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THE GEOCHEMICAL BACKGROUND IN ISTRIAN SOILS

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The geochemical background is postulated for two major groups of soils of the Istrian Peninsula, depending on the type of bedrock, or parent material as one of the main soil-forming factors. An effort is made to combine conceptual fundamentals of non-linear dynamic theory with the principles, methods and practical application of basic statistics in order to elucidate the nature and origin of elemental subpopulations hidden in the original geochemical data of Istrian topsoils. In this sense, the 4σ-outlier test and iterative 2σ-statistical technique are utilized, by which the outliers and anomalous values are removed from the total data set and assigned to the consequences of non-linear system dynamics, which prevents the development of a simple cause-and-effect relationship between geochemical variables. The geochemical background is then defined as the normal range of data of the remaining data set. As confirmed by the study, the carbonate-derived soils have a higher natural or geogenic baseline and are also more strongly loaded with heavy metals and other trace elements, in some places critically. On the other hand, flysch-derived soils, except for higher Ca contents, are actually depleted in many elements and also devoid of outliers. Such behaviour implies »dilution« due to the characteristic nature of the weathering of the underlying parent material and other soil-forming processes controlling their fate. In a general sense, the character of the probability distribution curves among chemical elements in the topsoil (or soils in general) can be used as reliable indicator of their evolutionary trends, that is, their enrichment or depletion, or, as regards the geochemical background, the equilibrium between the two, which in the case studied depends principally upon the contrasting Istrian bedrock lithology.

Key words: geochemical background, topsoil, parent material, geogene influence, human impact, normal distribution, normal range, Istria, Croatia

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U radu je razmatran geokemijski šum zasebno za dvije skupine tala na Istarskom poluotoku, ovisno o tipu geološke podloge, odnosno ishodišnog materijala kao jednog od glavnih čimbenika u razvitku tla. Povezana je teorija nelinearnih dinamičkih sustava s načelima, metodama i praktičnom primjenom elementarne statistike s ciljem da se razjasni priroda i porijeklo elementnih subpopulacija skrivenih u izvornim geokemijskim podacima površinskog horizonta istarskih tala. U tu svrhu korištene su statističke metode – 4σ-test za određivanje ekstremnih vrijednosti i 2σ-metoda iteracije – kojima su ekstremi i anomalne vrijednosti odvojeni od glavnog skupa podataka i pripisani posljedicama nelinearne sistemske dinamike koje su brana uspostavi jednostavnih, uzročno-posljedičnih odnosa među geokemijskim varijablama. U skladu s navedenim, geokemijski šum je određen kao raspon normalnih vrijednosti reduciranog skupa podataka nastalog nakon oba statistička postupka. Pokazalo se da tla razvijena na karbonatnim stijenama imaju višu prirodnu razinu kemijskih elemenata, a također sadrže i veću koncentraciju teških metala i elemenata u tragovima koja je na pojedinim lokacijama i ekstremno visoka. S druge strane, tla razvijena na flišu, s izuzetkom povišenog sadržaja kalcija, u stvarnosti su siromašnija sadržajem većine elemenata i ne sadrže ekstremnih vrijednosti. Takvo ponašanje ukazuje na »razrjeđenje« zbog karakteristične prirode trošenja ishodišnog materijala i drugih čimbenika koji utječu na raspodjelu elemenata u površinskom horizontu tla. U općem slučaju, karakter krivulje statističke distribucije elemenata kemijskih elemenata u površinskom horizontu (i u tlu općenito) može se uzti kao pouzdan pokazatelj evolucijskih trendova, odnosno obogaćenja ili osiromašenja pojedinim elementima ili, kad je riječ o geokemijskom šumu, ravnoteže među ovim procesima. Kod tala na području Istre na ove odnose primarno utječe izrazita razlika u karakteru geološke podloge.

Ključne riječi: geokemijski šum, površinski horizont tla, ishodišni materijal, geogeni utjecaj, antropogeni utjecaj, normalna raspodjela, raspon normalnih vrijednosti, Istra, Hrvatska

1. INTRODUCTION

The soil is a thin part of the earth's surface system interacting both between the lithosphere and the atmosphere (including the hydrosphere and the biosphere), and between nature and man. In both cases it forms a subtle ecosystem whose mineral and chemical contents reflect natural, or geogenic, as well as non-natural, or anthropogenic influences. Distinguishing between them is of primary importance in overall geochemical investigations, particularly with environmental and ecological objectives, as it imposes the judgment of critical values, or some sort of boundary concentrations, functioning as a separation criterion. In the statistical treatment of geochemical and environmental data this partition is usually thought of as removing the main population, often called the »background« or »baseline«, from the rest of the data body. But, as will be shown later in the text, this procedure is fraught with implications that go far beyond the sphere of simple statistical computations.

A very sensitive and vulnerable medium, the soil strives to accommodate its physical and chemical properties to continuous environmental perturbations driven by the interaction of a complex suite of parameters such as parent geology, relief, organisms, climate, human impact and time, which operate in concert during pedogenesis (JENNY, 1980). From this vantage point soil geochemistry would emerge as a specific pattern – a mixture of elemental populations with variable concentration ranges – reflecting the dynamics of pedogenetic and related earth surface processes. The emphasis on the pattern-process interaction as one of the inherent characteristics of open natural systems is crucial, implying that the relationship between background and non-background values must be viewed through the lens of system response to external stimuli. This reaction may be either linear and thus self-stabilizing, or nonlinear and thus driven to the point of instability, far from equilibrium, in either spatial or temporal domains. Accordingly, the system's state is reflected in the character of fluctuations and, in reference to this, in distribution functions of diverse parameters (state variables) that describe the system behavior, such as, in the case considered, the content of major and trace elements in soils.

On its most fundamental level, the relationship between the fluctuations and probability functions can easily be assimilated from the conceptual framework of open system thermodynamics (e.g., NICOLIS & PRIGOGINE, 1977; PRIGOGINE, 1978; PRIGOGINE & STENGERS, 1984). Some of the concepts including equilibria, feedbacks, thresholds and, in more recent times, non–linear dynamic systems, dissipative structures, or self-organized criticalities, have been diffused rapidly through the earth sciences, particularly geomorphology, during the last few decades (see, e.g. KARCZ, 1980; HUGGET, 1988; PHILLIPS, 1992a; 1992b; 1995; 1996; RENWICK, 1992; AHNERT, 1994; SCHEIDEGGER, 1997; and others). Having soon become the main tenets of the so-called complexity theory (see MANSON, 2001; MIKULECKY, 2002) which emerged as a promising scientific trend in the nineties, these ideas captured the immediate attention of a number of researchers in the soil sciences (for example IBAÑEZ *et al.*, 1994; PHILLIPS, 1993a; 1993b; 1998; HUGGET, 1998) who recognized their potential explanatory value in probing the hitherto unresolved questions of the formation of soil landscapes. But, apart from merely triggering a new insight and understanding into the dynamics of soil-forming factors, especially with reference to the recent paradigm shift from the more traditional, developmental (equilibrium) to a modern, evolutionary (nonequilibrium) view of pedogenesis (HUGGET, 1998), the new approach could not avoid having to cope with practical problems of the proper definition and numerical expression of the geochemical background. This problem seems to have a heavy impact on geochemical and environmental research because, apart from its essentially geochemical overtones, a critical value has been thought of largely as a statistical question whose solution must be sought by related methods and techniques. This said, it seems a paramount task to give a solid ground to a simple and comprehensible overarching frame within which complex soil geochemistry could be formulated and related to the basic statistical laws applicable in geochemical exploration.

As mentioned above in brief, the primary objective of this work is to set a realistic and plausible boundary between the geochemical background and »anomalous« populations in the topsoil material sampled over a relatively small, but geographically well defined part of the karstic soil landscape exemplified by the territory of the Istrian Peninsula. An effort is made to combine the conceptual and theoretical basis of nonlinear dynamic theory with principles, methods and practical applications of basic statistics in order to elucidate the nature and origins of particular element subpopulations concealed in a total sample collective. The paper focuses its dicussion on the two lithologically and pedologically contrasted portions of the selected study area – one that is occupied dominantly by terra rossa and brown soils overlying an extensive carbonaceous rock complex, and the other that is represented by rendzinas, regosols and related soils developed on a carbonate-siliciclastic flysch bedrock. It is expected that the choice of particular area which is spatially homogeneous in the sense of climatological, lithological and pedological characteristics would keep the range of background values within the relatively stable limits with regard to the impact of natural factors, so that anthropogenic impacts could be more explicitly outlined in the topsoil geochemistry. The original data collectives are treated by the method of iterative truncating of the highest values in order to isolate the strings of decreasing non-background concentration values down to the stable, homogeneous, normally distributed remainder which could be safely defined as the natural baseline or geochemical background. The 4σ-outlier test and iterative 2σ-statistical technique are used, while the outliers and extremes detected by the applied methods are assigned to the human-affected changes in the soil landscape.

2. THERMODYNAMIC APPROACH TO GEOCHEMICAL BACKGROUND

2.1. Background, normality and linearity

Provided that, due to the regularly small disturbances that occur in the process of weathering, transport and deposition, elemental concentrations fluctuate more or less uniformly around some central value, creating a kind of steady-state equilibrium between input and output phases in an open soil system, it is relatively easy to define the range of background concentrations on a regular statistical basis. Some recent studies offer excellent reviews of relevant statistical and other methodologies as well as many problems raised in this respect (see MATSCHULLAT *et al.*, 2000; REIMANN & FILZMOSER, 2000). Essentially, the idea of geochemical background revolves around the normal range of values which is characterized by linear relationships between the observed parameters. On this basis, a simple correlation can be drawn between normality (homogeneity) and linearity – small impacts produce small effects with diminishing probability of large perturbations in state variables (element contents). Small fluctuations are related to the stability domain of an open system, often called the thermodynamic branch (KARCZ, 1980), within which regular causes produce expected effects. Viewed through the lens of nonlinear dynamic theory, however, soil landscapes rarely behave in such a simple, predictable manner. Such behaviour is often in sharp contrast with the case when the effects of major changes are reverberating through the soil system, driving the fluctuations into the nonlinear realm, beyond some threshold value. The fate of such a system is inherently unpredictable due to uncertainties involved in the relationship between effects and their causes. As a result, a major shift in the compositional properties usually occurs which is manifested by departure of their probability distributions from normality, showing heavy upper tails with outliers and extremes. As before, the thresholds or criticalities can also be assessed through convenient statistical methods and procedures (MATSCHULLAT *et al.*, 2000). Putting both examples together, two main populations of geochemical data can be recognized in the soil samples and consecutively separated on a statistical basis – one that is equilibrium-dominated, deterministic in nature and thus predictable, and another that is nonequilibrium-dominated, stochastic in nature and thus unpredictable. The former converges on the geochemical background, while the latter diverges from the background assuming the form of »anomaly«.

This said, one may assume as a first approximation that the background concentration levels of most elements in soils reflect a balanced, uniform regime of earth surface processes tarrying in a Gaussian domain, away from thresholds. Due to some kind of »pedogenic inertia« (CHADWICK & CHOROVER, 2001) caused by a variety of relaxation times and pathways these values defy, at least within a limited period of time, significant influence by local variations of the soil-forming factors. However, because of lithological, geomorphological and other differences, most geochemical and environmental data from local, or even regional, compartments typically display a certain degree of spatial contingency (REIMANN & FILZMOSER, 2000; PHILLIPS, 2002). When combined with external forces such as climate or human impacts periodically disturbing the system, the variations may be enhanced by irregular geochemical fluxes and other rapid, irreversible changes. In turn, the elemental populations in the soil are affected by their, as a rule, not obeying the law of normal distribution.

Following this line of reasoning, the soil can be described as a vulnerable medium displaying a complex, dynamic behaviour, so that a number of coexisting elemental populations reflect simultaneously linear and nonlinear responses and relationships between constantly changing entities or variables. Various types of soils are often scattered in a seemingly random spatial fashion, sometimes reminiscent of a patch mosaic comparable to the »leopard spots« typical of many soil maps. They reflect various phases of »crystallization« of a soil ecosystem after the change (phase transition) into a new stable phase (cf. GREEN & NEWTH, 2001). The latter is subsequently added to the previous changes joining the soil geochemistry into an aggregate of two or more populations of any particular element, which indicate enrichment, depletion, or equilibrium between the two. Soil diversity arising through the successive (multiple) steady states over long timescales is quite in accordance with the contemporary evolutionary view of soil formation which maintains that soil at any particular point in time may exist in one of several possible states (pedons, soil profiles) as a result of two or more evolutionary pathways (HUGGET, 1998). Put differently, nonlinear responses in soil systems increase their variability over time – the older the soil, the more random and variable its composition appears (PHILLIPS, 1996). The pattern implied by the coexistence and juxtaposition of a number of elemental subpopulations may, in all probability, leave its traces in the geochemical signature.

With this in mind, a recurring issue in relation to the probability distribution as discussed in this work is that of ergodicity. The ergodic hypothesis is indispensable in solving the-so called ergodic problem, that is, decoding the temporal and spatial changes in a (soil) system. It is based on the assumption that the statistical properties of time series are essentially the same as the properties of a set of observations of the same phenomenon taken over a spatial ensemble (CHORLEY & KENNEDY, 1971; VAN LITH, 2001). This statement suggests that under certain circumstances sampling in space is equivalent to sampling through time, meaning that space-time transformations are acceptable and temporal variations can be simply understood from spatial evidence. If the element concentrations in the topsoil are measured in a given area the probability distributions can indicate the fate of that element in a certain period of time. Thus, a study area of the size of the Istrian Peninsula contains a range of soil ages that must embrace representatives of a number of stages in soil development. The search for systematic variations in probability distribution curves may offer a deeper insight into the kind and direction of natural processes in which the chemical elements participate in the evolving soil (leaching, eluviation, illuviation etc.) and help to separate these form the more recent, anthropogenic influence.

