Normalization and Trace Element Contamination of Soils in a Karstic Polje - An Example from the Sinjsko Polje, Croatia

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Abstract

Estimation of the anthropogenic over natural contribution in the chemical content of soils and sediments is very important but not easy to measure. Normalization based on either aluminium or iron, as reference conservative elements having supposed natural distributions, is a useful tool in solving this problem. However, several independent factors can influence the normalization procedure, which if not taken into account could lead to completely erroneous conclusions about the origin of the particular elevated concentrations of certain elements. Therefore, a great deal of caution should be exercised during application of the normalization procedure. Analytical data from 95 soil samples from the Sinjsko polje enabled us to critically apply this procedure. Linear regression analysis, evaluation of enrichment factors and trend surface analysis with the construction of appropriate maps were used to test the procedure. Presuming an existing linear dependence between the conservative element and the heavy metal it is possible with the use of linear regression to simultaneously define the heavy metal geochemical background (baseline) and to isolate natural and/or anthropogenic outliers (anomalies). Coupled with geographic plotting facilities this type of outlier-screening is used to locate areas of man made pollution.

Statistical treatment of selected elements included the calculation of means, standard deviations and other estimates of basic statistic parameters. Evaluation of enrichment factors reveals the dependence of this parameter upon four main factors: the choice of reference element; the choice of reference material; the homogeneity of reference element distribution in the study area; and correlation of particular element with reference element. Examination of trends is a common procedure in the analysis of geochemical maps. Its purpose is to segregate the underlying trend that possibly pervades the study area, from the local variations, that is, the "noise" or "background".

Statistical analysis, as suggested by the results in this work, would be more properly used over general areas in the karstic terrain, with different geological, geomorphologic and hydrogeological characteristics, rather than being focused on the relatively small phenomena such as poljes, with many local geologic, hydrogeological and geochemical constraints.

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1. INTRODUCTION

One of the main characteristics of soil as a part of the environment is that it serves as a purification medium for water on its way from the surface to the underground. So, soils are also sinks for many materials transported onto the land. Many substances that occur naturally, such as trace metals and nutrients, may be mobilized as a result of natural processes, as well as human activities. Before anthropogenic contributions to soils can be assessed, contributions due to natural processes must be estimated. For most continental areas natural trace element concentrations can range over two orders of magnitude, causing confusion in data interpretation regarding anthropogenic loading (WINDOM et al., 1989). However, the natural value or background is more a range than a single value, and it strongly depends on local factors and the particular environment. A background range, or soil (sediment) baseline, which is probably more correct, is thus close to the definition of the threshold in exploration geochemistry, which is defined as a value that separates anomalous samples, or areas, from background (SINCLAIR, 1991). In an ideal situation, geochemical threshold levels should be selected on the basis of orientation survey information with a careful inspection of data from both the numerical and spatial viewpoints. The current range, availability and power of computers permits the easy ordering and manipulation of data (after, if necessary, transformation to a normal distribution), allowing the direct isolation of the top-most 2% of the data. This avoids the mean plus two standard deviation rule which has led to many misinterpretations in the past. In fact, so widespread was the application of the rule that many users of exploration geochemical data believed that the threshold was the mean plus two standard deviation level, rather then a carefully selected value based on geochemical and geological evaluation of the data.

Both exploration and environmental geochemists identify the geochemical background as being of prime importance. Statistical outliers and geochemical anomalies are relatively rare events and difficult to study statistically due to the fact that anomalous populations could have several different sources. It is far better to reliably define the geochemical background and then focus on individuals which are above background. These are, by definition, anomalies that require atten-

tion and interpretation in terms of mineral occurrence, lithology, or secondary geochemical environment (GARRETT, 1989).

In order to show the importance of background or baseline for global geochemical mapping, the leaders and cooperators of IGCP-259 "World Geochemical Map" (after the termination of this project), proposed a new project as an extension and the logical continuation of the previous one. The new IGCP-360 has been named "Global Geochemical Baselines" in order to stress the importance of geochemical background for the geochemical mapping of the globe. Firstly, the new project definitely recognizes the karstic terrain as a peculiar area in the geochemical sense, and secondly, soils developed on carbonate rocks, as a specific geochemical environment, which was pointed out by PIRC & MAKSIMOVIĆ (1985), PIRC et al. (1989, 1991) and PROHIĆ (1989), PROHIĆ & JURAČIĆ (1990) and PROHIĆ et al. (1990), among others. Critical examination is required for establishing geochemical baselines in the karstic environment.

There are several sources of trace elements in the environment, both natural and man made: soil parent material (rocks), commercial fertilizers, liming materials, sewage sludges, animal wastes, pesticides, irrigation waters, coal combustion residues, metal-smelting industries, car emissions, and others. With the exception of the parent material, all are anthropogenic in nature. The first seven sources are the primary input sources in agro-ecosystems. The rest may have an impact on the natural ecosystem, as well as on urban and rural areas. Free of human interference, the trace element content of the soil is largely dependent on that of the rocks from which the soil parent material was derived, and on the process of weathering to which the soil-forming materials have been subjected. The more aged and older the soil, the less may be influence of parent rocks (ADRIANO, 1986). Metals such as zirconium, rubidium, and strontium, which are derived from rock material by natural weathering processes, constitute this group. The second group is made up of metals which have become enriched chiefly as a result of human activities, and includes, among others, chromium, cobalt, nickel, copper, zinc, cadmium, mercury, and lead.

These two groups often overlap; for example, the enrichment of mobile elements such as manganese and iron, which may also have had an additional anthropogenic origin. By their own accumulation, these metals can cause other elements to accumulate. Even the precipitation of carbonates can be influenced by "anthropogenic" means and in turn influence the metal levels (FÖRSTNER & WITTMANN, 1981). The concentrations of trace elements in soils are dominantly determined by inorganic detrital, rather then organic and nondetrital materials. The inorganic detritus is the result of chemical and physical weathering of the continents, and is composed mostly of a limited number of silicate minerals, such as quartz, feldspars, micas, clay

minerals, metal oxides and sulphide minerals. In some areas and for some soil types, carbonate minerals represent an important component. Of the materials contained in natural sediments, quartz, feldspar and carbonates are relatively poor when compared to the other phases, and thus serve to dilute soil metal concentration (WINDOM et al., 1989). Nonetheless, when attempting to determine the "extent of pollution" recorded in the soil by means of trace metal load in sediments, it is of primary importance to establish the natural level of these substances, i.e. the "pre-civilization" level, and then subtract it from existing values for metal concentrations in order to derive the total enrichment caused by anthropogenic influences. The trace element content of soils is, thus, a composite of natural and contaminant source material and reaction products, and is mostly associated with the fine-grained fraction.

Whereas fine-grained sediment, or the fine-grained fraction of mixed sediment, is potentially a sensitive indicator of sediment contamination, pollution assessment is made difficult by the need to differentiate contaminant levels from background levels in sediments of different origins and textural characteristics. Without correction for variable background levels, meaningful comparison of trace element concentrations are impeded by large levels of bias and variability. Several attempts have been made to solve this problem which is briefly called the "background question".

GARRETT (1989) uses, as he named, the chi-square plot, which is a relatively simple approach based on a multivariate probability plot where each multi-element geochemical sample is represented as a single value. The resulting diagram would be interpreted much as a univariate probability plot, where the presence of more than one straight-line segment is taken as evidence of multiple populations, and outliers, as individuals or small groups, are separated from the remaining data by gaps on the plot. The purpose of this procedure is to identify statistical outliers which are candidates for interpretation as true geochemical anomalies, and to isolate a multi-element subset that is representative of the geochemical background.

Comparison of contaminant trace element levels over large distances and time periods requires a method separating contaminant, which is anthropogenic, from natural components that is applicable to the size of region under consideration. The aim is to facilitate the significant reduction of variability in trace element concentrations by regional definitions of baseline (HANSON et al., 1993). Although the validity of a regional definition of baseline may tend to decrease as the region becomes larger, we use this approach to describe a uniform baseline for soils in the Sinjsko Polje, which is representative of a typical karstic polje, using different approaches given in the literature. Our goal was to establish the best approach of data normalization that would prove applicable for a specific karstic environment.
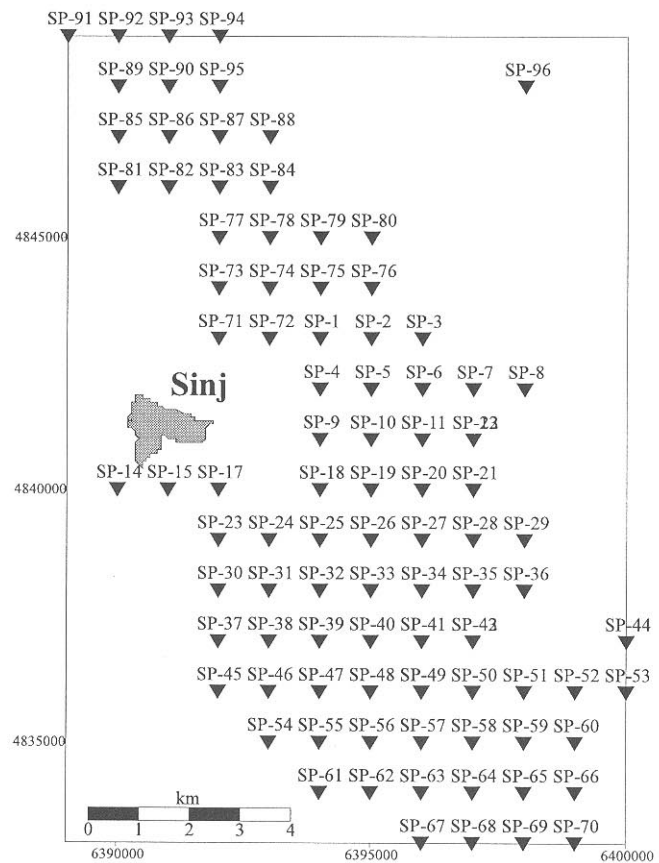
Fig. 1 Geographic location and soil sampling grid of Sinjsko Polje.

