NAT. CROAT. | VOL. 9 | No 1 | 41–59 | ZAGREB | March 31, 2000

ISSN 1330-0520
UDK 577:551.510.42˙504.54(497.5/1-15)

original scientific paper / izvorni znanstveni rad

GEOCHEMICAL BASELINE MAPPING AND LEAD POLLUTION ASSESSMENT OF SOILS ON THE KARST IN WESTERN CROATIA

SLOBODAN MIKO[1], ZORAN PEH[1], DRAGAN BUKOVEC[2], ESAD PROHIĆ[3] & ŽELJKO KASTMÜLLER[1]

[1]Institute of Geology, Sachsova 2, Zagreb, HR-10000, Croatia

[2]Croatian Natural History Museum, Demetrova 1, Zagreb, HR-10000, Croatia

[3]Faculty of Science, University of Zagreb, Zagreb, HR-10000, Croatia

Miko, S., Peh, Z., Bukovec, D., Prohić, E. & Kastmüller, Ž.: Geochemical baseline mapping and lead pollution assessment of soils on the karst in Western Croatia. Nat. Croat., Vol. 9, No. 1., 41–59, 2000, Zagreb.

The area studied follows the sharp geomorphological boundary at which an abrupt change occurs from a Mediterranean to a cold continental climate. The dominant soils are brown soils developed on limestone and melanosols developed on dolomite. Twenty five elements were analysed in the fine soil sample fraction (– 63 m) by ICP-AES after total dissolution in a mixture of concentrated acids (HF, HCl, HNO_3, $HClO_4$). The topsoil geochemical data sets of both western Croatia and the national park were processed through R-mode factor analysis to determine the patterns of geochemical association among elements and to detect and identify possible anomalies of elements that could be associated with airborne contamination. A four-factor model accounted for 75 % of the total variance. The association of Pb, Zn, Cd, As and P was interpreted as associated with airborne contamination and acid rain deposition. The factor score map of the Pb-Zn-Cd-As-P association shows high positive scores located along the climate boundary that passes through Risnjak National Park and further to the southeast over Mt Velebit. Along this regional climate barrier, the deposition of airborne contaminants carried by westerly winds from both regional (NE Italy) and local (Rijeka, oil refineries and oil- and coal-fired power plants) sources evidently occurred. With the aid of factor analysis it was possible clearly to identify areas influenced by airborne pollution. Total lead concentrations detected at altitudes higher than 1050 m above sea level in the national park were higher than 80 ppm (maximum 139 ppm Pb) while the regional mean Pb concentration is 43 ppm. Also a stoichiometric approach was applied to compensate for the influence of the amount of the clay fraction by modeling soil geochemical baselines on the basis of the calculation of the Pb enrichment factor (EF). As a basis for these calculations, reference soils with the presumed least anthropogenic influence from the island of Mljet (78 samples) were used. In the area of Risnjak National Park approximately 20% of the samples have an Pb EF higher than 2, which can be considered polluted, while the whole region of Western Croatia (not including Istria) has less than 3% of Pb enriched samples. All the samples from the area of Mt Velebit contain Pb within the baseline range (EF < 2).

Key words: acid rain, soils, airborne pollution, karst, geochemical baseline, lead, enrichment factor, Risnjak national park, Western Croatia

Miko, S., Peh, Z., Bukovec, D., Prohić, E. & Kastmüller, Ž.: Geokemijsko kartiranje i procjena onečišćenja olovom tala na kršu zapadne Hrvatske. Nat. Croat., Vol. 9, No. 1., 41–59, 2000, Zagreb.

Istraživano područje pruža se duž oštre geomorfološke granice koja označava nagli prijelaz iz mediteranske u hladnu kontinentalnu klimu. Dominantan tip tla čine smeđa tla razvijena na vapnencu i crnice razvijene na dolomitu. Analizirano je 25 elemenata u sitnoj frakciji uzorka (– 63 m). Uzorci su nakon otapanja u smjesi koncentriranih kiselina (HF, HCl, HNO_3 i $HClO_4$) podvrgnuti analizi metodom ICP-AES. Rezultati analize tla obrađeni su R-metodom faktorske analize kako bi se utvrdili oblici asocijacija među elementima te otkrile i protumačile moguće anomalije koje bi mogle potjecati od atmosferskog zagađenja. Ukupno 75 % ukupne varijabilnosti dobivenog faktorskog modela koncentrirano je u prva četiri faktora od kojih se Pb-Zn-Cd-As-P faktor može povezati s kiselim kišama i atmosferskim zagađenjem. Faktorska karta ove asocijacije elemenata dobro definira klimatsku granicu koja prolazi kroz Nacionalni park »Risnjak« pružajući se dalje prema jugu prema Velebitu. Duž ove regionalne klimatske barijere dolazi do obaranja aerosola nošenih zapadnim vjetrovima od regionalnih (SI Italija), ali i lokalnih (naftna industrija u Rijeci, termoelektrana u Plominu) zagađivača. Pomoću faktorske analize bilo je moguće jasno utvrditi područja zagađena putem zračnih struja. Ukupna koncentracija olova otkrivena na visinama preko 1050 m nad morem iznosi u Nacionalnom parku više od 80 ppm (max = 139 ppm), dok je prosječna regionalna koncentracija 43 ppm. U analizi je primijenjen i stehiometrijski pristup koji se sastoji u modeliranju osnovnih geokemijskih nivoa pomoću linearne regresije između metala i Al s ciljem neutraliziranja utjecaja glinovite komponente, a također i izračun faktora obogaćenja (EF) za olovo. Kao osnova za te izračune korištena su tla otoka Mljeta (78 uzoraka) za koja se pretpostavlja da odražavaju najmanji utjecaj antropogene komponente. U području Nacionalnog parka »Risnjak« približno 20 % uzoraka ima EF vrijednost za Pb višu od 2 (EF > 2), što se može smatrati kao zagađenje, dok čitavo područje zapadne Hrvatske (osim Istre) ima manje od 3 % olovom obogaćenih uzoraka. Svi uzorci s područja Velebita imaju vrijednost EF za olovo unutar područja geokemijskog šuma (EF < 2) pa se može smatrati da je utjecaj atmosferskog zagađenja u tom području manje izražen.

Ključne riječi: kisele kiše, tlo, atmosfersko zagađenje, krš, geokemijski šum, olovo, faktor obogaćenja, Nacionalni park »Risnjak«, zapadna Hrvatska

INTRODUCTION

Geochemical baseline mapping and environmental studies of carbonate terrain in Croatia in the past fifteen years (PIRC & MAKSIMOVIĆ, 1985; PIRC *et al.*, 1991; PROHIĆ *et al.*, 1997; PROHIĆ *et al.*, 1998; MIKO *et al.*, 1999) have shown that some areas previously considered well preserved natural karstic landscapes have been greatly affected by airborne pollution.