2.2. Anomalous populations and human impact

Having in mind that the »anomalous« population can originate from both sources mentioned earlier, namely »natural« and anthropogenic, indicating both mineralization and pollution, the above picture rarely escapes involvement by uncontrolled inputs into the soil system from the human activity. Various human drivers of change can bring about punctuated, incoherent and even catastrophic (hazardous) events throughout the soil landscape history, triggering huge fluctuations (outliers) with a highly nonlinear character. Such events can be spatially contingent, that is, local and rare, but they leave a deep impact on the symmetry of the probability distribution of element concentrations in soils. As is generally known, metal processing facilities, mining, and power plants produce a strong anthropogenic signal that is dispersed into the natural environment in a variety of ways. Contamination spread by airborne contaminants and depending on the character of the pollution source, size and density of emitted particles, direction and strength of wind and other causes (McMARTIN *et al.*, 2002) is but one. Some questions are raised in this respect about a distinction between natural and human impacts because a conclusive indicator of »unnatural« anomalies cannot be deduced from the distribution functions alone. In considering all practical issues and consequences, the human species can hardly be acquitted of being generally responsible for the most adverse impacts on landscape ecology, putting all natural factors behind it (see USHER, 2001). Accordingly, the highest deviations from background in both distribution tails – minima and maxima in the content of most of elements in soils – are, in one way or another, associated with pollution, land use, engineering or some other kind of human intervention in the natural ecosphere. This usually gives rise to a real problem in the definition of natural background, additionally encumbering the naturally complex soil landscape system that operates in accordance with the theoretically well established but in a real world still not satisfactorily applied non-linearity principle. The result is that the human-caused forces all too often offset the natural signal recorded in elemental dispersion through the soil profile.

3. STUDY AREA

The Istrian Peninsula is a prominent part of the Croatian Adriatic coast area occupying the farthest northwest rim of the country (Fig. 1). Because of its geographical as well as its geological position, the study area is distinguished by characteristic climate, lithology, tectonics, as well as a typical soil landscape. All these, together

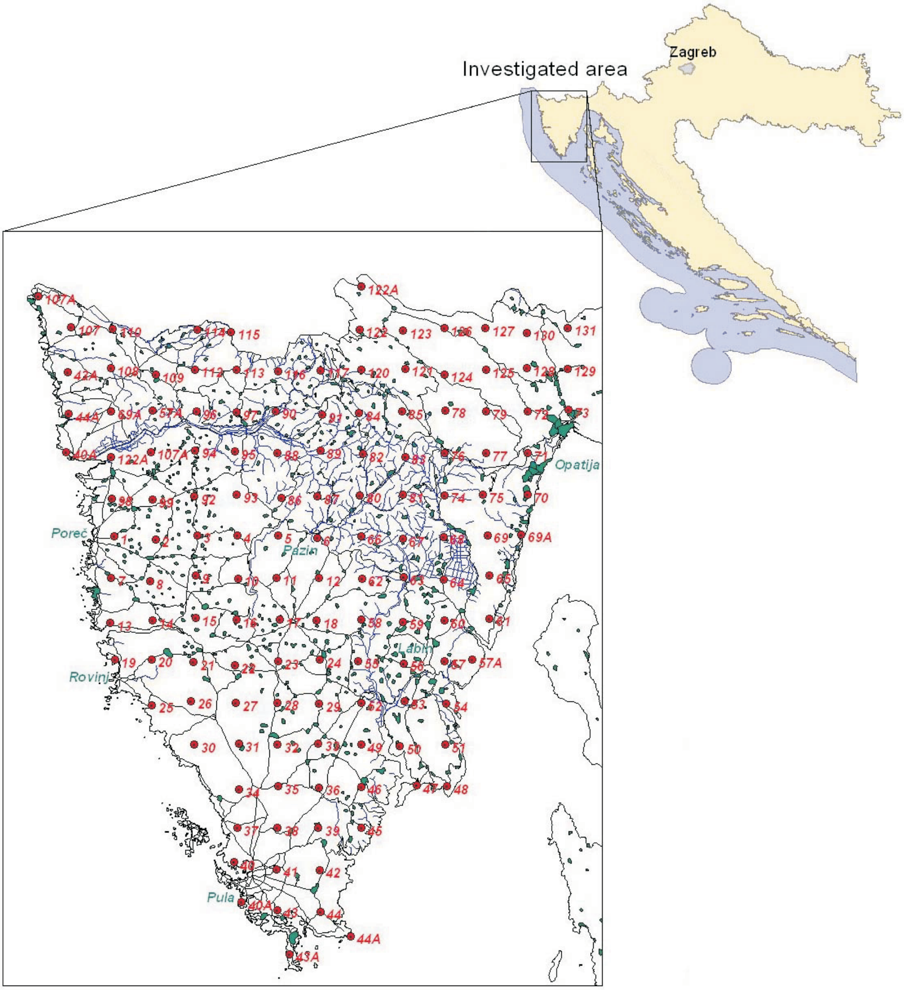

Fig. 1. General map of the study area with sample locations in a regular 5 5 km^2 grid

with an anthropogenic factor manifested more strongly along the coast than in the hinterland – industry (coal-fired power plant) in the east and extensive tourism in both east and west – leave a strong impact on the geochemistry of the Istrian soils.

3.1. Geological setting

Geologically, the Istrian Peninsula is for the most of its part a typical karst area composed predominantly of carbonate rocks, mostly limestone. Accordingly, it is distinguished by various karst phenomena, most intensely developed on the high mountainous ranges of Učka (1396 m) and Ćićarija (1272 m) in its northern and north-eastern portions. By contrast, the western and central exposures consist mostly of undulating planes and low hills with sinkholes as the prevalent feature of the rich karstic scenery.

Tectonic and lithologic attributes of the study area (Fig. 2) are conditioned by its specific geodynamic setting at the northwest fringes of the Adriatic carbonate platform. This is evinced by the recent geologic framework as well as vigorous seismotectonic activity along the most important reverse zones in the structural framework marking the contact area with the resisting rock masses of the Dinaric platform

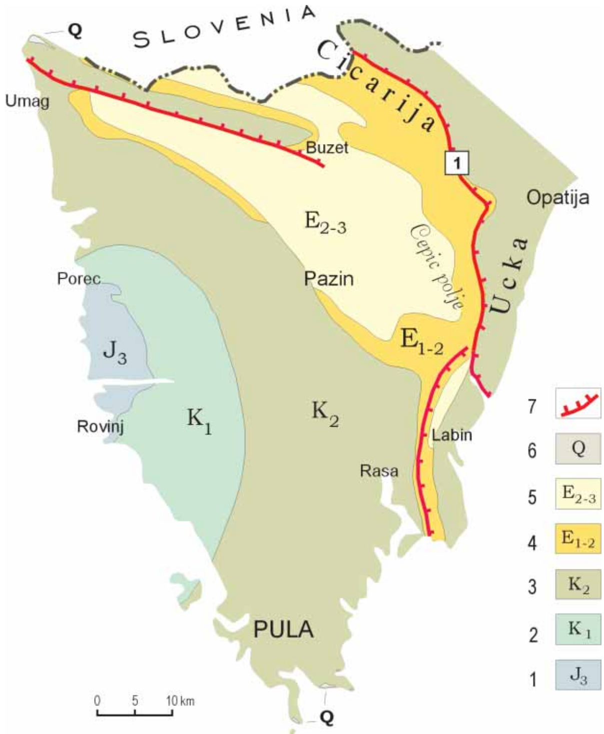

Fig. 2. Simplified geological map of the Istrian Peninsula (modified after Geological map of SFRJ 1:500.000, 1970; VELIĆ *et al.*, 1995; PRELOGOVIĆ *et al.*, 1995): 1) Upper Jurassic (Bathonian – Lower Kimmeridgian unit); 2) Lower Cretaceous (Upper Tithonian – Upper Aptian unit); 3) Upper Cretaceous (Upper Albian – Lower Campanian unit); 4) Paleocene –Eocene unit (Foraminifera limestones); 5) Paleocene – Eocene unit (Transitional beds and flysch); 6) Quaternary sediments (loess); 7) Faults; [1] Mt. Ćićarija – Mt. Učka – Labin fault.

(PRELOGOVIĆ *et al.*, 1995). Among these, the fault Ćićarija Mt. – Učka Mt. – Labin is most distinguished structurally, though the least active historically, as it separates the regional structural unit of Istria (the West Istrian Jurassic – Cretaceous anticline) from the rest of the Adriatic carbonate platform. The area to the southwest of this fault is largely undisturbed, probably as a consequence of deformation of the flysch basin which served as the buffer zone against the resisting Dinarides in the early times of the regional underthrusting during the Pyrenean tectonic phase (MATIČEC *et al.*, 1996). It consists of the Jurassic-Cretaceous-Palaeogene carbonate plain of southern and western Istria, and the Palaeogene flysch basin of central Istria (VELIĆ & TIŠLJAR, 1988; VELIĆ *et al.*, 1995). To the east and northeast the terrain is intensely disturbed, with mixed Cretaceous – Palaeogene, carbonate – clastic series building the overthrusted structures of Učka and Ćićarija Mountains. The same authors distinguish four phases of sedimentation and emersion in Istria that lasted from the Upper Jurassic to the end of the Middle Eocene, when the final emersion and uplift affected the whole area. These phases resulted in formation of four distinct sedimentary units, or megasequences, of different duration which can be specified successively as follows (Fig. 2): 1) the oldest, Bathonian – Lower Kimmeridgian regressive unit, characterized dominantly by shallow-water limestones and, due to the shallowing and coarsening upward trend, by regressive breccia with final occurrence of occasional bauxite deposits in its uppermost parts; 2) an Upper Thithonian – Upper Aptian transgressive-regressive unit, composed of various types of peritidal deposits, prevalently limestones, with subordinated early- and late diagenetic dolomites, emersional breccias and grainstones; 3) an Upper Albian – Lower Campanian transgressive-regressive unit, distinguished by great thickness (more than 1000-m) and facies heterogeneity, with a number of small bauxite deposits that formed due to regression, uplift and aerial exposure of carbonate rocks following Laramian movements during the late Senonian; 4) a Paleocene – Eocene unit, lithologically variable both laterally and vertically, consisting of a relatively thick succession of carbonate, clastic and transitional rocks. This megasequence can be, in a general sense, separated vertically into four lithostratigraphic subunits – from the lowest Liburnian deposits (fresh-water and brackish Palaeocene limestones), through Lower and Middle Eocene Foraminiferous limestones and Transitional beds (clayey limestones, calcareous marls and marls) of the Middle Eocene to the uppermost Flysch deposits of the Middle and Upper Eocene (marls and carbonate sandstones). Flysch appears as a result of fundamental geotectonic changes during the Eocene-Oligocene period and represents syntectonic deposits about 300–350 m thick (MARINČIĆ *et al.*, 1996).

The youngest, Quaternary, sediments are rare and scattered in different portions of the Istrian Peninsula. Their origin is various: the southernmoost (Premantura and Marlera capes) and north-western (Savudrija) coastal areas are covered by the Upper Pleistocene loess deposits up to 4-m thick; the Jurassic – Cretaceous – Palaeogene carbonate plain of southern and western Istria is strewn with numerous patches of terra rossa up to 14-m thick, accumulated in deep karst depressions; the river valleys of the Dragonja, Mirna, Raša and Pazinčica are filled with alluvial sediments, while lake sediments (sand and clay) form the valley infill of Čepić Polje in eastern Istria.

3.2. Istrian soils

Fitting in a particular environment forming an integral part of the Mediterranean region, the soils of the Istrian Peninsula have developed, or rather, evolved as a result of a number of specific constraints. Research has long recognised at least four distinguishing features applying to all Mediterranean soils in general, which to a great extant determine their nature. Among these are specific climate, strike and altitude of the mountain ranges (particularly in relation to the coastline), addition of external material (especially aeolian dust), and long term effects of land use, particularly of agricultural activity (see YAALON, 1997). What is characteristic of Istria as a relatively small region (about 3400 km^2) is its bedrock lithology, that is, the spatial extent and distribution of the two essentially different kinds of parent rocks, with different weathering styles, which serve as a primary source of material for the most part of its soil landscape. The colloquial names for different part of the peninsula – Red, Grey and White Istria – derive from the typical association of soils and soil units covering different kinds of bedrock, which roughly conforms with previously mentioned threefold division of Istria on tectonic/lithological basis.

The Jurassic-Cretaceous-Palaeogene carbonate plain of southern and western Istria (*Red Istria*) is dominated by two types of soils among which terra rossa represents the typical and most widespread soil unit in the Mediterranean area (Fig. 3). It is a reddish clayey or silty-clayey soil which dominates the western part of the carbonate plain occupying over 70% of surface area, with an increasing share of brown soils (calcocambisols) toward the east (ŠKORIĆ *et al.*, 1987; BOGUNOVIĆ *et al.*, 1997). It appears as a discontinuous surface layer filling the cracks and sinkholes in the carbonate bedrock usually up to 2.5 m thick, while greater accumulations more than ten meters thick can be found in a number of deep karst depressions formed as a result of netectonic, activity during the Quaternary (BENAC & DURN, 1997). The origin and genesis of terra rossa on the hard carbonate rock has long been disputed but is now firmly considered a polygenetic soil with considerable presence of external material added to the insoluble residue of carbonate rocks. Recent investigations into Istrian terra rossa supported the opinion that apart from the material derived from the chemical weathering of limestones and dolomites *in situ* other constituents might have contributed to their formation (DURN *et al.*, 1999). The analyses of particle size, mineralogy and geochemistry indicate that flysch and loess also might have contributed, as parent material for terra rossa. The former probably covered a significant part of the peninsula in the past before being eroded and reduced to its present position, while the latter was deposited recurrently in a broader area since the early Middle Pleistocene, particularly in the Upper Pleistocene. Actually, most of the Istrian red soils were formed before the Quaternary and represent the palaeosols but due to their very low resistance to erosion they were intensely eroded and washed away from elevated positions in more recent times (DURN, 1996).

