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BACKGROUND LEVELS OF TRACE ELEMENTS IN THE SOILS OF ŽITNÝ OSTROV, SLOVAKIA

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Abstract: Fifteen soil profiles of the area of Žitný ostrov have been investigated and the variability in the natural background of eighteen trace elements, viz. Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Ga, Hg, Ni, Pb, Sr, Sn, V, Zn and Zr has been examined. Analyses have been performed mainly using optical emission spectroscopy and atomic absorption spectrometry. Comparison shows a relative tendency of the studied soils toward enhanced values with regard to B and Cd, and depletion to Ba, Cr, V and Zr.The frequency distributions of the elements are positively skewed, and transformation of the data to their natural logarithms was effective to reduce the skewness and kurtosis values significantly, and to approach normal distribution more closely. The contents, thus, appear to be mostly log-normally distributed, and they were described in terms of log-derived mean and normal range. Statistically, no geographical relation have been found with the levels of the studied trace elements, with the exclusion of few elements in case of As, Pb, Zn and Zr, but there is a relative accumulation of some trace elements in the middle and lower parts of the area.

Key words: trace elements, soils, Žitný ostrov.

Introduction

The area of Žitný ostrov is economically very important for the country, because it is intensively and diversely agriculturally used. In addition, the area represents a big groundwater aquifer that is potentially used for drinking, domestic and irrigation purposes. Therefore, the study of trace element contents in the soils of the area becomes of special importance as a result of their anticipated impact on the other components of the environment (plants, animals and groundwater) and later on the human beings, particularly in the lack or absence of such studies in the area. Lastly, the dam construction on the Danube at Gabčíkovo has increased the tendency toward more comprehensive investigation of this region, and the present study comes under this task. No systematic study of the trace element contents of soils (in general) in the Žitný ostrov region has been reported, and the purpose of this paper is to present the current information on background levels (totals) of several trace elements in these soils, to compare them with the geological origin, with other soils elsewhere in the world, and to indicate the relationship between the trace elements and the physiographic regions of the studied area.

Main characteristics of the area

Žitný ostrov (Wheat Island) is situated in the southwestern part of Slovakia, enclosed between the Danube and Little Danube rivers (Fig. 1), with an extension of about 1742 km^2. The area is boardered on the NW by Bratislava, and on the SE by Komárno. It forms the lower part of the wider Danubian Lowland, and geomorphologically represents an independent unit within it (Hromádka 1956). It is virtually a young structural plain originated by the accumulative activity of the Danube (Lukniš & Mazúr 1959 have called it a terrestrial delta) during constantly occuring subsidence. The area has been divided by the previous authors, on the basis of different subsidence intensity, into three parts along its longitudinal axis, the upper part extends nearly up to Dunajská Streda, middle part nearly up to Čalovo and lower part up to Komárno.

The main characteristics of the area can be summarized as follows (Mucha et al. 1992):

- a low lying, gently sloping plain area;
- weak surface layer formed by fine humic materials and soils with variable thickness from tens of centimeters up to three meters;
- thick alluvial aquifer (the river Danube gravel deposits) with thickness from 5 meters up to over 300 meters, with great variability of particle size distribution

