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TRACE ELEMENT DISTRIBUTION IN SURFACE SEDIMENTS OF LAKE VRANA AND TOPSOIL OF CRES ISLAND, CROATIA

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This paper presents a study of major and trace element distribution and an evaluation of their environmental geochemical aspects in the surface sediments of Vrana Lake and the topsoil within its catchment area. The concentrations of 22 elements were determined in 30 lake sediment samples and 60 topsoil samples covering the lake catchment area and the whole island of Cres. The element to Al ratios fall into three main groups: the group of elements that show no difference in ratios in soils and lake sediments: Ni, Co, Mn, Th, Zn, Ba, Ti, K, V, Na, and H; elements that are enriched in the sediments: Ca, Sr, Cd, Pb, Ba and Mg; and elements that are depleted in the lake sediments: Cu, P, Fe, Cr, and La. Long-range air pollution is probably the main reason why the content of metals, especially lead, is increased in the lake sediments, although a local source, from road transport, as indicated by soil data from the catchment area, could also be an important source of Pb. Some pollutants in the soils of the catchment area, such as Cu and Hg from agro-chemical sources, were not determined in elevated concentrations in the lake sediments. Comparison of element/Al indexes from this study with the other studies of surface materials in the region show mutually similar sources, with loess and flysch as two geochemical end-members.

Key words: trace element distribution, lake sediments, soils, lead, normalization, atmospheric deposition

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U radu se daje pregled raspodjele glavnih elemenata i onih u tragovima u površinskim sedimentima Vranskog jezera i tlima na otoku Cresu, te se na temelju izrađenih analiza daje pregled mogućih geokemijskih promjena u okolišu. Određene su koncentracije 22 elementa u 30 uzoraka jezerskog sedimenta i 60 uzoraka tla koje pokriva slivno područje jezera i otoka Cresa. Na temelju omjera pojedinih elemenata i aluminija utvrđene su tri geokemijske grupe elemenata; prvu grupu čine elementi koji ne pokazuju razliku u omjerima element/Al u tlima i sedimentima: Ni, Co, Mn, Th, Zn, Ba, Ti, K, V, Na i H; elementi koji pokazuju obogaćenje u sedimentima: Ca, Sr, Cd, Pb, Ba i Mg, te grupa elemenata koja je obogaćena u tlima; Cu, P, Fe, Cr i La. Povišene koncentracije olova u jezerskim sedimentima moguće je tumačiti kao posljedicu atmosferskog taloženja iz udaljenih industrijskih izvora a koncentracije utvrđene u tlima, na lokacijama na širem području prometnice koja prolazi istočnom stranom slivnog područja jezera, upućuju i na mogućnost lokalnog utjecaja automobilskog prometa. Neki potencijalno toksični elementi (Hg i Cu) koji su utvrđeni u povišenim koncentracijama u tlima slivnog područja, nisu utvrđeni kao povišeni u samom jezerskom sedimentu. Usporedbom omjera element/Al dobivenih u ovom radu sa rezultatima istraživanja površinskih materijala drugih autora sa šireg područja pokazuju da detritični materijal potječe iz istih izvora sa lesom i naslagama fliša kao dva krajnja geokemijska člana.

Ključne riječi: raspodjela elemenata u tragovima, jezerski sedimenti, tla, olovo, normizacija, atmosfersko taloženje

INTRODUCTION

The Vrana Lake on Cres Island is one of the most interesting karst water phenomena within the Dinaric karst and Adriatic Islands. The lake depression contains approximately 220 million m^3 of fresh and extraordinary clean water whose hydrogeochemistry has been studied in detail by KAPELJ (1997). The largest portion of lake water recharge comes from precipitation (OŽANIĆ & RUBINIĆ, 1994; HERTELENDI *et al.*, 1995; BIONDIĆ *et al.*, 1997; KAPELJ, 1997), and according to the limnological properties the lake belongs to the monomictic and oligotrophic lake type.

The lake is a source of potable water for the islands of Cres and Lošinj. In view of this specific environment and its importance for the local water supply, an evaluation of environmental geochemical aspects concerning the lake sediments and the surrounding soils was attempted. This work summarizes some of the aspects and results of a complex study.

Since mineralogical composition indicated that the detrital fractions of the surface sediments of Vrana Lake and the surrounding soils have a similar origin (MESIĆ, 1999), a common geochemical baseline can be presumed for both materials. Having this in mind, a procedure using the ratio of an element and aluminum in the analyzed soil and sediment samples was applied to detect contributions to the lake that could be considered anomalous.

The basic geochemical approach is to normalize geochemical data by means of a conservative component whose levels are unaffected by contaminant inputs, for example, grain size, Al, Fe, Sc, Ni, TOC and Li. A conservative element is used assuming that it has had a uniform flux to the sediments over the past century from crustal rock sources. Consequently, changes in the water, salt, $CaCO_3$, or organic matter content, especially in the upper layers, can be compensated for (FÖRSTNER & WITTMANN, 1981). Aluminum is a conservative element frequently used for the normalization of trace element data due to its high natural abundance. Additionally, aluminum is a major constituent of soils and sediments as a structural element of clays. It has a strong positive correlation with many major and minor elements in soils and sediments, in which it is considered a natural content and is applied to reduce significantly data variability for the purposes of sample inter-comparison over small and larger regional areas. The association between Al and other elements can be therefore used as a basis for the comparison of natural elemental content in sediments and soils, which obviously have varying textural and mineralogical characteristics.

LAKE VRANA GEOLOGY, HYDROGEOLOGY, SEDIMENTS AND SOILS

Vrana Lake is a crypto-depression and occurs within the elongated Cres Island, composed mostly of karstified carbonate rocks, Upper Cretaceous rudist limestones and Eocene limestones, dolomites and Paleogene flysch deposits. During the exploration of the lake floor, Pliocene-Pleistocene lacustrine silty sediments, torrential slope detritus and recent lacustrine sediments were discovered (BIONDIĆ *et al.*, 1995; 1997). SCHMIDT *et al.* (2000) determined a calibrated ^{14}C date at the base of a 5m long core of approximately 16,000 years and determined in the central profundal zone of the lake by echography a lake sediment thickness of over 25 m. According to SCHMIDT *et al.* (2000), the upper 30 cm of lake sediment contains over 70% quartz and clay, 10% dolomite and less than 5% calcite, while deeper parts of the profile (to 1m depth) are dominated by calcite (more than 60%). In comparison with the ^{14}C dates and the results of echography, the hypothetical age of the lake (17,000 years) proposed by ŠEGOTA & FILIPČIĆ (2001) seems to be an underestimate.