The other widely distributed soil type on the Istrian carbonate plain is represented by brown soils but, typically, their appearance is more common with higher altitudes and greater distance from the coast. Their nature is also polygenetic, but slightly different bio-climatic conditions, that is, the absence of the characteristic Mediterranean (xeric) climatic regime farther from the coast, with richer vegetation

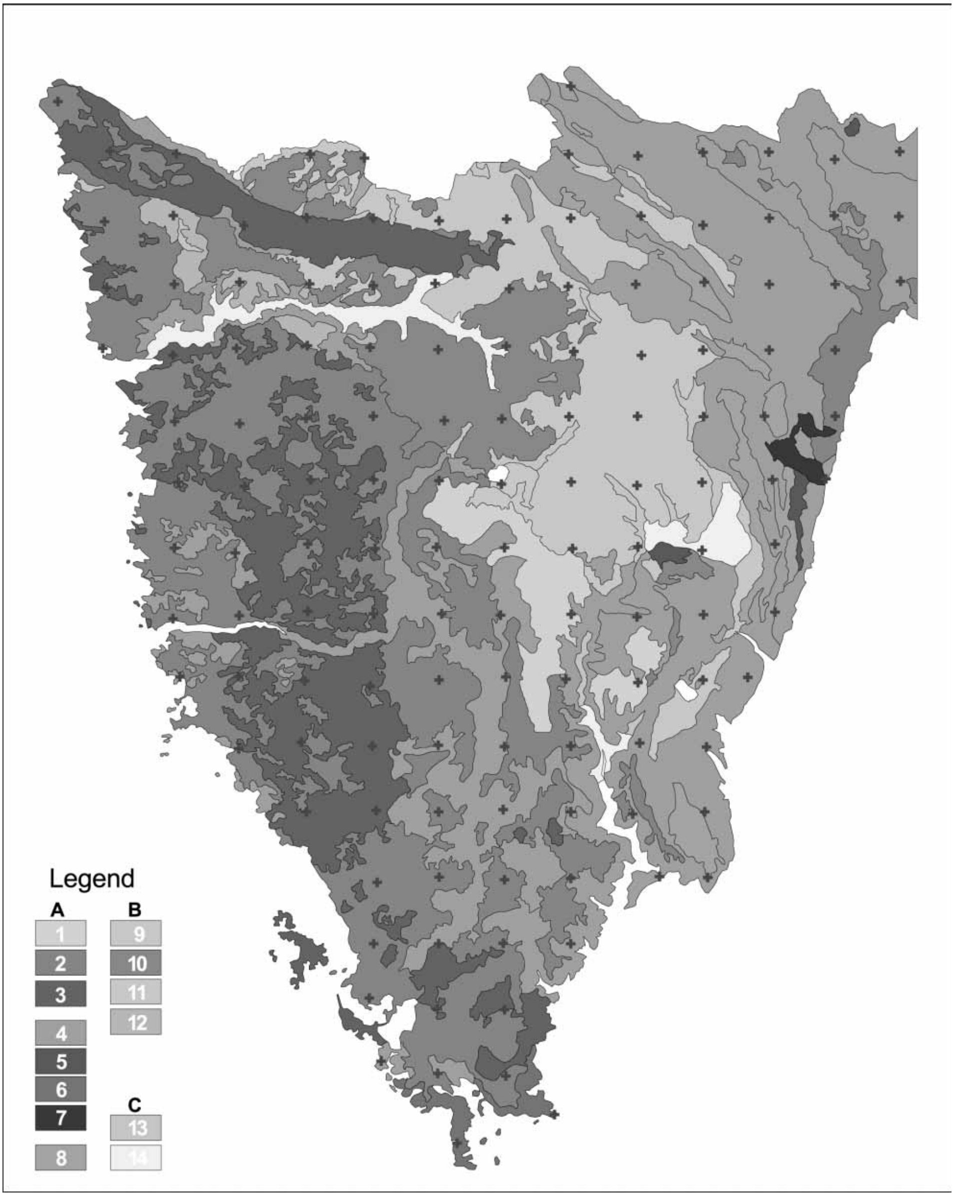

Fig. 3. Distribution of soils in Istria (modified after BOGUNOVIĆ *et al.*, 1997; ŠKORIĆ *et al.*, 1987): A) Carbonate-derived soils – 1) Terra rossa luvic; 2) Terra rossa luvic and typical, deep; 3) Terra rossa, typical, deep; 4) Calcocambisol; 5) Acrisol luvic and typical; 6) Eutric cambisol; 7) Rendzina on weathered carbonate rock; 8) Calcomelanosol, organomineral; B) Flysch-derived sols – 9) Rendzina on flysch and soft limestone; 10) Rigosol on flysch and soft limestone; 11) Rhegosol; 12) Vertisol; C) Colluvial-Alluvial soils – 13) Colluvium, calcareous; 14) Gley, vertic, partly hydroameliorated.

and humidity, impeded the process of complete rubification. More commonly than terra rossa these soils can be found on softer Palaeocene limestone and, especially, on dolomites which are distinguished by the different nature of weathering and, consequently, give more residue and saprolite material for soil formation.

The Cretaceous-Palaeogene carbonate-clastic zone of Učka and Ćićarija is virtually devoid of terra rossa. This zone is a domain of various types of brown soils developed on carbonate rock (calcocambisols) with occasional occurrence of black soils (calcomelanosols) in the highest regions (above 1000-m) where specific climatic and vegetation conditions permit accumulation of humus. Landscape is dominated by steep slopes and narrow valleys causing relatively rapid erosion, particularly in places with scarce plant cover. Since the weathering hardly keeps up with the rate of erosion these soils are mostly shallow and reaches of denuded, rocky, terrain are more common than in other parts of Istrian Peninsula (hence *White Istria*). Rendzinas also occur, developed on narrow zones of clastic rocks, prevalently marls, of very limited extension.

The Palaeogene flysch basin of central Istria (*Grey Istria*) is built mainly of soft rocks and is characterized by a quite different style of erosion and soil genesis. The main body of soil cover is composed of rendzinas and regosols depending on intensity of erosion (steepness) and extent of vegetation cover. Both cases represent immature soils though the latter is typical of flysch, where due to rapid erosion the marls and sandstones are recurrently being exposed on the surface and washed away, particularly on the southern and south-eastern steep slopes and in deep rills cut in soft calcareous marls (ŠKORIĆ, 1987). The mechanism of soil genesis differs greatly with respect to Red and White Istria. As contrasted to the hard carbonate bedrock elsewhere, where the bedrock weathering is mostly chemical (corrosion) the flysch rocks weather predominantly physically and the process penetrates into a much deeper layer of rock. This results in a higher Ca content which, prevented from being regularly leached into deeper horizons due to formation of clayey detritus (saprolith), creates the main geochemical signature of the flysch-derived soils over the Istrian Peninsula (PROHIĆ *et al.*, 1997; ZUPANČIČ & PIRC, 1997). Differences in the content of other elements such as Na or K may also be found significant, putting their concentration ranges on slightly different scales in the cross-comparison.

With respect to this, in assessing the pedo-geochemical baselines of the soils of the Istrian peninsula, the carbonate and flysch bedrock lithology are rather treated separately. The parent geology is considered the crucial environmental parameter in pedogenesis against which all other parameters, the human impact in particular, require evaluation.

4. MATERIALS AND METHODS

4.1. Sampling and geochemical analysis

Soils sampled in the study area include various soil types developed on both carbonate and flysch bedrock (Fig. 3). Most samples are terra rossa and brown soils collected on limestones and dolomites (109 locations), while the rest represent rendzina, regosol and related soils sampled on soft carbonate-siliciclastic rocks, predominantly calcareous marls (26 locations). All samples are collected at pre-assigned locations on a regular square grid 5 x 5 km as defined by the Geochemical Map Protocol for Croatia (PROHIĆ *et al.*, 1998). The topsoil material at each location is sampled from the upper 25 cm of the soil profile which, in most cases, cut through the full A-horizon, and occasionally through the upper part of the underlying B-horizon. The sample is represented by the composite homogenized of 5 subsamples from the area within 25m^2 around the site. A total of 135 samples was thus assembled encompassing the entire territory of Istrian Peninsula. The sample material was air-dried, disaggregated and finally dry-sieved to the fraction of <0.063 mm for further chemical analysis. Analytical work was performed at the ACME Analytical Laboratories in Vancouver, Canada. After near total (hot multi-acid mixture of $HClO_4$-HNO_3-HCl-HF at 200 °C) digestion the samples were subjected to multi-element analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES), while Hg was analysed by flameless AAS after digestion by aqua regia (HNO_3-HCl, 1:3). A total of 42 elements was analysed, but Au, Be, Bi, U and W, having invariable concentrations, and Ag, Sb, Sn and Cd, being mostly under the detection limit, were removed at once from further inspection. Only 24 elements were selected for evaluation of geochemical background. Herein, elements of a strongly anthropogenic signature are included, such as Pb, V, Cu, Hg and Cr; elements of a mostly geogenic origin, such as Ba, Sr, Ti, Al, Na, Ca, Mg, Fe, Mn, and Co; and also intermediate elements with both geogenic and anthropogenic influence, such as Zn and Ni. Apart from the chemical elements, pH level as a valuable environmental factor was also added to the analysis.

4.2. Choice of a method and its implications

There are essentially two types of methods applied in the evaluation of the geochemical background irrespective of the medium, or analyte, under survey. Very often, particularly in environmental and ecological studies, so-called geochemical methods are employed which make use of various geochemical data normalization procedures. In Croatian karst regions, including Istria, where contrasting sedimentary lithology and products of their weathering render direct application of mixed concentration values from different locations inappropriate, geochemical baselines for a number of elements, especially those of anthropogenic origin, have been usually evaluated with the use of some kind of enrichment factor (PROHIĆ *et al.*, 1995; MIKO *et al.*, 1999; 2000; 2001). In this case great expert knowledge is required for each particular local or regional problem concerning mineralization or pollution because the geochemical behaviour of each element depends on many environmental conditions.

Another type of background evaluation employs a statistical approach with a variety of techniques, tests and procedures. In scientific circles of late increasing importance is being ascribed to statistical methods as a powerful tool for assessing more realistic numerical values (ranges and limits). This is most likely initiated by the acknowledgement that the generally valid, or »global«, natural geochemical baseline such as that based on global marine »shale standard« or »average shale« (TUREKIAN & WEDEPOHL, 1961) and average soil (MARTIN & WHITFIELD, 1983), for example, does not actually apply worldwide because it is a function of regional variability and time (MATSCHULLAT *et al.*, 2000). To deal effectively with such spatial and temporal incoherence, the data collectives need to be subjected to a locality-oriented examination, using tools capable of establishing boundaries within a data set as strictly as possible. Statistical methods generally stand as such a tool, though, admittedly, there exists a variety of approaches mainly because of the lack of a satisfactory definition of the geogenic background (regardless of the analyte examined). In overcoming the problem of the »selection of best statistics« the methods employed in this work are in full agreement with opinions treating the pedo-geochemical background as a range that can be determined statistically only for a defined spatial setting (MATSCHULATT *et al.*, 2000). This precludes the mixing of populations from spatially separated compartments, or even from within the same regional confines such as Istria with its contrasting lithologies, thus ensuring some degree of homogeneity. Also, the idea is accepted that multi-modal distributions reveal multifaceted process-response relationships in pedogenesis with each mode corresponding to a single relevant geochemical process (MATSCHULLAT *et al.*, 2000; REIMANN & FILZMOSER, 2000), even within a normal range of data. Finally, it was felt worth mentioning that anomalous values from anthropogenic influence may not be related only to the positive deviations from the once defined baseline range of any particular element, but also, on the contrary, that they may be the result of imbalances creating extremely low contents of some elements in the upper soil horizon. In this light, aside from simply recalculating the original data to define the normal range, the nature of probability distributions is examined for causes of skewed tendencies.

Putting all the above considerations together it is clear that some requirements must be satisfied before choosing an appropriate statistical method to calculate the background, particularly as regards its broad applicability and robustness. Moreover, in the computational process of what might be appropriately called partitioning the threshold population(s) from the background two main issues call for attention. One is the detection of outliers that are often the downright example of strong and persistent extraneous, most frequently human, interference in the data set. The other is treatment of the data remainder clean of outliers but still with some degree of residual skewness that is a clear indication of the anomaly still being present. In the former case, the 4σ-outlier test is a quick and clean-cut method for the detection and elimination of these data. The latter problem can also be effectively dealt with by the simple and relatively easy computational approach commonly known as the iterative 2σ-technique. The concluding data sub-collective can be considered a reliable explanation of the baseline range and its geogenic origin.

4.3. Partitioning the threshold population(s) from the background

The quantitative partitioning of »anomalous« values from the main data body can be thought a less biased method in treating the skewed density functions as compared to various graphical tools such as histograms, box-plots, or cumulative frequency curves because previously more or less subjectively classified outliers and extreme values can be now effectively eliminated in the process. Diagrammatic representation is, however, an indispensable tool that offers a quick and clear insight into the character of density distributions (see LEPELTIER, 1969; SINCLAIR, 1976;

TUKEY, 1977) and is thus always recommended as the first step in the analysis (see REIMANN & FILZMOSER, 2000). However, quantitative methods, such as, for example, the test applying the criterion of four standard deviation from the mean (4σ), are more direct in this respect. The 4σ-outlier test can be applied as an objective numerical method because of the omission of all values digressing four standard deviation beyond the mean without much vagueness. This figure is a clean-cut number that has been accepted as a convention – just as many other statistical measures, including 2σ standardized unit variance – conveying the idea of extremely high improbability of the event occurrence. As a matter of fact, the 4σ-deviation from the mean results in probability of less than one case in a ten thousand ($p<0.000032$), which is a quite respectable safety margin to separate objectively the extreme events (processes) of unmistakably anthropogenic origin from the rest of the measured data. After removing the outliers classified in this manner some researchers tend to accept the postulated range of *mean* ± 2σ of the final sub-collective as a normal range for (pedo)geogenic background. However, removing the outliers does not necessarily ensure the normal range of the remaining data subset. Mathematically robust as it is this procedure still leaves the area between the two standard deviations weighed down with the possibility of hidden non-linear tendencies. Residual skewness always indicates the presence of an anomaly, which is a sensible rationale for further partitioning of data until the final sub-collective roughly complies to the Gaussian law, its density distribution approaching normality – having ideally one mode and decent symmetry.

