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Vertical distribution patterns of trace and major elements within soil profile in Lithuania

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The vertical distribution of the total contents assayed by *Dc-Arc ES* analysis of 28 trace elements and 6 major elements measured by *ICP-MS* within 53 complete soil profiles in Lithuania are presented. Models of the soil profiles were created, each having the master soil horizons A, E, B and C. Median values of elements in the master horizons of different texture were used in place of missing samples, while aberrant samples were discarded. The absolute average deviation (σ) was taken to measure the variability of the data subsets and thus to check the reliability of location of the element contents within the soil profile. Within the context of the different actions of the various soil-forming processes (podzolization, lessivage, gleyfication, humification and so on) the general patterns of vertical element distribution were revealed. Element depletion is dominant in the soils of Lithuania. The most easily removed are the alkaline elements Ca and Mg, while U, B, Th, As, Co, Cr, Sr, Y, Mo, La, Sc, Yb, Ti, P and K are depleted through the whole soil profile. Ag, Pb, Sn and Mn were defined as the accumulative elements in the surface A-horizon and might be influenced by anthropogenic or biogenic processes. A relative accumulation of Zr, Ba and Nb was observed in the surface A-horizon, and this seems to be related to the weathering of resistant minerals. Levels of Fe, Li, Al, V, Zn, Ga, Ni, Cu and Rb were ascribed to elements precipitated in the soil illuvial B-horizon due to soil formation processes. Na, K, Sr, B, U, As, Co Rb and Yb were found to be the most immobile elements within typical soil profiles, while Ag, Zn, Sc, Ba, Cu, Zr, Fe La, Th and Ca are the most mobile elements and affected by a variety of natural and human factors.

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Key words: Lithuania, complete soil profile, accumulative elements, removable elements, total element contents, variability.

INTRODUCTION

The vertical distribution of elements in complete soil profiles is investigated nowadays for a variety of purposes. Modern agricultural recommendations are derived from the last century's research into soil fertility, regarding the total depth reached by plant roots. Recent investigations are aimed more at the release and immobilization of contaminants added to soil with sewage sludge or fertilizers (Agbenin and Felix-Henningsen, 2001; Morera *et al*., 2001; Kaschl *et al*., 2002). Depletion and redistribution of nutrients has been observed in soil after clear-cutting down and firing of forests, as well as after afforestation (Kutiel and Inbar, 1993; Berthelsen and Steinnes, 1995; Lahdenperä, 1999; Andersen *et al*., 2002). The impact of airborn dust on undisturbed soil and the behaviour of heavy metals within soil profile has been investigated mainly in supposedly non-polluted forests and boggy sites, which are rich in organic soil matter (Shotyk *et al*., 1992; Blaser *et al*., 2000; Hernandez *et al*., 2003). The enrichment of surface soil horizons in certain metals has been reported: by lead and cadmium in France, and by lead and zinc, as well as by arsenic and cupper, though to a lesser extent, in Switzerland. The spatial distribution of elements and an increase in nickel, iron and chromium in the mineral-humus soil horizons of Western Poland has been related to the vertical distribution of these partly aerially-derived elements (Degorski, 1998). Understanding the location of trace elements in soil profiles also helps to provide correlations within geochemical maps of trace element contents, obtained by stream sediment and topsoil analyses (Berrow and Mitchell, 1991).

This study analyses the patterns of spatial element distribution, established during national geochemical mapping across Lithuania, the data being derived from topsoil and stream sediments (Kadūnas *et al*., 1999). This study of vertical element distribution also helped to evaluate both the natural and human factors acting on soil chemistry prior to calculation of element background values in topsoil. Assessment of the element distri-