2. DESCRIPTION OF THE AREA

The territory comprising the Sinjsko Polje and its surroundings measures 25 x 35 km. It is situated mostly in the Dalmatian part of the Republic of Croatia with a small NE extension into Herzegovina (Bosnia). The basin, elongated in the SSE direction, lies between the Dinara mountain in the northeast, Svilaja in the west and Mosor in the south. Northeast of the Dinara range, a small section of the Livno Polje was not mapped (Fig. 1). The geology is shown on the geologic map 1:100,000, sheets Sinj (PAPEŠ et al., 1984) and Omiš (MARINČIĆ et al., 1982). The surroundings of the depression consist largely of Mesozoic carbonate rocks of chiefly Cretaceous and Jurassic age, with a subordinate extent of Palaeozoic and Tertiary (flysch) clastics. The surface of the Sinjsko Polje is covered in part by Tertiary marls (with coal) and largely by Pliocene-Quaternary lacustrine and fluvial deposits (Fig. 2). The territory belongs to the High Karst of the Outer Dinarides with prevailing NW-SE directions of structures which bend in the south toward an E-W direction. The surroundings are intensely karstified, with the karst hydrography dominated by the Cetina river. The soils comprise rendzinas, brown and red soils on limestones and dolomites, and minor terra rossa on carbonate beds, and rankers, brown acid soils and podzolic brown soils on clastic rocks. In the depression, hydromorphic soils are common (Fig. 3).

A number of industries and intense agriculture, especially vine and vegetable growing, are characteris-

tic. The soils on the surrounding carbonates and on the gravel plains are mostly brown soils on limestone, lessivated brown soils and in places terra rossa. In the area of the lake, soils are hydromorphic (PIRC, 1993).

3. SAMPLING AND ANALYTICAL METHODOLOGY

Grid sampling of soils was taken after analysis of variance sampling designs, followed by the subsequent analysis of these materials. The analysis of variance designs that were used in the study are of the unbalanced, nested type. The grids applied were 1x1 and 2x2 km. The point of origin of this grid was randomly determined for the project of the Geochemical Map of Istria.

AOV sampling was applied to sample sites of this grid according to MIESCH (1976), so that at a number of randomly selected grid sites a second sample was collected 100 meters away, either (randomly) to the north, east, south or west of the sample point. Then a number of randomly selected samples were split into two subsamples which were separately analyzed. This procedure permitted the break-down of the total variance within the analyzed samples into the component between areas, then into the component within areas and between grid points, within grid points and between samples 100 m apart, and the component between analytical replicates, which is the analytical error. The scheme for partition of the total variance within the data is thus:

$$S^2_{total}/S^2_{regional}+S^2_{grid}+S^2_{local}+S^2_{lab}$$

The total variance can be separated in this design into components as follows (PIRC, 1993):

$$S^2_{total}=S^2_{25x25km\,cells} + S^2_{5x5km\,cells} + S^2_{1x1km\,cells} + S^2_{0.2x0.2km\,cells} + S^2_{lab}$$

The statistical significance of components is established by the F test.

3.1. SAMPLE MATERIALS: SOIL

Soil was collected by channel sampling of the upper 15 cm (below the Ol and Of horizons, if present) of the soil profile (PIRC et al., 1991). At each sampling site, a sample of about 1 kg was collected with comprised sampled material from 5 sampling points, one at the exact location of the site, and another four at 10 m N, E, S and W from the central point. Compositing was used to reduce local variability. The air dried soil fraction that passed through the 2 mm sieve was reduced by repeated quartering and milling to 0.062 mm for analysis. Samples were collected during 1989. It is important to mention that the samples had been taken before the aggression and war started in the region, so it can be concluded that the samples were not contaminated by the activity of war.

The grids applied were 1x1 and 2x2 km for depressions which are, as a rule, of smaller sizes, and 5x5 km for the surrounding elevated terrain. The point of origin of this grid was randomly determined for the project of the experimental geochemical map of Istria.
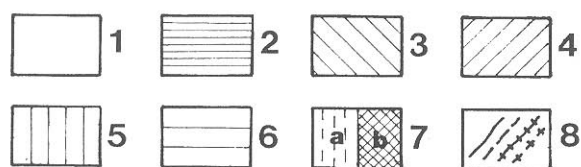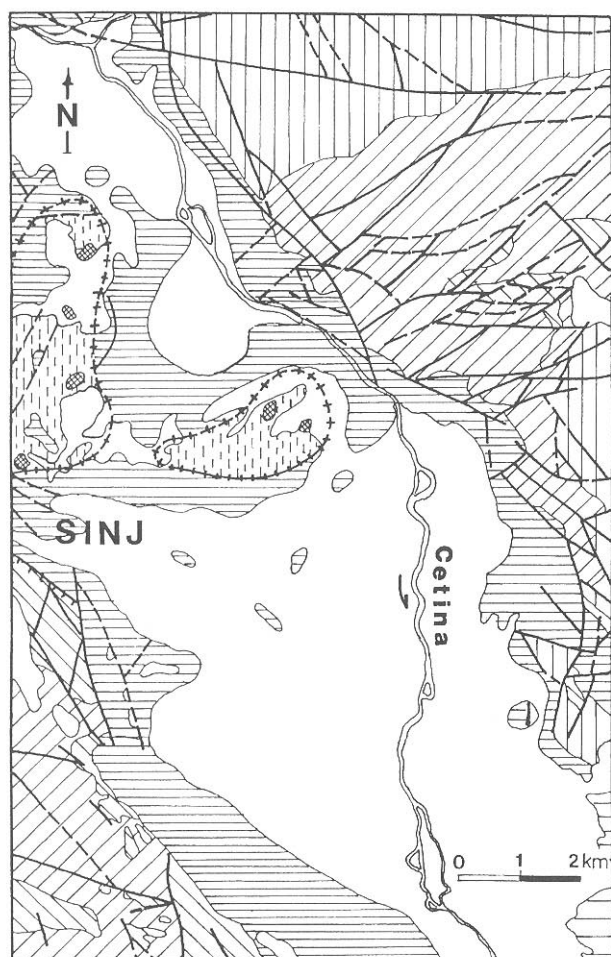

Fig. 2 Simplified geologic map of the study area (after MARINČIĆ et al., 1976; PAPEŠ et al., 1982). Legend: 1) Quaternary sediments - alluvium, proluvium and terra rossa; 2) Miocene sediments - marl, limestone, sand and clay with coal; 3) Eocene and Palaeocene sedimentary rocks - Promina clastites, foraminiferal limestones; 4) Upper Cretaceous sedimentary rocks - limestones; 5) Lower Cretaceous sedimentary rocks - limestones and dolomites; 6) Jurassic sedimentary rocks - massive limestones, limestones with dolomite lenses; 7) Permian and Triassic rocks - a) Clastic sedimentary rocks with gypsum and anhidrite, b) Spilitized diabases; 8) Faults and diapiric contacts, observed and inferred.
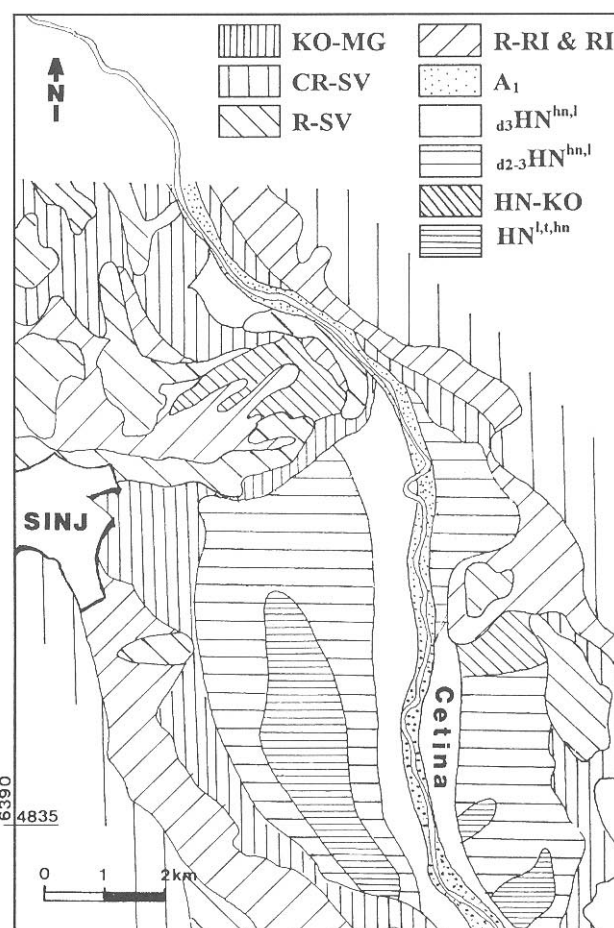

Fig. 3 Simplified pedologic map (after MARTINOVIĆ et al., 1983). Soil mapping units: KO-MG colluvium, carbonate, nongleyic-eugley, mineral, anthropogenized; CR-SV terra rossa-calcocambisol; R-SV rendzina-regosol on limestone; R-RI & RI rendzina-regosol on marl; A_1 fluvisol, carbonate; $_{d3}HN^{hn,l}$ hydromeliorated fluvisol-eugley(80:20); $_{d2-3}HN^{hn,l}$ eugley-fluvisol (90:10) hydromeliorated; HN-KO eugley-colluvium (70:30) hydromeliorated; $HN^{l,t,hn}$ eugley-peaty gley (90:10) hydromeliorated.

3.2. ANALYTICAL METHODS

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

3.3. QUALITY ASSURANCE AND CONTROL

Quality assurance was maintained by minimizing human error through good training and the care of collectors and lab workers who did the sample preparation, by using composite samples to reduce the local variability, and by submitting samples for analysis in random succession in order to evenly distribute the error due to the shift of analytical conditions across samples.

