sediments in the context of production-related activities (mining, smelting, etc.) and consumption-related activities (use, wear and disposal of consumer and commercial products). Sources of soil contamination in urban areas have been discussed by THORNTON (1990), and are grouped as follows: construction of buildings and demolition, household activities, waste disposal, transport, industry, and power stations. Among the aforementioned, factors influencing the B and CP soils would be industry and waste disposal (B – all sorts of liquid chemicals; CP – useless old tyres).

Over the last few decades much attention has been directed towards the geochemical patterns of soil pollution as soils are the ultimate sink for metals in the terrestrial environment (WARREN & BIRCH, 1987; LI & THORNTON, 2001; OREŠČANIN et al., 2003; MARTLEY et al., 2004). A growing body of literature is focused on assessing soil pollution by copper (KUO et al., 1983; MERRINGTON & ALLOWAY, 1994; GRAEDEL et al., 2002; SPATARI et al., 2002; BERTRAM et al., 2002; HU et al., 2006; LI et al., 2006).

So far, there has been no local sampling dealing with soil geochemistry in the Moslavina region. Garešnica is a city where the key sources of employment and income are the aforementioned B and CP factories as well as several others from the wood processing and textile industries. In spite of a general opinion that the county has a good environment, it must have been influenced by the presence of such longterm industry. Copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn) are the principal metals of concern in environmental surveys because they are often the main metal constituents of air pollutants and have known toxicities to biota (ADRIANO, 1986).

This paper evaluates the influence of three decades of industrial activities on neighbouring soil in the context of metal pollution, starting with the geochemical and mineralogical characterisation of soil in the vicinity of the B and CP factories. Soil samples from a nearby control site are used in the discussion as being representative of natural background levels. Using statistical methods, total and extractable trace metal concentrations are discussed with respect to soil mineralogy, bedrock lithology and anthropogenic setting.

2. MATERIALS AND METHODS

2.1. Site description and sampling strategy

The study area is located in the south-western corner of the Pannonian Basin near the eastern flanks of Moslavačka Gora hill. In the wider area around the sampling sites, Quaternary, Neogene sediments and sedimentary rocks together with the older Moslavačka Gora crystalline complex, comprising granite and medium-grade metamorphic rocks occur. Since the Basic Geological Map SFRY sheet Kutina for that area, although produced in the late 1980's, has never been published, for the broad information on surface geology, we are dependent on the neighbouring map (sheet Bjelovar – KOROLIJA & CRNKO, 1985), and related Explanatory notes (KOROLIJA et al., 1986) for general information on surface geology. However, very useful information about the geol-

ogy of area was published in the Croatian Geological Society Excursion guide book for the Moslavačka Gora (CRNKO, 1998) and by JURAK et al. (2006) where the youngest sediments are methodically described according to unpublished Geological Map for the Kutina sheet.

The Quaternary sediments extensively cover the research area and occur in different facies including the alluvium of recent flows, colluvium – proluvium deposits and organogenic swamp and flood-plain sediments. Alluvial sediments occur in the recent river valleys streaming from the Moslavačka Gora and feeding the Garešnica River which passes through the study area (Fig. 1). The sediments are composed of gravels, sands and silts of variable lithological composition comprising fragments of metamorphic and igneous rocks, limestones, sandstones and fossil fragments. In the Pleistocene, swamp and terrestrial loess produce a non-uniform complex alternating with terrestrial silts, swamp silts to clays and alluvial (mud and gravel) deposits (Fig. 1).

The Neogene is characterised by sediments (gravels, sands, silt and clays) and sedimentary rocks (limestones, marl, silty marl, sandstone and conglomerate) (Fig. 1). Differences in the local source area accompanied by separation processes and possible contributions from distant sources, (KOVAČIĆ & GRIZELJ, 2006) influence the local variability of sediments and sedimentary rocks.

The crystalline complex of the Moslavačka Gora is composed of granite and varieties of medium-grade metamorphic rocks including gneiss, migmatite, amphibolite, mica- and cordierite-schists (Fig. 1). Weathering of granite and medium grade metamorphic rocks of the Moslavačka Gora crystalline complex mainly contribute (*d*) to the materials comprising the sediments and sedimentary rocks of the research area.

The investigated area is covered by humic cambisols (ŠPOLJAR, 1999) characterised by their high moisture content as a consequence of high precipitation, flooding and high groundwater level (ŠKORIĆ, 1986). In Figure 1 numbers 1–15 is soil samples collected in the vicinity of the B and CP factories, constituting a total of 30 samples. The samples were collected every ten metres avoiding the local industrial infrastructure. Control samples (K) 1–5 were taken randomly in the forest soil developed upon the swamp and terrestrial loess, and recent flood sediments rich in siliceous fragments of acid igneous and medium-grade metamorphic rocks. Urban and control soil samples were all rather similar in their visual appearance, i.e. texture. However, the control samples were somewhat darker and more waterlogged in comparison to the urban soils groups.