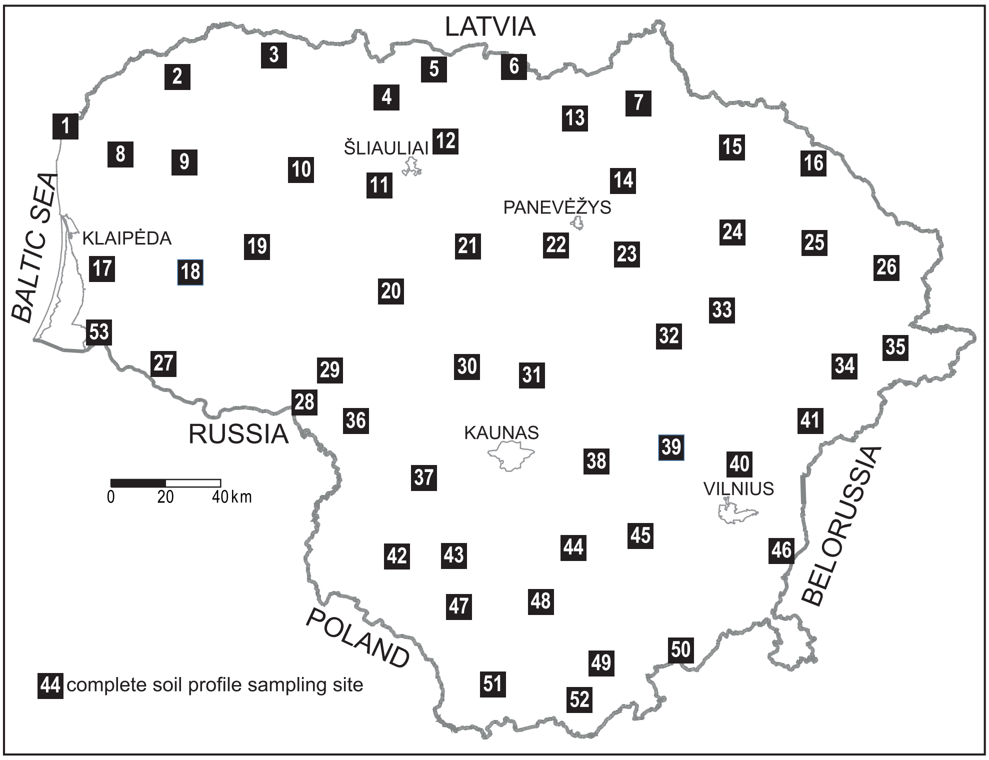

Fig. 1. Total distribution of soil profile sampling sites in Lithuania

bution within soil profiles provide a basis for establishing long-term and wide spread predictable changes in soil and groundwater quality. This study also updates understanding of element migration through multi-layered mineral media in a boreal climate zone with an excess of precipitation.

METHODS

Pedological studies of complete soil profiles were carried out within the project "Geochemical Atlas of Lithuania" (Kadūnas *et al*., 1999). 249 soil samples were taken from the master horizons A, E, B, BC and C of 53 complete soil profiles. The selection of sampling sites was designed to cover the national territory evenly and to represent the dominant soil types (Fig. 1). Both forest and agricultural soils were collected according to the dominant land use and soil parent material in the sampling area; and site selection was carried out to establish a maximum distance to roads, villages, industry and others sources of human activity.

Descriptions of soil profile texture was made in the field using national soil maps at a scale of 1:50 000, and later the grain-size classes were revised in selected samples by a combined sieve and pipette method in the laboratory. The samples were analysed in the Spectral Laboratory of the Institute of Geology and Geography of Lithuania by *Dc-Arc ES* for the total content of 28 trace elements. The loss on ignition (LOI) was calculated after soil burning at a temperature of 450°C, and determination of pH was made using glass electrodes in a 1:5 suspension of soil in water. The total content of major and trace elements in a 4-acid digestion (HNO_3-$HClO_4$-HF-HCl) was determined in Acme Analytical Laboratories Ltd. of Canada by *ICP-MS* to provide internationally comparable data. Data on the major elements Al, Ca, Fe, K, Mg, Na from Acme Laboratory and data on the trace elements Ag, As, B, Ba, Co, Cr, Cu, Ga, Y, Yb, La, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sc, Sn, Sr, Th, Ti, U, V, Zn, Zr from Spectral Laboratory is discussed here.

The entire dataset was separated into subsets for the master soil horizons A, E, B and C and statistical parameters (median, arithmetical average and standard deviation) were calculated. The same statistical data was calculated for the different soil horizons according to the soil texture, i.e. for sand, sandy loam and loam/clay horizons separately. The median values of elements in the master horizons of different texture are shown in Table 1.

In reality, not all soil profiles consist of the same sequence of horizons, thus, from the data, 53 soil profile models with 159 samples were created, each of them having samples from all the master horizons A, E, B and C. The atypical samples, e.g. of buried organic horizons and of soil layers with specific diagnostic properties, were not included in the soil profile models. Missing samples of some master horizons were replaced with element median values of the corresponding soil horizon of corresponding texture. Most of the modifications were done for the E-horizon.