The unique positions of Risnjak National Park and the Velebit protected area (Fig. 1), on the geomorphological boundary between the coastal Mediterranean part of Croatia and the continental hinterland have evidently caused a considerable atmospheric fallout impact on their soil cover. The sources of this atmospheric pollution are both local and regional. In a regional sense the geomorphological boundary extends along the Dinaric mountain chain that arches along the Adriatic coast and is the first barrier to atmospheric pollutants from the whole north eastern part of It-

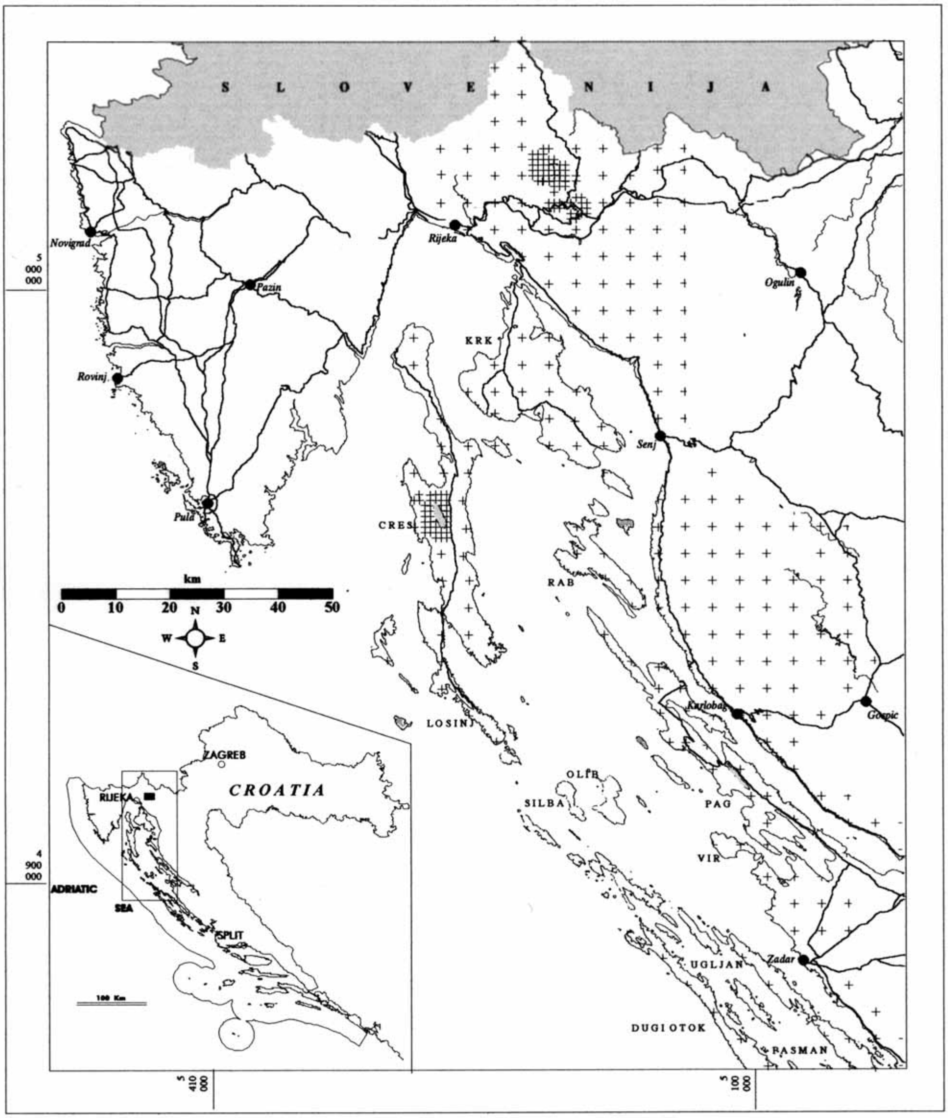

Fig. 1. Map of Croatia and location of the studied areas (W. Croatia open rectangle and Risnjak national park, filled box on the small map); + topsoil sampling sites (5x5 km and 1x1 km grids).

aly. During the last three decades the forests of this region have been declining (PRPIĆ, 1987; PRPIĆ *et al.*, 1991). This phenomenon is especially marked in the fir and beech-fir forests while fir is the most endangered of the tree species. Studies of soil acidity and heavy metal humus concentrations (GLAVAČ *et al.*, 1987; VRBEK &

GAŠPARAC, 1992) indicate that the region of Gorski Kotar is subject to moderate air pollution. Topoclimatic analysis of Risnjak National Park (ANTONIĆ, 1996) shows pronounced exposures to west cyclone incomings and forest decline as a consequence of acid rain deposition. Moreover, the major Van Bebber cyclone path for this region, the so-called Genova cyclone, crosses the area from west to east (PANDŽIĆ, 1989). According to ROBINSON (1984), this cyclone could be a major transporter of the air pollutants that are being deposited on the geomorphological barrier of Gorski Kotar.

The vulnerability of karstic landscapes is due to the very shallow acid soil (pH 4.5–6.5) developed on the carbonate rocks and its limited ability to buffer the effects of airborne pollution.

In the past decades it has been recognized that atmophile trace metals such as As, Hg, Pb, Zn, Cd and Cu contribute most to soil pollution as atmospheric fallout (LANTZY & MACKENZIE, 1979; FÖRSTNER, 1995; WILSON & BELL, 1996; MATSCHULLAT & BOZAU, 1996; KUBIN & LIPPO, 1996).

To assess the pollution impact on the soil cover of Risnjak National Park and the regional climate boundary, data obtained during the geochemical baseline survey were subjected to R-mode factor analysis within which the airborne element association (Pb, Zn, P, As, and Cd) was singled out and the distribution of the resulting factor scores interpreted as pollution impact. In addition, a stoichiometric approach was applied by modeling soil geochemical baselines on the basis of the calculation of the Pb enrichment factor (HASSAN & ISMAIL, 1993; PROHIĆ *et al.*, 1995; MIKO *et al.*, 1999). As a basis for these calculations, reference soils with the presumed least anthropogenic influence from the island of Mljet (78 samples) were used.

GEOLOGY

Western Croatia is distinguished by various features characteristic of karst landscapes. These phenomena are most developed and most numerous in the zone of the so-called »high« Dinaric karst spreading over the elongated coastal mountains such as Velebit. The area consists mainly of Mesozoic limestone and dolomites, occasionally with flysch and associated sedimentary, mostly carbonate, clastic rocks, such as breccias and conglomerates. The oldest, Upper Paleozoic rocks i.e., sandstone, shales and siltstones are exposed only in the hinterland (Gorski kotar and Lika).

Upper Triassic and Liassic dolomites intercalated with limestone cover almost the entire area within the boundaries of the national park. Further to the west and northwest, the dolomite series of Triassic and Liassic age is progressively replaced by limestone, which prevails to the Cretaceous in an uninterrupted stratigraphic sequence. Intensive erosion of limestone in the entire area resulted in a typical karst hydrogeology and geomorphology.

SOILS, CLIMATE AND VEGETATION

Since more than 75 % of the studied part of Western Croatia is built of Jurassic and Cretaceous limestone, the prevailing soil types are brown soils developed on limestone (calcocambisols), while at lower altitudes with a Mediterranean climate various terra rossa type soils have developed. Occurrences of dolomites are usually covered by rendzinas and organic-mineral melanosols. Both organic and organic-mineral melanosols are developed on limestone and dolomites at higher altitudes. The area is covered mainly by very shallow soils developed on Mesozoic limestone and dolomite, among which the following soil types predominate: melanosol, calcocambisol and luvisol (Martinović *et al.*, 1994). On silicate Permian bedrock, acid brown soils (dystric cambisols) have developed.

The macroclimate of the karst mountainous region of Western Croatia is perhumid: moderately cold, with high precipitation (over 3500 mm annually), high relative humidity, high and enduring snow cover and frequent frost over the entire, relatively short growing season. Spatial topoclimatic contrasts are very strong because the relief is extremely rugged, due to the geological porosity and relatively high precipitation. The vegetation complex belongs to the North Dinaric inland type, with the largest part of the area covered by beech, fir and spruce monodominant forests, beech-fir mixed forests and mountain pine woods. The vegetation pattern is mosaic due to the topoclimatic contrasts (Antonić, 1996; Antonić *et al.*, 1997).

Transition to the Mediterranean macroclimatic types follows decreasing altitude toward the west with oro-Mediterranean (moderately cold and dry with xeric beech forests), sub-Mediterranean (moderately warm and dry with sclerophyllous deciduous oak forests), and eu-Mediterranean (warm and dry with evergreen oak forests) macroclimates.