At each location, after removing the top 5–10 cm of vegetative cover, approximately 1 kg of soil sample was taken with the sampling shovel. All samples were dried at 105 °C, then sieved through 0.5 mm and disaggregated in an agate mortar for further analysis.

2.2. Analytical methods

All solid samples were analysed for multi-element composition (Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Ga, As, Rb, Sr, Y, Zr) by energy dispersive X-ray fluorescence

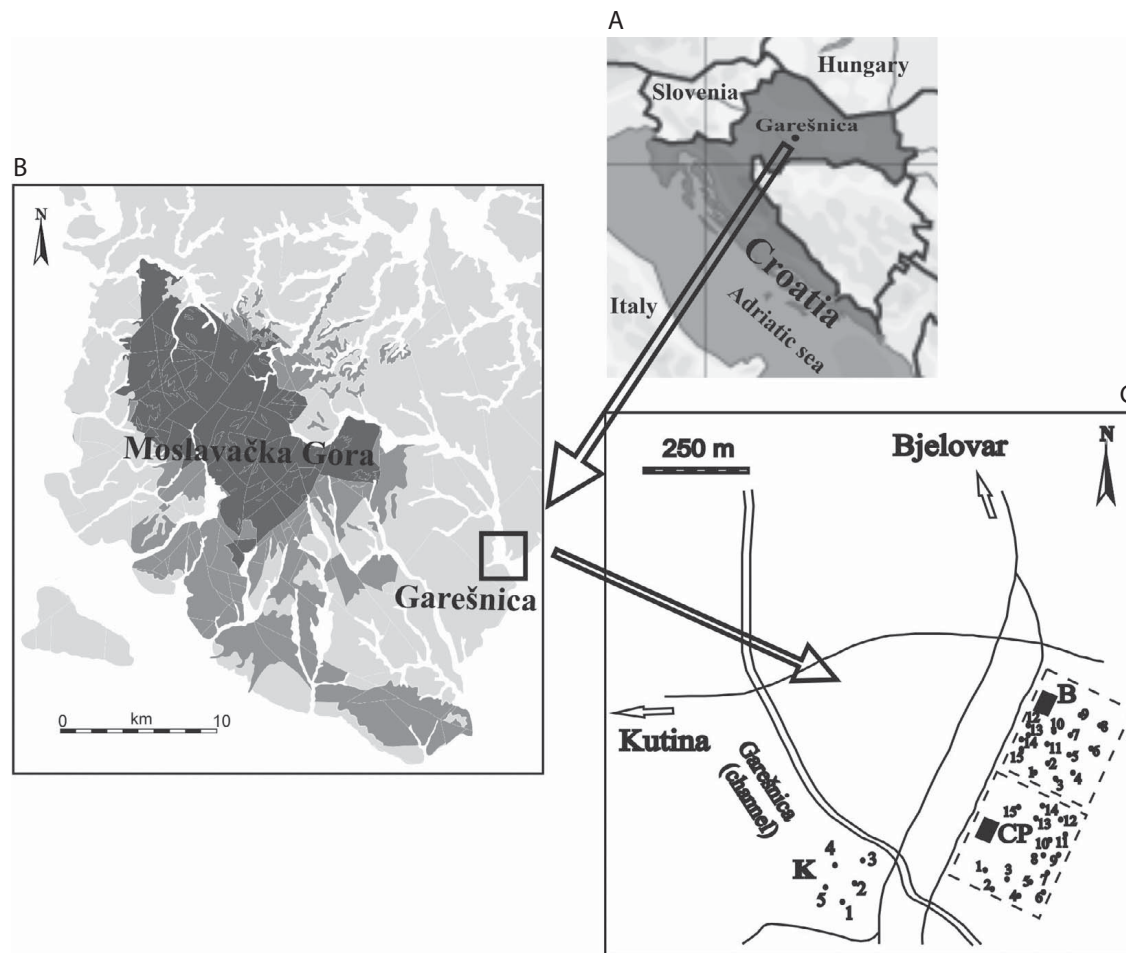


Figure 1: (A) The location of Garešnica within Croatia; (B) geological sketch map of Moslavačka Gora mountain showing the research area, crystalline rocks (black), Neogene sediments and sedimentary rocks (dark gray), Pleistocene loess (light gray), alluvial sediments of recent river valleys (white); (C) sketch map of the research site with sampling localities (B – the 'Bakrotisak' factory, CP – the 'Croatia Protpekt' factory, K – control samples).