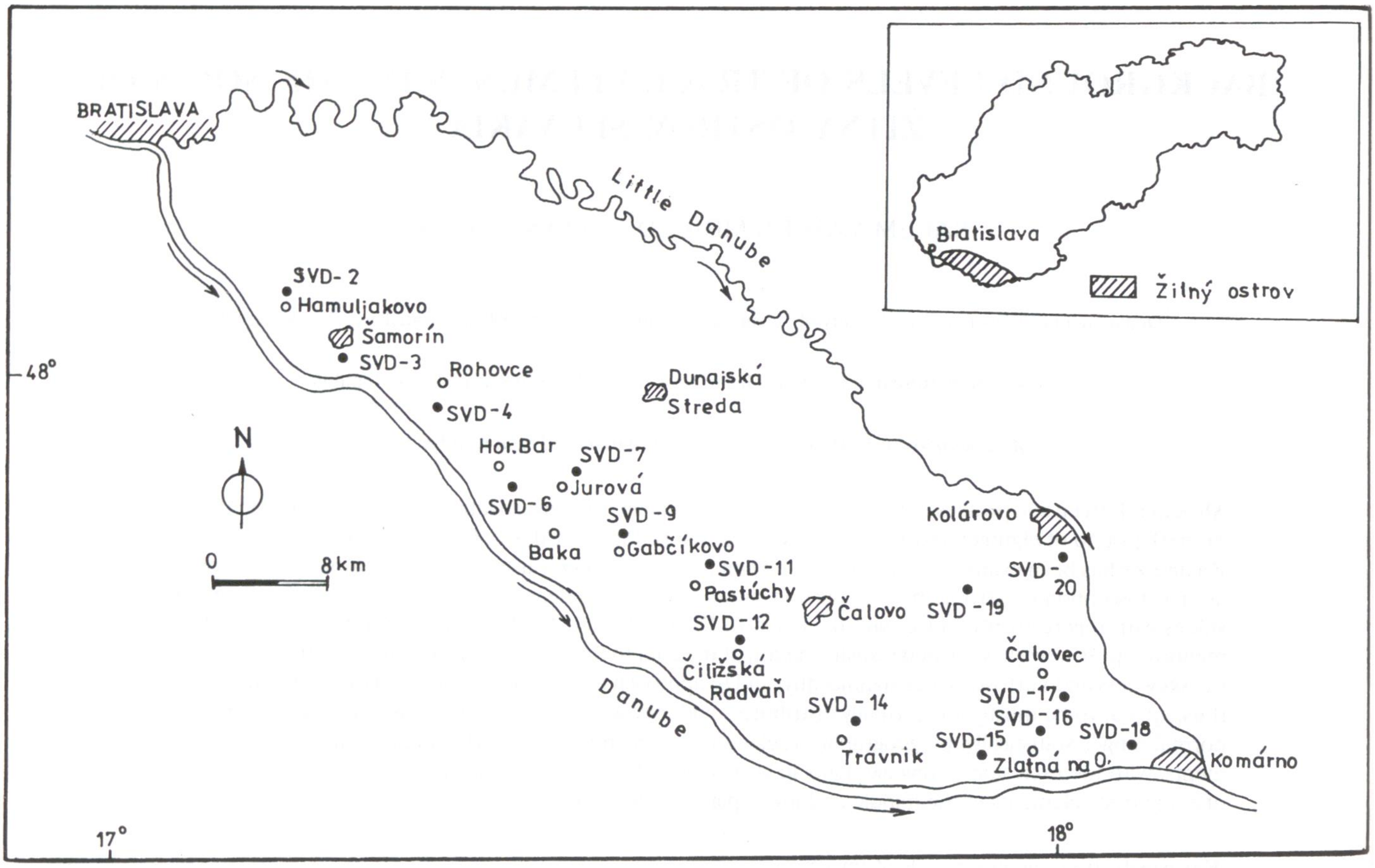

Fig. 1. Žitný ostrov and the locations of the soil profiles investigated.

and extremely high conductivity intercalated by fine lenticular sands and meander deposits;

- continental climate of Central European type, with well differentiated meteorological seasons, with 550 mm average rainfall, 830 mm average evapotranspiration and mean annual temperature above 9 °C. Hence, an evaporative regime is prevailed;
- groundwater is affected quantitatively and qualitatively by the Danube water.