These sediments are characterized by the dominance of the epidote group of minerals and amphibole in the heavy mineral fraction (MESIĆ, 1999), which is similar to the terra rossa types of soils and loess (DURN, 1996). The soils developed on carbonate bedrock in the wider region surrounding the lake consist predominantly of brown soils developed on limestone, rendzina on limestone and dolomite and terra rossa in the southern parts of the lake region (BOGUNOVIĆ *et al.*, 1996). The karst morphology is covered by sparse vegetation as a consequence of deforestation and the carbonate bedrock often lacks regolith.

SAMPLING AND ANALYTICAL METHODS

The lake sediments were collected along five profiles perpendicularly to the long axis of the lake. The spacing between the sampling profiles and points was irregular (Fig. 1). The samples were collected from a boat with the aid of manual dredge. The sediment sampling depth varied and the collected samples are a mixture of the top calcite-poor layer and the underlying calcite-rich layer. A total of 30 samples were collected.

The 36 topsoil samples (from 0 to 20 cm) were collected in the surroundings of Vrana Lake on a regular 1×1 km grid (Fig 1.). In most cases shallow brown soils on limestone and dolomite, and terra rossa predominate. All samples are a composite of at least three sub-samples covering a surface of 10×10 m. Also, the data from the regional geochemical baseline program during which sampling of topsoil (25 sampling sites) was performed on a regular 5×5 km grid (Fig. 1) on the whole of Cres Island (MIKO *et al.*, 2001) were used in evaluation of the data from the area surrounding the lake. The topsoil sampling and analysis were done in accordance with the geochemical sampling protocol used at the Institute of Geology, Zagreb (HALAMIĆ *et al.*, 2000) which is a modification of the FOREGS geochemistry mapping field manual (SALMINEN *et al.*, 1998). The soil and lake sediment samples were air-dried and the fraction was sieved to less than 63mm.

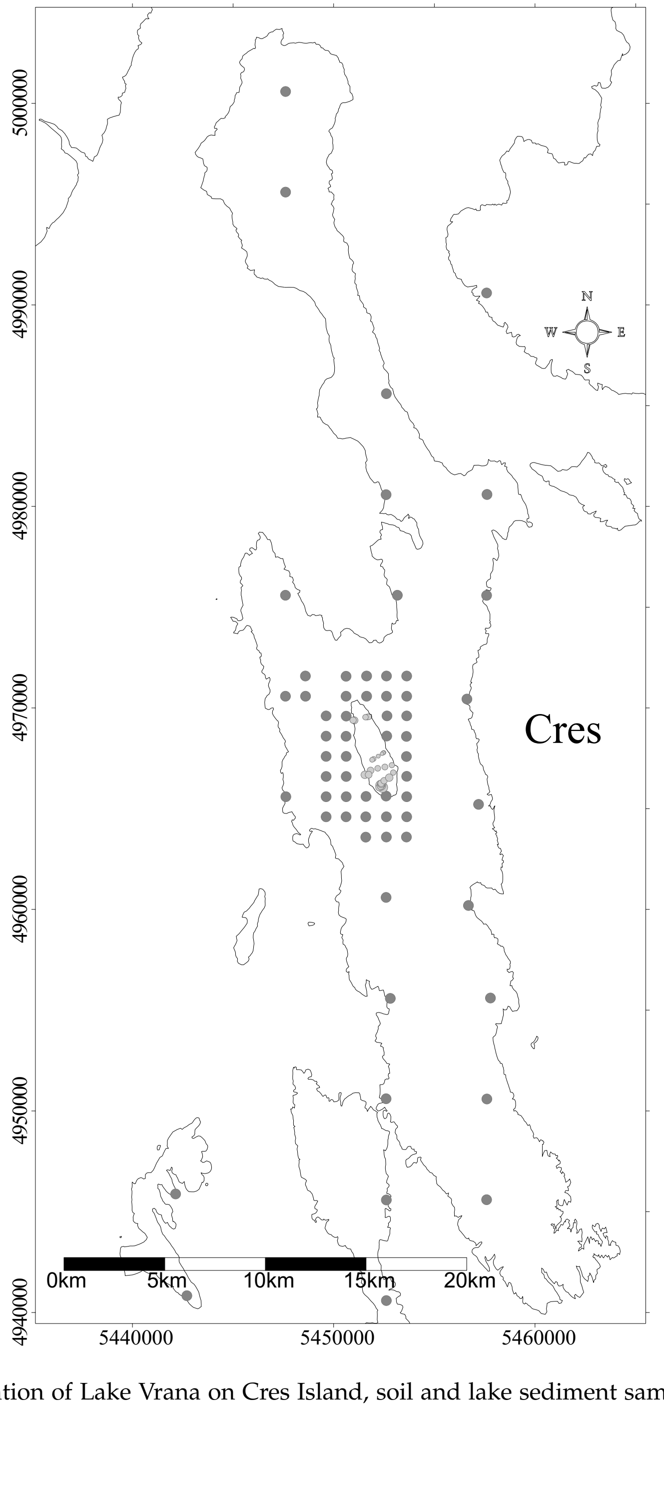

Fig. 1. Location of Lake Vrana on Cres Island, soil and lake sediment sampling sites.

The sieved soil samples and sediments were dissolved by a mixture of acids ($HClO_4$-HNO_3-HCl-HF) at 200 °C. The elements Al, Fe, Ca, Mg, Na, K, Ti, P, Pb, Zn, Cu, Co, Ni, Cd, Th, Sr, Cd, V, La, and Ba, were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES. Mercury was analyzed by flameless AAS. Accuracy of analyses was controlled using certified geological reference materials i.e. soils from the USGS; GXR-2, GXR 5, and SJS-1, and for most elements analyzed in the reference soil materials it is in the range of +/–10 % of the certified values. The precision of the analyses was determined by repeated analysis of both certified reference samples and randomly selected soil samples, the resulting coefficient of variation was on average approximately 5%.

RESULTS AND DISCUSION

The geochemical study of the surface sediments of Vrana Lake and soils on Cres Island was done by analyzing the distribution of some of the major (Al, Fe, Ca, Mg, Na, K, Ti, P) and trace (Pb, Zn, Cu, Co, Ni, Cd, Th, Sr, Cd, V, La, Ba, Hg) elements. The summary statistics of the analytical results for the lake sediments, soils within the lake catchment area (1 × 1 km grid) and the regional topsoil (5 × 5 km grid) is given in Tab. 1, together with the summary statistics for the same ele-

Tab. 1. Mean major and trace element concentrations in surface Vrana Lake sediments, topsoil from the Vrana Lake catchment area (1 ×1 km grid), topsoil from Cres Island (5 ×5 km grid) and North Adriatic Sea marine surface sediments (data from DOLENC *et al.*, 1998).