The absolute average deviation (σ) was used to measure the variability of the data and to check the probability of location of the element contents within the soil profile. The parameter σ was calculated by the formula:

Table 1

Median values of elements in the master soil horizons of different texture

Elements [ppm]	A-horizon				E-horizon				B-horizon				C-horizon		
	sand	sandy loam	loam/ clay	whole set	sand	sandy loam	loam/ clay	all	sand	sandy loam	loam/ clay	all	sand	loam/ clay	all
	$n = 10$	$n = 29$	$n = 14$	$n = 53$	$n = 13$	$n = 12$	$n = 18$	$n = 43$	$n = 15$	$n = 6$	$n = 31$	$n = 52$	$n = 13$	$n = 40$	$n = 53$
Ag	0.088	0.105	0.088	0.096	0.079	0.079	0.076	0.079	0.079	0.098	0.076	0.084	0.094	0.064	0.068
As	2.0	2.9	4.0	2.9	2.4	3.6	4.2	3.6	2.5	3.75	4	3.4	2.7	4.8	4.4
B	22	30	36	30	22	32	37	32	27	34	49	43	24	50	46
Ba	198	365	475	342	230	358	435	347	228	252	337	298	253	325	312
Co	2.6	6.4	7.2	6.7	3.1	7.1	8.2	7.0	4.5	7.5	8.9	8.4	3.4	9.4	8.6
Cr	14	40	45	41	18	45	48	42	22	43	63	50	19	55	52
Cu	4.9	7.7	9.5	7.8	3.0	6.6	9.7	6.7	5.0	8.9	12.7	11.4	4.0	12.7	11.7
Ga	5.0	7.8	8.0	7.8	5.4	8.2	9.1	7.6	6.2	8.3	10.6	9.7	4.2	10.1	9.7
Y	8.0	15.6	18.5	15.3	5.9	17.6	17.3	15.6	8.0	18.6	17.4	15.4	9.4	21.8	18.9
Yb	1.34	2.28	2.47	2.21	1.00	2.29	2.54	2.16	1.30	2.46	2.57	2.32	1.39	2.75	2.62
La	16.8	25.6	27.2	24.6	17.0	22.0	26.6	22.8	18.0	27.4	26.9	25.2	17.9	32.2	28.7
Li	10.7	17.1	20.0	17.3	11.9	16.9	19.2	16.6	14.0	18.6	24.1	19.7	12.5	21.4	19.2
Mn	406	475	454	464	168	420	459	387	350	477	423	423	281	489	458
Mo	0.65	0.75	0.77	0.75	0.62	0.67	0.71	0.68	0.69	0.83	0.79	0.78	0.64	0.98	0.95
Nb	12.6	13.5	13.8	13.3	10.9	13.7	14.7	13.6	10.8	13.8	13.3	11.8	12.9	13.7	13.6
Ni	6.3	13.6	17.9	14.2	7.5	15.8	19.2	15.7	9.9	22.4	29.4	23.3	7.0	25.3	24.4
P	446	558	475	506	403	356	358	372	403	474	404	405	471	582	539
Pb	17.7	19.5	18.7	19.0	12.9	15.1	17.9	15.8	14.7	19.1	16.7	15.8	11.4	15.6	14.9
Rb	31	65	77	65	42	69	90	68	40	65	87	68	41	83	77
Sc	1.92	6.12	8.20	5.97	1.49	5.82	8.12	5.89	2.48	5.08	8.09	6.44	2.14	8.14	7.21
Sn	2.05	2.41	2.40	2.28	1.87	2.58	2.69	2.32	2.10	2.83	3.35	2.75	1.93	2.47	2.29
Sr	54	83	91	82	65	81	92	80	68	83	86	83	64	103	97
Th	2.1	4.6	5.3	4.6	3.9	5.1	6.4	5.0	4.0	5.4	6.4	5.8	3.7	6.7	6.0
Ti	1287	3040	3022	2688	1297	2699	3196	2716	1085	2360	3023	2635	1389	3026	2922
U	1.3	2.3	2.6	2.3	2.2	2.4	2.7	2.4	2.2	2.3	3.0	2.8	2.3	3.6	3.2
V	17	40	46	40	17	43	55	47	27	50	71	65	18	67	62
Zn	16	35	34	33	12	30	46	33	18	34	48	39	10	38	37
Zr	168	273	260	254	208	290	241	235	135	269	212	191	154	194	191
[%]															
Al	1.63	3.04	4.15	3.14	1.79	3.26	4.24	3.37	2.16	3.13	4.65	3.59	1.75	4.02	3.86
Ca	0.21	0.45	0.66	0.46	0.18	0.34	0.49	0.33	0.24	0.46	0.53	0.44	0.23	4.23	1.91
Fe	0.42	1.19	1.71	1.21	0.45	1.12	1.80	1.26	0.69	1.28	2.25	1.67	0.34	1.96	1.65
K	1.07	1.80	2.12	1.80	1.14	2.01	2.16	1.93	1.33	1.71	2.34	1.97	1.18	2.14	2.08
Mg	0.06	0.29	0.54	0.30	0.08	0.26	0.50	0.33	0.18	0.39	0.67	0.52	0.08	1.23	0.95
Na	0.27	0.43	0.46	0.43	0.38	0.50	0.46	0.44	0.37	0.45	0.43	0.42	0.38	0.44	0.42

$$\bar{\sigma} = \frac{1}{n}\sum\left|x-\bar{x}\right|$$

where: n — the number of samples, x — the element content in the n-sample and $\bar{x}$ — the arithmetical average.