MATERIALS AND METHODS

The topsoil samples used in this study were collected on a 5 5 km grid for the General Geochemical Map of Croatia, and the soil samples from Risnjak National Park on a 1 1 km grid (Fig. 1) were collected during a project which was aimed at the characterization of soils in Croatian national parks. It should be noted that 90% of the soil samples in the national park were taken at altitudes higher than 1050 m above sea level, and the topmost sample was taken at 1410 m above sea level. The detailed descriptions of initial geochemical regolith mapping protocols for carbonate terrains is given in detail by Pirc *et al.* (1991), Prohić *et al.* (1997), Prohić *et al.* (1998) and baseline mapping by Prohić *et al.* (1995), Miko *et al.* (1999) and Peh & Miko (1999).

The topsoil samples were taken at each sampling site from 3 to 5 shallow pits (mollic horizon, from 0 to 20 cm deep) and the material of the organic layer, if present, was excluded. All samples are a composite of at least 3 sub-samples covering a surface of 10 10 m. The soil samples were air-dried and the fraction sieved to–63m was analysed.

Sieved soil samples were analyzed after near total (hot 4 acid mixture: $HClO_4$-HNO_3-HCl-HF at 200 °C) digestion for 35 elements by inductively-coupled plasma atomic emission spectrometry (ICP-AES) in the ACME Labs in Vancouver.

The accuracy and reproducibility of analysis were controlled by analysis of USGS geological reference soil standards (GXR-2, SJS-1 and GXR-5) in the analyzed sample batches. The accuracy of analysis expressed as the ratio between measured and recommended values of elements in the standard samples was in the range 10 % and the obtained precision on replicate samples was even below 5 % for most elements. From the 35 element analytical package, 11 elements are excluded since 25 % or more of their values are below detection limit. The following elements were used in this study: Al, As, Ba, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Th, V, Ti, Sc, Sr, Pb, Zn, and P.

For decades, both exploration and environmental geochemical studies frequently use R-mode factor analysis as a multivariate mathematical technique to reveal the underlying structure of a specific set of data (Davis, 1986). As such, it is commonly used as a tool of data reduction, with a purpose of providing a clearer insight into the basic relationships among variables (R-mode) or samples (Q-mode). A simply structured factor model containing only a few heavily loaded factors is always indicative of the strong dependence among elements and in this case was used to delineate polluted areas.

Factor scores of element associations present the most straightforward way of portraying the influence of each independent factor in every single sample, or observation point. When plotted on a map they disclose the manner of some significant local or regional geochemical signatures. The factor-score maps display most conspicuously the process dynamics responsible for the characteristic institution of the factor model (Dillon & Goldstein, 1984). Prior to factor analysis the probabilty distributions were determined and the elements that showed positively skewed distributions (Cu, Pb, Zn, As, Sr, Cd, Ca, La, Mg, Ba and P) were log-transformed. Positive skewness of distributions of some elements was not lost after logarithmic transformation (Ca, Mg, Ba, Zn, Pb).

The airborne athropogene impact of Pb on soils can be also evaluated by calculation of enrichment factor (Hassan & Ismail, 1993) and was performed for this area. The enrichment factor (EF) used in this case is the concentration ratio of Pb in each individual sample ($C_{n\ sample}$) to the conservative element (Al) in the sample ($C_{cons.sample}$) with respect to same ratio of Pb and Al in a reference material ($C_{n\ ref.}/C_{cons.ref.}$) (Förstner & Wittmann, 1981; Li, 1981):

$$EF = (C_{n\ sample}/C_{cons.sample}) \ / \ (C_{n\ ref.}/C_{cons.ref.})$$

The definition of the enrichment factor indicates that this parameter depends on the choice of referent element and the choice of reference material.

The influence of reference element choice upon the value of the enrichment factor is discussed in papers of numerous authors, but Al is the commonest in use and its correlation with the clay content in sediments and soils is well established (Windom *et al.*, 1989; Prohić *et al.*, 1995, Prohić *et al.*, 1998, Miko *et al.*, 1999, Durn *et al.*, 1999). The normalisation procedure used in the evaluation of anthrophogenic Pb impact utilized baseline values established on the basis of 85 (1 1 km sampling grid) soil samples from the island of Mljet (Peh & Miko, 1999). This island was chosen as the baseline reference site for geochemical baseline mapping of carbonate terrains in Croatia because of its remoteness from possible anthropogene sources and a favorable soil cover and bedrock that contain the major units of both found in Croatia. GOLCHERT *et al.* (1991) distinguish three categories of enrichment factors: EF 2, 2 < EF < 10 and EF 10, where an EF lower than 2 indicates a natural variation of an element and those higher than 10 indicate severe pollution.

The geochemical maps were produced with the aid of SURFER mapping software. Gridding was performed by linear kriging with grid cell resolution of 2 2 km.

RESULTS AND DISCUSSION

Tab. 1. summarizes the main statistical parameters for the elements used in this study for Risnjak National Park (50 samples) and Western Croatia (292 samples).

Tab. 1. Summary statistics for the analyzed elements in topsoil samples of Risnjak National Park and Western Croatia.

	Risnjak national park (n = 50)					Western Croatia (n = 292)
	Min.	Max.	Std. Dev.	Skewness	Mean	Mean
Cu (ppm)	5	386	52	6.66	32	40
Pb (ppm)	25	139	27	0.87	70	43
Zn (ppm)	22	289	54	0.77	124	107
Ni (ppm)	7	118	29	0.40	55	72
Co (ppm)	2	25	5	–0.02	12	16
Cd (ppm)	0.4	3.0	0.7	0.64	1.3	1.1
As (ppm)	5	66	11	1.86	20	15
Th (ppm)	2	27	4	0.57	12	13
Sr (ppm)	32	102	19	–0.52	75	89
V (ppm)	30	299	50	1.00	127	131
Mn (ppm)	59	2545	561	1.06	779	904
Cr (ppm)	18	97	18	–1.04	67	107
Ba (ppm)	58	1249	179	3.48	295	269
Zr (ppm)	16	123	21	0.44	63	68
Sc (ppm)	3	16	3	–0.49	10	11
Al (%)	1.62	8.97	1.59	–1.27	6.40	7.54
Fe (%)	0.74	5.86	1.12	–0.23	3.49	4.01
Ca (%)	0.08	12.10	2.24	2.93	1.65	2.64
K (%)	0.25	2.42	0.40	0.10	1.25	1.26
Mg (%)	0.17	7.41	1.27	3.19	1.25	1.19
Na (%)	0.09	0.87	0.22	0.09	0.48	0.49
Ti (%)	0.10	0.66	0.11	–0.77	0.41	0.41
P (%)	0.032	0.187	0.038	1.40	0.075	0.077

The analyzed air-transported elements Pb and As, and to a lesser extent Zn and Cd, have higher mean concentrations in the Risnjak National Park area (Tab. 1). The most striking difference is expressed by Pb in samples taken at altitudes higher than 1050 m above sea level, where most samples have concentrations above 80 ppm, which is almost twice the mean content of lead (43 ppm) in the whole region. The mean concentrations of Al, Cr, Ni, Co and Cu have higher regional averages as a consequence of their accumulation during pedogenesis of the coastal terra rossa soils that make almost 50 % of the regional data set. Because presentation of single element maps would not fit in the scope of this paper, only factor score maps of environmentally relevant elemental associations, resulting from R-mode factor analysis, will be presented as well as that of Pb. The total data set processed

Tab. 2. Varimax rotated factor loadings matrix for the topsoil geochemical data from Risnjak National Park and Western Croatia (n = 342).