	Cres soils 5 × 5 km grid	Vrana lake soils 1 × 1 km grid	Vrana lake sediments	N. Adriatic marine sediments DOLENC *et al.*, 1998
Cu mg/kg	39	63	19	19
Pb mg/kg	43	44	31	18
Zn mg/kg	99	122	69	76
Ni mg/kg	75	82	41	45
Co mg/kg	19	17	8	7
Mn mg/kg	928	882	461	446
Fe %	4.05	4.13	2.00	2.09
Th mg/kg	13	14	7	7
Sr mg/kg	97	97	104	456
Cd mg/kg	1.06	0.92	0.88	No data
V mg/kg	131	149	78	76
Ca %	3.50	4.00	16.66	11.02
P %	0.091	0.099	0.026	0.043
La mg/kg	49	46	20	26
Cr mg/kg	113	121	60	74
Mg %	1.95	2.23	2.59	2.04
Ba mg/kg	257	272	155	182
Ti %	0.40	0.41	0.19	0.23
Na mg/kg	0.58	0.42	0.25	No data
K %	1.28	1.50	0.83	1.33
Hg µg/kg	No data	292	107	395
Al %	7.58	7.62	4.21	4.23

Tab. 2. Mean element/Al ratios in surface Vrana Lake sediments, topsoil from the Vrana Lake catchment area (1 × 1 km grid), topsoil from Cres Island (5 × 5 km grid) and North Adriatic Sea marine surface sediments (data from DOLENC *et al.*, 1998).

	Cres soils 5 × 5 km grid	Vrana lake soils 1 × 1 km grid	Vrana lake sediments N = 30	N. Adriatic marine sediments DOLENC *et al.*, 1998
Cu/Al	5.17	8.79	5.17	4.27
Pb/Al	5.93	6.46	8.65	4.17
Zn/Al	13.4	17.0	17.7	17.6
Ni/Al	9.71	10.78	9.99	10.32
Co/Al	2.43	2.27	2.16	1.70
Mn/Al	122	118	120	109
Fe/Al	0.53	0.54	0.49	0.49
Th/Al	1.66	1.87	1.86	1.87
Sr/Al	15	16	55	124
Cd/Al	0.14	0.14	0.31	No data
V/Al	17.3	20.1	19.3	17.5
Ca/Al	0.97	1.57	11.63	2.93
P/Al	0.0135	0.0137	0.0042	0.0105
La/Al	6.72	5.88	4.76	6.54
Cr/Al	14.9	15.9	15.3	17.3
Mg/Al	0.56	0.89	1.43	0.53
Ba/Al	33.9	36.4	41.1	43.4
Ti/Al	0.052	0.054	0.051	0.055
Na/Al	0.079	0.058	0.078	No data
K/Al	0.17	0.20	0.21	0.31
Hg/Al	No data	38	33	95
Ba/Sr	3.10	3.02	1.57	0.51
Cr/V	0.88	0.80	0.79	1.01

ments in surface marine sediments from the northern Adriatic given by DOLENC *et al.* (1998). The comparison of the data is possible since the marine sediments were analyzed in the same manner (dissolution and analytical techniques) hence the comparison can be used for an environmental geochemical assessment in the wider region. In order to compare the geochemistry of the different materials from this region the chemical composition of both sediments and soils is discussed on the basis of element/Al ratios (Tab. 2). The element/Al ratio is used to compensate for the carbonate dilution in the sediments (Fig. 2) and allows comparison with the soils. The element/Al ratios should show differences due to the variability of source materials for the sediments and the soils as well as anthropogenic influences. The correlation between Ca and Al and the other elements analyzed in the lake sediments is shown in Tab. 3, which indicates (high positive correlation coefficients) that the clay fraction controls the geochemistry of most of the elements.

There are two main types of recent surface lake sediments obtained by dredge sampling in the Vrana Lake; those with high carbonate content (Ca 10%), which occur on the steep zone along the lake shore and consist of carbonate sand detritus with low organic matter content (< 5%). The sediments in the central part of the lake depression consist of finer sediments with CaO contents of less than 10% and

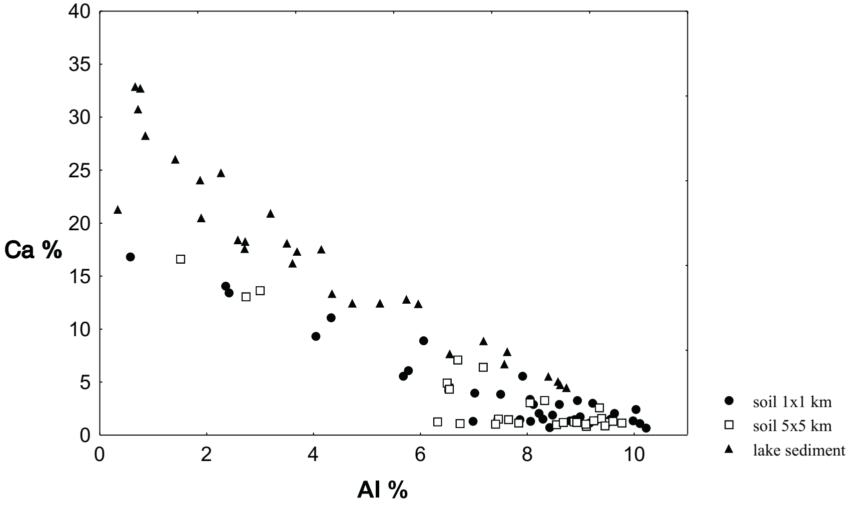

Fig. 2. The Ca vs. Al plot showing the carbonate dilution effect in lake sediments and soils sampled on a 1 ×1 km grid (catchment area soils) and 5 ×5 km grid (Cres soils).

with organic matter content higher than 10%. Also, some of the sampled sediments have a high Ca content and a low Mg content (< 1%), while others have both high Mg and Ca content (Fig. 3). This variability can be explained by the nature of the

Tab. 3. Correlation (Pearson r) between Ca and Al and other analyzed elements in surface lake sediments showing the carbonate dilution effect.

	Ca	Al
Cu	–0.921	0.973
Pb	–0.869	0.871
Zn	–0.945	0.979
Ni	–0.945	0.999
Co	–0.948	0.991
Mn	–0.818	0.794
Fe	–0.938	0.994
As	–0.760	0.777
Sr	0.868	–0.766
Cd	–0.789	0.813
V	–0.953	0.998
La	–0.953	0.997
Cr	–0.955	0.999
Mg	–0.359	0.071
Ba	–0.945	0.997
Ti	–0.966	0.994
Na	–0.932	0.918
K	–0.957	0.996
Hg	–0.480	0.471