Materials and methods

Soils

The groundwater regime in the area has very important influence on the geochemical processes that lead to the evolution of different soil types. Groundwater is characterized by its fluctuation in correspondence to the fluctuation in the water level of Danube river. Generally, groundwater fluctuates during the year between 4 - 7 m in the upper part of the isle, 2 - 4 m in the middle part and 0 - 2 m in the lower part. Groundwater at zero point of infiltration (in Danube) is low mineralized, slightly alkaline with Ca^{2+}, HCO^{3-} chemistry. Due to interaction in the system precipitation - plant - soil - groundwater, the chemistry of groundwater gradually changes (Ca^{2+}, Mg^{2+}- Ca^{2+}, Mg^{2+}, Na^{+}, HCO^{3-}) with raising mineralization. Zonal character in groundwater chemistry is reflected in soil chemistry. So, in the middle and lower parts of the area with shallower groundwater table hydromorphism is more pronounced.

Soils of Žitný ostrov are relatively variegated (Fulajtár & Čurlík 1992) and depend on the geological, hydrogeological (and hydrogeochemical) and climatic conditions prevailed in the area. The older part of the area (Pleistocene core) is characterized by typical automorphic soils of chernozemic type, while the lower Holocene sediments along rivers are characterized by Fluvisols.

There is a gradual increase in semi-hydromorphic soil toward the lower part of the area in accordance with groundwater table which becomes more much close to the surface in this direction. Thus, in the upper part with deeper groundwater table automorphic soils prevail, represented by Calcaro-haplic Chernozem and Haplic Phaeozem. Passing through Haplic Phaeozem , in the middle part Fluvi-haplic Phaeozem and Fluvi-calcaric Phaeozem are also occurred. In the lower part with shallower groundwater and more pronounced hydromorphism Fluvi-mollic Gleysols are developed. Gleysols and Histosols (peat) occur at places with water logging (old river arms, swamps). The studied soils belong to five soil types: Calcaric Fluvisol, Calcaro-haplic Chernozem, Fluvi-haplic-calcaric Phaeozem, Fluvi-gleyic-calcaric

Table 1: General characteristics of the studied profiles.

profile	location	FAO soil classification	parent material	texture	pH	groundwater table	plant
SVD-2	Hamuliakovo	Jc	A	l	8.4	5-6	corn
SVD-3	Šamorín	Jc	B	ls	8.7	3-4	wheat
SVD-4	Rohovce	Chc	B	l	8.8	2-3	barley
SVD-6	Horný Bar	Hgcf	C	l	8.5	1-2	sunflower
SVD-7	Jurová	Hgcf	C	lc	8.4	1-2	sugar-beet
SVD-9	Gabčíkovo	Gmcf	A	lc	8.4	1-2	sugar-beet
SVD-11	Padaň	Hgcf	A	l	8.4	1-2	corn
SVD-12	Čiližská Radvaň	Hgcf	A	c	8.4	0-1	wheat
SVD-14	Trávnik	Hhcf	C	lc	8.8	0-1	wheat
SVD-15	Zlatná na Ostrove	Hgcf	C	l	9.0	2-3	wheat
SVD-16	Zlatná na Ostrove	Hhcf	C	c	9.0	1-2	soya-bean
SVD-17	Čalovo	Hgcf	C	lc	8.7	2-3	wheat
SVD-18	Komárno	Hhcf	D	lc	8.9	1-2	wheat
SVD-19	Zemianská Olša	Hgcf	A	c	8.6	0-1	corn
SVD-20	Kolárovo	Jc	A	lc	8.5	1-2	sugar-beet

FAO soil classification: B - light calcareous alluvial sediments; Jc - Calcaric Fluvisol; C - loess; Chc - Calcaro-haplic Chernozem; D - calcareous alluvial gravel-sand; Hhcf - Fluvi-haplic-calcaric Phaeozem Texture; Hgcf - Fluvi-gleyic-calcaric Phaeozem; ls - loamy sandy; Gmcf - Fluvi-mollic-calcaric Gleysol; l - loamy. Parent materials: lc - loamy clayey; A - mildly heavy calcareous alluvial sediments; c - clayey .

Phaeozem, and Fluvi-mollic-calcaric Gleysol. The pH of these soils ranges between 8 - 9 indicating slightly alkaline conditions. All soils are calcareous. Their parent materials are light to heavy calcareous alluvial sediments. Texture is relatively diverse, loamy sandy, loamy, loamy clayey and clayey. Location of the soil profiles studied and their general characteristics are listed in Tab. 1.