Instead of measured concentrations, selected ratios were used to avoid the influence of measurement units in the (σ) calculations. Several absolute average deviations were applied in order to smooth out unusual fluctuations in element content and reveal regularities in element distribution within the soil profile:

σ1 — the variability of elements in the whole dataset (the ratio of element content in each real sample to the element median value of the C-horizon data subset (rx/C_{Md}) is used in the calculation);

σ2 — the variability of elements in the whole model dataset (the ratio of element content in each sample of this set to the element median value of the C-horizon data subset (tx/C_{Md}) is used in the calculation);

σ3 — the variability in the element contents within the model soil profile in comparison to the soil parent material of the same profile (the ratio of element content in the master hori-

Table 2

Total contents of some elements in soil profile No. 35 (Stagni-Eutric Podzoluvisol)

Horizon	Depth [cm]	Texture	pH	Ca [%]	Zr [ppm]	Ni [ppm]	V [ppm]	Ga [ppm]	Li [ppm]
Ap	0–26	sandy loam	7.35	0.49	316	12.0	40	6.5	14.4
AE	26–40	loam	6.9	0.37	351	12.2	51	6.8	15.6
E	40–44	loam	7.05	0.36	352	13.7	55	6.6	12.7
Bt	44–75	silty clay loam	7.45	0.42	270	23.2	71	10.1	20.3
BCkg	75–105	clay loam	8.65	1.91	243	34.9	116	16.5	24.3

The suffix letters used to qualify the master horizons: p — disturbed by ploughing; t — illuvial accumulation of clay; k — accumulation of calcium carbonate; g — gleyic properties pattern expressed by mottles reflecting variations in oxidation and reduction

Table 3

Total contents of some elements in soil profile No. 33 (Eutric Podzoluvisol)

Horizon	Depth [cm]	Texture	pH	Fe [%]	Ba [ppm]	As [ppm]	Cu [ppm]	U [ppm]	Sc [ppm]
Ap	0–27	sandy loam	6.7	1.07	317	2.6	7.7	2.6	4.80
AE	27–35	loam	6.35	1.56	443	3.6	13.8	2.2	6.40
Bs	35–64	clay loam	6.65	2.64	543	4.7	33.0	3.0	8.73
Ck	64–100	sandy clay loam	8.7	1.54	196	4.1	25.5	2.8	5.50

s — accumulation of sesquioxides; other explanations as on Table 2

Table 4

Total contents of some elements in soil profile No. 8 (Stagnic Luvisol)

Horizon	Depth [cm]	Texture	pH	Co [ppm]	Cr [ppm]	B [ppm]	Nb [ppm]	Ni [ppm]	V [ppm]
Ap	0–30	sandy loam	7.2	6.9	38	27	15.4	15	36
E	30–53	loam	7.4	8.8	60	35	21.5	24	57
Ej	53–65	loam	7.8	8.7	58	30	21.2	20	40
Bt	65–76	silt loam	8.4	14.4	106	58	23.1	48	96
Ck	76–100	clay loam	8.5	12.6	64	45	10.6	37	77

j — stagnic properties expressed by occurrence of jarosite; other explanations as on Table 2

Table 5

Total contents of some elements in soil profile No. 37 (Carbi-Gleyic Podzol)

Horizon	Depth [cm]	Texture	LOI [%]	Sn [ppm]	P [ppm]	Mn [ppm]	La [ppm]	Y [ppm]	Zn [ppm]
Ap	0–25	sand	4.5	2.20	573	191	25.8	11.5	11.5
Ob	25–35	org. matter	34.1	0.92	1188	73	19.1	9.9	7.9
E	25–45	sand	2.1	1.76	490	142	10.8	5.9	9.8
Bh	45–50	sand	1.9	1.96	324	157	16.7	8.4	9.8
Bs	50–68	sand	1.4	1.58	325	148	17.7	7.5	9.9
BC	68–106	sand	0.3	1.50	319	160	18.9	10.0	11.0
Cr	106–136	sand	0.3	2.09	299	189	35.9	12.0	12.0

b — buried soil horizon; h — accumulation of organic matter in mineral horizon; r — strong reduction as a result of ground water permanent presence; LOI — loss on ignition; other explanations as on Tables 2 and 3

zon sample to the real element content in the C-horizon (A*x*/C*x*, E*x*/C*x*, B*x*/C*x*,) is used in the calculation);

σ4 — the variability of elements within the model soil profile by the master horizons (horizon by horizon) as the ratios of element contents between the contiguous master horizons (A*x*/E*x*, E*x*/B*x*, B*x*/C*x*,) is used in the calculation.