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Cu	0.59*	0.39	–0.02	0.26	0.57
Ni	0.85*	0.30	0.03	0.25	0.88
Co	0.76*	0.08	–0.05	0.05	0.58
Mn	0.63*	0.31	0.11	0.37	0.64
Fe	0.85*	–0.20	0.10	0.33	0.88
Th	0.69*	–0.46	0.13	0.19	0.73
V	0.80*	–0.10	0.03	0.37	0.79
Cr	0.88*	0.12	–0.04	–0.05	0.80
Ti	0.71*	–0.53*	0.21	0.15	0.86
Al	0.83*	–0.30	0.20	0.24	0.87
Zr	0.73*	–0.33	–0.08	0.20	0.69
Sc	0.86*	–0.16	0.20	0.27	0.87
Ca	–0.03	0.92*	–0.07	0.08	0.85
Mg	–0.24	0.55*	0.02	0.22	0.41
Sr	0.18	0.25	0.76*	–0.12	0.69
Na	–0.04	–0.31	0.76*	–0.22	0.73
K	0.36	–0.35	(0.48)	0.14	0.50
Ba	0.23	–0.54*	0.58*	0.09	0.70
Pb	0.19	–0.16	–0.13	0.86*	0.82
Zn	0.54*	0.08	0.05	0.72*	0.82
As	0.44	–0.05	–0.13	0.54*	0.50
Cd	0.41	0.24	–0.24	0.64*	0.70
P	0.21	0.30	0.01	0.69*	0.62
% of Var.	35.39	13.17	8.73	14.49	

through R-mode factor analysis resulted in a four-factor model that accounts for 71.8 % of the total variance (Tab. 2).

The first factor accounts for 35.4 % of the total data variability and for most of the variation of the 12 elements in data set. The association of Al, Sc, Zr, Ti, Cr, V, Th, Fe, Mn, Co, Ni and Cu can be basically interpreted as a measure of soil maturity and clay content. The distribution of high positive scores of this elemental asso-

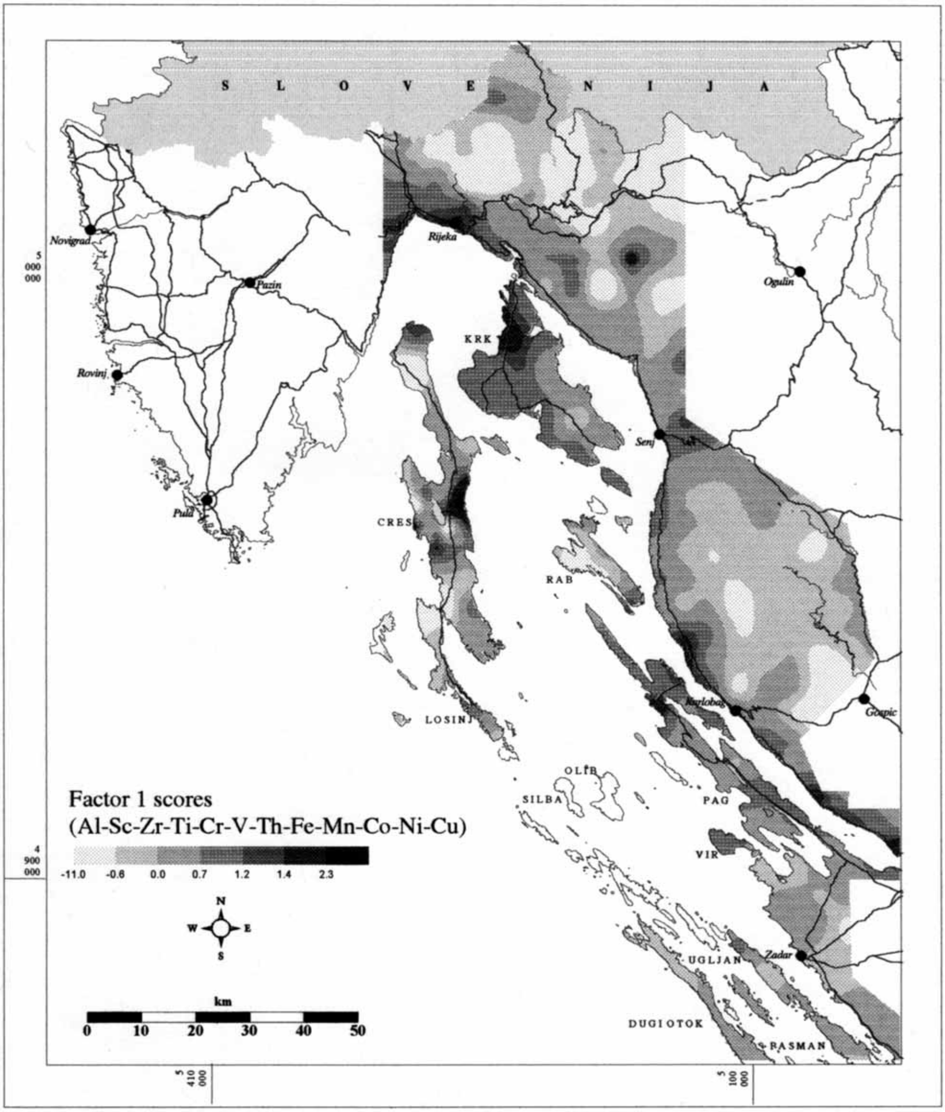

Fig. 2. Factor score map of the Al-Sc-Zr-Ti-Cr-V-Th-Fe-Mn-Co-Ni-Cu association.

ciation corresponds to the distribution of the coastal terra rossa soils. High negative scores reflect mountain soils and soils developed on clastic rocks of all stratigraphic positions as well as soils developed on alluvial plains in karst poljes (Fig. 2). The Ca-Mg-(Ba-Th) association (factor 2) accounts for 13.2 % and is related to soils developed on clastic sedimentary rocks (Eocene flysch) and soils developed on dolomites. The distribution of factor scores of the Sr, Na, K and Ba association (factor 3)

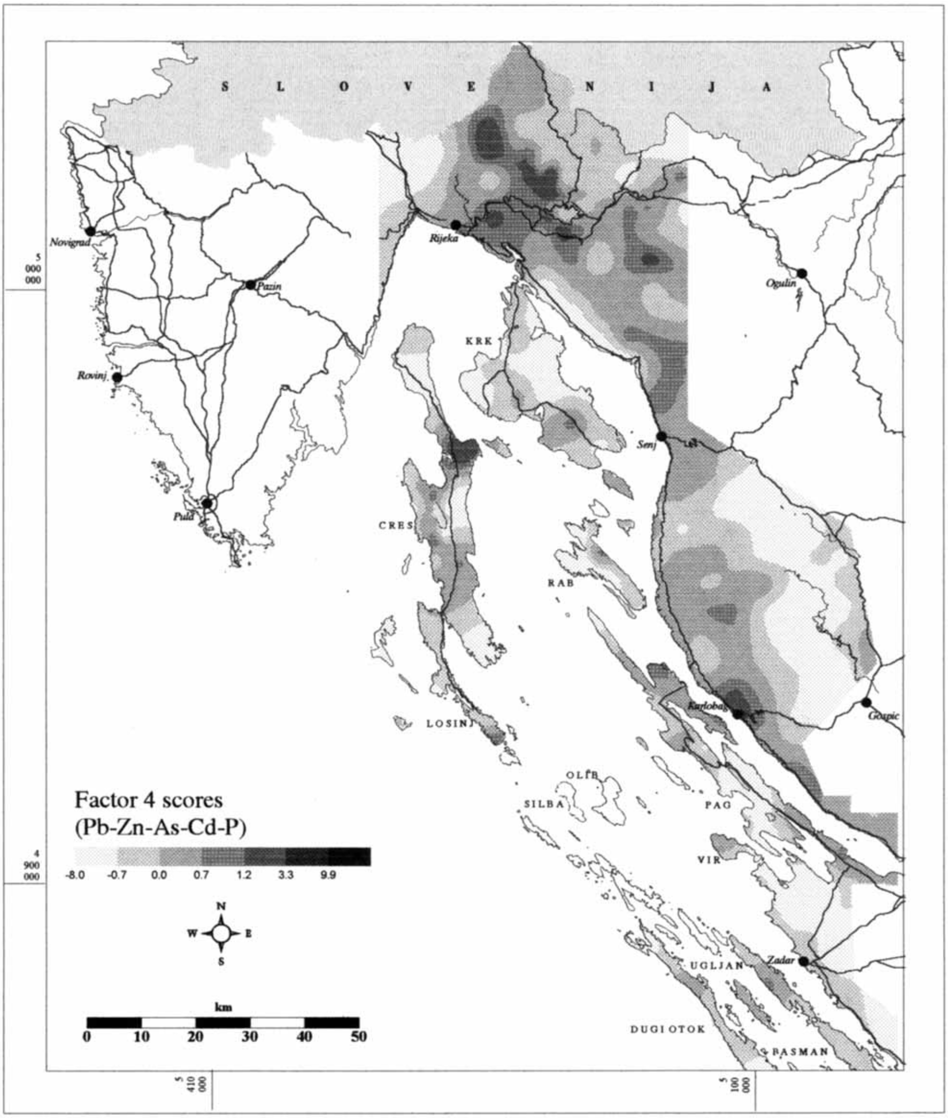

Fig. 3. Factor score map of the Pb-Zn-As-Cd-P association.

is indicative of low bedrock permeability and in general corresponds with higher positive score values for the less permeable bedrock (Paleozoic clastic rocks and Eocene flysch rocks, dolomites). This factor accounts for 8.7 % of total data variability.