(EDXRF). They were prepared for analysis as follows: 4 grams of each powdered sample (particle size <0.071 mm) were pressed into pellets of 20 mm in diameter (15 tons pressure, 30 s dwelling time). No binder material was added. The samples were placed in standard sample holders and loaded into the MiniPal 4 X-ray fluorescence spectrometer (PANalytical, Almelo, Netherlands). Spectral data were analysed by MiniPal/MiniMate software version 3.0.–63(2.64) (PANalytical). A calibration model for qualitative and quantitative analyses was created on the basis of measurements of the following standard reference materials: IAEA-SL1 (lake sediment), IAEA-Soil 7, IAEA 405 (stream sediments) and IAEA SL 3 (lake sediment). All four standard reference materials were supplied by the International Atomic Energy Agency (Vienna, Austria). Accuracy of the measurements was checked firstly by measuring the standard reference materials included in the calibration as unknown samples, while the second check was done by the measurement of 'NIST-2702' ('inorganic in marine sediments') standard reference material (National Institute of Standards and Technology, Broadway, Boulder, CO, USA) which was not included in the calibration of the spectrometer and could represent a real unknown sample. The goodness of the fit was checked from the following values: K Factor; RMS value, Relative RMS (%) and coefficient of correlation.

The leaching procedure was as follows: 1 gram of each powdered soil sample (dry weight) was subjected to extraction with 1M NH_4OAc -pH 7 (exchangeable fraction). The extracts were diluted to 100 mL with double distilled water divided into two subsamples, and adjusted to pH 3 and 11 by the addition of concentrated $\text{HNO}_3/\text{NH}_4\text{OH}$, respectively. After the pH adjustment, samples were preconcentrated by 1 mL of freshly prepared 1% w/v solution of ammonium-pyrolidinedithiocarbamate (APDC). After the complexation which lasted 20 min, the suspension was filtered through a Millipore filter (0.45 mm) in order to obtain thin targets that were irradiated by X-ray for 300 s. All targets were analysed by EDXRF. The obtained results were multiplied by the dilution factor and the percentage of the extracted element was calculated from the formula: $(\text{C}_{\text{tot}} - \text{C}_e / \text{C}_{\text{tot}}) * 100$ (where C_{tot} – mass concentration of the element in bulk sample, C_e – mass concentration of the element extracted from the soil).

X-ray diffraction analysis was carried out on a Philips PW 3040/60 X'Pert PRO powder diffractometer (PANalytical) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54055$ Å) at 40 kV and 40 mA. For identification of phyllosilicates the samples were additionally treated in ethyleneglycol vapour for 24 hours, and heated at 400 and 550 °C for 30 minutes in each case.

The cation exchange capacity was determined by mixing the samples with a 0.01 mol dm⁻³ solution of copper ethylenediamine complex [Cu(en)₂]²⁺ (AMMANN et al., 2005). The subsequent change in Cu²⁺ concentration due to sample adsorption was determined by UV-VIS spectrophotometer Hach DR/4000 U 8 (Hach Company, Loveland, CO, USA) at 548 nm absorption line. The pH of the [Cu(en)₂]²⁺ solution upon mixing with each sample was around 7.

Loss on ignition, as an indicator of the organic matter content of samples, was determined by heating in an oven at 375 °C over 24 h.

Data processing was performed with the STATISTICA Version 7 software.

3. RESULTS AND DISCUSSION

The evaluation of possible trace metal pollution linked to industrial activity was studied by a comparison of soil around the B and CP factories with the K samples collected from a nearby forest (Fig. 1). Numerous papers deal with soil metal concentrations above what would naturally occur, comparing them with the quantified geochemical (natural) background levels reflecting natural processes uninfluenced by human activities (SALOMONS & FÖRSTNER, 1984; HANSON et al., 1993; DASKALAKIS & O'CONNOR, 1995; PROHIĆ et al., 1995; MATSCHULLAT et al., 2000; MIKO et al., 2001; REIMANN & GARRETT, 2005; REIMANN et al., 2005). Since the K samples were collected from the forest assumed to represent the study area in its supposed pre-industrialization state, their geochemical features will be discussed first, followed by explanation of the chemical and mineralogical nature of the urban soil changes presumably caused by the industrial activity. As the first step in data analysis is estimating the distribution of the measured variables (REIMANN & FILZMOSER, 2000), the Shapiro-Wilk W test shows moderate to perfect normality for all variables in the K samples, except for potassium and cobalt; e.g. the results of the test for Cu and Zn are as follows: SW-W = 0.97 and 0.88, $p = 0.91$ and 0.34 , respectively. However, the K data (as well as the B and CP data), like any other environmental data, are characterised by the problem of small sample size (GLEIT, 1985), in which case disproving normality by the hypothesis test is rather difficult. Therefore, distribution-free nonparametric procedures were employed here. The Kendall's Tau correlation matrix was calculated for Al, Fe, Ni, Rb, LOI, Cu, Zn, Pb, and As. The first five variables in a row represent conservative components, the values of which are commonly unaffected by contaminant inputs, whereas the last four are selected trace metals which are commonly enriched as a result of human activities (SALOMONS & FÖRSTNER, 1984; PROHIĆ et al., 1995). The results (Table 1) demonstrate a very strong positive correlation between Cu and Rb (>0.99), strong correlations (0.95) for the pairs Fe-Rb and Fe-Cu, and finally less strong, but still statistically significant correlations (0.84) for the Al-Rb, Al-LOI, Al-Cu, and Al-Zn pairs. Remaining correlations are all positive (except for Fe-Ni = -0.11), but not statistically significant. These associations to a large extent have resulted