The approach to the normal range of data as performed in this work is iterative, with successive inspection and testing of the newly emerged subsets of data. The procedure of omitting all values (previously standardized to zero mean and unit variance because of easier examination) that exceed the *mean* ± 2σ interval of each subsequent subset is reiterated in the process until no value further from the mean than 2σ remains in the data set. This is a close approximation to the technique of truncating the upper tail of the density distribution of a variable with immediate testing of the residual subset for normal distribution (PEH, 1997). The process is repeated until the distribution becomes normal and the last truncated value before assumption of normality is accepted as the upper limit for the background. In either case, what can be said of the final subgroup is that it is actually »forced« to enter the normal range with both upper and lower ends approximately equally deviating from the mean. All values lying within the calculated normal range are accepted as the »true« geogenic background – for an element, in an analysed medium, within defined spatial limits – describing the linear (pedogeogenic) process with its expected natural response. All others, including the values exceeding 4σ calculated in the original data set (which are outright outliers), can be seen as anomalous. As an addition, their anomalousness can be categorized, or classified, by the process of partitioning in as many classes as there are steps needed to reduce the original data collective into non-anomalous subgroup corresponding to the background. The whole procedure may be recognized as an approximation to normality, sometimes with a considerable loss of data, or, speaking in terms of non-linear physics, as a collapsing of a complex, non-linear, into a simple, linear realm of system relationships.

Data comprised in a reduced package between upper and lower baseline limits will usually retain a greater portion of the original data set, which may be a convincing argument for the prevalence of equilibrium tendencies and adjustments between gains and losses determining the elemental composition in analysed soils. On the other hand, data lost due to partitioning are likely to reflect directly the degree of non-equilibrium and complexity shared by the analysed element in the soil system – the greater the loss of data, the farther away from equilibrium the element is. It must be noted, however, that even in the new data set fitted by partitioning into a normal range of $-2\sigma < mean < +2\sigma$, elements may not attain the perfect normal density distribution. The real data rarely, if ever, behave in such an ideal manner, especially if data collectives are small. Original data sets of Istrian soils contain as many as 109 cases for soils from carbonate bedrock that have been reduced by over 30% for some elements after partitioning, while in the case of the flysch-derived soils it is even smaller, consisting of only 26 cases at the onset. That the normality of such small sub-collectives may be rejected by statistical tests for normality (see REIMANN & FILZMOSER, 2000) does not preclude the linear character of related processes, since the fitted data fluctuate within the normal range. Inability of attaining the normal distribution originates from the presence of more than one mode in a truncated distribution, suggesting more than one process that fluctuates within the boundaries of linear domain.

5. RESULTS

5.1. Preliminary statistics

Due to the different nature of the soils derived from the two contrasted types of Istrian bedrock all statistics are displayed and the background calculations performed separately for the two original data sets. The results are presented in such a way that immediate comparison among the variables is possible within and across both sets – soils derived from the carbonate bedrock vs. soils derived from the flysch bedrock. The small number of cases (only 26) in the »flysch« data set may be accused of causing the low stability of correlation matrices and subsequent geochemical maps (if generated). However, as the searched numerical model is not supposed to be self-referential, the data, however scarce, are saved by reason of comparative study. Such limitation in size is inevitable in the current phase of research since the same grid density is used in sample collection in both kinds of underlying bedrock regardless of their area of extent.

In Tab. 1 the summary statistics are given for original data sets before partitioning. Data matrix contains the basic statistical parameters, together with p-values for a Shapiro-Wilk (S-W) test for normal distribution, and skewness which is a measure of asymmetry. The results of the 4σ-outlier test are added to the basic statistics in a separate spreadsheet (Tab. 2) as the first step in cleaning the raw data before computation of the normal range for each element. Calculation of the upper 2σ-limit of range (critical deviation from the original mean) is not included, however, convey-

Tab. 1: Descriptive statistics for geochemical data on Istrian soils – Original data set

	Mean	Median	Min	Max	StdDev	CV (%)	Skew	W–S
Carbonate data set – 109 cases								
pH	6.13	6.22	4.30	7.56	0.73	9.79	-0.30	*0.129
Fe (%)	4.10	4.01	2.47	7.25	0.74	14.46	1.31	0
Ca (%)	0.89	0.82	0.28	2.24	0.40	32.60	1.34	0
Mg (%)	0.59	0.54	0.25	1.08	0.19	26.89	0.52	0.001
Ti (%)	0.421	0.420	0.276	0.626	0.046	8.17	0.58	0
Al (%)	8.05	7.84	5.36	11.71	1.09	10.09	0.88	0
Na (%)	0.727	0.699	0.249	1.516	0.222	23.76	0.74	0.014
K (%)	1.43	1.43	0.83	2.12	0.23	12.16	0.29	*0.218
P (%)	0.053	0.049	0.021	0.169	0.023	27.65	2.53	0
Cu (ppm)	30.72	29	10	74	10.55	23.91	1.57	0
Pb (ppm)	40.70	38	27	233	20.14	19.73	8.24	0
Zn (ppm)	96.99	92	59	186	22.86	17.43	1.41	0
Ni (ppm)	80.88	74	40	207	25.66	21.48	2.34	0
Co (ppm)	19.06	18	9	43	4.99	17.67	1.79	0
Mn (ppm)	978.45	976	438	2284	287.45	20.62	1.53	0
As (ppm)	20.26	18	9	105	10.25	27.46	5.50	0
Th (ppm)	16.71	17	9	24	2.70	12.85	-0.17	*0.118
Sr (ppm)	96.07	90	55	375	33.96	18.04	5.52	0
V (ppm)	161.44	153	85	397	49.40	18.96	2.52	0
La (ppm)	55.92	55	34	91	8.38	11.07	0.36	0.009
Cr (ppm)	127.95	121	79	273	29.20	15.04	2.47	0
Ba (ppm)	317.29	317	195	433	41.62	10.10	0.10	*0.924
Zr (ppm)	63.60	61.10	35.4	120.3	14.93	17.96	1.05	0
Sc (ppm)	14.11	14	11	17	1.51	11.54	-0.23	0
Hg (ppb)	67.89	45	15	660	91.59	61.50	5.23	0
Flysch data set – 26 cases								
pH	7.23	7.66	4.84	7.98	0.96	9.51	-1.86	0
Fe (%)	2.97	2.77	1.82	4.74	0.73	18.98	0.87	*0.094
Ca (%)	9.35	10.27	0.20	18.43	6.15	57.17	-0.23	0.035
Mg (%)	0.71	0.70	0.32	1.02	0.14	14.68	-0.17	*0.327
Ti (%)	0.277	0.252	0.189	0.429	0.065	19.65	0.67	*0.057
Al (%)	5.27	5.034	3.86	7.13	1.05	16.91	0.47	0.047
Na (%)	0.550	0.545	0.232	0.829	0.146	21.64	-0.16	*0.800
K (%)	1.50	1.51	0.99	2.06	0.22	11.37	-0.04	*0.547
P (%)	0.042	0.044	0.015	0.075	0.014	25.78	0.12	*0.769
Cu (ppm)	34.35	30.5	16	68	10.87	22.96	1.44	0.006
Pb (ppm)	20.81	18.5	12	53	8.55	20.07	2.33	0
Zn (ppm)	72.77	70	45	130	18.93	18.74	1.24	0.034
Ni (ppm)	80.35	72.5	32	148	25.91	23.64	1.14	0.006
Co (ppm)	15.58	14	9	32	6.03	26.78	1.75	0
Mn (ppm)	905.31	754.5	454	2478	468.03	33.80	2.25	0
As (ppm)	7.77	8	4	11	2.12	22.01	-0.03	*0.204
Th (ppm)	6.65	7	3	11	2.07	25.26	0.10	*0.377
Sr (ppm)	214.27	186	58	588	124.25	45.55	1.05	0.045
V (ppm)	101.62	98	64	169	24.57	17.76	1.09	*0.060
La (ppm)	25.08	22.5	26	39	6.79	23.10	0.62	0.022
Cr (ppm)	104.46	97	73	163	23.57	17.49	1.03	0.034
Ba (ppm)	232.58	240	164	367	55.05	18.68	0.87	0.026
Zr (ppm)	42.86	38.95	31.7	66.5	8.69	16.15	1.19	0.002
Sc (ppm)	10.73	10	7	15	2.32	18.61	0.42	*0.073
Hg (ppb)	39.04	35	20	70	13.57	29.86	0.47	*0.124

* = normal distribution according to W-S test

Tab. 2: Outliers in geochemical data – *Total data set*

	Carbonate data set					*Flysch data set*	
	4σ–limit	Outliers	Sample	(ppm)	(σ)	4σ–limit	Outliers
pH	9.07	none	none	–	–	11.09	
Fe (%)	7.07	1	53	7.25	4.25	5.90	
Ca (%)	2.47	none	none		9.34	33.94	
Mg (%)	1.34	none	none	–	–	1.28	
Ti (%)	0.61	1	53	0.63	4.42	0.54	
Al (%)	12.40	none	none	–	–	9.47	
Na (%)	1.62	none	none	–	–	1.13	
K (%)	2.35	none	none	–	–	2.39	
P (%)	0.15	1	74	0.17	5.04	0.10	
Cu (ppm)	72.94	1	35	74	4.10	77.83	
Pb (ppm)	121.25	1	6	233	9.55	55.01	
Zn (ppm)	138.42	none	none	–	–	148.51	
Ni (ppm)	183.52	2	65(53)	204(197)	4.91(4.60)	184.00	None
Co (ppm)	39.04	1	62	43	4.79	39.72	
Mn (ppm)	2128.23	1	108	2284	4.54	2777.44	
As (ppm)	61.27	1	53	105	8.26	16.26	
Th (ppm)	27.50	none	none	–	–	14.96	
Sr (ppm)	231.93	1	53	375	8.21	711.28	
V (ppm)	359.04	2	65(53)	397(391)	4.77(4.65)	199.88	
La (ppm)	89.45	1	53	91	4.19	52.25	
Cr (ppm)	244.76	2	47(53)	273(253)	4.97(4.28)	198.73	
Ba (ppm)	483.76	none	none	–	–	452.78	
Zr (ppm)	123.30	none	none	–	–	77.63	
Sc (ppm)	20.16	none	none	–	–	20.03	
Hg (ppb)	434.26	2	47(74)	645(660)	6.30(6.46)	93.30	

ing no essential information in this instance, and being largely affected by the high values beyond the natural baseline even after elimination of outliers.

Even the precursory inspections into Tab. 1 and supplementary box-plots (Figs. 4a and b) reveal a great variation among the element contents in both data matrices, though slightly greater in the »carbonate« set judging by the coefficient of variation CV (calculated as »average«σ/*mean*, in %), which is used as a more suitable measure of dispersion alleviating the comparison within and across both data sets at once (WEBSTER, 2001). In general, many elements show strongly skewed density distributions with apparent difference between mean and median values. In a number of cases multi-modality is clearly detected revealing the presence of several causes (processes) that dictate the character of elemental density distributions. If compared, the element contents in soils developed on carbonate bedrock seem not only enriched for most elements except, typically, for Ca, Mg, Sr, and K but also display density distributions that are farther from the normal range than in soils developed over the flysch parent material. Conversely, quite a number of elements

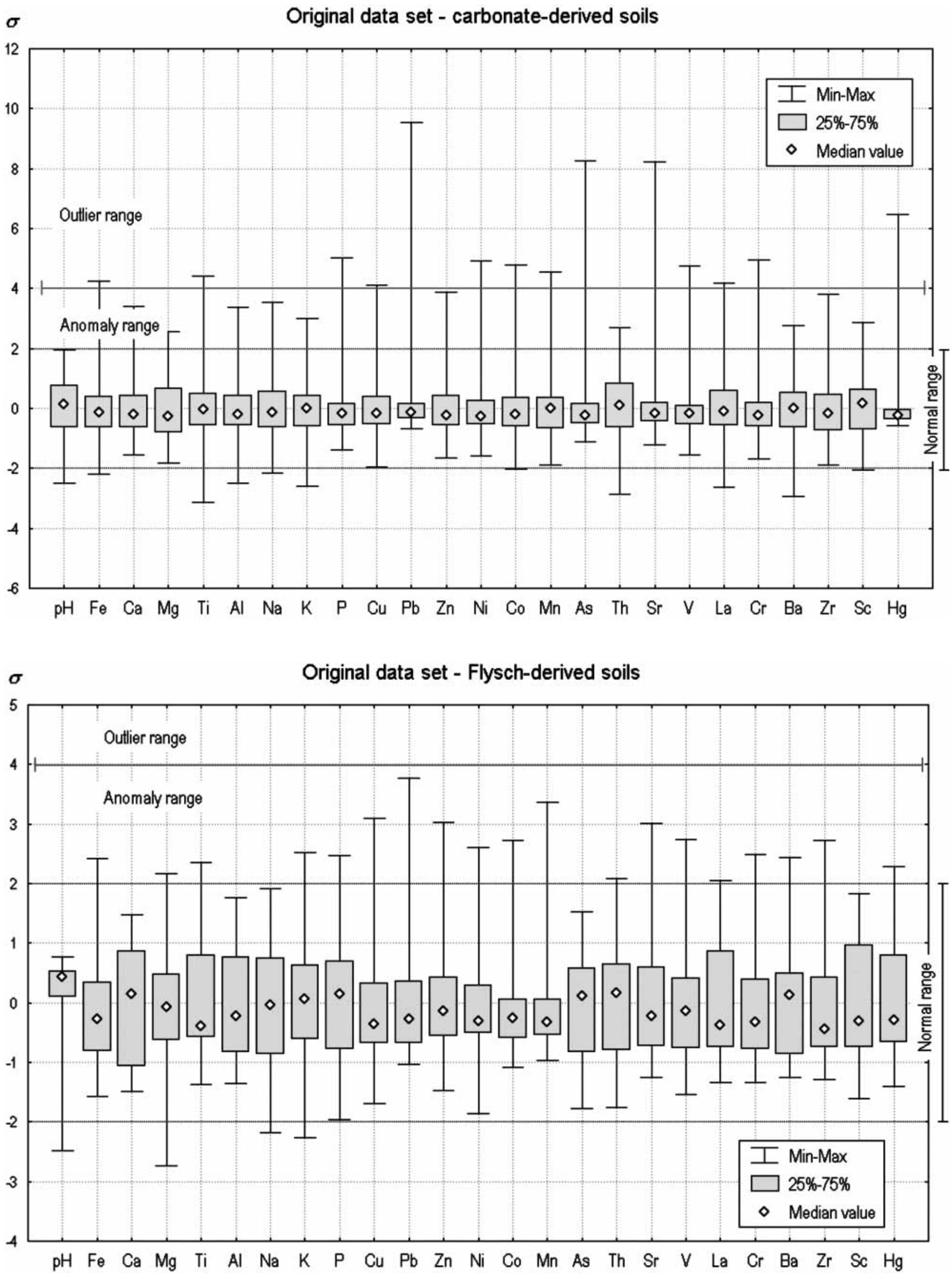

Fig. 4. Original data set – Boxplot comparison of major and trace elements measured in: a) carbonate-derived soils; b) flysch-derived soils. Element concentrations are standardized.