TOTAL ELEMENT CONTENTS IN THE SOIL HORIZONS

All the soils in Lithuania are developed on the more or less mechanically-comminuted and re-sorted Quaternary deposits of the various stages of Weichselian and Saalian glaciations: basal and marginal glacial loam and sandy loam, glaciofluvial sand and gravel, glaciolacustrine sand and clay, i.e. a more or less uniform parent material (Guobytė, 1998).

In reality, not only vertical but also horizontal (spatial) chemical variation in the soils is apparent and this means that variations should also be interpreted in the light of pedochemical processes such as podzolization, lessivage, gleyfication and humification (Gregorauskienė, 1997).

The effect of podzolization could clearly be identified by the element distribution in the soil profiles that are developed on marginal tills of various ages on the East Lithuanian highland. An almost equal element depletion is observed in the moderately drained cultivated Stagni-Eutric Podzoluvisol developed on the marginal till of the oldest stage of the Late Weichselian Glaciation (Table 2). Carbonates are leached to a depth of 75 cm and the Ca value in the BCkg-horizon is 5.3 times higher than in the E-horizon. The higher values of Zr in the upper soil horizons, particularly in the eluvial E-horizon, reflect also a relative increase in the content of minerals resistant to weathering. On the other hand, V, Ga, Li, Ni and other elements are related to the clay fraction and accumulate in the illuvial Bt-horizon. The textural changes also indicate the possible vertical translocation of elements related to the fine-grained soil fraction.

The element depletion in the freely drained cultivated Eutric Podzoluvisol, developed on the younger marginal till, in comparison to the previously mentioned soil is also recognized by pH_{H_2O} values.

The latter values indicate very alkaline conditions present in the parent material, while neutral-subacid conditions are present in the upper part of the soil profile (Table 3). In the context of the general depletion, the illuvial Bs-horizon is clearly enriched in Fe, U, Ba, As, Sc, Cu and other elements that bind to clay minerals and oxides-hydroxides, especially when compared to the eluvial AE-horizon.

The vertical movement of elements (Co, Cr, B, Ni, Nb and V) prevailing in the fine fraction of the soil is noticeable in the moderately drained cultivated Stagnic Luvisol formed on the young basal till composed of two distinct units, temporarily suffering a water excess (Table 4). These trace elements are leached from the overlying water-saturated Ej-horizon when changing from oxidising to reducing conditions and *vice versa* and accumulated in the underlying Bt-horizon enriched in clay and silt particles.

A similar mobility of trace elements is noticed in the Carbi-Gleyic Podzol formed on the glaciolacustrine sand of the South Lithuanian phase (Table 5). The gleyic Cr-horizon, permanently groundwater-saturated, contains increased amounts of elements leached from the upper horizons. This sampling site was on an arable field cultivated in the former forest, thus here we can observe the influence of soil organic matter on the redistribution of elements, both geogenic and agrogenic in origin. The buried discontinuous Ob-horizon (partly mineralized roots and peat) contains much biogenic P and is depleted in Sn, Mn, and Zn. The ploughed A-horizon is enriched in agrogenic La, Y, Sn and Zn. The same pattern is observed in the Cr-horizon, i.e the agrogenic elements migrate easily through the sand soil profile into those parts of the soil that are lower than the groundwater level.

Organic matter in soil is important as regards the sorption capacity of chemical elements, and this affects the redistribution of elements within the soil profile (Shotyk *et al*., 1992). The accumulation of airborne and agrogenic elements contaminants in soil organic matter may be seen in the poorly drained cultivated Anthric Histosol on the calcareous basal till of the South Lithuanian phase (Table 6). The contents of Ag, Pb, Sn, Cr and Zn increase several times in the surface-ploughed A-horizon when compared to the lower non-cultivated histic H-horizon consisting of peat.

Element redistribution through the calcification process is observed in the poorly drained cultivated Stagni-Calcaric Cambisol on the youngest calcareous basal till of the North Lithuanian phase (Table 7). A continuous powder-like calcic horizon is found here at a depth of 60–62 cm. The precipitation of carbonates via evaporation from the carbonate-saturated pore water takes place during summertime (the average soil temperature in July is +18°C) at the upper boundary of the permanently wet BC-horizon. Nodules and thin 'veins' of calcite are observed in the upper part of section, at a depth of 36–60 cm.