Table 1: The Kendall's Tau correlation matrix for the K soil group (numbers in bold are significant at $p < 0.05$; number of samples is 5).

	Al (%)	Fe (%)	Ni (ppm)	Rb (ppm)	LOI (%)	Cu (ppm)	Zn (ppm)	Pb (ppm)	As (ppm)
Al (%)	1.00								
Fe (%)	0.76	1.00							
Ni (ppm)	0.12	-0.11	1.00						
Rb (ppm)	0.84	0.95	0.00	1.00					
LOI (%)	0.84	0.53	0.40	0.60	1.00				
Cu (ppm)	0.84	0.95	0.00	>0.99	0.60	1.00			
Zn (ppm)	0.84	0.53	0.00	0.60	0.60	0.60	1.00		
Pb (ppm)	0.36	0.32	0.20	0.40	0.00	0.40	0.40	1.00	
As (ppm)	0.60	0.53	0.00	0.60	0.60	0.60	0.20	0.00	1.00

from natural processes occurring in soils formed by the weathering of acid igneous rocks (LOUGHNAN, 1969; HANSON et al., 1993), thereby confirming that the chemical composition of the K soil group could represent local-scale background data.

Cation exchange capacity (CEC) determination for the K soil yielded 16.1 mEq/100g, and 4.6 mEq/100g for the soil after the removal of organic matter. The original soil CEC corresponds to soils of loam and silty loam textures. The significant reduction of CEC upon organic matter removal indicates the dominant role of organic matter in the adsorption capacity of the investigated soil. Indeed, the mineral composition of the K soil comprises quartz, plagioclase, chlorite, mica/illite and kaolinite (Fig. 2) without the presence of swelling clay minerals which are strong adsorbents. Thus, the determined mineral composition supports low CEC values strongly reflecting the occurrence of the phyllosilicate minerals with general CEC values ranging from 5 to 25 mEq/100g (VAN OLPHEN & FRIPIAT, 1979; YONG & WARKENTIN, 1975).

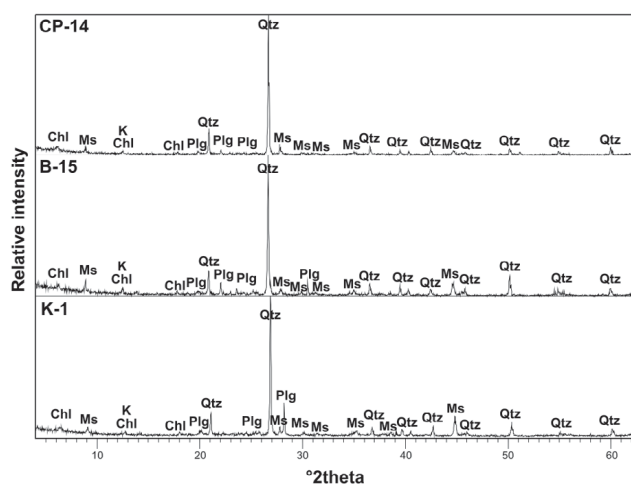


Figure 2: XRD patterns representing mineral composition of the K soil (K-1), and two urban soil samples (B-15 and CP-14) selected on the basis of their enrichment in Cu (Qtz – quartz; Chl – chlorite; Ms – muscovite/illite; K – kaolinite, Plg – plagioclase).

Table 2: Basic statistical parameters (SD – standard deviation) of the measured variables (LOI – loss on ignition) in three soil groups defined by sampling localities (K – check samples, number of samples 5; B – soil surrounding the B factory, number of samples 15; CP – soil surrounding the CP factory, number of samples 15).