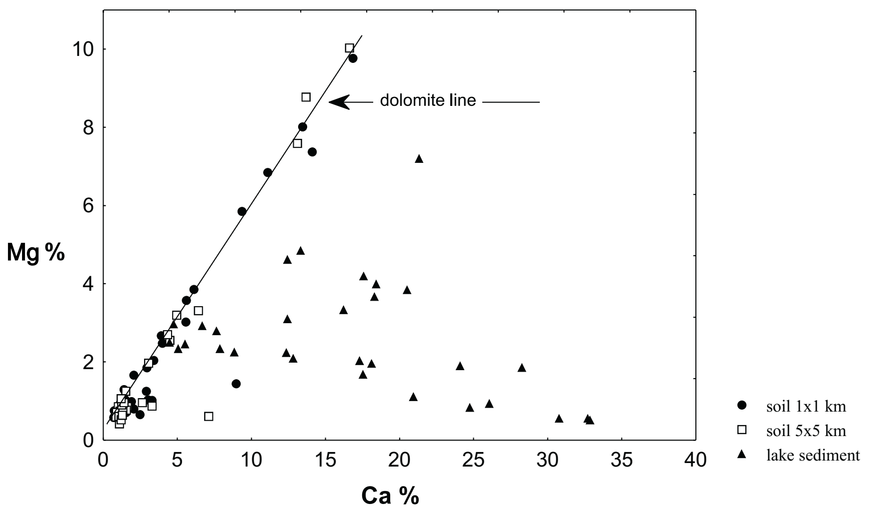

Fig. 3. The Ca vs. Mg plot showing the dolomite contributions to the lake sediments and soils sampled on a 1x1km grid (catchment area soils) and 5x5 km grid (Cres soils).

sediments and the robust method of sampling applied. The sediments with high Ca and Mg have a principal source in the weathering products of dolomite rocks located on the southern and southwestern shores of the lake. The physical weathering of these rocks was intensified considerably after the forest and soil covers were removed by farming practices in the past. The sediments with high Ca and low Mg content are pre-deforestation lake sediments during which calcite precipitation was the major process of lake sediment formation. During sampling, older calcite-rich sediments were obtained, probably due to the weight of the dredge sampler, which penetrated through the overlying unconsolidated sapropel type of sediment (SCHMIDT *et al.*, 2000). From the Ca vs. Mg plot (Fig. 3) it is obvious that the sampled lake sediments are different mixtures of various sediments located within the lake, older calcite rich sediments, more recent detrital /sapropel type clay rich sediments and sediments with a dolomite influence.

Major element geochemistry is of lake sediments characterized by large ranges of Al from < 1% to 9%, Ca from 5% to 35%, Mg from 0.5 to 10% (Figs 2 and 3). The soil samples show far less variability, with the exception of several rendzina samples developed on dolomite bedrock, which contain higher concentrations of Ca and Mg. In general the average contents of both major and trace elements in soils of the Vrana Lake catchment area and those of the whole of the Cres island region do not differ significantly. Only Cu and Zn are present in some 20–30% higher average contents (Tab. 1) in the lake catchment area, due to the abandoned vineyards in the northern and southern parts of the lake. Trace and major element average values (Tab. 1) of the lake sediments are in very good agreement with those given by DOLENC *et al.* (1998) for the surface north Adriatic Sea sediments. A major difference occurs in the content of Pb, which has a mean content of 31 mg/kg in the lake sedi-

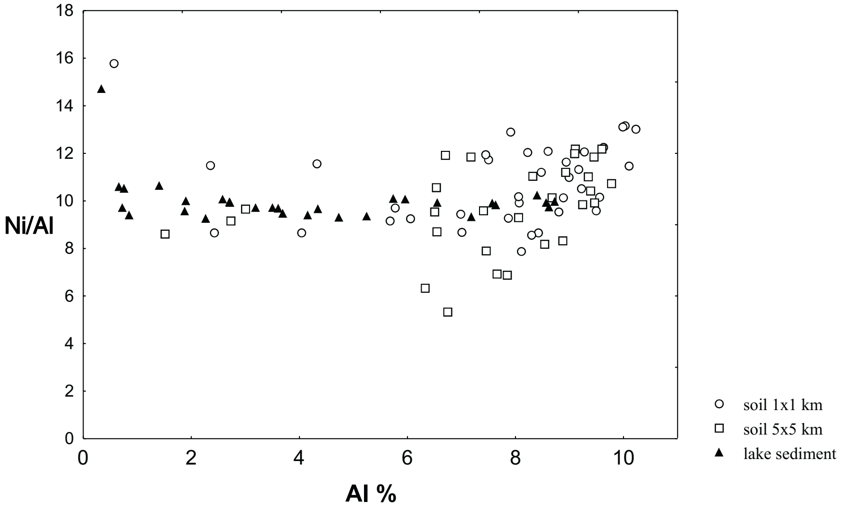

Fig. 4. The distribution of the Ni/Al ratio values in respect to Al in soils and lake sediments.

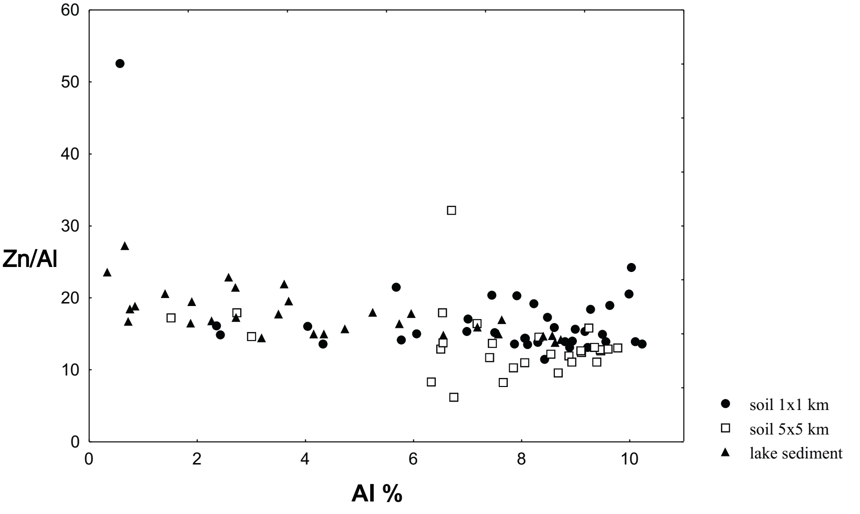

Fig. 5. The distribution of the Zn/Al ratio values in respect to Al in soils and lake sediments.

ments and 18 mg/kg in marine sediments. The mean Hg concentration (395 μg/kg) in North Adriatic sediments is higher than in the lake sediments (107 μg/kg). The difference in Hg content is the consequence of Hg rich sediments from Trieste Bay where the Soča River deposits sediments from the Idrija mercury-mining region. Lake sediments were found to have accumulated lead pollution from the atmo-