Factor 4 is highly loaded with the air-borne Pb-Zn-As-Cd-P association of elements. This association accounts for 14.5 % of the total data variability. A geogene source of high concentrations for this association of elements is excluded since a carbonate bedrock with low content of trace elements could not contribute considerably to soils through weathering processes. The soils developed on carbonate rocks can be considered to be, in a sense, transported overburden since they are developed from various types of parent materials transported on carbonate terrain by different mechanisms (DURN *et al.*, 1999). The spatial distribution of factor 4 scores shows (Fig. 3) the highest positive values in the mountain region (Risnjak National Park) northwest of the industrial port of Rijeka and this pattern, less pronounced, follows the climatic boundary along the coastal mountain chain of Velebit to the southeast. High positive values are also found in the area of the town of Karlobag, which was the only gateway for southern Dalmatia during the Croatian war from 1991 to 1995. The area with high factor score values on Cres island is near a waste disposal site with uncontrolled incineration. The distribution pattern of the Pb-Zn-As-Cd-P association of elements in topsoils on the regional scale generally shows a trend towards higher positive scores at higher altitudes of the coastal mountain area of western Croatia. This association of elements with their pollution effects and geographical distribution corresponds to the situation in other mountainous regions of central Europe, where the resulting atmospheric inputs to soil are attributed to long range transport and the effect of acid deposition (e.g., FÖRSTNER, 1995; WILSON & BELL, 1996; MATSCHULLAT & BOZAU, 1996). There is no intention of using the data obtained to evaluate the amount of pollution that can be attributed to sources outside Western Croatia (Italy) since there is plenty of evidence that a (large) part of the pollution can be attributed to local sources. Namely, approximately 50 km to the southwest of the national park there is the coal fired Plomin electric power plant which fired a local high sulfur (average 12 %) coal for more than 20 years, as well as the oil refineries and other polluting industries in Rijeka.

The highest measured concentration of Pb within the boundaries of Risnjak National Park was 139 ppm in a brown soil at the altitude of 1390 m above sea level. The distribution of Pb in the national park and Western Croatia is presented in Fig 4. The geochemistry of Istria is excluded from this discussion since it was presented in detail in papers by PROHIĆ *et al*. (1997), ZUPANČIČ & PIRC (1999) and MIKO *et al*. (1999). The distribution of lead, as stressed before, shows that the soils of this mountain region have been considerably affected by airborne pollution and the average total Pb content is twice the regional average (Tab. 1.). Other elements attributed to atmospheric pollution show a less pronounced increase in concentration. Concentrations of As are 25 percent higher than the regional average, Zn and Cd approximately 15 %, and the average P content does not differ from the regional average (Tab. 1.). To evaluate the relative intensity of Pb pollution in the region, the enrichment factors were calculated for each individual sample on the basis of 86 reference samples from Mljet island. The results are presented in Tab. 3. and the distribution of Pb enrichment factors in Western Croatia is given in Figs. 5 and 6. The Pb (EF) – Al diagram (Fig. 6) shows that only 19 samples from the data set have EFs for Pb higher than 2, 9 of which are situated within Risnjak National Park (approx. 20 % of samples). The other 10 samples represent only 3 % of the total data set from Western Croatia. All samples collected within the region of Mt. Velebit are below the EF = 2 boundary (Fig. 6), but since three samples at altitudes above

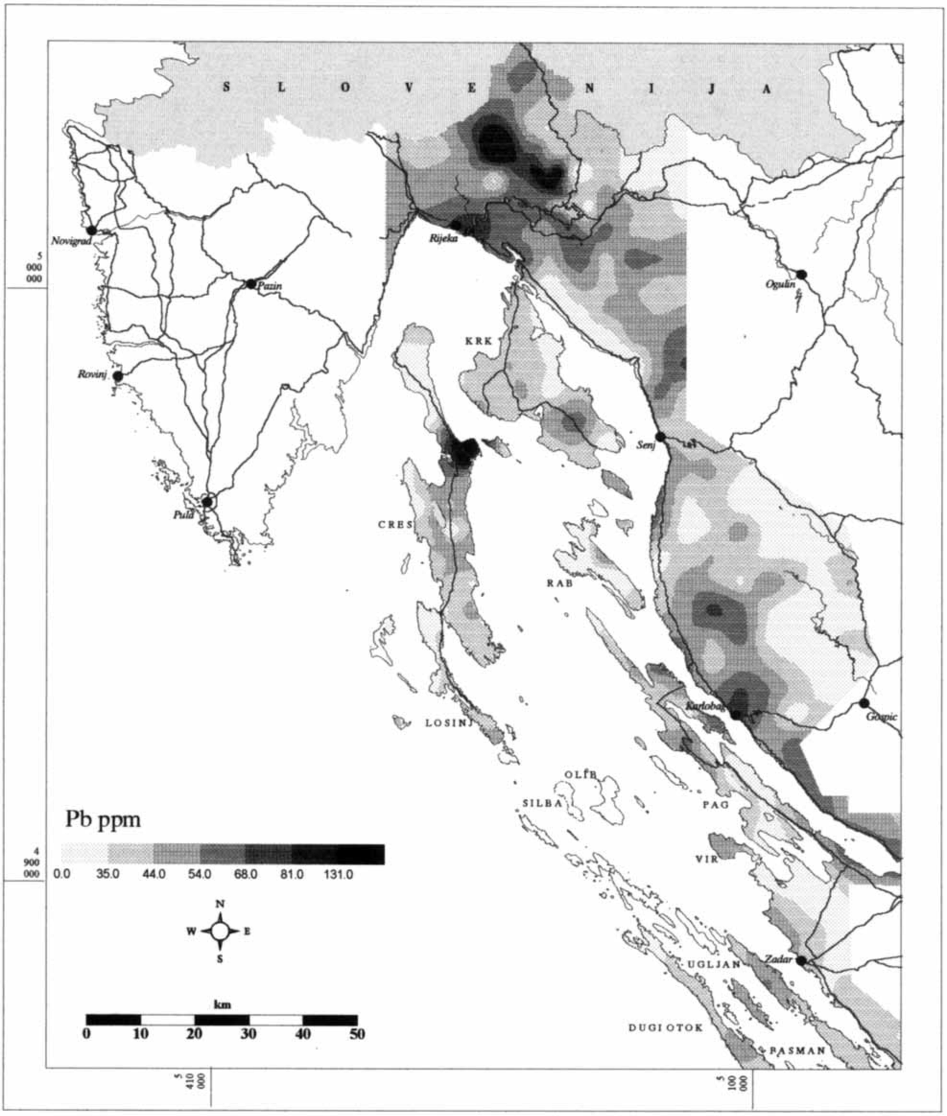

Fig. 4. Distribution of Pb in soils of Western Croatia.