	mean			median			min			max			SD		
	K	B	CP	K	B	CP	K	B	CP	K	B	CP	K	B	CP
Cu (ppm)	34.60	92.05	54.17	34.8	65.8	41.2	30.7	37.3	33.2	37.7	331.8	186.7	2.75	75.63	40.45
Zn (ppm)	146.00	161.61	160.77	145.0	156.7	156.6	135.3	129.2	132.7	162.1	213.9	224.3	9.87	23.88	21.50
Pb (ppm)	24.80	22.48	22.75	24.1	22.2	22.2	22.3	15.3	14.3	30.1	30.3	43.8	3.19	4.03	6.92
As (ppm)	13.26	13.74	13.19	13.4	13.3	13.2	12.1	12.1	11.3	14.4	15.5	15.1	1.04	1.25	1.10
Al (%)	13.86	14.07	13.78	13.9	13.7	13.9	13.4	12.1	11.8	14.2	15.8	15.2	0.29	0.94	0.80
K (%)	1.96	2.01	1.96	2.0	2.0	2.0	1.9	1.7	1.6	2.0	2.2	2.1	0.05	0.13	0.13
Ca (%)	0.50	0.97	0.72	0.5	1.0	0.7	0.4	0.6	0.6	0.6	1.5	1.4	0.10	0.26	0.21
Ti (ppm)	6453.04	6015.73	6097.66	6452.6	6033.9	6088.2	6386.8	5688.2	5803.4	6512.1	6208.0	6318.4	45.36	123.56	130.12
V (ppm)	164.20	155.70	157.69	162.1	153.9	157.4	156.0	139.5	147.3	172.9	170.6	169.2	7.12	9.47	5.54
Cr (ppm)	152.36	160.95	149.26	151.5	160.3	150.2	144.7	145.9	129.2	161.7	192.9	172.3	7.22	10.76	12.71
Mn (ppm)	791.26	857.29	895.46	834.1	825.1	875.0	601.0	757.8	756.2	1021.3	1025.9	1333.6	170.00	78.71	136.70
Fe (%)	4.34	4.77	4.56	4.4	4.8	4.6	4.1	4.2	3.8	4.5	5.3	5.1	0.18	0.35	0.30
Co (ppm)	16.56	18.18	17.23	16.7	18.2	17.4	15.6	16.1	14.9	17.1	19.6	19.2	0.56	1.10	0.99
Ni (ppm)	70.70	75.32	73.76	70.8	76.3	72.0	66.7	67.9	67.7	76.0	84.8	82.8	3.93	4.55	4.34
Ga (ppm)	24.48	22.07	22.83	24.3	21.8	23.1	23.5	18.6	18.5	25.5	25.9	25.0	0.78	1.77	1.59
Rb (ppm)	157.26	145.34	146.16	156.9	144.3	147.5	148.0	123.6	116.5	170.4	160.4	165.7	8.61	10.05	11.97
Sr (ppm)	130.66	132.37	135.99	131.0	132.1	136.7	128.8	123.2	129.4	131.7	138.2	141.3	1.20	4.27	3.33
Y (ppm)	101.52	101.52	106.21	102.5	105.3	107.3	93.1	80.0	88.8	111.1	118.9	126.4	7.17	13.71	9.67
Zr (ppm)	1044.26	832.51	914.93	1027.2	867.9	912.2	930.6	602.7	643.7	1207.0	1040.7	1360.9	103.19	145.09	171.55
LOI (%)	7.98	6.05	6.54	8.1	6.0	6.2	7.2	4.2	3.8	8.5	7.4	8.9	0.51	1.06	1.64

As regards the properties of the B and CP soil groups, a rough inspection of trace metal contents (Table 2) shows that Cu and Zn mean and median values calculated for the B and CP soil groups exceed the values of the control K group. The Kruskal-Wallis test confirms that only Cu has higher, statistically significant ($p < 0.001$) values in the B soil compared to the K soil. This finding obviously indicates a contamination to varying extents which is discussed in further detail below. An opposite trend is shown by Pb and As being lower or equal in the B and CP compared with the K group. In view of the fact that there is a local road along the forest where the K samples were taken (Fig. 1), their slightly higher Pb values are not surprising. Lead is known to deposit within 100 m of a road (THORNTON, 1990). LOI values (Table 2), ascribed to organic matter content, and were found to be higher in the K group than in the other two groups.

The mineralogy of the B and CP soil samples does not significantly differ from the K group containing quartz, plagioclase, chlorite, mica/illite and kaolinite (Fig. 2). The presence of swelling clay minerals was not observed. As for the K group, the mineral composition does not presume high adsorption capacities and the CEC values determined for the K soil could be considered representative of both the CP and B soil samples.