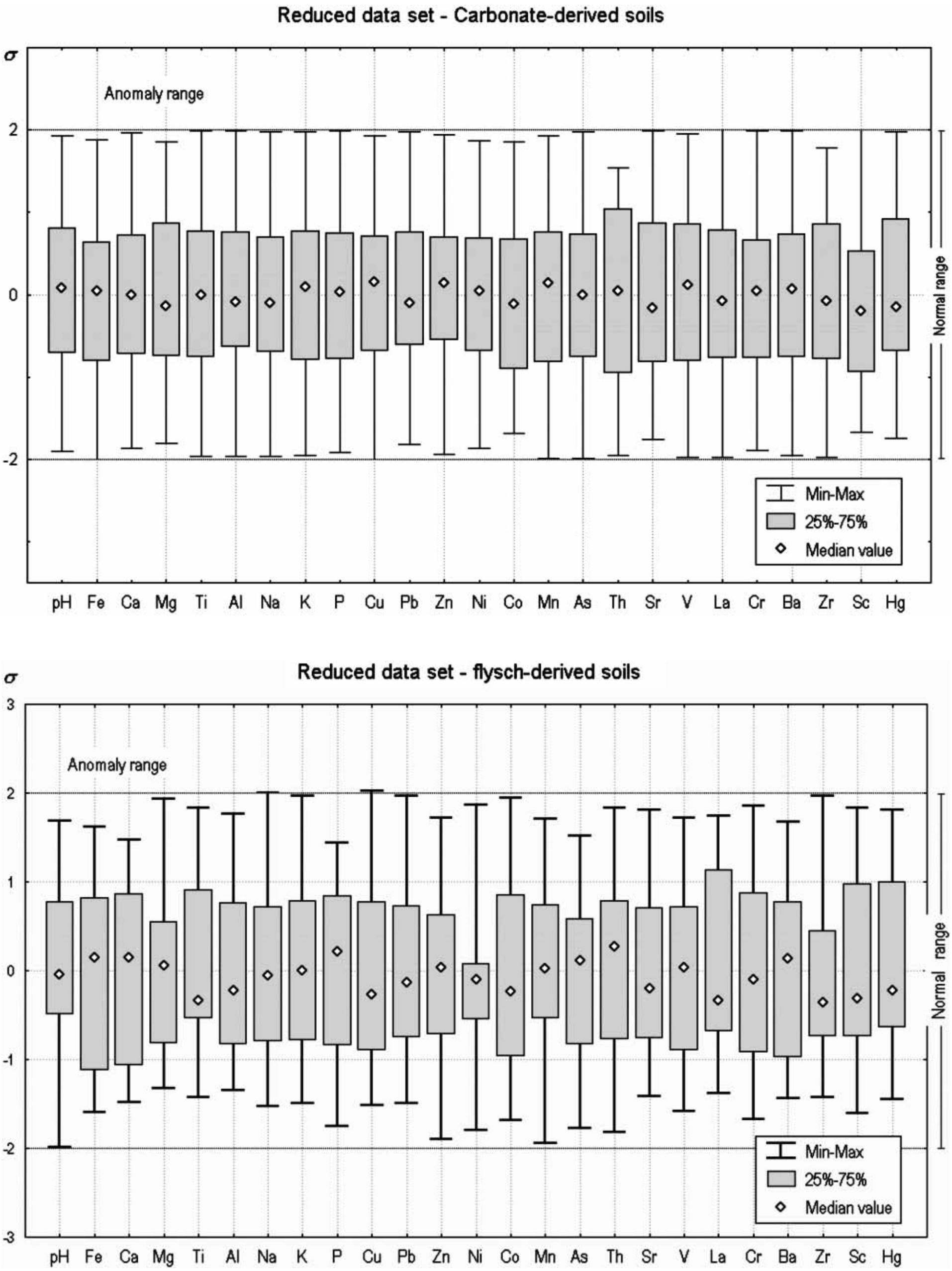

Fig. 5. Reduced data set (geochemical background) – Boxplot comparison of major and trace elements measured in: a) carbonate-derived soils; b) flysch-derived soils. Element concentrations are standardized.

of the latter group appear to be normally distributed – all major elements except Ca and Al, together with some trace elements including As, Th, V, Sc, and even Hg. Most elements analysed from red and brown soils do not even remotely approach normal distribution– only K among major, and Th and Ba among trace elements. On the contrary, their pH index is distributed normally (W-S>0.05, marked by *), while in their flysch counterpart non-normality is prominent showing markedly negative skewness. Also, if pH indices are compared, the higher alkalinity of the soils from the flysch environment is quite noticeable.

The difference between the two data collectives is particularly evident as regards the variation producing the outliers. A cursory glance at the Tab. 2 shows a number of elements from the carbonate-derived soils containing one or two outliers – Fe, Ti and P among major, and Cu, Pb, Ni(2), Co, Mn, As, Sr, V(2), La, Cr(2) and Hg among trace elements. Some of these are the true extremes having concentrations more than twice beyond their calculated 4σ–outlier limit, obviously a heavy impact of human activity on the vulnerable karstic environment – Pb (9.55 σ), As (8.26 σ) and Sr (8.21 σ). It must be noted here that σ values are obtained as the result of data standardization to unit variance. Almost half of the outliers (eight out of 19) are related to the same spot from which sample 53 was collected, that is, from the industrial zone of the Raša port with nearby coal-fired Vlaška (now abandoned), and more distant Plomin power plants, indicating heavy contamination of the area (Fig. 6a and b). On the other hand, not a single outlier is detected within the flysch-derived soil samples. Despite the low number of samples the element contents in the »flysch« data set seem less varied, showing no extremes, even in the presence of possible human activity (such as agriculture).

5.2. Normal range of data

After elimination of outliers and iterative reduction of thusly altered data matrices both »types« of soils are represented by their normal ranges of data. Their most instructive statistical parameters are summarized in Tabes 3 and 4, and graphically in Figures 5a and b by the respective box-plot diagrams. Some elements suffered a considerable loss of data, amounting to 37% for Zn in the carbonate-derived soils, although much greater values are reported from other surveys (cf. MATSCHULATT *et al.*, 2000). Information thus sacrificed for the sake of acquiring the normal range of data did not, however, result in simultaneous attainment of the normal distribution for all elements invariably. Most elements acquired, and still others approached, normal distribution through the process of fitting to normal distribution, particularly for the flysch-derived soils. In the reduced »flysch« data set 18 out of 24 elements show p-values >0.05 for the Shapiro-Wilk test, compared to 11 out of 24 in the original data set, which is a significant increase. In the case of carbonate-derived soils the improvement is even better – 13 elements compared to only four out of 24 in the original data set. A mismatch between the calculated normal range of data and normal distribution for other elements is indicative of inherent non-homogeneity of their background populations. This derives from the residual multi-modality of their distributions inherited from the original population and is reflected in the number of stages applied iteratively in setting the limits of the normal range

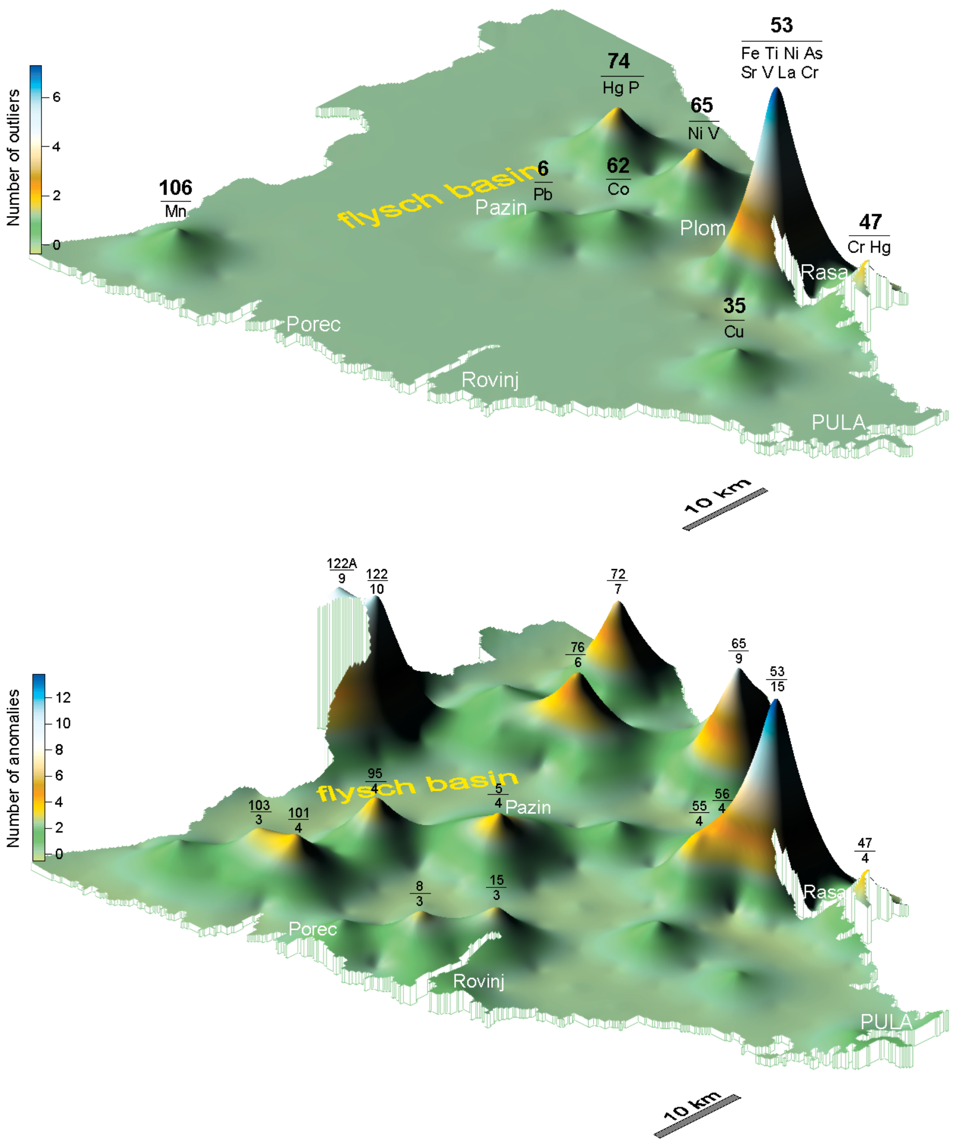

Fig. 6. Metal and trace element loading on the surface unit (25 km^2) of the Istrian Peninsula represented by the number of: (a) outliers (>4σ); (b) anomalies (>2σ).