Control of the accuracy of the ICP-AES was achieved by blind determinations of the geological standard materials: BUTR 8, GXR 6, SJS-1, SO-2, GXR-6, MAG-1, SCo-1, SGR-1, SJS-1 and SO-1 in 1992, (recommended values in ABBEY, 1983). Accuracy is sometimes not easily assessed owing to contrasting indications of particular standards. In the first approximation it is acceptable for most of the determined elements. Detailed comparisons of elemental abundance should be made, however, on the grounds of careful consideration of the indications of the standards.

Precision was monitored by analysis of variance estimation of laboratory error, i.e. the variance component between the analytical splits. So, the precision is expressed as variance joined to the laboratory error, which for aluminium is 3%, scandium 4%, iron 2%, lead 15%, cadmium 44%, copper 3% of the total variance respectively (note that these values are for the entire region of poljes in Slovenia and Montenegro batched together). Generally, laboratory error greater than 50% of total variance is considered too high, and analytical results insufficient either for estimating mean concentrations, or for the construction of geochemical maps (PIRC, 1993). It can be seen that the precision for cadmium is close to this limit, so that data for this element should be interpreted with extreme caution. The reason why we included cadmium in our study is its very peculiar distribution in the Sinjsko Polje which, although being expected according to the field studies, still represents an open question. So we decided to reanalyze the samples from the Sinjsko Polje for cadmium. The laboratory error of ICP for lead is 15%, which is not too high taking into account the difficulties connected with the analysis of lead in the emission spectra, but for regional studies it is rather satisfactory. For other elements the precision is below 5%, which is considered excellent.

3.4. DATA PROCESSING

Data processing of seven elements selected from the batch of the 35 analyzed elements was mainly done using the STATISTICA version 4.3 program and the resulting element maps are colored maps drawn by ROCKWARE and SURFER contouring programs. The raw data single-element maps were drawn using an inverse-distance weighting cell averaging computer routine (ROCKWARE) with contours drawn (SURFER) at the 10th, 25th, 50th, 75th, 90th, 95th, and 99th percentiles of the cumulative element distribution which allows comparison of the spatial distribution patterns for different elements (HOWARTH, 1983). Maps of element distribution after outlier screening were drawn by the same procedure.

4. AN OVERVIEW OF THE GEOCHEMICAL DATA NORMALIZATION PROCEDURES

A variety of approaches for reducing natural variability have been used to improve the statistical power in data intercomparison. There is no consensus on the appropriate soil - sediment component to be used for normalization i.e. to factor out the variability in natural trace element concentrations. In most cases, the source of the natural material making up the sediment has been assumed to be constant, so the emphasis has been placed on accounting for the "grain size effect" (WINDOM et al., 1989). Metals are not homogeneously distributed over the various grain size fractions, and large differences in total concentrations are observed in sediment samples from a single locality. Within the grain size spectrum, the finer-grained fraction - consisting mainly of clay minerals - show relatively high metal contents. In the silt and fine sand fractions the metal concentrations generally decrease as that fraction is dominated by quartz components with low metal contents. In the coarser fraction, the presence of heavy minerals may cause the metal portion to increase still.

Different methods for grain size correction are presented in the literature and compiled by SALOMONS & FÖRSTNER (1984). These methods will reduce (not eliminate) the fraction of the sediments that is largely chemically inert, i. e. mostly the coarse-grained quartz, feldspar and carbonate minerals, and increase the substances active in metal enrichment, i. e. hydrates, sulphides, amorphous and organic materials. Analyses have been carried out often on a specific size fraction to correct for natural variability, but this approach requires a separation step and the results are often confusing since concentrations in a certain size fraction do not reflect the concentration in the total sediment (WINDOM et al., 1989).

The basic geochemical approach to normalize geochemical data is by means of conservative components whose levels are unaffected by contaminant inputs, for example, grain size, Al, Fe, Sc, Ni, TOC and Li. A conservative element is used as it is assumed 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). A conservative eleme-

nt which is often used as a normalizer of trace element data is aluminium, due to its high natural abundance and because it is not commonly associated with anthropogenic input. Additionally, aluminium is a major constituent of soils and sediments as a structural element of clays. Aluminium was most recently used by WINDOM et al. (1989), in the study of estuarine and coastal marine sediments, ESSER et al. (1991), in study of soil contamination, and HANSON et al. (1993), who studied contamination of estuarine and coastal marine sediments. It has strong positive correlation with many major and minor elements in soils, which are considered as natural content and is used to significantly reduce data variability for the purposes of sample intercomparison over small (WINDOM et al., 1989, SCHROPP et al., 1990) and larger (HANSON et al, 1993) regional areas. The association between Al and other elements has a geochemical foundation which can be used as a basis for developing statistical models of the natural elemental content in sediments of varying textural and mineralogical characteristics. Linear regression was used to estimate model parameters for each metal with aluminium (HANSON et al, 1993).

On sediment samples from the Ems River Estuary in Northern Germany a series of potential reference elements - Cs, Eu, Fe, Rb, Sc, Sm and Th (measured by neutron activation analysis) - were tested by ACKERMANN (1980). This study suggests that cesium appears to be the preferred reference element for two reasons: it is particularly well correlated with the <20µm fraction and the ratio, s(100%)/s(0%) is greater than for any other elements. The main disadvantage is that cesium is not analyzed in routine studies. Due to the very close geochemical relationship between scandium and aluminium (which is most often taken as a reference value), the measurement of these components seems to be recommended (THOMAS & MARTIN, 1982; GUEGUENIAT et al., 1983; GOLCHERT et al., 1991). Scandium has the advantage over its geochemical counterpart aluminium when standardization of trace elements is made due to all the obstacles which could arise when comparing the major and trace elements (analytical concentration range, differences in precision and accuracy, difficulties in making simultaneous analysis for most techniques). Additionally, ash content can be used as a "conservative parameter" (SHOTYK et al., 1990), the content of the element of interest in the supposed nonpolluted area (FULLER et al., 1990), concentration of titanium (TIAN et al., 1993), cerium (REHM et al., 1984), strontium (WINDOM et al., 1989), lithium (LORING, 1990), nickel (WU, 1984), iron (VAN ALSENOY et al., 1993; DASKALAKIS & O'CONNOR, 1995) and rubidium (RANDLE et al., 1993), among others. Apart from the inorganic component of soils, particle-bound TOC was also used for normalizing trace element data (WINDOM et al., 1989) assuming that it acts as a matrix on particle surfaces for complex formation. One weakness of TOC as a normalizer, however is the fact that TOC itself is subject to considerable

augmentation by human activity and is often a contaminant (DASKALAKIS & O'CONNOR 1995). An excellent review of standardization techniques is given by VERTAČNIK (1994). Generally, it appears that corrections made with conservative elements are especially valuable. If separation of coarser grain size, for example down to <63µm, is carried out prior to correction, still better results may be obtained.

The numerical approach to the problem of normalization with conservative elements is linear regression analysis. A baseline model was considered acceptable when the covariation with a conservative element was statistically significant, and the linear regression intercept was close to zero (HANSON et al., 1993; DASKALIS & O'CONNOR, 1995).

Another problem associated with the natural versus anthropogenic contributions to or share of the trace element contents in sediments and soils is the quantification of environmental impact. The basic idea is to make the comparison with a standard reference earth material. It is assumed that this standard material is not contaminated, and its trace element content can be taken as "background values". Several possibilities have been discussed to establish background values for trace elements (FÖRSTNER & WITTMANN, 1981; PROHIĆ, 1989; PROHIĆ & JURAČIĆ, 1989):

1. average shale composition as a global standard value;

2. fossil aquatic sediments from a defined environment as a standard;

3. recent deposits in relatively unpolluted areas;

4. short, dated sedimentary cores which provide a historical record of events.

A first attempt to quantify the extent of heavy metal pollution in sediment on a more global scale was made by FÖRSTNER & MÜLLER (1973) by the comparison of heavy metal consumption with the natural concentration of the respective elements in unpolluted sediments, which is then recorded in the "Index of Relative Pollution Potential". A similar approach was used by NIKOFOROVA & SMIRNOVA (1975) by calculating the "Technophility Index" which is the ratio of the annual output of a metal to its "Clarke" (mean concentration in the earth's crust). The higher the TI of a metal, the more intensively it is involved in technological migration. A quantitative measure of the metal pollution in aquatic sediments has been introduced by MÜLLER (1979), known as the "Index of Geoaccumulation" (I_{geo}):

$$I_{geo} = \log_2 \frac{C_n}{15 \times B_n}$$

C_n is the measured concentration of the element "n" in the pelitic sediment fraction <2mm, and B_n is the geochemical background value in fossil argillaceous sediment ("average shale"). The factor "1.5" is used because of possible variations of the background data

due to lithogenic effects. The I_{geo} consists of 7 grades, whereby the highest grade (6) reflects 100-fold enrichment above the background values (SALOMONS & FÖRSTNER 1984).

Another way to quantify the possible environmental impact by measuring the trace element content in sediments is the so called "Sediment enrichment factor" or simply "Enrichment factor" (Ef) which is the concentration ratio of a given element ($C_{nsample}$) to the conservative element in sample ($C_{cons.sample}$) with respect to the same ratio in a standard material $C_{n\ ref.}/C_{cons.\ ref.}$ (FÖRSTNER & WITTMANN, 1981; LI, 1981):

$$Ef = \frac{C_{nsample}/C_{cons.sample}}{C_{n\ ref}/C_{cons.ref}}$$

A quantitative elaboration of enrichment factors is not an easy task and mostly depends on local conditions with respect to the type of environment, soil or sediment type, main goals of the study etc. However, GOLCHERT et al., (1991) distinguished three categories of enrichment factors : Ef≤2, 2<Ef<10 and EF≥10. HASSAN & ISMAEL (1993) showed how different materials used as reference materials can give quite different, even erroneous conclusions about the origin of the particular elements. That is why the choice of reference material and appropriate conservative element is crucial to the final conclusions, a fact which is, in many papers, still not sufficiently evaluated. In this study we have tried to critically apply several approaches before recommending, in our opinion the best one for the given material in a given environment. Finally, in this study, the average shale (TUREKIAN & WEDEPOHL, 1961) was chosen as the normalizing standard. The average crustal igneous rock often used in similar investigations is not used here, because the average shale is presumed to be a more closer representative of continental soils (LANTZY & MACKENZIE, 1979) then the average igneous crustal rocks.