Next, when testing the normality of analysed variables in urban soil of the B group, a striking departure from the nor-

mality was discovered for Cu ($SW-W = 0.69$, $p < 0.001$), a moderate one in case of Al, K, Cr, Mn, As, and Y, whereas the rest exhibit normal distribution (e.g. Zn: $SW-W = 0.94$, $p = 0.50$). The non-normal distribution of Cu is consistent with the results of the Kruskal-Wallis test, additionally underpinning the postulation that copper contamination occurs in the B soil group. Concerning the CP group, the greatest departure from normality was again discovered for Cu ($SW-W = 0.49$, $p < 0.001$), a moderate one in case of Zn ($SW-W = 0.82$, $p = 0.008$), K, Ca, Mn, Fe, Pb, and Ga, whereas the rest exhibit normal distribution. Generally, this finding could be attributed mostly to natural geochemical processes commonly occurring in weathering profiles (LOUGHNAN, 1969), and to a lesser degree to the copper contamination which is mainly of anthropogenic origin (HALAMIĆ et al., 2003). A similar conclusion could be drawn from the Kendall's Tau correlation matrix calculated for the B and CP groups. The general assessment of its results is as follows (Table 3):

- the highest correlation (0.77) found for the Al-Rb pair in the CP group, defining the geogenic association, is statistically significant, yet lower than the weakest (0.84) significant correlation found for the K group (including the pairs Al-LOI, Al-Cu, and Al-Zn; see the text above);
- correlations among the conservative components (Al, Fe, Ni, and Rb) are mostly low, non-significant and even negative, showing relationships that cannot be explained by common geochemical processes in weathering profiles;

Table 3: The Kendall's Tau correlation matrix for the B and CP (in italics) soil groups (numbers in bold are significant at $p < 0.05$; number of samples in each group is 15).

	Al (%)	Fe (%)	Ni (ppm)	Rb (ppm)	LOI (%)	Cu (ppm)	Zn (ppm)	Pb (ppm)	As (ppm)									
Al (%)	1.00	<i>1.00</i>																
Fe (%)	0.59	0.62	1.00	<i>1.00</i>														
Ni (ppm)	0.13	<i>-0.04</i>	0.23	<i>-0.16</i>	1.00	<i>1.00</i>												
Rb (ppm)	0.73	0.77	0.66	0.70	0.17	<i>0.08</i>	1.00	1.00										
LOI (%)	0.33	<i>0.03</i>	0.19	<i>0.31</i>	<i>-0.13</i>	<i>0.02</i>	0.38	<i>0.18</i>	1.00									
Cu (ppm)	0.06	<i>-0.09</i>	<i>-0.17</i>	<i>0.10</i>	<i>-0.29</i>	<i>0.29</i>	0.00	<i>0.09</i>	0.27	0.30	1.00	1.00						
Zn (ppm)	0.27	<i>-0.28</i>	0.23	<i>0.04</i>	<i>-0.10</i>	<i>0.06</i>	0.38	<i>-0.09</i>	0.46	0.39	0.58	<i>0.37</i>	1.00	1.00				
Pb (ppm)	<i>-0.08</i>	<i>0.07</i>	<i>-0.17</i>	<i>0.19</i>	-0.46	<i>-0.15</i>	<i>-0.02</i>	<i>0.05</i>	0.33	0.47	0.48	0.39	0.40	0.43	1.00	1.00		
As (ppm)	0.44	0.22	0.24	0.41	<i>-0.12</i>	<i>-0.08</i>	0.50	<i>0.18</i>	0.66	0.26	0.25	0.38	0.33	0.34	0.35	0.48	1.00	1.00

- with the exception of a significant correlation between Rb and Zn (0.38) in the B group, all other correlations of either Cu or Zn with respect to the conservative elements are low, non-significant and even negative, presumably due to processes other than geogenic ones (HALAMIĆ et al., 2003);
- a positive correlation between organic matter content and Zn retention by soil (ADRIANO, 1986) is confirmed in this study since significant LOI-Zn correlations are found for both soil groups (0.46 and 0.39, respectively). Furthermore, it is of interest to note that Cu shows no significant correlation to LOI as opposed to the fact that copper is one of metals exceptionally tightly bound by humates (SALOMONS & FÖRSTNER, 1984). Trace metal correlations in the K group (Table 1) are non-significant, ranging from 0.00 to 0.60, whereas their values in the B and CP groups (Table 3) are significantly positive (the pairs Cu-Zn and Cu-Pb in particular), which would indicate an anthropogenic influence on the trace metal composition of the investigated urban soil (HALAMIĆ et al., 2003).

From this, it can be inferred that a considerable part of the enrichment of Cu (Table 2) in the B soil group (and partly in the CP group, too), as compared with the respective contents in the soils from northwestern Croatia (HALAMIĆ et al., 2003), is due to input from the B's industrial emissions. HALAMIĆ et al. (2003) found the Cu content varying from 5 to 248 ppm, with the mean and median values of 25 and 22 ppm, respectively. Similarly, ADRIANO (1986) points out that the Cu content of most soils generally falls in the 20 to 40 ppm range, and that soils derived from acid igneous rocks contain lower concentrations of Cu than those developed from basic igneous rocks.