Chemical analysis

Fifteen soil profiles have been investigated from the area of Žitný ostrov by terms of their A horizons, transitional A/C horizons, and C horizons. Sixty one samples have been chemically analysed for different trace elements in the laboratories of Geological Institute, Faculty of Sciences (Medveď et al. 1992). Elements Ag, B, Ba, Be, Co, Cr, Cu, Ga, Ni, Pb, Sn, Sr, V and Zr have been analysed by optical emission spectroscopy (OES) using grid spectrometer PGS 2 with DC arc and intensity of 6 A during 90 seconds. Atomic absorption spectrometry (AAS) has been applied for the analysis of As, Cd, Hg, and Zn using PERKIN-ELMER 380 spectrometer. Both As and Hg were analysed using separate techniques. Absorption signals of As have been obtained by hydride techniques after dissolution of the sample. Hg was determined from solid samples after thermal evaporation in oxygen flow and its concentration in an amalgamator. The other elements were determined after total dissolution of the sample by atomization in an acetylene-air flame.

For the aim of these analyses a soil subsample (approx. 5 g) of the <2 mm (fine earth) air-dried fraction of the soil was ground to a fine powder (<0.2 μm) and homogenized in an agate mortar. Samples have been dried at 28 - 30 °C prior to ignition at 650 °C for two hours. The total dissolution of the soil samples has been performed by mixture of HNO_3, $HClO_4$, and HF acids.

Manipulation and presentation of data

The frequency distribution of the presented data was found to be mostly asymmetric (positively skewed), hence the data have been transformed to their natural logarithms which can reduce both the skewness and kurtosis and approach normality more much closely. For these elements log-normally distributed, the log-derived mean and normal range have been determined according to Berrow & Reaves (1986). Approximately 95 % of the data will lie within the normal range.

Table 2: Total trace element contents of the present study and compared data (ppm).

	A	B	C	D	E	F	Ratio
Ag	**0.52** (0.15-6.70)	**0.05** (0.01-8.0)		0.41	0.057	0.07	7.428
As	**13.02** (5.96-30.18)	**6.0** (0.10-40.0)	5	8.37	7.7	1.8	7.233
B	**41.68** (12.0-91.0)	**20.0** (2.0-270.0)	10	16	100	10	4.168
Ba	**258.39** (128-430)	**500.00** (100-3000)	500	605	460	425	0.607
Be	**2.16** (1.10-3.6)	**0.30** (0.01-40.0)	6	2.72	2	2.8	0.771
Cd	**2.06** (1.13-2.90)	**0.35** (0.01-2.0)	0.5	0.77	0.17	0.2	10.3
Co	**10.72** (8.0-14.0)	**8.0** (0.05-65.0)	10	16.5	14	25	0.428
Cr	**50.36** (27.06-84.35)	**70.0** (5.0-1500)	200	97.5	72	100	0.503
Cu	**28.44** (13.40-142.82)	**30.0** (2.0-250)	20	20	33	55	0.517
Ga	**12.11** (7.90-20.0)	**20** (2-100)	20	31.1	18	15	0.807
Hg	**0.108** (0.016-3.044)	**0.06** (0.01-5)	-	-	0.19	0.08	1.35
Ni	**34.06** (20.8-159)	**50** (2-750)	40	25.4	52	75	0.454
Pb	**26.86** (12.2-46.5)	**35** (2-300)	10	28	19	12.5	2.148
Sn	**5.51** (2.7-8.9)	**4** (1-200)	10	3.82	4.6	2	2.75
Sr	**125.24** (17.4-399.5)	**250** (4-2000)	300	206	325	375	0.333
V	**63.21** (39-104)	**90** (3-500)	100	194	105	135	0.468
Zn	**84.65** (47.42-178.73)	90(1-900)	50	93.8	95	70	1.209
Zr	**236.77** (132-430)	400(60-2000)	300	604	150	165	1.434

A - average concentrations and ranges of the present study; B - normal range in soil (Bowen 1979), median (range); C - Andrews & Jones (1968); D - average concentrations of Scottish soils (Ure et al. 1979); E - mean sediment (Wedepohl 1968); F - crustal abundance (Taylor 1964).