1000 m (Fig. 5) show a slight enrichment (EF = 1.7), a possible airborne Pb contribution should not be excluded. The distribution of the Pb enrichment factor also gives the sharpest outline of Pb pollution in the Risnjak National Park area (Fig. 5).

The correlation between Pb and Zn on one side and altitude on the other is expressed by moderate correlation coefficients of 0.54 and 0.42 (Tab. 4.), respectively. The observed high correlation of Pb with P (Fig. 7) is in accordance with the geo-

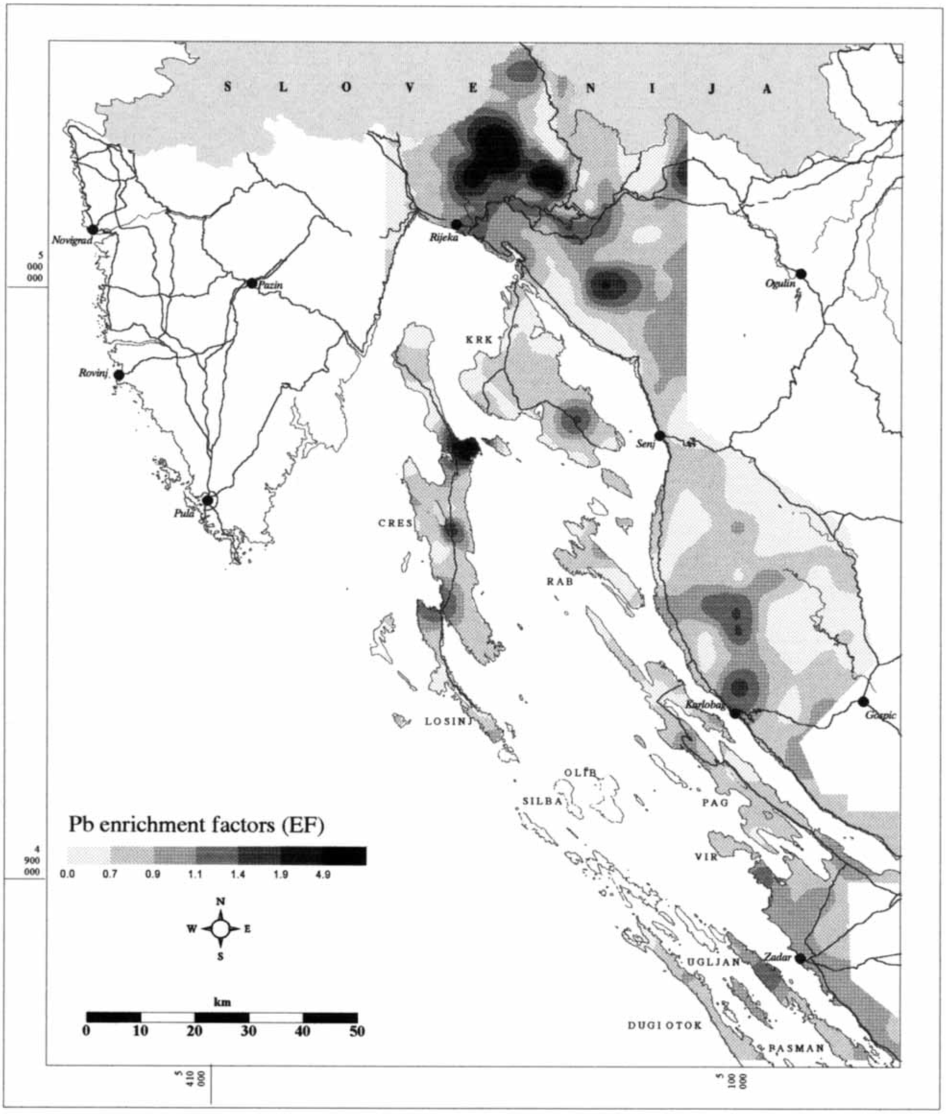

Fig. 5. Distribution of the Pb enrichment factor.

Tab. 3. Comparison of Pb concentrations and enrichment factors (EF) for the studied region.

		Pb (EF)			Pb (ppm)		
	n	Means	Std. Dev.	Variance	Means	Std. Dev.	Variance
W. CROATIA	268	0.91	0.50	0.25	43.3	16.43	287.08
RISNJAK	46	1.90	1.99	3.98	68.1	29.35	861.53
VELEBIT	37	0.85	0.26	0.06	46.5	12.05	145.19

chemistry of Pb in acid soils where the most stable Pb solid phases are phosphates such as $Pb_3(PO)_4$, $Pb_5(PO_4)_3Cl$ and $PbAl_3(PO_4)_2(OH)_5$ H_2O (SPOSITO, 1983), while in calcareous soils $PbCO_3$ can be important (ADRIANO, 1986). The role of phosphate is important in this case since it is a significant sink for Pb in the environment, and soils with high phosphate concentrations will immobilize Pb making it unavailable

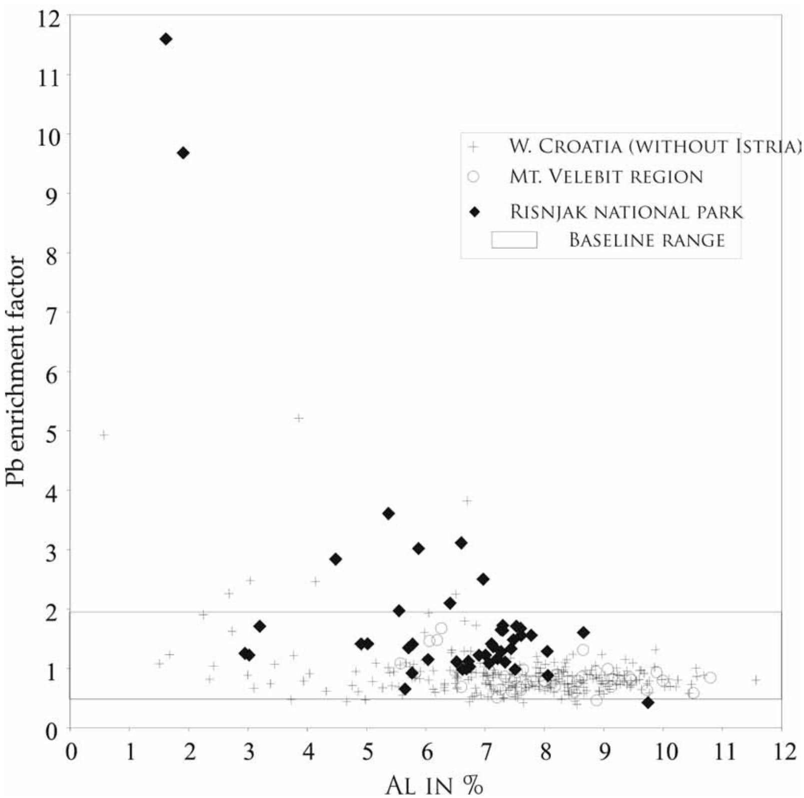

Fig. 6. Pb (EF)-Al plot for soils in the studied regions.

Tab. 4. Correlation coefficients for topsoil geochemical data of Risnjak National Park and neighboring terrain (area corresponds to that presented on the geological map in Fig. 1, n = 117).