The soil-forming processes are clearly reflected in the chemical composition of the loam-clay soils, i.e. the total contents of the major and trace elements show element redistribution through a soil profile. The element distribution is more even in sandy soils, this type of soil having a more homogenous texture. The variations of most elements within a profile reflect rather analytical error fluctuation at (and below) the detection limits. However, in the very well-drained forested Hapli-Albic Arenosol on the glaciofluvial sand (remade by eolian processes) of the oldest stage of the Late Weichselian Glaciation, the total element contents (Al, Sr and some others) differ notably between the contiguous soil horizons (Table 8). The significant increase of Zr and Yb may be related to the weathering-resistant minerals while an increase of airborne Pb, Ag and Sn is observed in the surface mineral A-horizon and has accumulated in the forest litter.

Table 6

Total contents of some elements in soil profile No. 43 (Anthric Histosol)

Horizon	Depth [cm]	Texture	pH	LOI [%]	Ag [ppm]	Pb [ppm]	Sn [ppm]	Cr [ppm]	Zn [ppm]
Ap	0–16	org. matter	7.35	46.0	0.130	36.7	3.24	48.6	151
Hb	16–44	org. matter	7	49.5	0.076	5.1	1.16	19.7	40
BCg	44–62	clay loam	8.15	4.0	0.054	13.4	1.82	38.4	59
Cg	62–82	clay loam	8.55	4.5	0.048	10.5	1.81	45.8	38

other explanations as on Tables 2 and 5

Table 7

Total contents of some elements in soil profile No. 3 (Stagni-Calcaric Cambisol)

Horizon	Depth [cm]	Texture	pH	LOI [%]	Ca [%]	Mg [%]	Ti [%]	Al [%]	Cu [p]pm
Ap	0–20	loam	7.25	7.0	0.76	0.62	0.298	4.38	12.1
Bt	20–36	clay loam	8.05	7.5	0.71	1.83	0.278	8.34	20.4
Bgk	36–60	clay loam	8.8	5.5	7.66	2.35	0.406	6.78	12.3
Bk	60–62	clay loam	8.85	5.3	16.29	1.92	0.218	4.35	7.1
BCg	62–98	clay loam	8.9	4.2	4.16	2.11	0.326	5.22	49.8

other explanations as on Table 2

Table 8

Total contents of some elements in soil profile No. 49 (Hapli-Albic Arenosol)

Horizon	Depth [cm]	Texture	pH	LOI [%]	Al [%]	Pb [ppm]	Ag [ppm]	Sr [ppm]	Zr [ppm]
A	3–23	sand	5.4	1	1.35	10.4	0.089	46	257
E	23–44	sand	5.45	0.2	1.43	7.0	0.050	48	210
B	44–70	sand	5.75	0.2	1.44	8.0	0.060	43	135
BC	70–120	sand	5.75	0.2	1.55	8.0	0.060	64	110

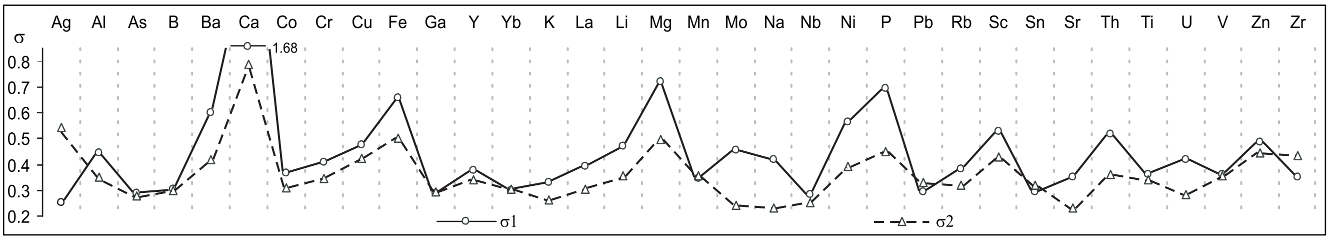

Fig. 2. Variability of element contents in the whole real dataset (σ1) and in the whole dataset of the 53 model soil profiles (σ2)

REGULARITIES OF VERTICAL ELEMENT DISTRIBUTION

The variability in element contents in the whole dataset of the 53 model soil profiles has been analysed. Variations in Ca, Mg and Ba contents related to the individual characteristic of the calcareous soil parent material were smoothed, eliminating samples from specific soil-diagnostic horizons (Fig. 2). But, the variability in Fe, Ni, Sc, U and Th related to the particular development of the B-horizon was also decreased. In the same way, fluctuations in Mo and P, being clearly related to the buried organic matter in the soil in some variable soil layers, were also smoothed. The variability in Ag, Zr and, to a slight extent, in Pb and Sn, was increased mainly because of the soil texture heterogeneity in the dataset and the local human impact on some samples of the real soil profiles.