The following values have been determined for the total trace element contents: minimum, maximum, range, mean, median, mode, standard deviation and coefficient of variation. The frequency histograms of the eighteen studied trace elements have been also presented in this work. Student's test has been applied for the comparison of the total trace element contents among the three different geographical parts of the studied area (Davis 1986), their means have been listed and also presented as bar - chart figure.

Results and discussion

In Tab. 2 the averages and ranges of the total trace element contents of the studied soils are compared with two compilations (Bowen 1979 ; Andrews-Jones 1968), with those of the Scottish soils (Ure et al. 1979), with the mean sediment (Wedepohl 1968), and with values of the contents of the Earth crust (Taylor 1964).

Generally, there is an agreement among the contents of the studied soils and other compared soils. However, our soils show a tendency of enhanced contents with regard to B and Cd, and decrease for Ba, Cr, V and Zr relative to other soils. They show, also, close similarity to the mean sediment.

The studied trace element contents have been compared with their equivalents in the Earth crust and their ratios computed, in a similar approach to that applied by Ure et al. (1979). These authors have arbitrarily chosen the limits of the ratio ≥ 2 and ≤ 0.5 to indicate average soil contents significantly higher or lower, respectively, than crustal abundance values, in order to make allowance for uncertainties in the values, and these limits have been adopted in this study also. Mean soil total contents of the elements Ba, Be, Cr, Cu, Ga, Hg, Zn, Zr, V and Pb are close to the crustal abundance, which agrees with the conclusion drawn by Mitchell (1964) which states that argillaceous materials generally contain constituent elements at about the average level for rocks as a whole. However, the rest of elements show dissimilarities of enhancement for Ag, As, B, Cd and Sn or depletion in case of Co, Ni and Sr relative to the Earth crust. So, it seems possible to conclude, on the basis of

Table 3: Main statistical features of the distribution of the studied elements.

	minimum	maximum	range	mean	medium	mode	S.D.	C.V.
Ag	0.15	6.7	6.55	0.520	0.30	0.39	0.029	178.769
As	5.96	30.18	24.22	13.027	11.8	10.56	4.140	31.785
B	12	91	79	41.688	40	39	14.691	35.242
Ba	128	430	302	258.393	255	251	66.659	25.797
Be	1.1	3.6	2.5	2.167	2.2	2.4	0.531	24.528
Cd	1.13	2.9	1.77	2.06	2.1	2.2	0.322	15.638
Co	8	14	6	10.723	10.7	11.1	1.391	12.978
Cr	27.06	84.35	57.29	50.361	51.19	56.14	13.427	26.661
Cu	13.4	142.82	129.42	28.441	25.45	35.9	17.040	59.912
Ga	7.9	20.0	12.1	12.114	12	11	2.625	21.675
Hg	0.016	3.044	3.028	0.108	0.048	0.068	0.384	352.876
Ni	20.8	159	138.2	34.063	30.6	30.6	18.229	53.516
Pb	12.2	46.5	34.3	26.868	26.4	26.5	6.006	22.356
Sn	2.7	8.9	6.2	5.519	5.5	5.5	1.280	23.196
Sr	17.4	399.5	382.1	125.244	101	140.5	75.622	60.38
V	39	104	65	63.213	62	58	13.384	21.173
Zn	47.42	178.73	131.31	84.654	81.98	81.86	24.694	29.170
Zr	132	430	298	236.77	234	220	54.214	22.897

these results that generally total trace element contents represent the background levels in the studied soils, with few exceptions which may reveal that both man induced and natural activities have played their role in influencing the content of the chemical constituents of the studied soils. The elevated values of some trace elements could be attributed to their strong chemical affinities to be accumulated by soil organic matter, and locally due to some anthropogenic contamination, particularly in case of Ag, As and Cd (Mejeed & Čurlík 1993).