– if high, it is suggestive of data fragmentation and occasional gaps which separate individual cases rather than their subgroups (see Tables 3 and 4). This is an unfavourable situation demonstrating miscellaneous influences often from unknown and untraceable sources. A truly homogeneous, unimodal, elemental distribution is

Tab. 3: Reduced data set – *carbonate-derived soils*

	N	Nfit	Loss(%)	Mean	Median	StdDev	CV	Upper2σ	Skew	S–W	HI
pH	103	3	5.5	6.17	6.22	0.65	8.75	7.47	–0.16	0.018	1
Fe (%)	91	5	16.5	3.96	3.98	0.42	8.71	4.83	0.00	*0.122	33
Ca (%)	93	4	14.7	0.77	0.78	0.23	24.10	1.23	0.13	*0.124	45
Mg (%)	86	14	21.1	0.51	0.51	0.12	19.65	0.77	0.28	0.003	29
Ti (%)	88	7	19.3	0.419	0.419	0.027	5.44	0.473	0.02	*0.211	24
Al (%)	92	4	15.6	7.84	7.78	0.63	6.50	9.10	0.14	*0.080	22
Na (%)	93	7	14.7	0.688	0.673	0.150	18.16	0.988	0.04	*0.079	35
K (%)	80	9	26.6	1.43	1.44	0.12	6.78	1.66	–0.12	*0.148	22
P (%)	91	5	16.5	0.047	0.047	0.010	17.17	0.07	0.03	*0.187	59
Cu (ppm)	88	6	19.3	27.69	28.50	5.35	15.68	38.40	–0.18	*0.102	48
Pb (ppm)	101	3	7.3	37.56	37.00	5.79	12.54	49.14	0.14	0.037	79
Zn (ppm)	69	10	36.7	87.97	89.00	7.22	6.79	102.41	0.04	*0.170	45
Ni (ppm)	84	6	22.9	72.02	72.5	10.19	11.21	90.39	–0.06	*0.073	56
Co (ppm)	93	4	14.7	18.29	18.00	2.54	11.22	23.37	0.19	0.003	46
Mn (ppm)	90	7	17.4	939.68	960.00	151.17	13.88	1242.02	–0.07	0.027	46
As (ppm)	93	5	14.7	18.04	18.00	4.03	18.27	26.10	0.11	*0.093	75
Th (ppm)	97	2	11.0	16.91	17.00	2.01	10.00	20.92	–0.08	0.001	13
Sr (ppm)	87	7	20.2	91.72	90.00	10.68	10.11	113.50	0.07	0.008	70
V (ppm)	80	7	26.6	147.63	149.50	15.53	9.93	178.68	–0.17	0.044	55
La (ppm)	95	4	12.8	56.44	56.00	5.78	8.30	68.00	0.16	0.047	25
Cr (ppm)	81	7	25.7	116.53	117.00	9.79	7.17	136.11	0.02	*0.066	50
Ba (ppm)	92	5	15.6	313.49	315.00	28.33	7.43	370.15	–0.11	*0.231	15
Zr (ppm)	85	7	22.0	58.53	57.90	7.99	11.67	74.51	0.03	0.048	38
Sc (ppm)	93	3	14.7	14.28	14.00	1.36	8.96	17.00	–0.23	0	0
Hg (ppb)	74	8	32.1	41.42	40.00	9.38	19.41	60.18	0.30	0	91

N = number of samples; Nfit = stages in fitting; CV = coefficient of variation (in%); HI = human influence (in%).

thus far from being a rule even in the case of the fitted background populations despite the fact that their normality may not be rejected by the required statistical tests (Fig. 7). The »flysch« background data, being plagued by the small number of cases, are particularly susceptible to the residual difference between the mean and median values, dragging a bias that was not successfully eliminated in the process of the background calculation.

An overall impression betrayed by the calculated background values as compared to the original data set is that of a rather uniform decline in variance for the majority of elements. A distinct drop is observable only with Hg measured in the »carbonate« data set while the most varying elements from the »flysch« soils – Ca and Sr – defy any appreciable attempt at homogenising their variance (Tables 3 and

Tab. 4. Reduced data set – *flysch-derived soils*

Element	N	Nfit	Loss(%)	Mean	Median	StdDev	CV	Upper2σ	Skew	W–S	HI
pH	20	4	23.1	7.68	7.68	0.18	1.73	8.04	–0.39	*0.553	–1
Fe (%)	19	6	26.9	2.68	2.73	0.34	1.36	3.36	0.00	*0.309	29
Ca (%)	26	0	0	9.35	10.27	6.15	57.17	21.64	–0.23	0.035	–17
Mg (%)	21	4	19.2	0.69	0.69	0.08	9.41	0.85	0.30	*0.269	17
Ti (%)	25	1	3.8	0.271	0.252	0.058	18.02	0.387	0.50	0.039	10
Al (%)	26	0	0	5.27	5.04	1.05	16.91	7.37	0.47	0.047	–3
Na (%)	24	2	3.8	0.552	0.545	0.124	18.85	0.799	–0.07	*0.242	4
K (%)	21	4	19.2	1.54	1.54	0.13	7.11	1.79	0.02	*0.216	13
P (%)	24	2	7.7	0.041	0.044	0.011	26.33	0.063	–0.35	*0.174	16
Cu (ppm)	20	4	19.2	30.80	30.00	4.36	11.23	39.52	0.42	*0.326	42
Pb (ppm)	22	3	15.4	18.05	17.50	4.04	17.93	26.13	0.54	*0.239	51
Zn (ppm)	23	2	11.5	67.57	68.00	11.89	13.80	91.35	–0.06	*0.796	30
Ni (ppm)	21	2	19.2	73.10	72.00	11.19	11.11	95.47	0.40	*0.160	35
Co (ppm)	23	1	11.5	13.65	13.00	2.76	20.19	19.17	0.31	*0.341	40
Mn (ppm)	21	4	19.2	719.48	723.00	136.54	17.09	992.55	–0.23	*0.837	60
As (ppm)	26	0	0	7.77	8.00	2.12	22.01	12.01	–0.03	*0.204	–9
Th (ppm)	25	1	3.8	6.48	7.00	1.92	24.40	10.32	–0.10	*0.213	6
Sr (ppm)	25	1	3.8	199.32	179.00	100.15	42.52	399.62	0.22	*0.189	32
V (ppm)	21	3	19.2	94.62	95.00	12.98	11.39	120.58	–0.04	*0.604	29
La (ppm)	24	2	7.7	23.96	22.00	5.76	20.32	35.48	0.55	0.014	9
Cr (ppm)	21	4	19.2	95.29	94.00	13.35	11.31	121.99	0.11	*0.601	25
Ba (ppm)	23	2	11.5	217.87	223.00	37.60	15.71	293.07	–0.01	0.034	20
Zr (ppm)	24	2	7.7	41.24	38.80	6.71	12.89	54.65	1.02	0.003	18
Sc (ppm)	26	0	0	10.73	10.00	2.32	8.96	15.38	0.42	*0.073	–3
Hg (ppb)	25	1	3.8	37.80	35.00	12.25	28.40	62.31	0.26	*0.069	11

N = number of samples; Nfit = stages in fitting; CV = coefficient of variation (in%); HI = human influence (in%)

4). As for the latter group, elements such as P, Al, Ti, Pb, As, Hg and Th also resist being homogenized significantly. It must be said, however, that the degree of variation (CV) for many elements from both data collectives remains below 20% in their original spread, indicating, accordingly, that respective deviations in the reduced data sets do not change this trend significantly, regardless of the soil »type«. It must be noted also that the basic geochemical signatures for the carbonate- vs. flysch-derived soils remain the same after the analysis, meaning that the relationship among elements as regards their contents does not change substantially. The background values for the former group always tend to settle for higher values (means, medi-

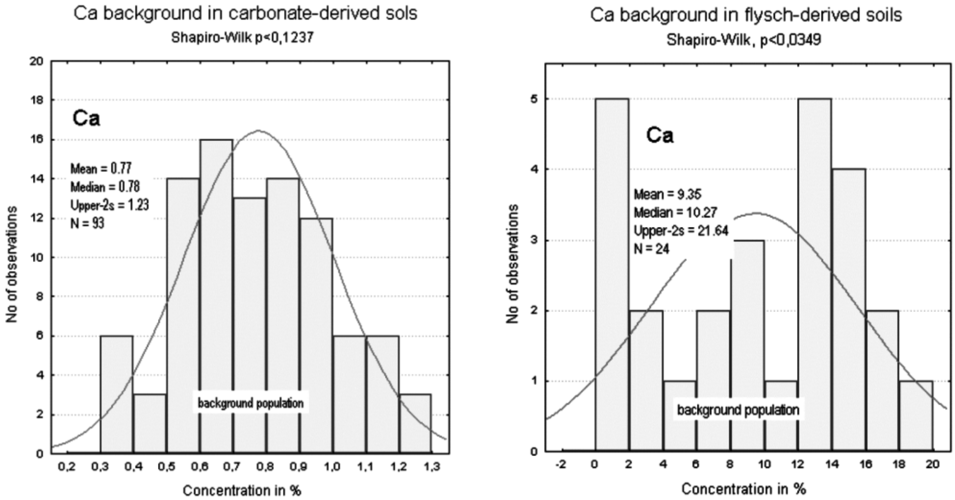

Fig. 7. Histogram comparison showing the frequency distribution of Ca-background subpopulation (normal range of data) in the carbonate- and flysch-derived soils of the Istrian Peninsula.

ans and upper 2σ-limits) except for the well known reversed geochemical signature of Ca, Mg, Sr and K, being accompanied by Cu and Ni.

6. DISCUSSION

Having considered the given results a major question arises as to how to estimate the anthropogenic vs. geogenic influences from the difference between the original and reduced data collectives in the most explicit way. In all cases the applied statistical method leads to a more or less clear distinction between the postulated background and original data set. If the calculated upper 2σ limits of the background are used for comparison with the original maximum values (including outliers) then the anthropogenic contribution for each element can be easily recalculated and the obtained amounts argued for their real nature. In this way the normal, or geogenic, range of values in the topsoil is put in direct contrast to the maximum values determined earlier either as outliers, or (in most cases) in the >2σ anomalous range. Geogenic influence can be calculated as ratio $2\sigma_{BCK}/Max_{ORIG}$ and converted into percent values for each observed element (cf. MATSCHULLAT, 1997; MATSCHULLAT *et al.*, 2000). Difference in the unit value indicates the anthropogenic impact (HI). This procedure gives some intriguing results for the soils from the Istrian peninsula (see Tables 3 and 4). For geogenic elements these values are not expected to be significantly high, and if they appear so, they give a quite unrealistic or even strange impression as to their natural dispersion in the topsoil. The prominent example is Ca whose maximum value in carbonate-derived soils reaches 2.24%

while the postulated geogene background range totals only 1.23%, which is in excess by 45%. For geogene elements such an increase gives a somewhat unrealistic picture for which human-caused forces cannot offer a plausible explanation. It is frequently indicative of an anomalous population originating from some diverse rock types and their weathering products as a »pollution« source (REIMANN & FILZMOSER, 2000). Elevation in Ca content can indeed be traced in most cases to the occurrence of nearby outcrops of calcareous marls or marly limestones at the boundary to the flysch series situated above the sample point (e.g. samples 124 and 74 with 2.24% and 2.13% Ca, respectively), whose weathering products were partly transported mechanically downslope to the spot. Higher accumulation of Ca in some red soil specimens developed on carbonate bedrock (e.g. sample 25 with 2.14% Ca) is not unusual considering the colluvial origin of terra rossa in many instances. Sr also shows high deviation from the background but being the element (together with Ba) whose content is influenced mostly by the underlying bedrock lithology, its 70% variation from the background limit (113 ppm) in carbonate-derived soils is not explicable by indirect geogenic influence only, especially if the outlying value (375 ppm) has the same source as the majority of detected Istrian outliers (sample 53 in the Plomin-Labin-Raša area, most probably polluted by the now abandoned Vlaška coal-fired power plant, 2 km northeast from the port of Raša; Fig. 6). Distribution patterns of other geogene elements that may be governed either by specific residual minerals in the »carbonate« soils (such as Ti, Al, Fe and Mn), or by bedrock permeability and pH level (such as Mg) (PROHIĆ *et al.*, 1997) reveal indirect geogene influences ranging from 22 to 35% higher than the postulated background. These values are quite realistic for minor local disturbances, and in the case of Mn (46%) they probably reflect the ubiquitous tendency of manganese oxides and hydroxides (particularly in terra rossa) to concentrate in the form of concretions and coatings on various soil features (DURN *et al.*, 2001). As for elements of mostly anthropogenic origin, the human impact is obvious in a number of elements (especially Hg, Pb, As, Cr and P) behaving in accordance with their worldwide reputation of being strong contaminants (see Tab. 3).

The flysch-derived Istrian soils are recognizable for being devoid of virtually any significant variation beyond the natural background, a phenomenon that is reflected in relatively small increments or even with a »decrease« in anthropogenic contributions. A meaningful variation is shown only in a minority of elements including Mn (60%, probably from enrichment with carbonate material), Pb (51%, airborne pollution), Cu and Co (about 40%, agriculture and industry). Others have the 2σ–background limits very close to maximum values in the original data set, even overlapping it, which results in »negative« influence« (Ca, Al, As and Sc). The actual cause for such a geochemical signature may exist in the specific nature of erosion and soil-forming processes changing the flysch soil landscape too rapidly and unpredictably to allow the attainment of the equilibrium tendencies.

Here we come to the point where the process dynamics of the uppermost part of the soil profile as seen in the shape of elemental probability (density) distribution curves (or proxy histograms) invokes the problem of its evolutionary trajectory (age), or time needed for particular earth surface process to leave intelligible imprints in the soil properties. The topsoil as defined in this work (top 25 cm of the soil profile) is an interacting zone, penetrating sometimes into the upper parts of the B-horizon, where natural and anthropogenic signals are mixed with various intensity and extent so that variations in heavy metal loading together with processes of their leaching and distribution according to depth evade the simple and straightforward linear, cause-and-effect relationship. It may be hard to define how old the topsoil horizon really is, owing to its dynamic nature which arises from almost incessant fluctuations of external factors and considerably affects its geochemical signature. The distinction between both geogenic and anthropogenic influence, and stable (steady-state) vs. unstable soil evolution by evaluating the pedogenic background can be tentatively established via the ergodic principle as indicated in the introductory notes. Distribution curves of observed elements implicitly reflect these changes through the space-for-time-substitution indicating the degree of pedogenic development (PHILLIPS, 2000). In the above example, the flysch–derived soils are placed in sharp contrast to their carbonate counterpart simply by their strong dynamism that involves both the processes of progressive and regressive pedogenesis in the scheme of soil formation (BIRKELAND, 1999). As expounded earlier, the Istrian flysch basin is distinguished by the high weatherability of its soft marls and weakly consolidated (calcareous) sandstones undergoing intense erosive processes. The soils forming on its surface can be described as incipient and undeveloped due to occasional bedrock exposure by the rapid erosion, slope transport, and subsequent mixing of the fresh parent material with already formed regolith. The colluvial soils formed on slopes can be both cumulative and non-cumulative depending on their position uphill or downhill. Thus the topsoil can be built up by accumulating the parent material downslope or be destroyed by surface erosion and removal of the weathered products from the upper slope, with human agency helping the process through agriculture or forest clearing. In both cases the elemental probability distributions will be composed of overprinted subpopulations originating from fusion of different phases over a relatively short period of time. This may be indicative of the effects of progressive-regressive pedogenesis due to rapid erosion or accumulation, initialising or abandoning agriculture, deforestation or afforestation of land, and other short time changes driven by external natural and human agencies. On the other hand, the anomalous values (of geogene elements), if they appear, may originate more from irregular fluctuations due to various stages of mixing and »rejuvenation« of the uppermost soil horizon by addition of parent material than from the time-independent, steady, evolutionary changes reflected in its geochemistry (Fig. 8). The calculated background range for geogene elements will very probably closely correspond to their natural spread in parent material, which is a matter for more detailed mass-balance studies involving the complete soil profile, but not within the scope of this study. As for elements of anthropogenic signature their fate will also be influenced by the same pattern of rapid topsoil changes and mixing processes leading to a certain dilution of the highest concentration values and possible anomalies. The less »mature« or undeveloped soils are generally recognized for not showing the typical enrichment in heavy metals but rather stable or even depleted concentrations (MCMARTIN *et al.*, 2002) though the characteristic skewness