5. STATISTICAL TREATMENT OF THE RESULTS AND INTERPRETATION

5.1. LINEAR REGRESSION ANALYSIS

Considering the presumption of an existing linear dependence between the conservative element and the heavy metal it is possible with the use of linear regression to simultaneously define the heavy metal geochemical background (baseline) and to isolate natural and/or anthropogenic outliers (anomalies). Coupled with geographic plotting facilities this type of outlier-screening is used to locate areas of man-made pollution.

Statistical treatment of selected elements included the calculation of means, standard deviations from the mean, and other estimates of basic statistic parameters (Table 1). After the assessment of population normality, performed through normal probability plots of raw data (Fig. 4), the data for Cu and Pb were log-transformed and used in further analysis. Correlation coefficients for the selected elements are given in Table 2. Linear regression analysis results (Table 3), display coefficients of determination (r^2) for metal correlation with aluminium and iron before and after outlier removal.

The choice of aluminium as the conservative element is mainly due to the fact that its levels are relatively unaffected by pollution, its accuracy determination and precision (3% error) by ICP analysis. Aluminium also serves as a measure of the clay content (DASKALAKIS & O'CONNOR, 1995) and its strong correlation with other elements (Tables 2 and 3). Alternatively, iron could have been used as a conservative element but since most elements have a slightly stronger correlation with aluminium (Tables 2 and 3) it seemed a more appropriate choice.

To have a valid regression model not only do the r^2 have to be high, but it is also important that the residuals are independent, have zero mean and constant variance (DILLON & GOLDSTEIN, 1984; ROCK, 1988; BARNETT & LEWIS, 1994). The autocorrelation was thus tested by Durbin-Watson statistics (Table 3) and heteroscedasticity by visual checks of residuals of selected elements plotted against the independent variable (Al).

The identification of outliers which have disproportionate influence on the estimated background model was performed through graphic analysis of residuals with normal probability plots (relative cumulative percentages are expressed as -3σ to +3σ from the mean - normal expected value). In the case of normal error structure the residuals plot on a straight line, and outlier (anomalous) values are marked as departures at either end of the plot (DILLON & GOLDSTEIN 1984; BARNETT & LEWIS 1994). Usually these departures occur at the lower and upper 5% (±2σ) of the normal expected distribution. When these dissimilar samples are identified, they are removed from the data set leaving a

	Cu	Pb	Zn	Ni	Cr	Cd	Al	Fe
n	95	95	95	95	95	95	95	95
Mean	106	50	114	71	142	1.18	5.92	2.96
Median	76	49	115	68	98	1.00	5.95	3.08
Min.	11	9	28	9	16	0.20	0.82	0.43
Max	923	220	208	160	2270	3.50	11.30	6.67
Std. dev.	109	28	43	35	227	0.96	2.59	1.28
Skewness	4.84	3.11	0.04	0.33	6.17	0.62	-0.06	0.07
Kurtosis	33.32	16.55	-0.78	-0.42	41.30	-0.77	-0.71	-0.26

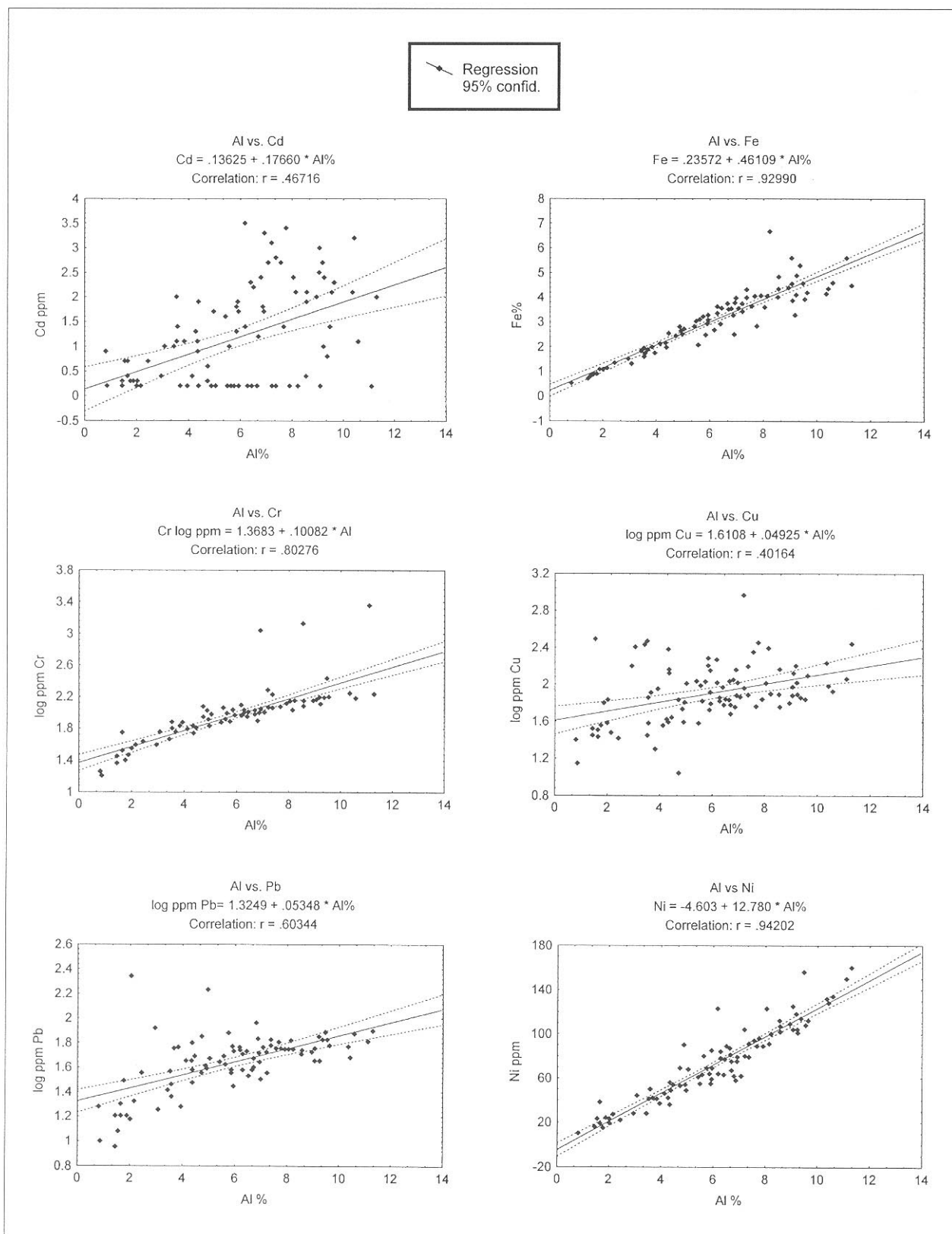Table 1 Basic statistics of all elements in ppm, Al and Fe in %.

Al vs. Cd
Cd = .13625 + .17660 * Al%
Correlation: r = .46716

Al vs. Fe
Fe = .23572 + .46109 * Al%
Correlation: r = .92990

Al vs. Cr
Cr log ppm = 1.3683 + .10082 * Al
Correlation: r = .80276

Al vs. Cu
log ppm Cu = 1.6108 + .04925 * Al%
Correlation: r = .40164

Al vs. Pb
log ppm Pb= 1.3249 + .05348 * Al%
Correlation: r = .60344

Al vs Ni
Ni = -4.603 + 12.780 * Al%
Correlation: r = .94202

Fig. 4 Linear regressions and corresponding equations of metals on aluminium for ninety-five samples in Sinjsko Polje.

background population whose residuals plot on a straight line on the normal probability plot. After outlier screening/trimming contour maps of background element distributions are drawn. Residual maps of the linear regression model (with Al as the independent variable) for each element reflect the deviations from the background (Figs. 6e and h, 8b) and are an additional product of this analysis. To demonstrate how normalization through linear regression modeling of trace elements as univariate dependent variables, and aluminium as the independent (conservative) variable functions, a choice of elements with high (Ni, Zn), medium (Cr, Pb)

	Al	Fe	Cu	Pb	Ni	Cd	Zn	Cr
Al								
Fe	0.93							
Cu	0.40	0.32						
Pb	0.60	0.57	0.26					
Ni	0.94	0.88	0.42	0.52				
Cd	0.47	0.36	0.43	0.32	0.43			
Zn	0.87	0.84	0.41	0.65	0.84	0.50		
Cr	0.80	0.75	0.36	0.49	0.80	0.28	0.68	

Table 2 Sinjsko Polje soil correlation coefficients (all are significant at p<0.05, n=95). Cu, Pb and Cr are log-transformed.

and weak (Cu, Cd) association with aluminium was made (Tables 2 and 3).

The results of the linear regression models for Cu, Pb, Cd, Ni, Cr, Zn and Fe with Al as the independent (normalizing) variable after outlier removal show that except for Cu, Pb and Cd, aluminium accounts for more than 80% of the element concentration variability ($r^2 >$ 0.8). For Pb fifty-seven percent (r^2=0.57) of variability is accounted for by Al, while Cu and Cd exhibit very weak correlation with both Al and Fe ($r^2 >$ 0.2; Table 3). The results of the analysis of selected elements are plotted against aluminium (Fig. 4). The poor correlation of Cd and Cu with Al is probably due to the anthropogenic contributions of these elements to the soils which are not a function of the soil clay content. Although it has been suggested (WINDOM et al., 1989; HANSON et al., 1993) that weak correlations of Cd with Al are a consequence of its association with organic matter, others (DASKALAKIS & O'CONNOR, 1995) think the that low molar concentration of Cd in natural materials makes it more susceptible to contamination than elements (Cr, Ni, Pb, Zn) whose concentrations are buffered by their higher natural abundance. The disrupted association of Cu and Al (even after data trimming r^2=0.29) is readily explained by extensive use of copper vitriol by local farmers in vineyards situated on the slopes that surround the Sinjsko Polje valley (Fig 6d, e, f).