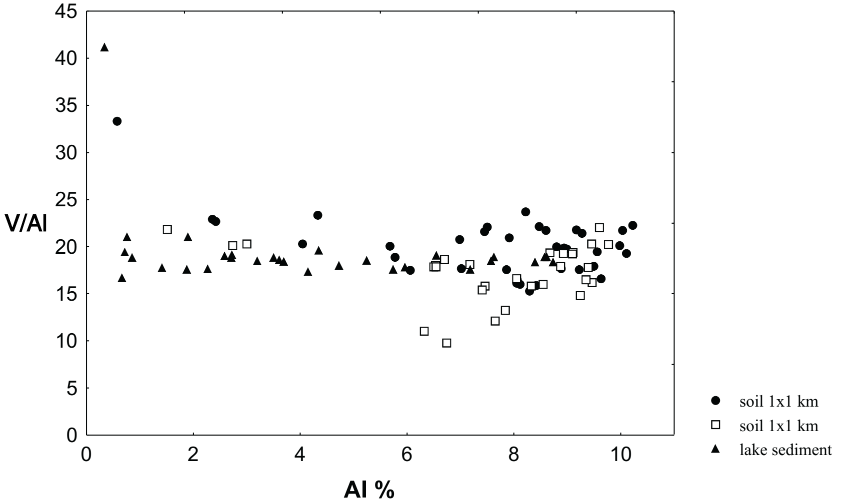

Fig. 6. The distribution of the V/Al ratio values in respect to Al in soils and lake sediments.

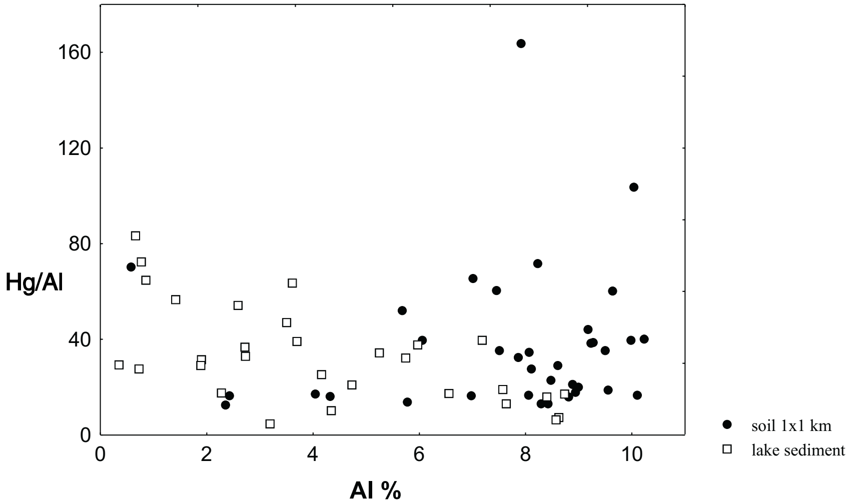

Fig. 7. The distribution of the Hg/Al ratio values in respect to Al in soils and lake sediments.

spheric fallout (SHOTYK *et al.*, 1998; BRÄNVALL *et al.*, 2001) in the past four thousand years in the northern hemisphere.

It was possible to evaluate the environmental changes in the local trace element geochemistry of both soils and sediments because of the positive correlation of Al with most of the elements analysed (except Ca, Mg and Sr) in both soils and sedi-

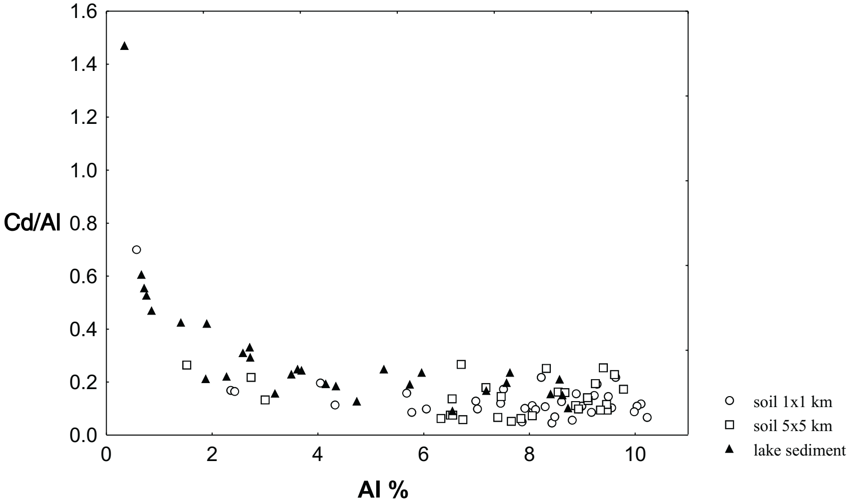

Fig. 8. The distribution of the Cd/Al ratio values in respect to Al in soils and lake sediments.

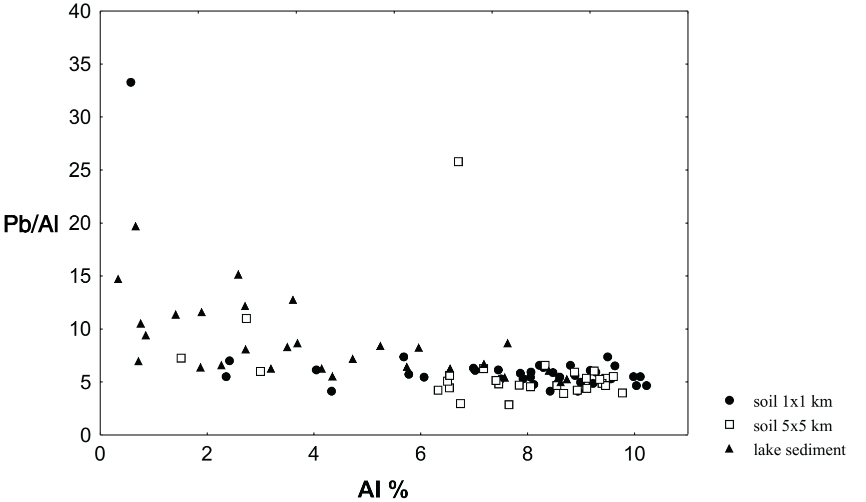

Fig. 9. The distribution of the Pb/Al ratio values in respect to Al in soils and lake sediments.

ments (Tab. 3). Aluminium can be regarded as best representing the detrital component of the sediments, since it is assumed to be present in the alumosilicate phases that, together with quartz, are the principal constituents of the soils in the catchment area. Under the assumption that the sediment detrital mineralogy (and therefore geochemistry) of most of the lake sediments is similar to the surrounding soils,

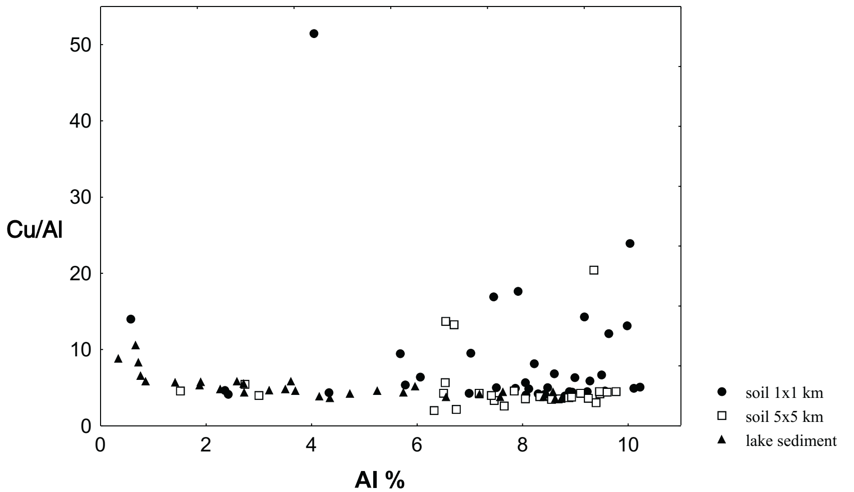

Fig. 10. The distribution of the Cu/Al ratio values in respect to Al in soils and lake sediments.