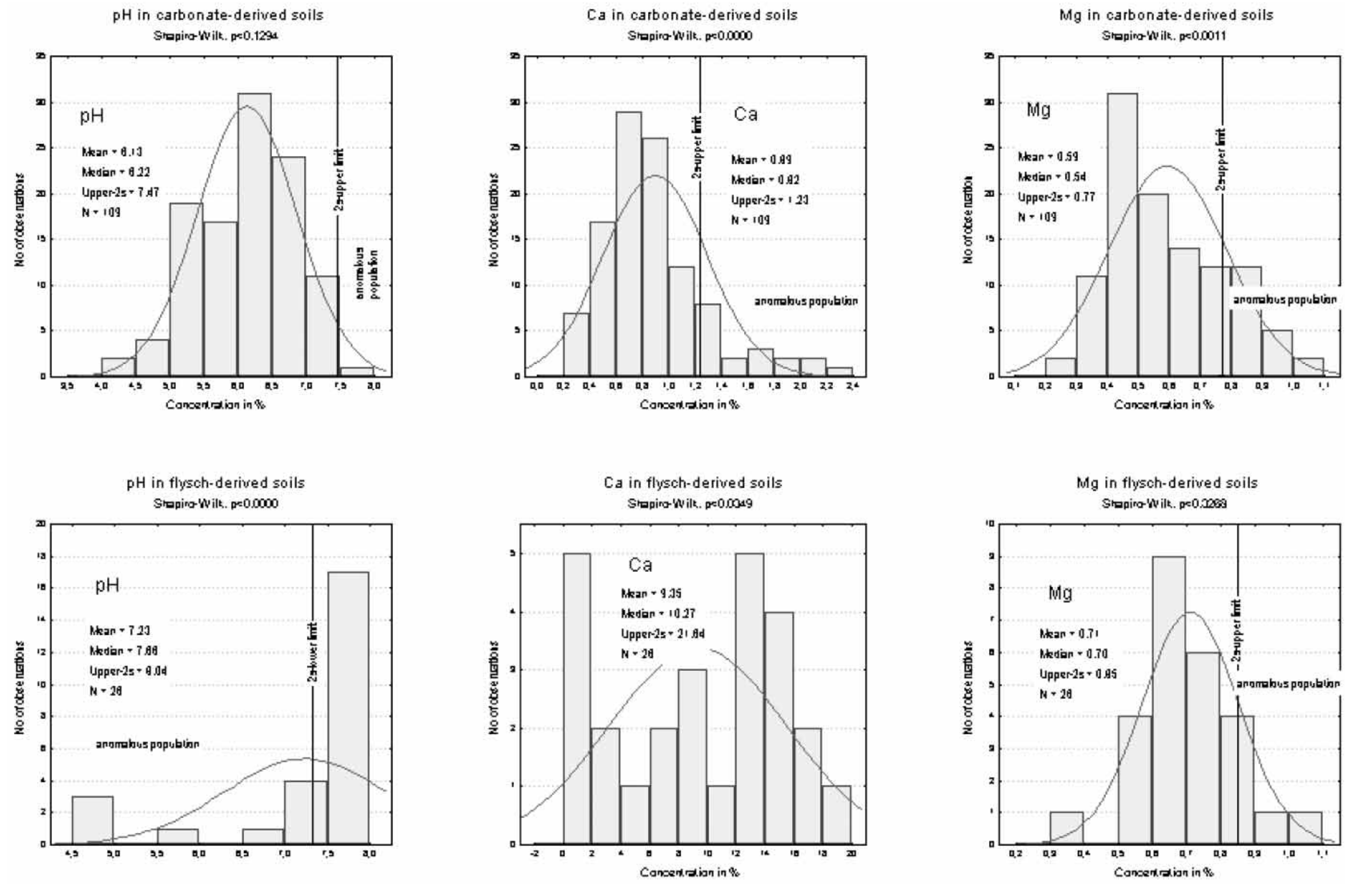

Fig. 8. Histogram comparison showing the frequency distribution of pH, and total content of Ca and Mg (total set of data) in the carbonate- and flysch-derived soils of the Istrian Peninsula.

of their probability distributions remains as a persistent mark of anthropogenic input. For example, the lower anthropogenic impact of Hg, As, Pb (Tabs. 3 and 4) and other heavy metals loaded in the flysch-derived soils as compared to the carbonate bedrock environment is not likely to be explained otherwise than by the damping effect that the above processes exert on atmospheric fallout and other sources of these elements in the uppermost horizon of the flysch soil landscape.

The carbonate-derived soils, and in particular the various terra rossa varieties, are evolved in a quite different pedoenvironment, that is, the geomorphologically stable surface of predominantly low and mild relief of the south-western and central Istrian carbonate plain with a completely different style of soil formation. There is a considerable body of evidence of their greater age with regard to the »flysch« soils during which erosion might have reduced a great part of a once perhaps continuous surface layer formed as a result of accumulation from various sources (DURN, 1999). Of these, a considerable portion is represented by aeolian fines, which, being deposited since the early Middle Pleistocene, together with an insoluble residue of carbonate rocks and flysch material are responsible for the polygenesis of paleosols and modern red and brown soils. As their recent discontinuous surface layer shows, the soil cover gradually lost material through erosion, so that in most places the former B-horizon eventually became the modern, non-cumulative topsoil. During this period the main pedogenic processes such as leaching of carbonates, eluviation and rubification gradually moved deeper by the thinning of the soil cover, but it is impossible to say exactly how intensely the characteristic features of primary deeper horizons were overprinted by younger pedogenic changes. In a supposed stable environmental situation it is expected that geochemical signature in the youngest, topmost horizon of the carbonate-derived soils would follow the trend of the soil development inherited from the past. Eventually, it would probably attain the steady-state equilibrium with prevailing environmental conditions (BIRKELAND, 1999) so that the anomalous values, additions and losses, can be more distinctly reflected and separated from the background levels than in the case of the flysch parent material. Leaching of carbonates and other solutes, and the accompanying pH conditions are clear evidence for this (Fig. 8). Here one can surmise a steady loss of Ca, and Mg in time judging from their positively skewed density distribution curves. Starting from some hypothetical initial conditions in the past, with concentrations lingering far above the upper 2σ-limit of background range (>1.23 ppm), Ca has been removing steadily from the topsoil downward by the percolating water causing the majority of concentration values to cluster through time around a progressively decreasing median, leaving behind a tail indicating the points in space (and time) where leaching was temporarily obstructed or counteracted by addition of Ca. Removal of Ca must have been relatively swift in contrast to Mg as the content of the latter in soils over the carbonate parent material or neighbouring flysch deposits does not exceed 1.1% (Tab. 1). Nevertheless, the Mg probability distribution curve in the original data set reveals stable depletion (Fig. 8) leading to the background limit of 0.77% Mg in the recent topsoil. By contrast, Na and K are more in balance as their losses are constantly supplied from other sources (by air) fitting their frequency distributions close to normal (Na), or normal

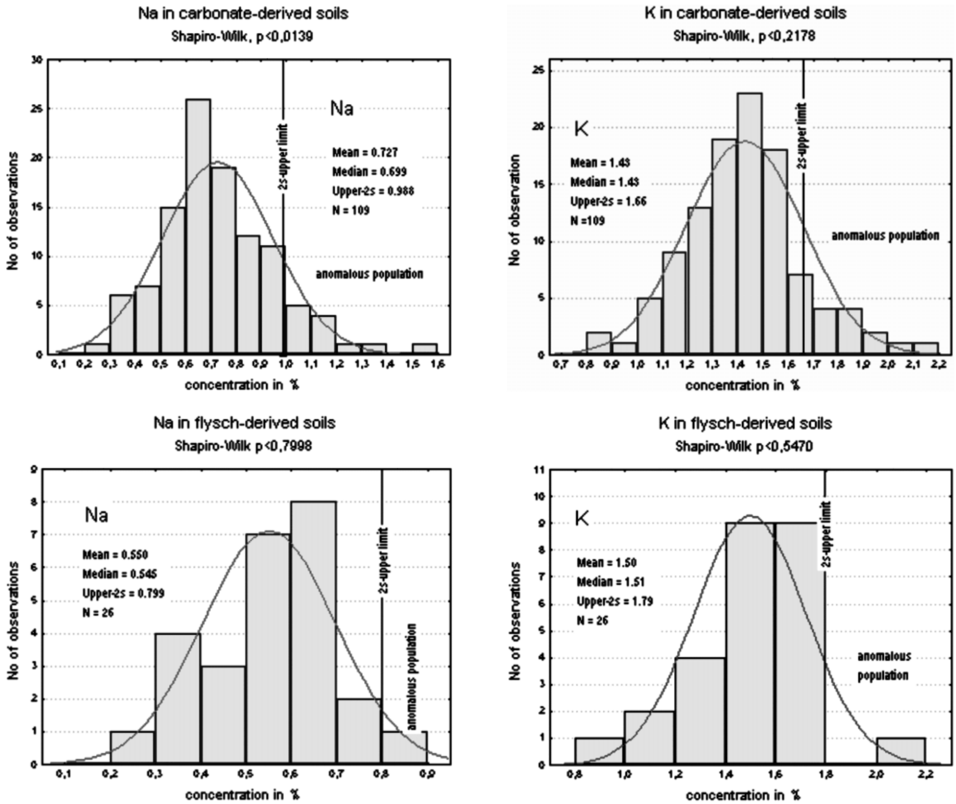

Fig. 9. Histogram comparison showing the frequency distribution of the total content of Na and K being, or approaching to, normal (total set of data) in the carbonate- and flysch-derived soils of the Istrian Peninsula.

(K) (Fig. 9). The pH level is also well balanced through time though its slightly negatively skewed distribution curve indicates progressive and steady acidification of the upper horizon, evidenced by a few strongly acid samples (pH<5), which is in accordance with the process of leaching. Values around pH=6.2 (mean and median of the reduced data set) are typical of carbonate-derived Istrian soils but the upper background limit of pH=7.5 is already well within the alkaline zone. If compared, the soils from the central Istrian flysch belt are prevalently basic with a maximum value pH=8 and strong negative skewness (Fig. 8), despite occasional non-outlier acidification (samples 83, 86 and 116 with pH<5.0, all in a dense deciduous forest). Distribution curves of solutes disclose the marks of impeded soil development in this kind of environment – carbonates have no time to leach properly and the steady-state equilibrium cannot be attained (Fig. 9). All tend to capture normal distribution (Tab. 1), some with small negative skewness, indicating the constant supply of fresh parent material.

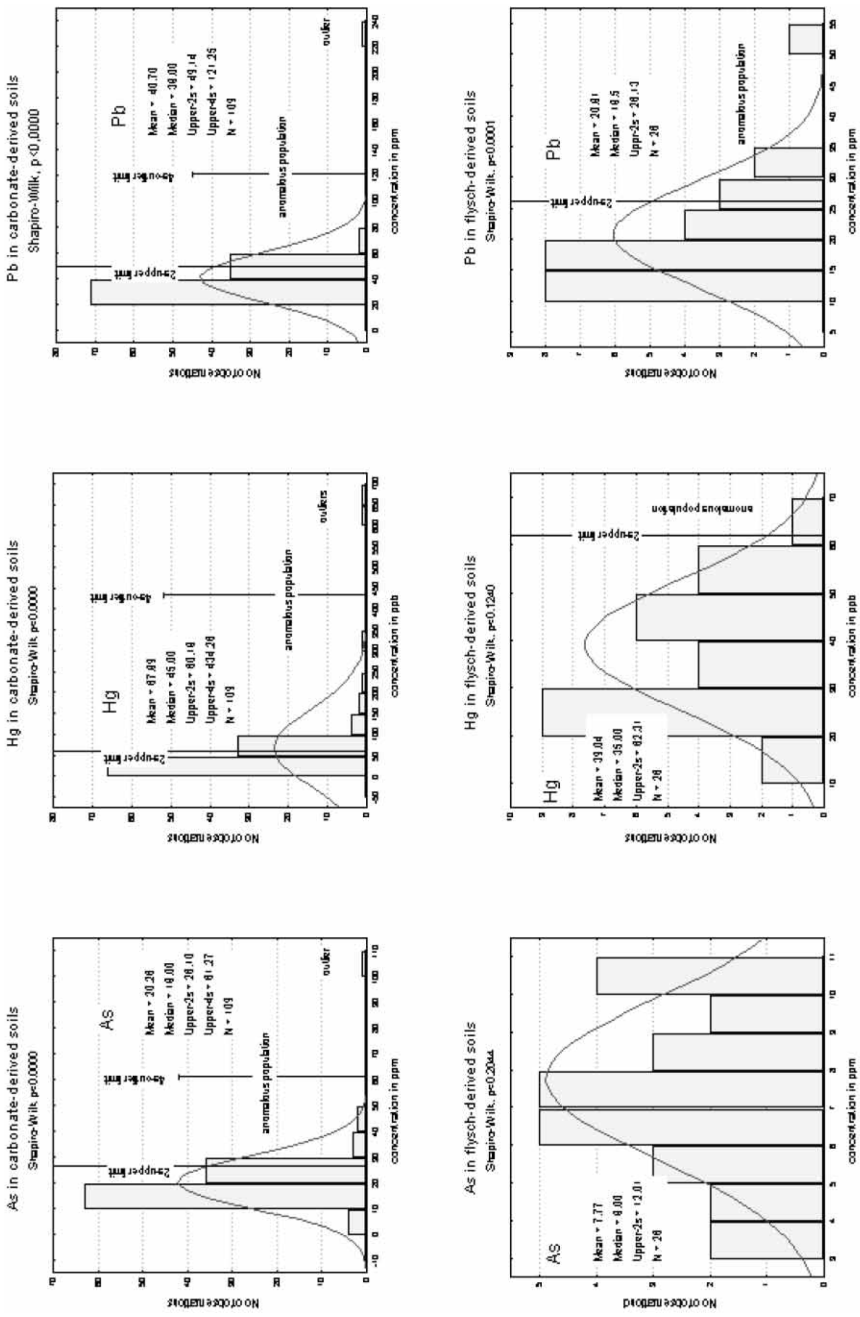

Fig. 10. Histogram comparison showing the frequency distribution of the total content of some trace elements (total set of data) in the carbonate- and flysch-derived soils of the Istrian Peninsula. Note the high positive skewness due to the outliers in the »carbonate« data set and the presence of multi-modality in their »flysch« counterparts.