The procedure of outlier identification and background distribution modelling of a single element can be readily visualized using chromium as an example. The initial normal probability plot of residuals indicates the presence of three individual samples that are grossly separated from the main mass of data (Fig. 5a, b, c). Despite the better correlation of the log-transformed Cr

data with Al (Table 2) the transform was not applied in the analysis since the three outliers severely influence the distribution and when removed the data does not range over more than one order of magnitude. The normal probability plot of residuals for the remaining subset of 92 samples implies the presence of another four anomalous samples, with 82% of Cr variability associated with Al (Fig. 5b). Finally, the trimming of the data by removal of the four extreme samples from the data set resulted in a background data subset with r^2 = 0.93, and a normal probability plot of residuals close to a straight line indicating normality (Fig. 5c). The trimming phases can also be easily visualized through the differences in contour maps. The same trimming procedures were applied to the other elements and the results are presented as initial contour maps (all data plotted) and as resulting maps after outlier removal (Figs. 6 and 8). The amount of extreme data in all cases varies between 5 and 8%.

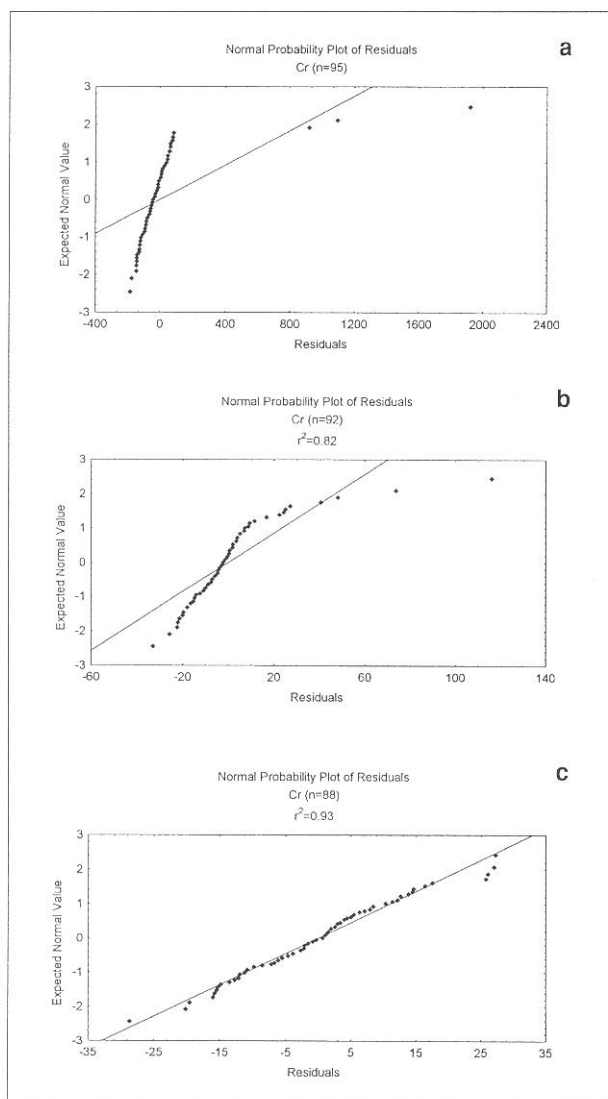## 5.2. BASIC STATISTICS AND ANALYSIS OF ENRICHMENT FACTOR

The basic statistical parameters for 8 investigated elements in 95 soil samples are shown in Table 1. Inspection of the mean values reveals that values for Cu, Pb, Zn, Ni and Cd are higher than in either reference material; standard shale (TUREKIAN & WEDEPOHL, 1961) or standard soil (MARTIN & WHITFIELD, 1983). The mean value for Cr is close to the values in the standard materials, while the found concentrations of Al and Fe are higher in both the standard shale and standard soil materials. In Table 2. soil correlation coefficients significant at p<0.05, n=95, are presented. It can be seen that Al and Fe have excellent correlation

	all data (n=95) norm. to Al	Durbin-Watson d*	all data (n=95) norm. to Fe	after outlier subtraction norm. to Al
Fe	0.86	1.58		
Cu	0.16	1.93	0.10	0.29
Pb	0.36	1.98	0.32	0.57
Ni	0.88	1.73	0.77	0.94
Cd	0.22	1.86	0.13	0.27
Cr	0.64	1.95	0.56	0.82(0.93)*
Zn	0.75	1.35	0.70	0.86

Table 3 Coeffecients of Determination (r^2) for metal correlations with aluminium or iron, and Durbin-Watson statistic for autocorrelation of residuals. Cu, Pb and Cr are log-transformed.

*Durbin-Watson statistic: number of explanatory variables k"=1, d_L =1.64 and d_U =1.69 are critical bounds which indicate the presence or absence of autocorrelation and the stability of R^2, if d>d_U no autocorrelation is present and the R^2 are stable (DILLON & GOLDSTEIN, 1984).

*Non-transformed Cr data was used in the analysis (see text), and two outlier removal steps were used.

Fig. 5 Normal probability plots of residuals for Cr vs. Al. a) Normal probability plots of residuals for original data. b) Normal probability plots of residuals after gross outlier removal with subset of size 92. c) Normal probability plots of residuals for the accepted background model with subset of size 88.

(r=0.93). Aluminium shows excellent correlation with nickel (r=0.94) and very good correlations with zinc (r=0.87) and chromium (r=0.80). Iron correlates very well with both nickel (r=0.88) and zinc (r=0.84). Correlation coefficients for copper, lead and cadmium with respect to aluminium and iron are generally low.

In the normalization procedural part of this paper we mentioned that one commonly used way of expression of anthropogenic over natural influence in sediments is the "Sediment enrichment factor" or simply "Enrichment factor" (Ef). It represents a concentration ratio of a given element to the conservative element in a sample with respect to the same ratio in the standard material. From the definition of the enrichment factor it is clearly seen that this parameter depends, at least, on four factors: 1) the choice of reference element, 2) the choice of reference material, 3) the homogeneity of reference element distribution in the study area, and 4) correlation of particular element with reference element.

The influence of reference element choice upon the value of the enrichment factor is shown in Table 4 and Fig 7. Enrichment factors based on iron as a reference element are, for all selected heavy metals, slightly lower or almost the same and for Zn even higher than as with Al (Fig 7). This can be explained by the fact

	Cu	(σ)	Pb	(σ)	Cd	(σ)	Ni	(σ)	Cr	(σ)	Zn	(σ)	Fe	(σ)
Metal/Al (mean in Sinjsko Polje samples)	18.24	15.19	9.97	11.20	0.21	0.32	11.87	2.27	27	57	20.9	6.2	0.51	0.06
Metal/Al (shale)[*]	4.31		1.92		0.03		6.51		8.6		9.1		0.47	
Metal/Al (soil)[*]	4.80		4.90				7.00		9.8		13.0		0.52	
Ef(Al)shale* (mean)	4.96	6.16	5.21	5.21	7.34	5.85	1.83	0.35	3.13	6.69	2.30	0.68	1.19	0.15
Ef(Al) soil*** (mean)	3.80	3.16	2.03	2.88			1.69	0.32	2.75	5.88	1.61	0.48		
Ef(Fe)shale** (mean)	4.52	5.45	4.67	4.67	6.72	5.11	1.56	0.35	2.95	6.66	1.95	0.53		

Table 4 Level of pollution of soils from Sinjsko Polje.

*   Ef(Al)shale =[Conc. metal$_{sample}$/Al$_{sample}$]/[metal$_{(average shale)}$/Al$_{(average shale)}$]