In Figure 3 concentrations of Cu and Zn have been plotted as a function of sampling localities. From this, it can be clearly seen that both variables show concordant patterns in the two sites that is in a reasonably good agreement with their correlations (Table 3). With respect to fairly low and uniform Cu and Zn values in the CP group, there is a sharp increase in Cu values at the sites CP13 (104.9 ppm) and CP14 (186.7 ppm) located near the fence surrounding the B factory (Fig. 1). These results additionally confirm that the copper contamination of the investigated urban soil is solely due to the B's industrial activity.

The next step to confirm this is the leaching analysis. It is well known that the exchangeable phase represents the most mobile fraction of elements which is introduced by anthropogenic activities and bound to the sediment in adsorbed form (SALOMONS & FÖRSTNER, 1984). Leaching analysis was carried out on several samples from both urban soil groups, selected according to their lowest and highest total Cu values (Fig. 3) in order to maximise the possible difference in trace metal leachate concentrations. Figure 4 presents the data concerning the copper leachate levels measured in selected samples of the B soil group. It clearly shows that the patterns of the total Cu, NH_4OAc -extractable Cu and the percentage of Cu constituting exchangeable phase are fairly similar; in other words, sampling localities with elevated total Cu values contain much more bioavailable Cu than those with background total Cu levels. This finding is consistent with a highly significant positive Kendall's Tau correlation coefficient (>0.99) between the extracted and total Cu levels in the B soil group. Hereby, these data definitely confirm strong human influence on soil composition in the vicinity of the B factory. Referring to the CP group, leaching analysis of Zn found a highly significant negative correlation (>-0.99) between extracted and total Zn values, suggesting that their origin would be geogenic. The Kendall's Tau correlation coefficients calculated for extracted and total Cu (the CP group)

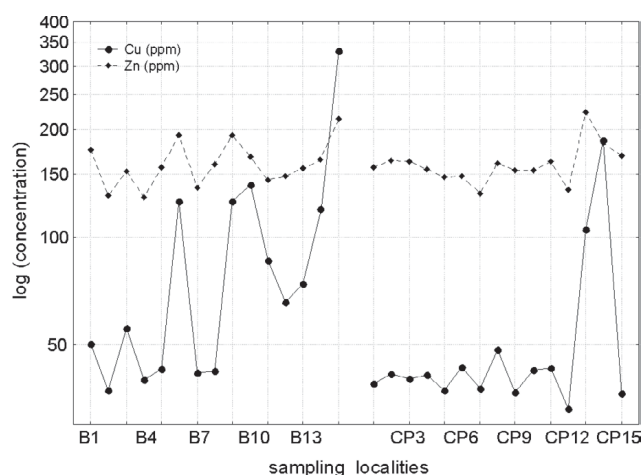


Figure 3: Total Cu and Zn concentrations in the urban soil groups.

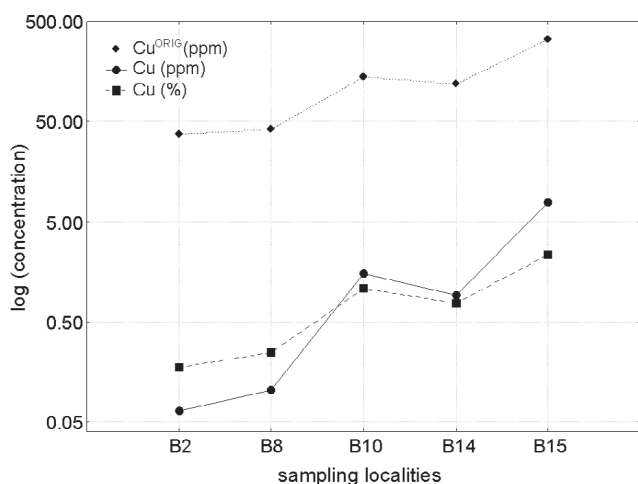


Figure 4: The results of leaching analysis carried out on several samples of the B soil group (Cu^{ORIG} – Cu total concentration in soil, Cu (ppm) – Cu concentration in leachates (exchangeable phase), Cu (%) – percentage of Cu constituting exchangeable phase).

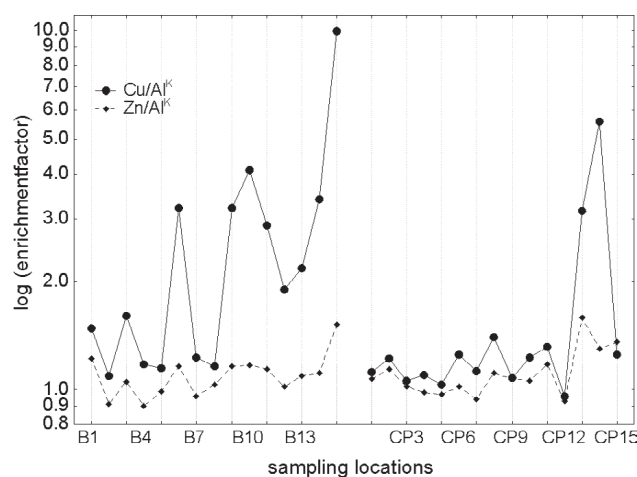


Figure 5: Enrichment factor values of Cu and Zn calculated for the B and CP soil groups. $\text{Metal}/\text{Al}^{\text{K}} = (\text{conc. metal}_{\text{sample}}/\text{Al}_{\text{sample}})/(\text{metal}_{\text{K soil}}/\text{Al}_{\text{K soil}})$.