	Altitude	Cu	Pb	Zn	As	Cd	P
Altitude	1.00						
Cu	–0.03	1.00					
Pb	0.54	0.38	1.00				
Zn	0.42	0.59	0.68	1.00			
As	0.15	0.43	0.48	0.51	1.00		
Cd	0.12	0.60	0.71	0.72	0.50	1.00	
P	–0.06	0.44	0.59	0.55	0.36	0.63	1.00

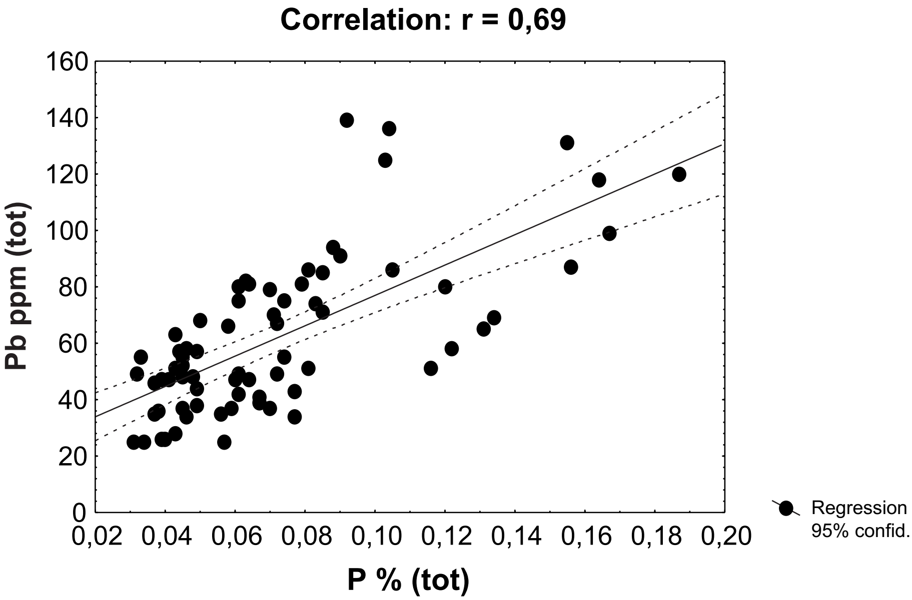

Fig. 7. Dependence of Pb and P in the analyzed soils.

in the soil solution (ADRIANO, 1986). The dependence of altitude and Pb topsoil concentrations, plotted as mean values of lead concentrations at different altitude level ranges for the region, best illustrates this relationship (Fig. 8). The high concentrations of Pb at lower altitudes are a consequence of pollution along the local roads that run along the coast. Acid rain fallout considerably contributes to the indigenous soil acidity, producing carbonic acid in soil solution as a consequence of

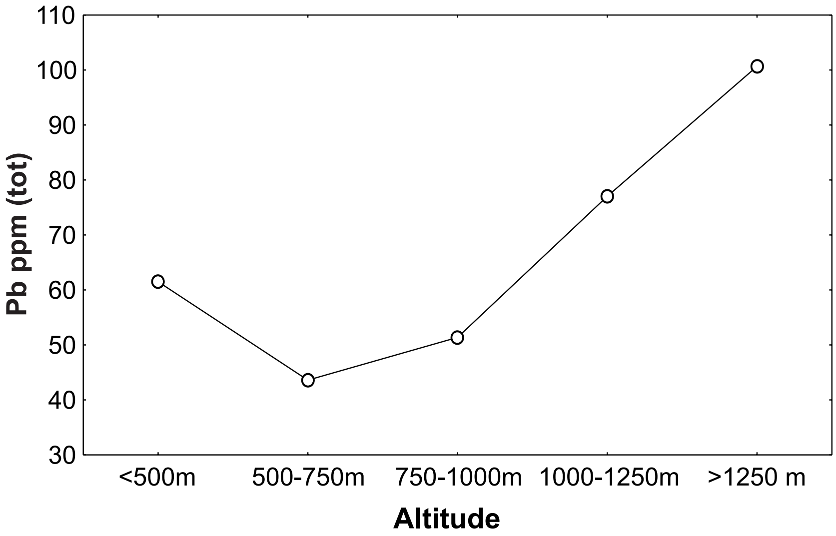

Fig. 8. Mean concentration of total Pb at various altitude ranges.

aerobic decay of organic mater. This in turn leads to the release of heavy metals and Al into solution, and due to the absence of a deeper soil cover, waters from these karst areas are drained directly into the aquifers.

CONCLUSIONS

A geochemical mapping program whose goal is to determine geochemical baselines e.i. the distribution range and variation of chemical elements in soils of the Croatian karst region was used in this case to assess the extent of environmental change in a protected natural reserve due to human influence (acid rain) on the distribution of Pb. The frequent fallout of acid rain, enriched by a combination of sulfuric, nitric, carbonic, chloride, fluoride, organic acids together with heavy metals, has considerably affected the topsoil of Risnjak National Park. Although acid rain precipitation was also observed in the Velebit region the analyzed soils do not exhibit Pb pollution as assessed by the statistical methods applied in this study. From the topsoil geochemistry in Western Croatia and Risnjak National Park, it is possible to draw the following conclusions.

The association of Al, Sc, Zr, Ti, Cr, V, Th, Fe, Mn, Co, Ni and Cu can be basically interpreted as the measure of soil maturity and clay content. The distribution of high positive scores of this elemental association corresponds to the distribution of coastal terra rossa soils. High negative scores reflect mountain soils and soils developed on clastic rocks of all stratigraphic positions, as well as soils developed on alluvial plains in karst poljes.

The spatial distribution pattern of the air-borne Pb-Zn-As-Cd-P association of elements is generally controlled by the abrupt climatic boundary that occurs along the Western Croatian coastal mountain range. Soil pollution in higher altitude mountain regions is analogous to the acid deposition observed in Central Europe.

The effect of probably both long-range and local transport of airborne pollution on the region of Risnjak National Park can be seen in the concentrations of Pb and As, and to a lesser extent of Cd and Zn. Total Pb concentrations detected at latitudes higher than 1050 m above sea level in the national park were higher than 80 ppm (max. conc. 139 ppm Pb) while the regional mean Pb concentration is 43 ppm.

The calculated enrichment factors for Pb show that only 19 samples from the data set have EFs higher than 2, 9 of which are situated within Risnjak National Park (approx. 20 % of samples). The other 10 samples represent only 3 % of the total data set from Western Croatia. All samples collected within the region of Mt. Velebit are below the EF = 2 boundary (Fig. 6) and therefore the region can be considered to be subject to a smaller atmospheric pollution impact. Three samples that show a slight increase in Pb EF (approximately 1.7) could indicate possible airborne Pb contribution in this region also.

ACKNOWLEDGMENTS

This study was funded by the Ministry of Science and Technology, Republic of Croatia project # 01810106, »The basic geochemical map of the Republic of Croatia«.

Received November 2, 1999

REFERENCES

ADRIANO, D. C., 1986: Trace Elements in the Terrestrial Environment. Springer-Verlag, Berlin, Heidelberg, 533 pp.

ANTONIĆ, O., 1996: Application of the spatial modelling in the Karst Bioclimatology. Cro. Met. J. **31**, 95–102.

ANTONIĆ, O., KUŠAN, V. & HRAŠOVEC, B., 1997: Microclimatic and topoclimatic differences between the phytocoenoses in the 'Viljska ponikva' sinkhole, Mt. Risnjak, Croatia. Cro. Met. J. **32**, 37–49.

DAVIS, J. C., 1986: Statistics and data analysis in geology. New York, John Wiley & Sons, 646 pp.

DILLON, W. R. & GOLDSTEIN, M., 1984: Multivariate analysis: Methods and applications. New York, John Wiley & Sons, 575 pp.

DURN, G., OTTNER, F. & SLOVENEC, D., 1999: Mineralogical and geochemical indicators of the polygenetic nature of terra rossa in Istria, Croatia. Geoderma, **91**, 125–150.

FÖRSTNER, U., 1995: Land contamination by metals – global scope and magnitude of problem. In: ALLEN, H. E., HUANG, C. P., BAILY, G. W., BOWERS, A. R., (Eds), Metal speciation and contamination of soil. CRC Press, 358 pp.

FÖRSTNER, U. & WITTMANN, G. T. W., 1981: Metal Pollution in the Aquatic Environment, Springer-Verlag, Berlin, Heidelberg, New York, 486 p.

GLAVAČ, V., KOENIES, H. & PRPIĆ, B., 1987: Zur Imissionsbelastung der industriefernen Buchen- und Buchen-Tannenwälder in den Dinarischen Gebirgen Nordwest – jugoslawiens. Verhandlungen d. Ges. f. Ökologie, 15. Jahrestagung in Graz 1985, Band XV, 237–247.