The main statistical features of the distribution of the studied elements are illustrated in Tab. 3. They show that the values of the mean, median and mode are, in general, very close. But, median values are less than the mean in case of Ba, Cu, Ni, Sr and Zn. Median values are, also, less than the mode for Cr, Cu and Sr, and higher than the mode for Ba, V and Zr. The dispersion of data as measured by standard deviation and coefficient of variation being widely different for each element.

The frequency distribution of the values of the studied trace elements was found to be positively skewed (except Cd which is insignificantly negatively skewed). Ahrens (1954a; 1954b) has concluded that the concentration of an element is log-normally distributed in a specific igneous rock and that this might also hold in spesific minerals and in some sediments. This concept have been objected by others like Miller & Goldberg (1955). But it has been later confirmed by pedologists who have found that the frequency distributions of trace element concentrations in soils are generally highly asymmetric (positively skewed) and that a logarithmic transformation is the most successful in normalising the distribution of the varieties (Archer & Hodgson 1987; Berrow & Reaves 1981, 1986; Reaves & Berrow 1984a, 1984b, 1984c; Kinniburgh & Beckett 1983; Davies 1983; Wakatsuki et al. 1978). Thus, our finding comes in consistence with the other mentioned studies, and hence our data were transformed to their natural logarithms in order to approach a normal distribution (Fig. 2). This data processing was active and successful to reduce significantly both skewness and kurtosis of most of the trace elements, viz. Ag, As, Ba, Co, Cu, Ga, Hg, Ni, Pb, Sr, V, Zn and Zr, particularly these elements show extreme enhanced contents in few cases which may reveal contamination due to some anthropogenic activities (Mejeed & Čurlík 1993) like Ag, As, Cu, Hg and Ni, because no attempt has been made to exclude such enhanced values from calculations. However, skewness and kurtosis values of Ba and Pb have only slightly enhanced, but those for B, Be, Cd, Cr and Sn show no signs of enhancement. Taking into con-

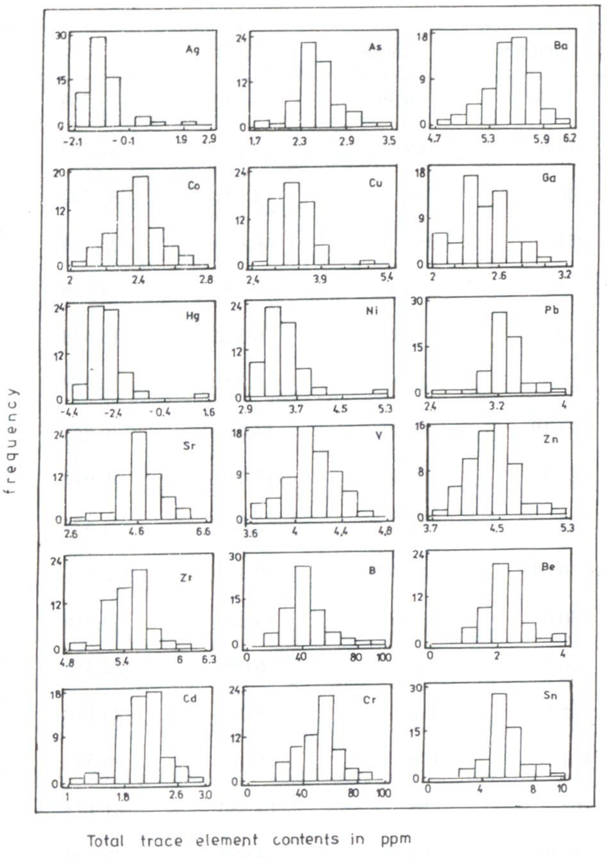

Fig. 2. Histograms showing the distribution of logarithms of concentrations of Ag, As, Ba, Co, Cu, Ga, Hg, Ni, Pb, Sr, V, Zn and Zr, and distribution of concentrations of B, Be, Cd, Cr and Sn.

sideration that skewness and kurtosis values of the lastly mentioned elements are primarily low, it seems then that their distribution is more close to the normal pattern than the log-normal one (Fig. 2). For log-normally distributed trace elements, log-derived means and normal ranges were computed (Tab. 4), because they are more suitable for the description of such frequency distribution than the mean and standard deviation of the untransformed data.