and Zn (the B group) levels are irregular and insignificantly low. Leaching analysis of the urban soil groups is strongly supported by XRD phase analysis (Fig. 2) which shows no other mineral phases except those originating from surrounding parent rocks. These mineral phases, especially phyllosilicate phases related to clay minerals, together with organic matter are adsorbents for the amount of elements derived from human activity.

Finally, the variation of Cu and Zn content in the investigated urban soils was expressed as metal/aluminium ratios (FÖRSTNER & WITTMANN, 1979; HANSON et al., 1993; DASKALAKIS & O'CONNOR, 1995). FÖRSTNER & WITTMANN (1979) emphasise that 'the ratio of the element under consideration to another element of little variability, e.g., an element with 'conservative behaviour', represents the 'sediment enrichment factor'. In other words, this factor, commonly called 'enrichment factor' (EF), is simply a way of quantifying the possible environmental impact. There are three categories of enrichment factors (GOLCHERT et al., 1991): $\text{EF} \leq 2$ mean no anthropogenic contribution, $2 < \text{EF} < 10$ indicates a possible anthropogenic contribution, and $\text{EF} \geq 10$ clearly indicates an anthropogenic contribution. PROHIĆ et al. (1995) point out that 'the choice of reference material and appropriate conservative element is crucial to the final conclusions'. In this paper, a standard reference material is represented by the K soil group, the trace element content of which can be taken as background values. The choice of Al as a reference element is based on the fact that it is often used as a normaliser of trace element data, due to its high natural abundance and because it is not associated with anthropogenic input (FÖRSTNER & WITTMANN, 1979; PROHIĆ et al., 1995). Linear regression analysis conducted for Cu regarding the B and CP soil group's shows that aluminium accounts for only 0.1% and 2% of the metal concentration variability, respectively. In the case of Zn, respective results are also low, i.e. 16% and 6%. In contrast, Al accounts for more than 80% of the Cu and Zn variability ($r^2 > 0.8$) in the K soil group. The poor correlation of Cu and Zn with Al in

the B and CP groups is evidence for the anthropogenic contribution of these trace metals to the investigated urban soils (FÖRSTNER & WITTMANN, 1979; PROHIĆ et al., 1995). In Figure 5 enrichment factors of Cu and Zn have been plotted as a function of sampling localities. Apart from their general similarity with total metal values (Fig. 3), Figure 5 suggests that approximately 40% of Cu samples of the B group fall in the category $2 < \text{EF} < 10$, whereas one sample shows $\text{EF} = 10$. Moreover, samples CP13 and CP14 also fall in the category $2 < \text{EF} < 10$. Therefore, it has been inferred on the basis of Cu EFs and the results of leaching analysis that Cu concentrations in the urban soil groups are elevated above natural levels as a result of factory B's industrial activity.

4. CONCLUSIONS

Analytical results show that natural geochemical processes occurring in weathering profiles are largely responsible for the overall geochemical and mineralogical composition of the investigated soils, but activities of the chemical industry left their impact on the soil in the vicinity of factory B.

In comparison with the background element composition of the control soils, the urban soil surrounding factory B shows elevated Cu values as a consequence of anthropogenic activity. The Kruskal-Wallis test confirmed this difference as statistically significant at $p < 0.001$.

The CEC values of the control soil samples are 16.1 mEq/100g, and 4.6 mEq/100g after the removal of organic matter. Mineral composition of the all three soil groups is represented by quartz, plagioclase, chlorite, mica/illite and kaolinite. The observed mineral composition corresponds well to the measured CEC value strongly suggesting the occurrence of phyllosilicate minerals with general CEC values ranging from 5 to 25 mEq/100g.

It is inferred that a highly significant positive Kendall's Tau correlation coefficient (> 0.99) between extracted and total Cu levels in the B soil group confirms the influence of factory B on the urban soil copper values. Furthermore, the

Kendall's Tau correlation coefficients between Cu and the conservative elements are mostly low, non-significant and even negative, showing relationships that cannot be explained by common geochemical processes in weathering profiles.

Data concerning Cu enrichment factors show that approximately 40% of samples of the B group fall in the category $2 < EF < 10$, whereas one sample shows $EF = 10$. The Cu content in the urban soil groups is found to be elevated above natural levels as a result of B's industrial activity.

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