**   Ef(Fe)shale =[Conc. metal$_{sample}$/Al$_{sample}$]/[metal$_{(average shale)}$/Al$_{(average shale)}$]
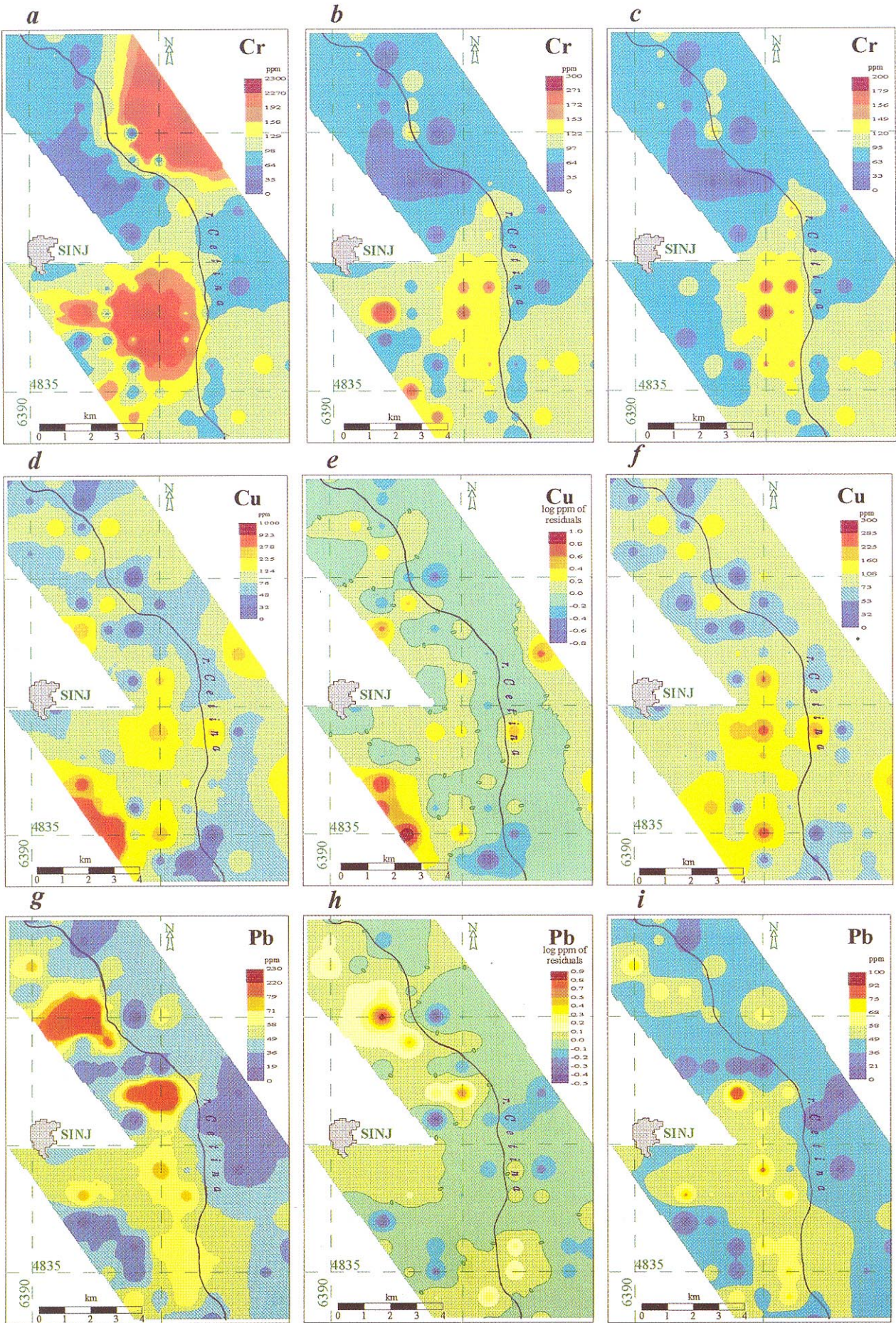
*** Ef(Al) soil =[Conc. metal$_{sample}$/Al$_{sample}$]/[metal$_{(average soil)}$/Al$_{(average soil)}$]

▲   Data from TUREKIAN & WEDEPOHL (1963)

♣   Data from MARTIN & WHITFIELD (1983).

Fig. 6 a) Distribution of Cr in soil all data; b) Cr distribution after first outlier trimming; c) background Cr distribution; d) Cu distribution - all data; e) Cu vs Al residual map reflecting deviations from background model; f) background Cu distribution; g) Pb distribution - all data; h) Pb vs. Al residual map reflecting deviations from background model; i) background Pb distribution.
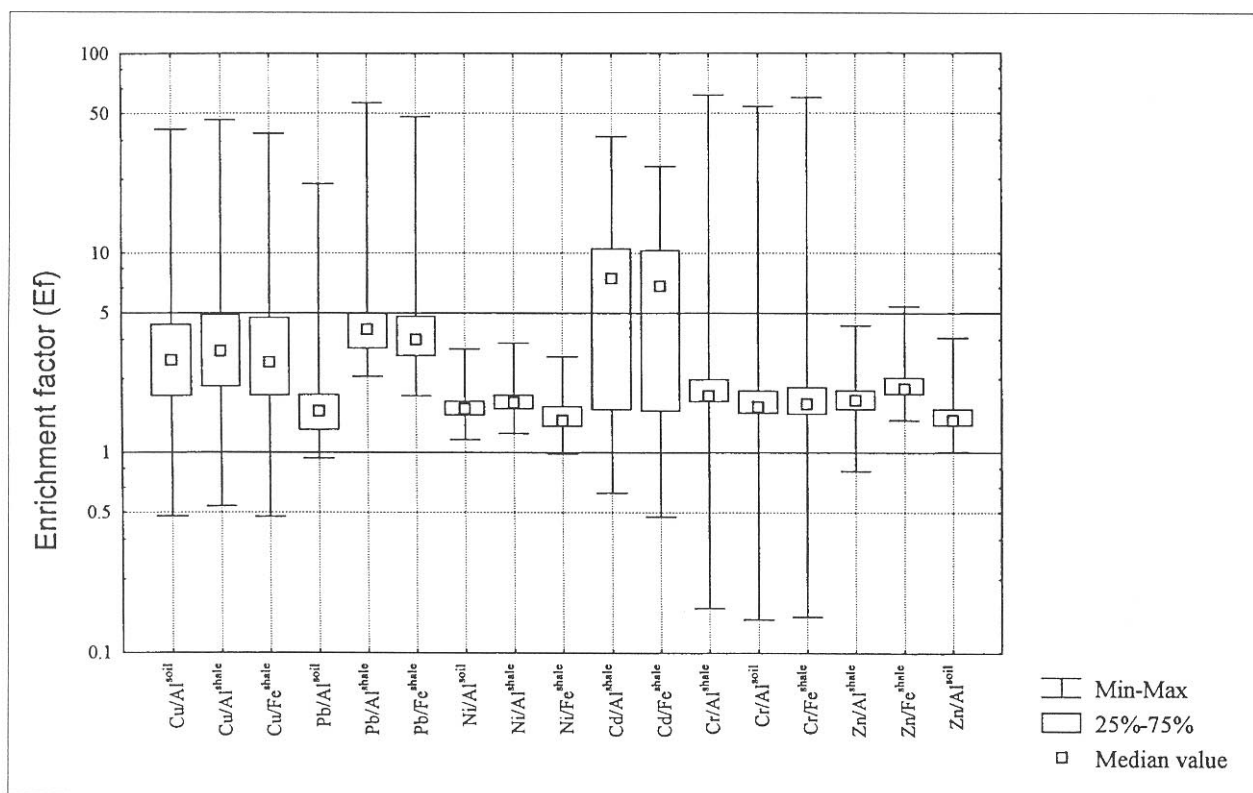
Fig. 7 Box and whiskers plot of enrichment factors (Ef). Metal/Al^{shale} =[Conc. metal$_{sample}$/Al$_{sample}$]/[metal$_{(average\ shale)}$/Al$_{(average\ shale)}$]; Metal/Fe^{shale} =[Conc. metal$_{sample}$/Al$_{sample}$]/[metal$_{(average\ shale)}$/Al$_{(average\ shale)}$]; Metal/Al^{soil} =[Conc. metal$_{sample}$/Al$_{sample}$]/[metal$_{(average\ soil)}$/Al$_{(average\ soil)}$].

that the iron concentration in investigated soils, expressed as its mean, is lower then in the standard reference materials (either shale or soil) while concentrations of most of the analyzed heavy metals are higher, which gives the lower numerator in the expression for the enrichment factor. Depletion of iron is influenced by the type of hydromorphic soil and pedogenic processes which take place in the temporary flooded area of the karstic polje.

The influence of standard reference material used in these calculations was shown by HASSAN (1993). The average shale after TUREKIAN & WEDEPOHL (1961) is most frequently used reference material in similar studies, since it is more representative of the continental soils than is the average crustal rock, as shown by LANTZY & MACKENZIE (1979). In addition, in this study we compared results with the average soil after MARTIN & WHITFIELD (1983) as a reference material. A ratio between a particular element and aluminium in soil is generally higher than in shale, so, consequently, the enrichment factors based on soil as a standard material are lower than ones based on standard shale. Although it seems that the choice of standard soil is more appropriate, as far as we are dealing with soils as sampling media, we equally used both standard

materials because one, shale, is widely accepted and checked as reference material, while other, soil, is only used recently, and needs more confirmation from other independent studies.

The third factor, homogeneity of the standard element distribution, is not considered, as far as we know, as a critical factor in the evaluation of enrichment factor. However, the enrichment factor shows the change of content of particular elements over the constant value (being the reference element value) which depends, as presumed, on general natural causes. But if these natural causes change locally, for different reasons they may mask the change of studied element and lead to completely erroneous conclusions about the origin of a particular element. To avoid these mistakes first of all the distribution of the standard element should be examined before it is utilized as the standard element. We show its dependence by plotting the aluminium distribution in the study area (Fig. 8i). The highest values are in the area southeast from Sinj, on the east bank of the river Cetina, and smaller area northeast from Sinj, on the west bank of the river Cetina. The first anomaly is caused by soil type, the second by geology or lithology type. The area southeast of Sinj is covered by hydromeliorated eugley-fluvisol in a 90:10 ratio and