Mean total contents of trace elements are mostly similar among the three different physiographic regions of Žitný ostrov (Tab. 5 and Fig. 3). Geographical difference was only highly significant (at 5 % level) in the case of As, Pb, Zn and Zr. Thus, samples from the lower part of Žitný ostrov have lower contents of As, Pb and Zn both than the upper and middle parts. While in the upper part Zr shows higher content and Pb lower content relative to the middle part. Therefore, it could be concluded that only Pb is significantly differentiated in each of the three regions. However, in spite of the limitation of the statistical method, some of the trace elements show relatively higher levels either in the middle part (Cu, Hg, Ni, Pb, Zn) or in the lower part (B, Ba, Cr, Sr).

Table 4: Values * of derived mean and normal range of the log normally distributed trace elements.

element	derived mean	normal range	
		L1	L2
Ag	0.343	0.086	1.364
As	12.465	6.979	22.264
Ba	249.635	146.936	424.113
Co	10.622	8.207	13.749
Cu	26.416	12.280	56.826
Ga	11.834	7.775	18.011
Hg	0.054	0.011	0.250
Ni	31.880	16.979	59.859
Pb	26.232	16.626	41.388
Sr	106.059	32.136	350.023
V	61.805	40.609	94.066
Zn	81.450	47.275	140.330
Zr	230.672	147.672	360.322

* These values have been determined in this manner: if x and s are the mean and standard deviation of the log-transformed data, then the derived mean = antilog x, and normal range is that between the limits $L1 = antilog\,(x - 2s)$ and $L2 = antilog\,(x + 2s)$.

Conclusions

The trace element contents of the studied soils are in good consistency with those compared from other sites in the world. From geological point of view, they are close to the values of mean sediment contents on one hand and to those of the Earth crust on the other, in spite of few differences of enhancement and depletion relative to the latter, which indicate that soils have been influenced by both natural and anthropogenic activities to some extent. Since, they could be considered to represent the background levels in the studied soils.

The frequency distributions of most of the trace elements are of log-normal type, which affirms many of the studies in this field. However, this does not preclude that few elements are more close to the normal distribution.

Statistically, distribution of the trace elements looks to be more homogeneous in the whole area and only few geographical differences among trace element contents have been found in case of As, Pb, Zn and Zr. However, there is a relative accumulation of many trace elements either in the middle or the lower parts.

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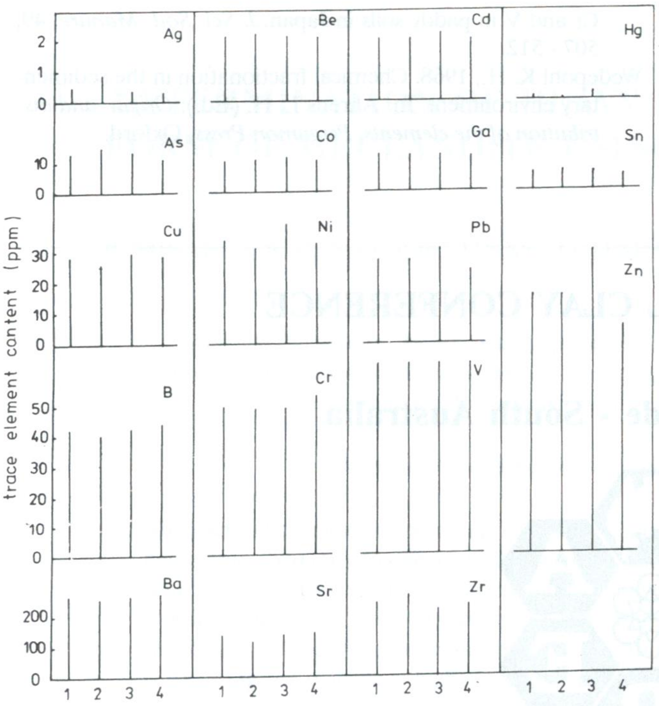