GOLCHERT, B., LANDSBERGER, S. & HOPKE, P. K. 1991: Determination of heavy metals in the Rock River (Illinois) through the analysis of sediments, Jour, Radioanal. Nucl. Chemistry – Art., **148**, 2, 319–337.

HASSAN, F. S. M. & ISMAIL, S. S. 1993: Use of geologically biased enrichment factors (Ef) as indicators of natural air pollutants. J. Radioanal. Nucl. Chem., – Art., **167**, 2, 237–246.

LANTZY, R. J. & MACKENZIE, F. T., 1979: Atmospheric trace metals: global cycles and assessment of man's impact. Geochim. Cosmochim. Acta. **43**, 511–525.

LI, Y-H., 1981: Geochemical cycles of elements and human perturbation. Geochim. Cosmochim. Acta, **45**, 2073–2084.

KUBIN, E. & LIPPO, H., 1996: Atmospheric heavy metal deposition in Finland from 1985 to 1990. Appl. Geochem. **11**, 155–161.

MARTINOVIĆ, J., VRANKOVIĆ, A. & PERNAR, N., 1994: The soils of the national park Risnjak (in Croatian). In Extended Abstracts Book »40 Years of the national park Risnjak, 1953–1993«, Crni Lug, 131–136.

MATSCHULLAT, J. & BOZAU, E., 1996: Atmospheric element input in the Eastern Ore Mountains. Appl. Geochem. **11**, 149–154.

MIKO, S., DURN, G. & PROHIĆ, E., 1999: Evaluation of terra rossa geochemical baselines from Croatian karst regions. J. Geochem. Explor., **66**, 173–182.

PANDŽIĆ, K., 1989: Factor analysis of the local climatic fields within global stream (PhD Dissertation). University of Zagreb, Faculty of Natural Sciences, Croatia.

PEH, Z. & MIKO, S., 1999: The geochemical atlas of Middle and Southern Dalmatia. Open file report (in Croatian), Institute of geology, Zagreb, 102 pp.

PIRC, S. & MAKSIMOVIĆ, Z., 1985: Methodology for geochemical mapping in Yugoslavia. In First Internat. Symp. Geoch. and Health, Thornton I. ed. Northwood: Science reviews, 31–44.

PIRC, S., MCNEAL, M. J., LENARČIČ, T., PROHIĆ, E. & SVRKOTA, R., 1991: Geochemical mapping of carbonate terrain. Bull. Inst. Mettal. Min., Applied Earth Sci. Vol. **100**, B–74-B- 83.

PROHIĆ, E., MIKO, S. & PEH, Z., 1995: Normalization and trace element contamination of soils in a karstic polje-an example from the Sinjsko Polje, Croatia. Geol. Croatica, **48**(1), 67–86.

PROHIĆ, E., HAUSBERGER, G. & DAVIS, J. C., 1997: Geochemical patterns in soils of the karst region, Croatia. J. Geochem. Explor. **60**, 127–138.

PROHIĆ, E., PEH, Z. & MIKO, S., 1998: Geochemical charecterization of karst polje – an example from Sinjsko polje, Croatia. Environmental Geology **33**(4), p 263–273.

PRPIĆ, B., 1987: Decline of forest trees in Croatia with the special emphasis on the load of 'Gorski kotar' area with the acid rain and heavy metals (in Croatian with English abstract). Šumarski list ,1–2, 53–60.

PRPIĆ, B., SELETKOVIĆ, Z. & IVKOV, M., 1991: Forest decline in Croatia and its relation to the biotical and abiotical factors today and in the past (in Croatian with English abstract). Šumarski list, 3–5, 107–129.

ROBINSON, E., 1984: Dispersion and fate of atmospheric pollutants. In: TRESHOW M. (ed.): Air pollution and plant life. J. Wiley, Chicester, 15–37.

SPOSITO, G., 1983: The chemical forms of trace elements in soils. In: THORTON, I., (ed): Applied environmental geochemistry, Academic Press, Toronto, 123–167.

VRBEK, B. & GAŠPARAC, M., 1992: New findings of heavy metals input in National park 'Risnjak' (in Croatian with English abstract). Radovi Šumarskog instituta **27**(1), 65–75.

WILSON, M. J. & BELL, N., 1996: Acid deposition and heavy metal mobilization. Appl. Geochem. **11**, 133–137.

WINDOM, H., SCHROPP, S., CALDER, F., RYAN, J., SMITH, R. Jr., BURNEY, L. LEWIS, F. & RAWLISON, C., 1989: Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern U.S., Environ. Sci. Technol., **23**(3), 314–320.

ZUPANČIČ, N. & PIRC, S. 1999: Calcium distribution in soils and stream sediments in Istria (Croatia) and the Slovenian littoral. J. Geochem. Explor. **65**, 205–218.

SAŽETAK

Geokemijsko kartiranje i procjena onečišćenja olovom tala na kršu zapadne Hrvatske

S. Miko, Z. Peh, D. Bukovec, E. Prohić & Ž. Kastmüller

Istaknut položaj Nacionalnog parka »Risnjak« i zaštićenog područja Velebita na geomorfološkoj granici između obalnog pojasa i planinskog zaleđa ima za posljedicu onečišćenje površinskog sloja tla. Sve češća pojava kiselih kiša obogaćenih kombinacijom anorganskih i organskih kiselina uz povišen sadržaj teških metala prijeti ozbiljim oštećenjem biljnog pokrivača. Premda su kisele kiše primijećene i na području Velebita, analize tla provedene u okviru izrade geokemijske baze podataka za područje čitave zemlje ne pokazuju takvo zagađenje teškim metalima, poglavito olovom, kao u Nacionalnom parku »Risnjak«, što se može zaključiti na osnovi statističkih metoda korištenih u ovom radu.

Rezultati faktorske analize navode na zaključak da se Al-Sc-Zr-Ti-Cr-V-Th-Fe-Mn-Co-Ni-Cu asocijacija elemenata (prvi faktor) može protumačiti kao mjera zrelosti tla, odnosno sadržaja glinovite komponente. Visoke pozitivne faktorske vrijednosti ovog faktora koincidiraju s rasprostranjenošću obalnih crvenica na karbonatnoj podlozi, dok visoke negativne vrijednosti upućuju na planinska tla koja su se razvila na klastičnim stijenama, ali i na tla nastala na aluvijalnim naplavinama krških polja.

Prostorna raspodjela atmofilne Pb-Zn-As-Cd-P asocijacije elemenata općenito je u izravnoj vezi s oštrom klimatskom granicom koja se pruža grebenom priobalnog planinskog lanca sjeverozapadne Hrvatske. Zagađenost tla u višim planinskim područjima analogna je pojavi zakiseljavanja u središnjoj Europi. Vjerojatan utjecaj udaljenog, ali i lokalnog donosa atmosferskih čestica u područje Risnjaka odražava se u povišenim koncentracijama Pb i As, a u manjoj mjeri Cd i Zn. Maksimalne ukupne kocentracije Pb u Nacionalnom parku, na visinama iznad 1050 m nadmorske visine, više su od 80 ppm (max = 139 ppm) dok su regionalne vrijednosti koncentracija Pb, prema Osnovnoj geokemijskoj karti RH, oko 43 ppm.

U području Nacionalnog parka »Risnjak« približno 20 % uzoraka ima EF vrijednost za Pb višu od 2 (EF > 2), što se može smatrati kao zagađenje, dok čitavo područje zapadne Hrvatske (osim Istre) ima manje od 3 % olovom obogaćenih uzoraka. Svi uzorci s područja Velebita imaju vrijednost EF za olovo unutar područja geokemijskog šuma (EF < 2) pa se može smatrati da je utjecaj atmosferskog zagađenja u tom području manje izražen.