Fig. 8 a) Distribution of Cd in soil -all data; b) Cd vs. Al residual map reflecting deviations from background model; c) background Cd distribution; d) enrichment factor distribution of Cd; e) enrichment factor distribution of Ni; f) enrichment factor distribution of Cu; g) enrichment factor distribution of Cr; h) enrichment factor distribution of Pb; i) distribution of Al in soil -all data.
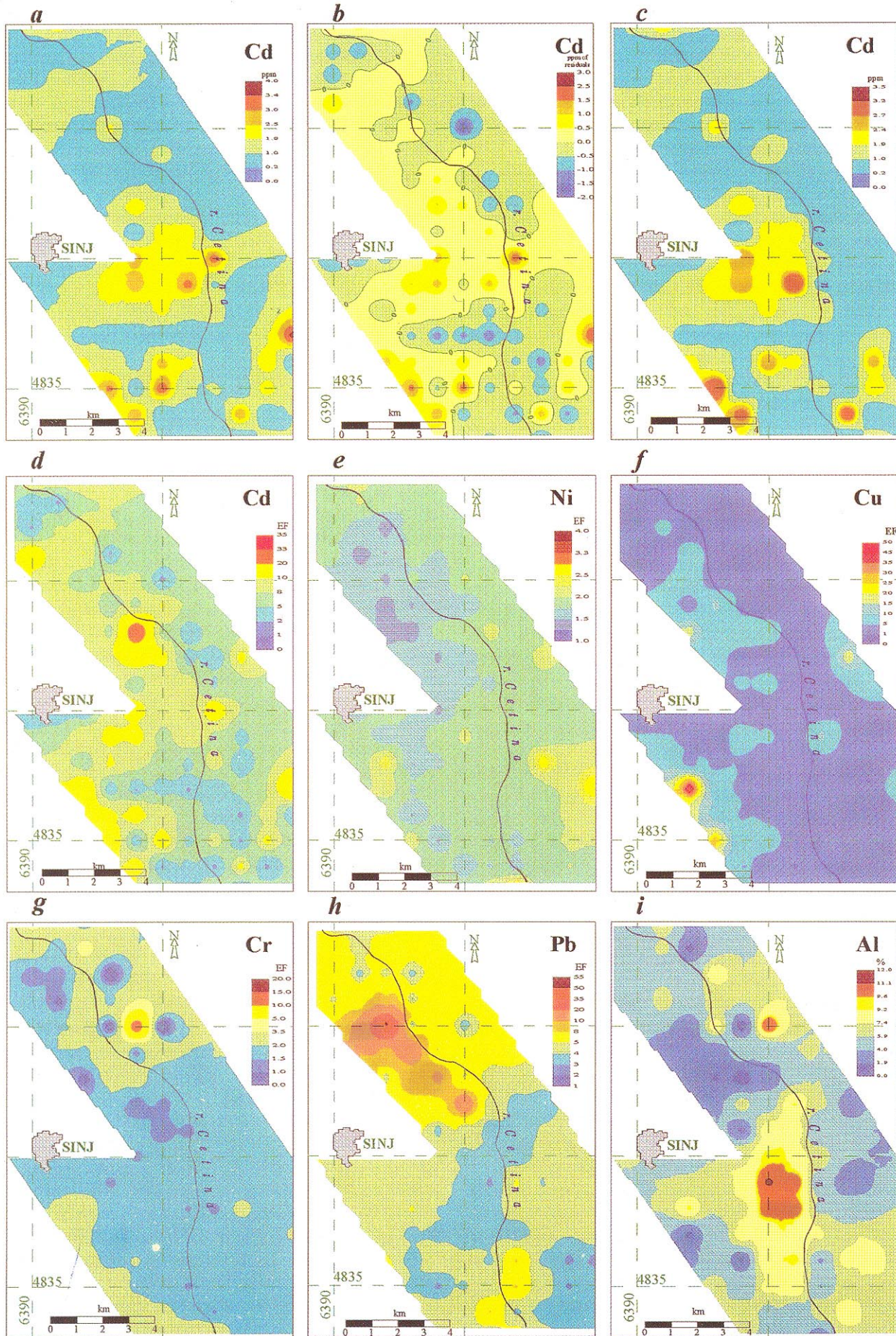
hydromeliorated eugley-peaty gley in 90:10 ratio (Fig. 3). Both types of hydromorphic soils are enriched in aluminium with respect to other types of soil in the carbonate environment. On the geological map of the studied area (Fig. 2) the area northeast of Sinj is shown as an area of discrete bauxite deposits which shows up as an aluminium anomaly in adjacent soil.

At first glance it seems that enrichment factor maps (Fig. 8) for cadmium, nickel, copper, chromium and lead, and map of the distribution of aluminium in soils are complete opposites. Following our previously established conclusions it seems that enrichment factor maps strongly depend on distribution of aluminium in the soils of study area. This conclusion, although true at least for some areas, is oversimplified and enrichment factor distributions are also influenced by man-made activities. Our approach tells us that enrichment factor maps are the results of, both, positively correlated anthropogenic contributions of particular elements and the negatively correlated distribution of the reference element in soils. Therefore we urge caution when evaluating the enrichment factor data.

In general, the statistical model presented here depends, as shown, on correlation with a conservative element, i.e. aluminium, or, alternately, with aluminosilicates, mostly clay minerals. The lack of good correlation is due to two main reasons : firstly, when particular element is not mainly bound to clay minerals but to some other mineral phase in the soil (or sediment), and secondly, when a particular element is enriched in soil (or sediment) due to the man-made activities. In the later case, the anthropogenic contribution to the element content is mainly bound to the exchangeable phase of the sediment (and soil) (FÖRSTNER & WHITTMANN, 1983; PROHIĆ, 1989). In order to show these dependencies, we chose elements with various correlations with aluminium, from copper, and cadmium (poor correlation r=0.40 and 0.47), lead (good r=0.60), and chromium (very good correlations r=0.80), to excellent (zinc r=0.87) and nickel (r=0.94). Of these elements, copper and lead, and probably partially chromium, are examples of elements with significant contributions from man-made activities, while cadmium is mostly bound to organic matter, although some could also have origin in pollution sources. Zinc and nickel are dominantly bound to the clay mineral fraction in soil.

Figures 8a-d shows development of the model for cadmium. Figure 8a is the map of the "raw" cadmium data, which shows high values of cadmium in the middle part of the polje, west rim of the polje and southeast from Sinj. Figure 8b is regression residual map, while c is a map of cadmium distribution after outlier subtraction (for explanation of this procedure see previous chapter on chromium example). The last map of cadmium, Fig. 8d, is the enrichment factor map, which shows an anomaly northeast of Sinj which was not previously apparent. The nickel enrichment factor map (Fig. 8e) probably represents the background distribution of this element. The copper enrichment factor map (Fig. 8f) illustrates the use of copper vitriol in vineyards on the slopes that surround the Sinjsko Polje valley. The map of the enrichment factors for lead (Fig. 8h) shows the pattern which can be explained by the theory of overbank sediments. Enrichment effects are shown along the upper course of the river Cetina, on its west bank for pollution coming from upper course of the river beyond the study area.

Quantitatively, the pollution levels for selected elements in soils of the Sinjsko Polje range from 1.61 for zinc to 7.34 for cadmium (Table 4). If we take the criteria given by GOLCHERT (1991) our values of the enrichment factors will fall into the second group of very probable influence of the man-made activities.

5.3. TREND SURFACE ANALYSIS

Examination of trends is a common procedure in the analysis of geochemical maps. Its purpose is to segregate the underlying trend that possibly pervades the study area, from the local variations, that is, the "noise" or "background"(MILLER & KAHN, 1962). Thereby, the original set of data, represented in the form of a geochemical map, can be separated into two parts - trend and residuals. The exact form of the computed surface is that for which the sum of squares of the residuals, that is, the differences between the original and calculated values, is the least. Trend surface, therefore, includes the regional or deterministic component in the total variability of the data, while the residuals contain local or irregular geochemical values, unrelated the principal distribution (NICHOL et al., 1969). Residuals, which represent the random deviations from the computed trend, consist of two components - one representing an error due to sampling and analytical methods, and another related to the real variation between the observed value and the calculated surface in the control point. The latter may be called "true" residuals. Computing the trend surface is sometimes necessary only to reveal whether regional variation exists and is persistent in the total variability. In such a case, the trend surface mapping serves as a quantitative analytical technique that can provide the desired answer (LUSTIG, 1969). If, however, the stress is laid on various causes of the total variability, then additional analysis is required to accommodate unexplained variance revealed after elimination of the regional trend.

One of the main problems arising from trend surface analysis is the proper choice of the polynomial approximating the original data (geochemical map). The polynomial of first, second or third degree (planes, quadratic and cubic surfaces) are most commonly used, although one usually never goes higher than the fifth or sixth degree. While the trend surfaces of successively higher orders more neatly fit the original data, they can create serious problems in interpretation. While they enable the regional features of an investigated area to be more thoroughly interpreted, they also diminish the

values of residuals and rule out the possibility of clearer insight into the character of anomalies and "outliers".

The first degree trend surface has some advantages in this respect. As a general linear model, conveniently expressed in the form of the equation $Z=A+Bx+Cy+\varepsilon$, where x and y represent geographic coordinates, it separates the linear component (plane), while all non-linear elements reduces to residuals - the unexplained part ε of the total variability (DAVIS, 1986). Segregation of the linear trend, containing deterministic component with normally distributed data (regression model), renders the possibility that the frequency distribution of residuals which, alternatively, represent random fluctuations around an equilibrium state, assume less skewed asymmetry with regard to the untrended data. Residuals can retain the positively skewed (lognormal) distribution even after the linear trend (and sometimes even the higher order trends) have been removed. However, non-linear relationships, being the cause of such a distribution, can arise from very different origins. So, for the trend itself to have been proved, it does not matter whether it is expressed as quadratic, cubic or some higher member of a polynomial. If the trend exists at all, then it can be shown by the first degree trend surface, and each successive member of a polynomial serves only to minimize the squared deviations from the trend more effectively, in which case the next polynomial member (p+1) fits better into the regression model than the former one (p).

To prove the trend, one can use the goodness-of-fit test. Application of the test in geochemical research usually involves the question of critical values on which basis one can deduce whether or not the predicted model succeeds in fitting the original data. Significance of obtained values is usually attested to by the statistical F-test, but it should be noted that a large number of data (control points) will almost invariably guarantee a statistically "significant" trend surface (TINKLER, 1969; UNWIN & LEWIN, 1971). The goodness-of-fit test applies the ratio of the sum of squared values of a computed trend against the sum of squared original data, and results are usually represented in the form of a determination coefficient $D=r^2$ (DAVIS, 1986). Here, r is the correlation coefficient between the trend surface map and the original geochemical map. If the test produces values of D that fall below 0.06 or 6% (r=0.24) for the linear surface, then the distribution of data points over the map is not significantly different from random at the $\alpha=0.05$ level (HOWARTH, 1967). In the case of original data being standardized, which is desirable if several geochemical maps are to be compared, the general linear model (plane) reduces itself to the form Z=0 because of total agreement with the plane of zero values in the original set of data (A=0, B=0, C=0). Obviously, the horizontal (Z=0) or gently dipping plane can be taken as an indicator of prevailing local effects or variations among control points.