Fig. 3. Bar-chart illustration of the distribution of elements in: 1 - whole area, 2 - upper part, 3 - middle part, and 4 - lower part of the area.

Table 5: Mean levels (ppm) of trace elements by region.

element	upper part	middle part	lower part
Ag	0.852	0.397	0.287
As	15.223	13.136^{bc}	10.852^{ac}
B	39.636	41.875	43.521
Ba	248.409	256.875	269
Be	2.245	2.162	2.095
Cd	2.003	2.159	2.052
Co	10.795	10.506	10.804
Cr	48.831	49.363	52.517
Cu	26.370	30.061	29.296
Ga	12.081	12.231	12.065
Hg	0.060	0.226	0.073
Ni	31.272	38.768	33.460
Pb	26.893^{ab}	31.303^{bc}	23.760^{ac}
Sn	5.854	5.456	5.243
Sr	113.3	126.819	135.574
V	62.5	62.687	64.260
Zn	83.828	100.072^{bc}	74.720^{ac}
Zr	258.227^{ab}	209.125	235.478

Explanations: ab - indicates significant difference between the upper and middle parts; ac - between the upper and lower parts; bc - between the lower and middle parts of the studied area.

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10TH INTERNATIONAL CLAY CONFERENCE

University of Adelaide - South Australia

Tenth International Clay Conference in Adelaide was organized by the *Association Internationale pour l'Etude des Argiles (AIPEA), Comission VII of the International Society of Soil Science* and by the *Australian Clay Minerals Society* on July 18 - 23, 1993. 315 participants from all over the world presented more than 370 papers either as lectures or posters. Ten keynote lectures were presented to open different sessions by T. J. Pinnavaia, K. Norrish, D. R. Veblen, H. H. Murray, S. Guggenheim, K. Wada, G. Lagaly, D. Nahon, U. Schwertmann and A. Chivas. Rich scientific program was divided into five main themes:

1. Clays in Geology
2. Clays in Industry and the Environtment
3. Soil Mineralogy
4. Surface and Interlayer Reactions
5. Structure, Chemistry and Nomenclature

and four symposias:

1. Poorly Crystalline Clays
2. Methods
3. Clay Minerals of Gondwanaland
4. Teaching in Clay Mineralogy

A special symposium organized in the late evening was named "**Clay Every Day**". It was chaired by well known Australian Journalist Robyn Williams who invited F. Veniale (Italy), Y. Tardy (France), J. Webb (Australia) and K. Tiller (Australia) to present popular lectures about the role of clays in our life.

The exciting scientific program was accompanyied by a pleasant social program like Welcome "Mixer", Coctail Reception, Happy Hours (hospitality offered by sponsors and companies exhibiting production in the Exposition area), and Conference Excursion to Middlebrook Winery near Adelaide.

Many field excursions showing the most interesting Australian geological treasures were combined with the famous Australian touristic atractions (Great Barrier Reef, Crocodile Dundee Country, Alice Springs etc., and of course wild kangaroos and koalas).

In the end of the Conference H. H. Murray was elected as new President of the AIPEA, and two AIPEA medals were given to Prof. S. Bailey and Prof. R. C. Reynolds.

The good work of the main organizers T. Eggleton (General Chairman), R. Fitzpatrick (General Secretary) and Elliservice Convention Management (technical organization of the Conference) brought the success of the 10th International Clay Conference and I believe that the most of the participants leaving Adelaide have decided to come again.

Vladimír Šucha