Comparison of the chemical composition of topsoil and soil parent material reveals dominant element depletion process in the soils of Lithuania: contents of trace elements in the topsoil are on average 8% lower, and of major elements 34% lower, than in the parent material (Gregorauskienė and Kadūnas, 2000). Only contents of trace elements related to weathering-resistant minerals (Zr, Ba and Nb) and the biogenic-anthropogenic elements (Ag, Pb, Sn and Mn) are higher in topsoil than in subsoil (Fig. 3).

The character and intensity of the depletion process depends also on the soil profile texture. Berrow and Mitchell (1991) has shown that such elements as Ti, Zr, La and Y, contained in resistant minerals, accumulate in silt and fine sand. This element removal is also clearly visible in the soils of Lithuania, particularly as regards the chemical composition of loam-clay soil (Kadūnas and Gregorauskienė, 1999). Nevertheless, the contents of Ag, Pb, Sn, Zr, Ba, Nb and Na in the topsoil are greater than in the soil parent material. The surface A-horizon of the sandy soil profile in addition is enriched with P, Mn, Zn, Yb, Al and Sc. The depletion in many other elements, e.g. Ca, Mg, Ni, As, Ga, and Mo, is less distinct. There are a few reasons for this phenomenon. Firstly, the chemical composition of the surface horizon in sandy soil reflects mainly the primary weathering-resistant silicates and a very small amount of clay minerals. Secondly, elements derived from forestry and agriculture practices noticeably precipitate in the topsoil. In loam-clay soil this precipitation is

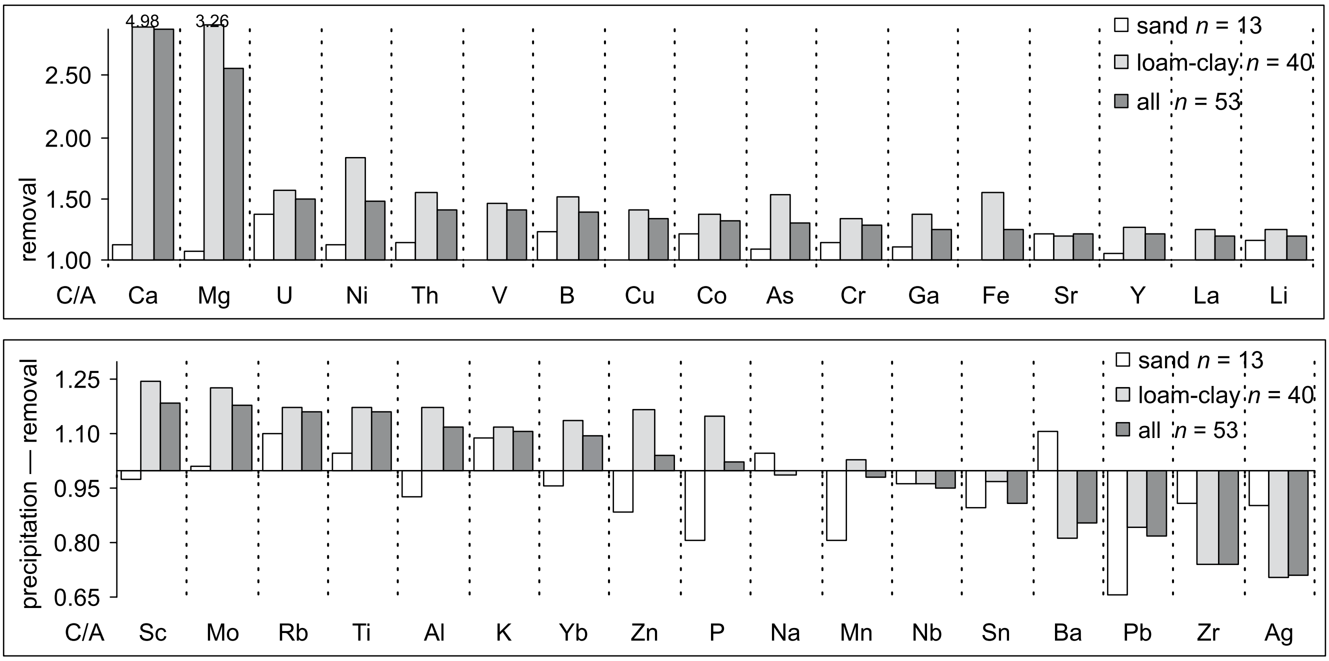

Fig. 3. Ratio of median values of elements in soil parent material (C-horizon) and topsoil (A-horizon) of soil with different texture