Contrastingly, trace elements in the carbonate-derived soils follow a different evolutionary pathway altogether, being, for the most part, directed by modern, human-influenced, environmental processes. Here, quite an opposite trend is indicated by their positively skewed frequency distribution curves when compared to most of the major (geogene) elements discussed above – that of accumulation in the topsoil. This process is usually far from being incremental, and undoubtedly has suffered strong acceleration since the onset of the industrial era. It disturbed particular places more heavily in the second half of the last century when most threshold values were crossed and outliers superimposed on the existent population (Fig. 10). Element Pb and sample 53 individually taken as a single variable and a single case are glaring examples (Fig. 6). The background values calculated for the majority of trace elements in this work indicate a safe upper 2σ–limit of their content belonging to the pre-industrial era but it is impossible to distinguish the small increments from the background population, or the existence of minor (extrinsic) concentration thresholds unless apparent gaps occur in the data set (Zn, Cr or V, for example). Such thresholds can be numerically assessed by locating stages during truncation of the original data set until the background population emerges. For example, the voids present in the frequency distribution of Zn and Mn (Fig. 11) are indicative of more than one threshold separating the background from anomalies accumulating in time. The same may be suggested by the presence of two or more modes (see also Fig. 10). Where progressive change (accumulation of an element) is absorbed by the soil system over time, meaning that the portion of the element content is transferred down to the B-horizon or even further below to the bedrock, the frequency distribution curve will be less skewed or even close to normal, reflecting a linear relationship, but such is more the behaviour of some geogene trace elements. However, normality as a reflec-

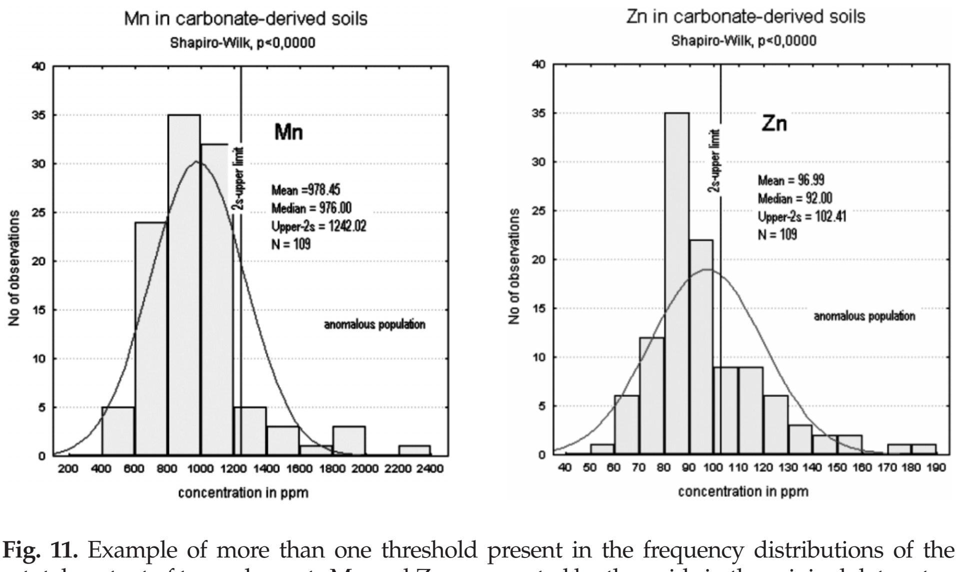

Fig. 11. Example of more than one threshold present in the frequency distributions of the total content of trace elements Mn and Zn represented by the voids in the original data set.

tion of a non-stressful, stable, natural environment is quite an unrealistic condition for most elements of an anthropogenic signature. Accumulation of trace elements in carbonate-derived soil is thus a strongly non-linear process driven by external disturbing forces that to a large extent obliterates their intrinsic behaviour.

7. CONCLUSION

The complex and polygenetic nature of the soil landscapes of the Istrian Peninsula is reflected in their geochemical signatures, which combine geogenic and anthropogenic signals to varying degrees. The criteria for identifying the asymmetrical contribution of both inputs, as well as for marking the baseline limits, may be sundry, but the fate of major and trace elements involved in various soil-forming processes can be very effectively studied via the character of their probability distribution curves (or proxy histograms). The geochemical background is effortlessly calculable by the statistical methods regardless of the soil type or any of the natural or anthropogenic factors under consideration, though the study clearly shows that the idealised impression of a simple, linear cause-and-effect relationship between geochemical or any other soil features is plainly nonexistent. The two main issues can be summarized by this work in respect to the geochemical background: the first is that the greater part of all measured concentration values fall within the normal range of data whose thresholds can be determined by simple mathematical computations; the second is that the soil complexity resists the building of stable, symmetrical probability distributions complying to the Gaussian law, even within the calculated background limits. Skewness of elemental distribution curves is the first and foremost signal of non-linear response to various, especially external, factors that disturb the soil system, because it indicates non-equilibrium dynamics reflecting either accumulation or depletion of an element involved in some soil forming or human-affected process. This explains complex and irregular temporal and spatial patterns caused by multiple responses in the soil evolution and by various modes of adjustment. The hope for their disentanglement is unsubstantiated without posing some limits as regards particular soil forming factors. In this work the setting was cleared from the start by sequestering the two types of parent material considered the most significant contributor to the specific behaviour of elements and character of their probability distributions. Thus the carbonate-derived and flysch-derived soils differ considerably from each other both in their background ranges and character of their elemental probability distributions, which is the result of different character of soil forming processes in the uppermost part of the soil horizon. The »immaturity« of the soils developed on the flysch parent material is seen in the low variation from the natural background – a consequence of the frequent reversal of developmental trends from progressive to regressive and vice versa. The normal range of the postulated geochemical background is not invariably followed by normal distribution of values within its limits, which suggests the presence of multi-modality. The latter points to instability of the main population due to the unyielding influence of more than one process on the local distribution of the given element. The »mature« or evolved soils overlying the carbonate parent rock show greater variation from the geogenic background and much more pronounced skewness being, though, more under the influence of anthropogenic sources often overprinting to a considerable degree, or even obliterating the natural signal. Outliers as the principal cause of skewed distribution are related specifically to these soils (their upper horizon) due to the fact that geogene processes cannot keep pace with recent, rapid anthropogenic change. By contrast, the undeveloped soils on flysch bedrock suppress the outlier outbreaks because of the dilution effect caused by weathering and transport of the easily erodible parent material and its subsequent mixing with already formed regolith. In both cases, the anthropogenic and natural signals are mixed together creating a multiple-causality problem enhancing the development of complex nonlinear soil dynamics. Since only the topsoil is taken into consideration the conclusions reached in this work inevitably suffers from the lack of data necessary for deeper evolutionary insight. Nevertheless, much can be deduced from the obtained results as regards the human impact on the environment, so that the calculated geochemical background (with its upper limit) offers trustworthy and plausible information on the natural or geogene limits of element content within the local boundaries of the study area.

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SAŽETAK

Pozadinski geokemijski šum u tlima Istre

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Kompleksna i poligenetska priroda tala Istarskog poluotoka odražava se u njihovim geokemijskim svojstvima u kojima je, osim prirodnih čimbenika, prisutan i utjecaj čovjekova djelovanja. Kriteriji prepoznavanja njihova, najčešće nejednolikog, doprinosa kao i označavanja razine pozadinskih (geogenih) koncentracija različiti su, no ponašanje pojedinih kemijskih elemenata koji sudjeluju u mnoštvu procesa razvitka tla nazire se i iz značajki njihovih krivulja raspodjele (ili histograma) te ga je moguće s tog aspekta i proučavati. Geokemijski šum koji predstavlja prirodnu koncentraciju elemenata u istraživanom mediju može se jednostavno i lako odrediti statističkim metodama, bez obzira na tip tla ili specifične prirodne i antropogene čimbenike, ali istraživanje provedeno u ovom radu jasno pokazuje da idealna predodžba o jednostavnom, linearnom uzročno-posljedičnom odnosu među geokemijskim ili bilo kojim drugim svojstvima tla ne odgovara stvarnom, prirodnom stanju.

U svezi s određivanjem pozadinskog geokemijskog šuma, ovaj rad pruža dvije osnovne informacije: prva je da se veći dio mjerenih vrijednosti koncentracija istraživanih elemenata nalazi unutar raspona normalnih vrijednosti, čije se granice mogu odrediti jednostavnim matematičkim izračunom; druga je da kompleksnost sustava tla ne dopušta stvaranje stabilnih simetričnih raspodjela vjerojatnosti koje se pokoravaju Gaussovom zakonu, čak i kad se radi o vrijednostima obuhvaćenim izračunatim granicama pozadinskog geokemijskog šuma. Asimetričnost krivulje raspodjele kemijskih elemenata prvi je i osnovni pokazatelj nelinearnih reakcija na različite, poglavito izvanjske, čimbenike koji remete pedosustav. Ona ukazuje na neravnotežnu dinamiku koja se odražava obogaćenjem ili osiromašenjem pojedinih elemenata uključenih u neki prirodni proces razvitka tla ili promjene prouzročene

čovjekovom djelatnošću. Međutim, razumijevanje ove kompleksne dinamike gotovo je nemoguće bez a priori određenih kriterija u odnosu na koje se ona promatra. Stoga je u ovom radu unaprijed je postavljena granica između dva tipa geološke podloge, odnosno matičnog materijala koji se smatra najznačajnijim čimbenikom u razvitku tla kao i specifičnom ponašanju elemenata u tlu i karakteru njihovih krivulja raspodjele. Tako se tla nastala na karbonatnoj i fliškoj podlozi međusobno bitno razlikuju, kako po rasponu pozadinskih vrijednosti koncentracija elemenata, tako i po tipu njihove raspodjele vjerojatnosti, što je posljedica kompleksne dinamike različitih procesa razvitka tla u površinskom djelu profila. »Nezrelost« tala razvijenih na fliškoj podlozi iskazuje se u nevelikim otklonima u odnosu na pozadinski geokemijski šum, što se može protumačiti kao posljedica čestih promjena razvojnih smjerova pedogeneze iz progresivnog u regresivni i obratno. »Normalni raspon« izračunatog geokemijskog šuma ($-2\sigma < \textit{mean} < 2\sigma$) ne mora nužno biti popraćen i normalnom raspodjelom vrijednosti unutar njegovih granica, na što upućuje prisutnost višestrukih modova u krivulji raspodjele vjerojatnosti. Ovi pak ukazuju na nestabilnost glavne populacije zbog utjecaja više od jednog procesa na lokalnu varijabilnost pojedinog elementa koji nije moguće odstraniti usprkos odbacivanju anomalnih vrijednosti. »Zrela« ili razvijena tla koja prekrivaju karbonatnu matičnu stijenu pokazuju veća odstupanja koncentracija od granica pozadinskog geokemijskog šuma, a krivulja raspodjele vjerojatnosti većine elemenata pokazuje jače izraženu asimetriju budući da je posljedica snažnijeg utjecaja antropogenih izvora koji prekrivaju ili čak brišu prirodni signal. Ekstremne vrijednosti kao glavni uzrok asimetrične raspodjele povezane su upravo s ovim tlima (njihovim površinskim horizontom) zahvaljujući činjenici da geogeni procesi ne mogu održati korak s današnjim, vrlo brzim antropogenim utjecajima koji izazivaju zagađenje okoliša. Upravo suprotno, u nerazvijenim tlima na fliškoj podlozi potisnute su pojave ekstremenih vrijednosti zahvaljujući učinku razrjeđenja prouzročenom brzom erozijom matične stijene (lapori) i miješanjem rastrošenog materijala s već formiranim regolitom. U oba slučaja, antropogeni i prirodni signal se miješaju, izazivajući problem mnogostruke kauzalnosti koja je uzrok kompleksne nelinearne dinamike u (geokemijskim) procesima razvitka tla. Budući da je samo površinski horizont tla podvrgnut istraživanju, zaključci izvedeni u ovom radu neizbježno trpe od nedostatka podataka nužnih za dublji uvid u evoluciju tla i ponašanje pojedinih kemijskih elemenata u profilu tla. Međutim, bez obzira na ovu činjenicu, dobiveni rezultati dovoljno jasno kazuju o utjecaju čovjeka na ranjivi krški okoliš, tako da izračunati pozadinski šum pruža vjerodostojne podatke o prirodnim (geogenim) rasponima koncentracija kemijskih elemenata u lokalnim okvirima u kojima je smješteno istraživano područje.

Original data set – Carbonate-derived soils

Original data set – Flysch-derived soils

Reduced data set – Carbonate-derived soils

Reduced data set – Flysch-derived soils