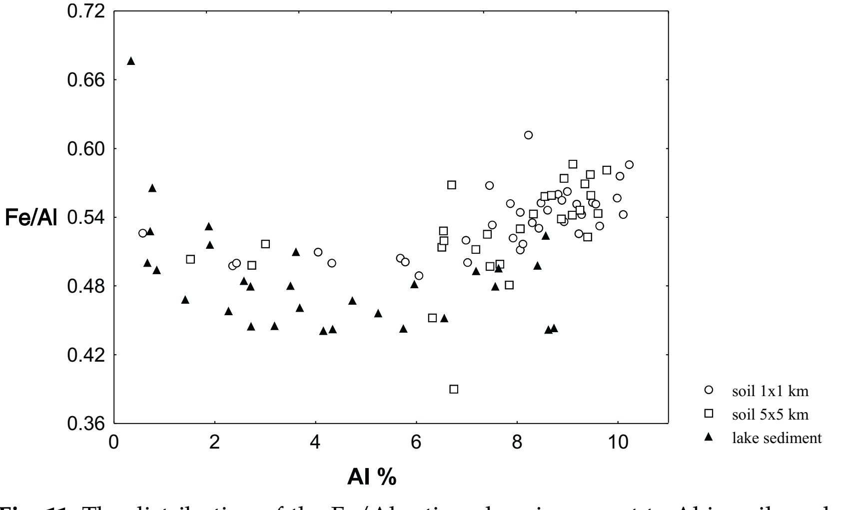

Fig. 11. The distribution of the Fe/Al ratio values in respect to Al in soils and lake sediments.

their main source, the less mobile elements such as Ti, Cr, V, Th and Ba should have similar element/Al ratios in both soils and sediments. With the application of the element to aluminium ratios it was possible to compare the trace element compositions of the lake sediments and the surrounding soils.

The mean element contents of soils and sediments differ considerably and are much higher in soils (Tab. 1). The element to Al ratios (Tab. 2) classify the elements

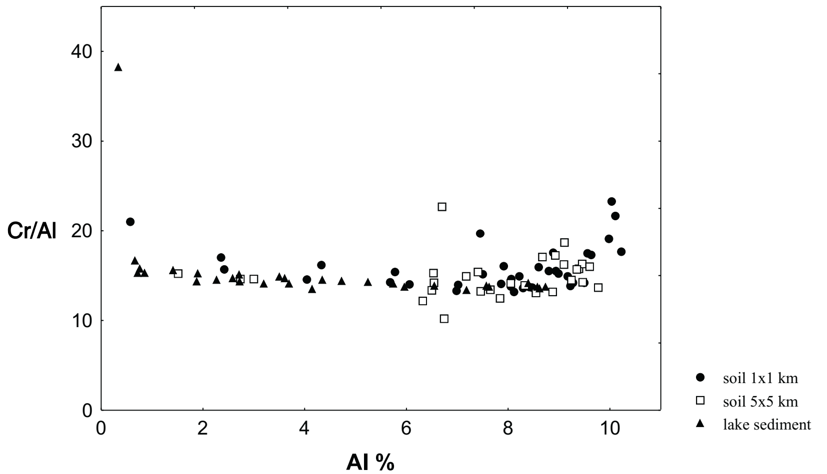

Fig. 12. The distribution of the Cr/Al ratio values in respect to Al in soils and lake sediments.

into three general groups, the group of elements that show no difference in ratios in soils and lake sediments: Ni (Fig. 4), Co, Mn, Th, Zn (Fig. 5), Ba, Ti, K, V (Fig. 6), Na, and Hg (Fig. 7); the elements that are enriched in the sediments: Ca, Sr, Cd (Fig. 8), Pb (Fig. 9), Ba and Mg; elements that can be considered depleted in the lake sediments: Cu (Fig. 10), P, Fe (Fig. 11), Cr (Fig. 12), and La. Tab. 2 also contains the element/Al ratios for the North Adriatic Sea sediments given by DOLENC *et al.* (1998) which show very similar ratios for conservative elements (Ti, Fe, Th, Ni, V) while diagenetic processes have depleted the surface marine sediments of Mn and Co, which have a similar geochemical behavior. Chromium/Al ratio is higher in the marine sediments probably due to sediment discharged from the Po River, and the high Cr/V index (Tab. 2) is also indicative of this influence as stressed by DINELLI & LUCCHINI (1999). The distribution range of Cu/Al, Pb/Al, V/Al, Ni/Al, Zn/Al and Cr/Al in soils, Vrana Lake sediments and marine sediments is given in Fig. 13.

The first group of element/Al indexes can be considered an indicator that implies the same general origin for the fine fractions of both sediments and soils. The second group is indicative of carbonate sediment accumulation (Ca, Mg, Ba, Sr) and accumulation that could be a consequence of atmospheric deposition (Pb, Cd). In the past decades it has been recognized that atmophile trace metals such as As, Cd, Hg, Pb, and Zn, contribute most to soil and lake sediment pollution in the shape of atmospheric fallout (MATSCHULLAT & BOZAU, 1996). Long-range air pollution is the main reason why the content of metals, especially lead, in lake sediments has increased (SHOTYK *et al.*, 1998; BRÄNVALL *et al.*, 2001). Most long-range pollution is deposited on Croatian coastal areas (MIKO *et al.*, 2000; 2001). This is probably the result of pollution from industrial activity. The distribution of Pb in the topsoil of Cres Island and the Vrana Lake catchment area and lake sediments are shown on the map in Fig. 14 and the corresponding Pb/Al ratios in Fig 15. The total concentrations