5.3.1. Trend-surface results

Trend surface analysis for five elements (Fig. 9a-i), Cd, Cu, Ni, Al and Pb - shows, in general terms, a very slight linear trend, or in some cases, no trend at all. There is no observable trend whatsoever in the case of two elements - Cd and Pb, which have very low values of the goodness-of-fit test. The determination coefficient D (in %) takes the values of 1.00 (r=0.10), and 0.64 (r=0.08) for Cd and Pb, respectively. The trend surface is a gently dipping plane tilted to the NNE (3.0°) in the former case, and ENE (4.4°) in the latter. No regional variation is present in the spatial distribution of these elements, which is a sure indicator of the total variability of the respective geochemical maps being contained in the local variations, possibly due to some kind of human activity in the area.

However, the remaining elements, including Ni, Cu and Al, all exhibit a slight linear trend. The determination coefficient gives the values of 8.41 (r=0.29) for Ni, 6.76 (r=0.26) for Cu, and 6.25 (r=0.25) for Al. While the first-degree trend surfaces for Ni and Al are almost of the same orientation - due NW which unmistakably reveals the course of the Cetina river as some agent contributing to their spatial distribution, for Cu the plane is inclined to the NE (13.9°) which is nearly perpendicular to the former two. It is fairly logical to assume that the regional trend, exhibited in the spatial distribution of Ni and Al appears to be strongly influenced by the Cetina river. The fact that the plane is tilted opposite to the river course can be explained in the way that there is some natural cause displaying the profound impact on the increase of Al and Ni concentrations down river and to the far end of the Sinjsko Polje.

In contrast, the NE tilt of the first-degree trend surface for Cu highlights the somewhat different nature of its distribution over the study area. Obviously, dissemination of Cu in the investigated area is in no way related to the factors involving the fluvial regime and accumulation of sediment along the river as may be supposed in the case of Ni and Al. On the contrary, high values of trend for Cu in the SW part of the Sinjsko Polje should probably be evaluated in light of increased agricultural activity (mostly vineyards) on the soils developed on the underlying Miocene marls. The trend, then, is basically not of regional, but of strictly local extent.

The noted discrepancies among the computed trends could well be accounted for by specific conditions related to the karstic areas. Namely, the borders between "regional" and "local" can be easily attenuated when related to such isolated parts of karstic terrain, such as relatively small karstic poljes. An area with prevailingly non-karstic characteristics surrounded with carbonate beds, sometimes with highly developed and deep karst, can virtually be an "island" bearing little or no geochemical resemblance to the outer regions, but behaving independently. It is expressly emphasized in the case of total isolation, when no drainage or other

ways of communication, exist in the area. That is, however, not the case here, judging from the computed trend surfaces for Ni and Al.

What is regional and what is local can become very questionable and must be determined separately for each element. Moreover, much attention should be focused on detrended values or residuals, for further explanations, such as in the case of Cu.

5.3.2. Nature of residuals

In the case of nonexistent, as well as very low or inconspicuous trends, residual values, naturally, can not be much different from the data accounting for the whole variability. In other words, the map of residuals will have almost the same appearance as the original map of untrended values. Examination of both will undoubtedly lead to the same conclusions. Spatial distribution of high and low concentrations of these elements remains practically unchanged, which is to say that the total variability of data is attributable to the local effects in the area of investigation.

However, differences become apparent, though not greatly, when examining the maps with more accentuated trend, such as in the case of Al, Ni and Cu. The only, but exceptionally important difference is indicated by increasing the already high untrended values after the trend is removed. In this way, the nature of residuals is still more effectively stressed because it reveals some influence of specific local variation in the research area. Obviously, for Ni and Al it must be connected with processes of sedimentation along the right bank of the river Cetina (probably with the overbank flow), and for Cu there must be some process of introducing this element in the soil through agricultural activity (pollution).

6. CONCLUSION

Estimation of the anthropogenic over natural contribution in the chemical content of sediments is very important but not easy to determine. Normalization based on either aluminium or iron as reference conservative elements, having supposed natural distributions is an useful tool in solving this problem. However, this should be undertaken with caution as several independent factors can influence this normalization which, if not taken into account, could lead to completely erroneous conclusions about the origin of particular elements. Analytical data from 95 soil samples from Sinjsko Polje enable us to critically evaluate this procedure. The following conclusions can be drawn from this study:

1. On the presumption of an existing linear dependence between the conservative element and the heavy metal it is possible with the use of linear regression to simultaneously define the heavy metal geochemical background and to isolate natural and/or anthropogenic outliers. It was possible to estimate the background populations and their spatial distributions for Cr, Ni, Zn and Pb after outlier removal. The process of baseline estimation was far less successful for Cd and Cu since Al accounted for less than 30% of their variability indicating that the area suffers from serious pollution by these metals and that their chemical mode of occurrence in the investigated area is not governed by the clay content in the soil.

2. Estimation of the enrichment factor depends upon four main factors, namely: the choice of reference element; the choice of reference material; the homogeneity of reference element distribution in the study area; correlation of a particular element with the reference element.

3. The results of trend surface analysis can be summarized as follows:

a) The regional trend in the study area is very slight (Ni, Cu and Al), or, in some cases, practically absent (Cd and Pb).

b) The spatial distribution of Cd and Pb is apparently in a domain of the strictly local control factors.

c) The slight trend shown by Ni and Al is undoubtedly related to the river Cetina, in contrast to the trend shown by Cu, which must be connected with the chemical pollution in vineyards, and should not be considered regional.

Statistical analysis, as suggested by the results in this work, would be more properly used over general areas in the karstic terrain, with different geological, geomorphologic and hydrogeological characteristics, rather than being focused on the relatively small phenomena such as poljes, with many local geologic, hydrogeological and geochemical features.
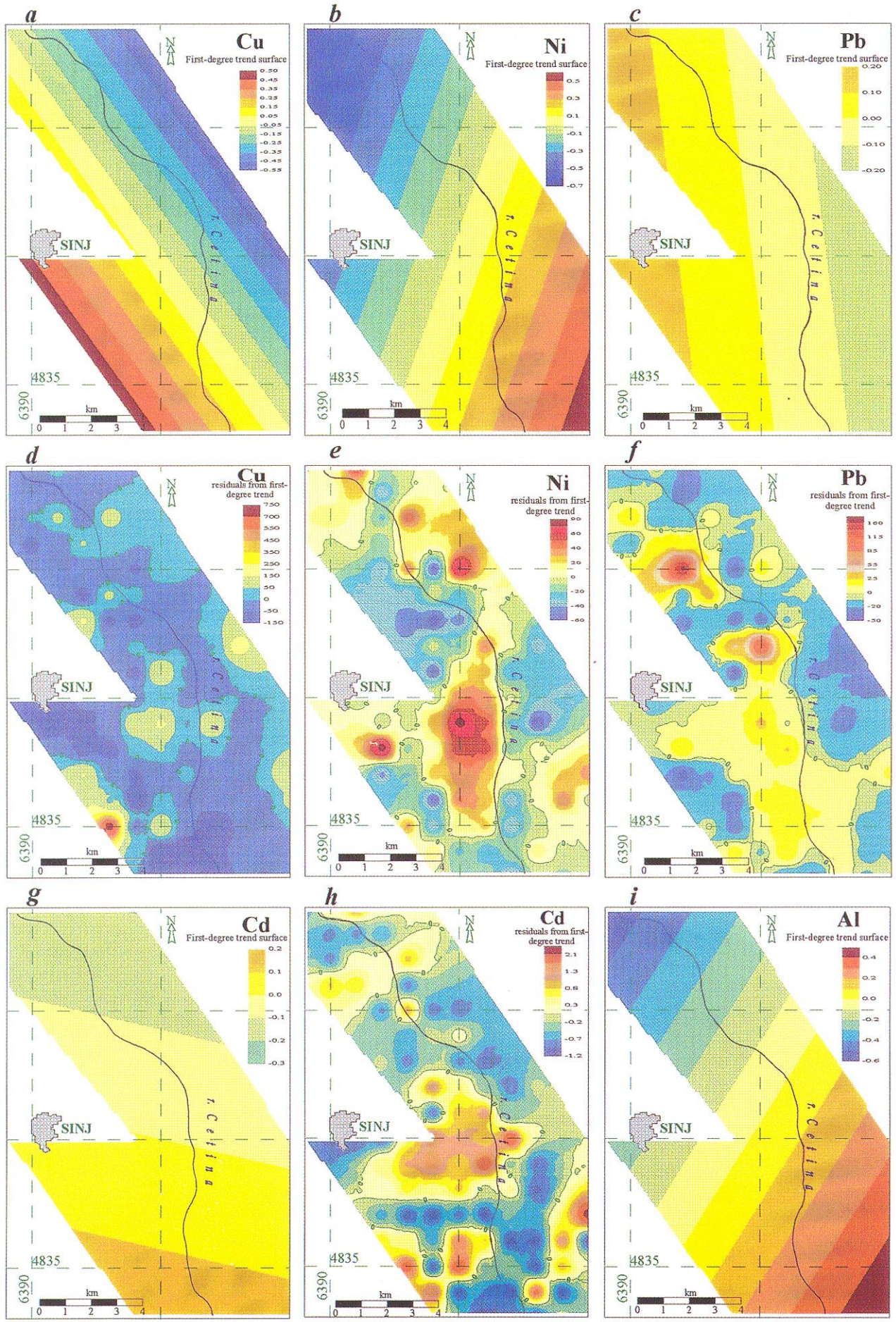
Fig. 9 a) First-degree trend surface for Cu; b) first-degree trend surface for Ni; c) First-degree trend surface for Pb; d) residuals from first-degree trend for Cu; e) residuals from first-degree trend for Ni; f) residuals from first-degree trend for Pb; g) first-degree trend surface for Cd; h) residuals from first-degree trend for Cd; i) first-degree trend surface for Al.

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