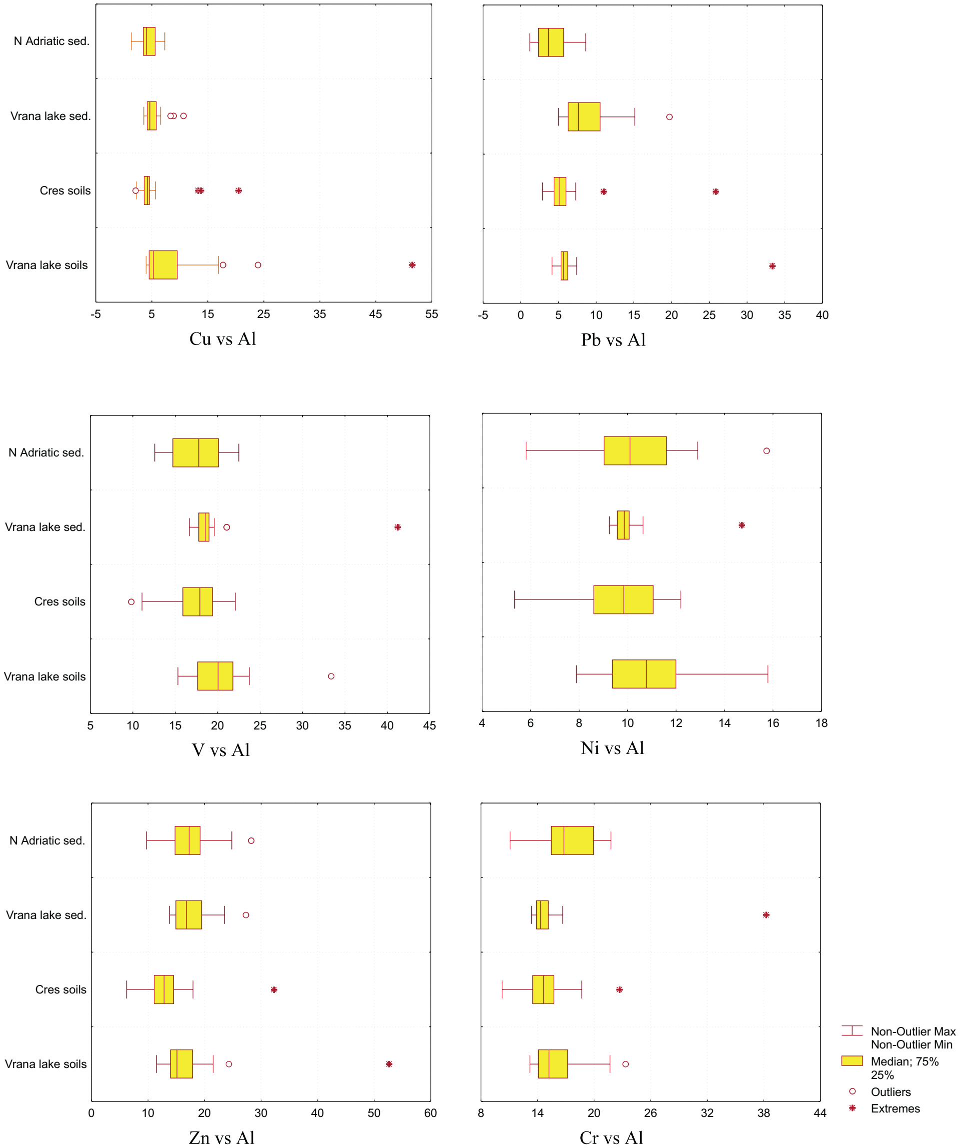

Fig. 13. A comparison of distribution ranges for Cu/Al, Pb/Al, V/Al, Ni/Al, Zn/Al and Cr/Al in soils from Cres island, Vrana Lake sediments and marine sediments (data for the Northern Adriatic Sea from DOLENC *et al.*, 1998).

of lead and the Pb/Al ratio in soils show no distinct patterns, with an anomalous sample taken near the port of Merag in the southeastern part of the studied terrain. In the lake sediments the Pb/Al ratio is high in the organic-rich sediments in the

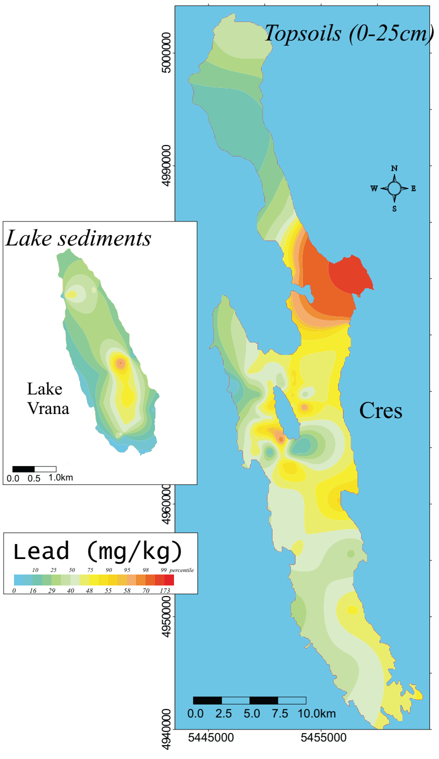

Fig. 14. Geochemical distribution map of Pb in soils and Vrana Lake sediments.

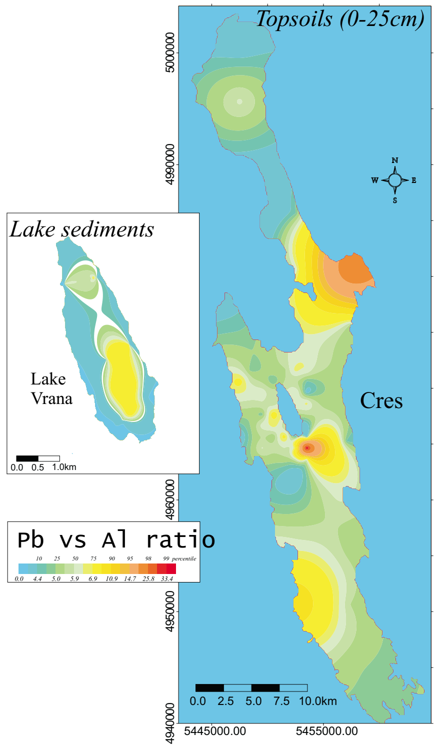

Fig. 15. Geochemical distribution map of Pb/Al ratios in soils and Vrana Lake sediments.

middle part of the lake (Fig. 15), and low in the coastal zone of the lake. Road transport is the main source of lead pollution in Europe. Even though more and more unleaded petrol is being used, all types of petrol still contain small amounts of lead, which is naturally present in crude oil. There are indications of a direct influence of road traffic on the soils in the south-eastern part of the lake catchment area where samples with higher Pb/Al ratios occur (Fig. 15) in the vicinity of the regional road from Cres to Osor. An anthropogenic influence of agricultural activity in the catchment area, which is evident in the soils in the form of Cu enrichment (Fig. 10), is probably the consequence of the application of Cu-based agro-chemicals in the past. The enrichment of Fe (Fig. 11) and Cr (Fig. 12) in soils on the other hand is a consequence of the natural pedogenic processes of rubification, which is characteristic of Mediterranean soils of this region (DURN, 1996; MIKO *et al.*, 1999).

The distribution maps of both total Cr content sediments (Fig. 16) show a slight enrichment in the central parts of the lake while the corresponding Cr/Al ratios indicate a slight depletion of Cr in the same areas (Fig. 17). The topsoil in the Vrana

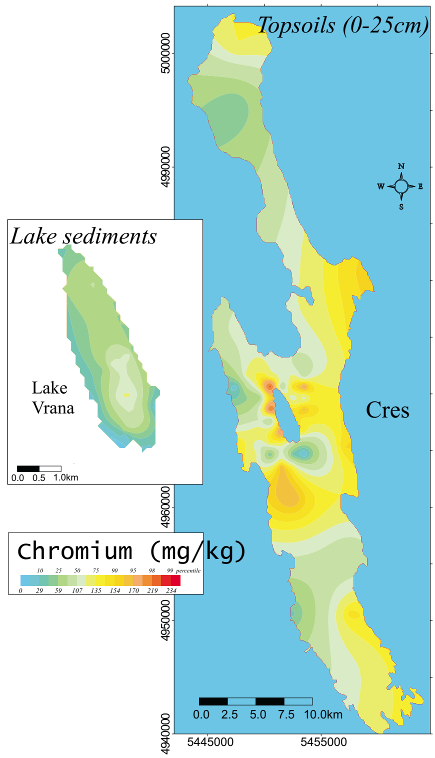

Fig. 16. Geochemical distribution map of Cr in soils and Vrana Lake sediments.

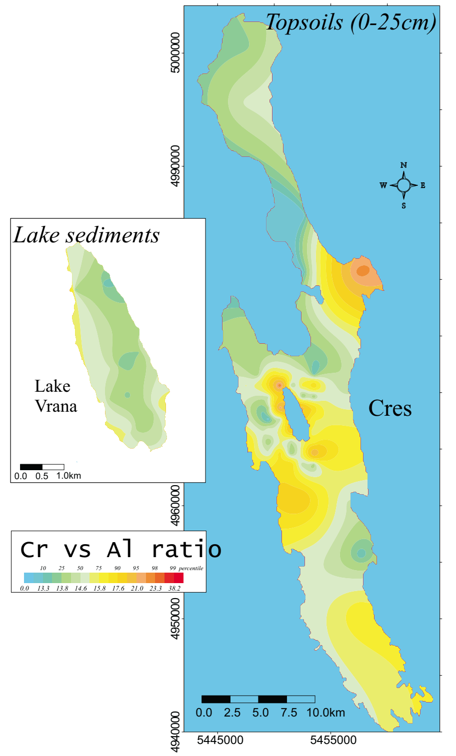

Fig. 17. Geochemical distribution map of Cr/Al ratios in soils and Vrana Lake sediments.

Lake catchment area (1 × 1km grid) has slightly higher concentrations of Cr (mean 121 mg/kg) than the topsoil from the rest Cres Island in general (mean 113 mg/kg). The Cr and V enrichment of the soils on the northwestern slopes of the Vrana Lake catchment area could be also due to the contribution of bauxite deposits that were mined in the past in that area. Fig. 18 shows the V/Al versus Ni/As plot of data from this study together with the data for surface marine sediments of the Northern Adriatic Sea obtained by DOLENC *et al.* (1998) and terra rossa, loess, and flysch sedimentary rocks from Istria by DURN (1996). Most of the soil and sediment V/Al indexes range from 15 to 24 and the Ni/Al from 6 to 13. Flinch samples plot outside these boundaries with high Ni indexes, while loess from the Premantura peninsula and Unije Island (to the south west of Cres Island) and the marine sediments sampled to the south of Istria (sample sites in DOLENC *et al.*, 1998) have low V/Al indexes (<15) and Ni/Al (<6). The plot indicates that the detrital influence is more under a regional influence and that the soils that exist today within the catchment area (especially the rendzina soils developed on dolomite) have less influence on the lake sediments sampled.

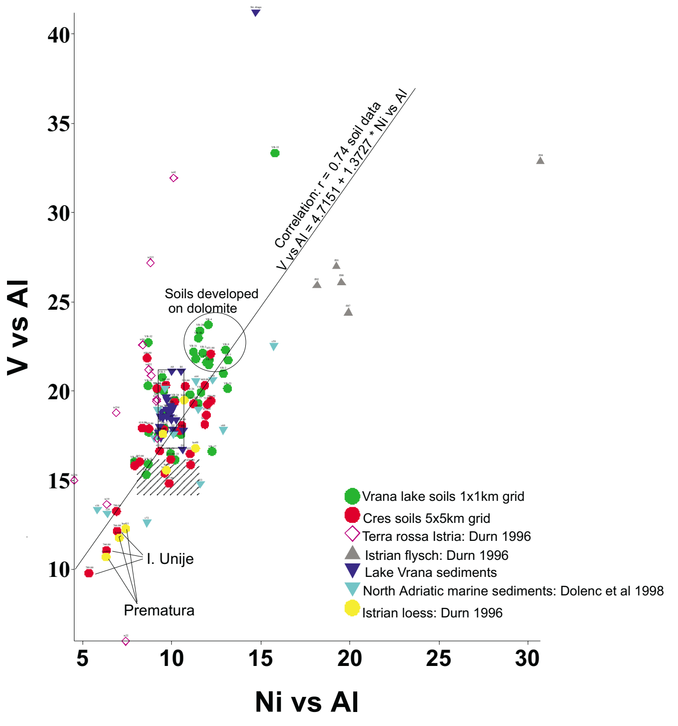

Fig. 18. The V/Al ratio vs. Ni/Al ratio in surficial materials of the northeastern Adriatic region. Open rectangle lake sediment data, open circle soils developed on dolomite in the Vrana Lake catchment area. Loess data from DURN (1996).

CONCLUSIONS

The mean element contents of soils and sediments differ considerably in the studied sediments of Lake Vrana and the topsoil of the lake catchment area, and are much higher in the soils. The element to Al ratios fall into three main groups, the group of elements that show no difference in ratios in soils and lake sediments: Ni, Co, Mn, Th, Zn, Ba, Ti, K, V, Na, and Hg; elements that are enriched in the sediments: Ca, Sr, Cd, Pb, Ba and Mg; and elements that are depleted in the lake sediments: Cu, P, Fe, Cr, and La.

Long-range air pollution during the past and in recent times is probably main reason why the content of metals, especially lead, in lake sediments has increased, although a local source from road transport as indicated by soil data from the catchment area could also be an important source of the Pb. Some pollutants in catchment area soils, such as Cu and Hg from agro-chemical sources, were not determined in elevated concentrations in the lake sediments. Comparison of element/Al indexes from this study with the other studies of surface materials in the region show mutually similar sources, with loess and flysch as the two geochemical end-members.

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