n — number of samples

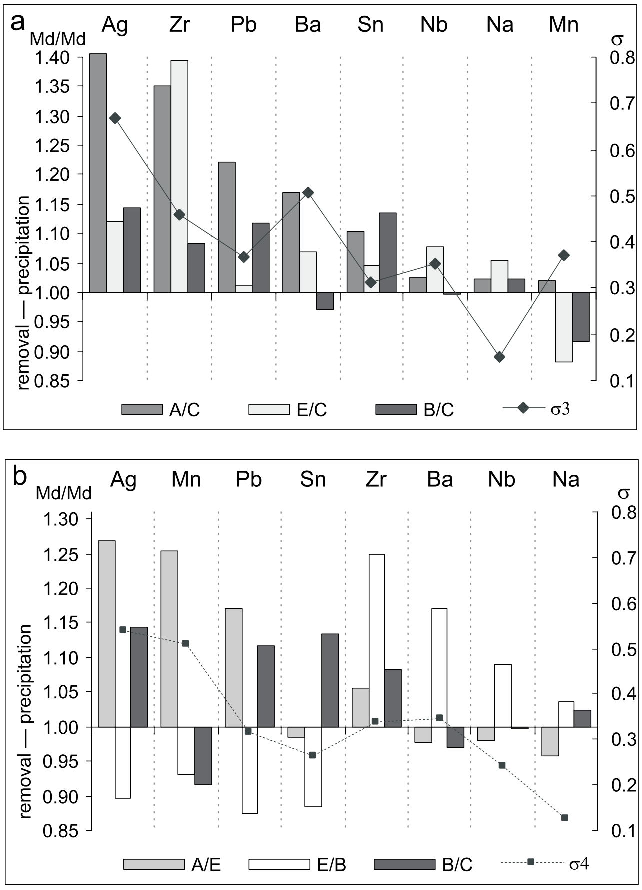

Fig. 4. Accumulative elements in the topsoil A-horizon: a — by the ratio of the soil horizon medians to the median value in the soil parent material; b — by the ratio of the median values of contiguous soil horizons

Md — the median values; σ — the absolute average deviation

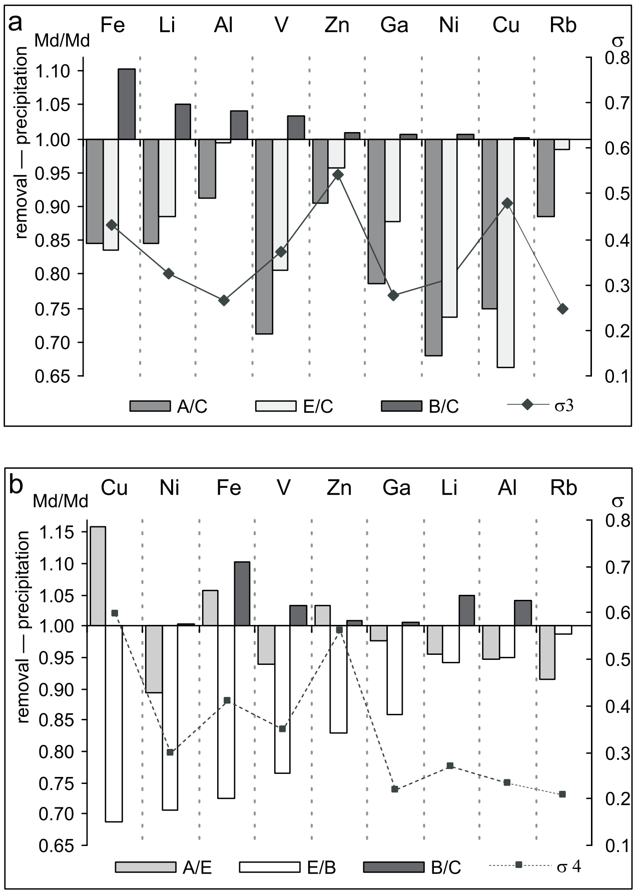

Fig. 5. Accumulative elements in the soil illuvial B-horizon: a — by the ratio of the soil horizon medians to the median value in the soil parent material; b — by the ratio of the median values of contiguous soil horizons

Explanations as on Figure 4

camouflaged by an active depletion of the weathered non-silicate primary minerals.

The elements were grouped according to their location within the model soil profile. The elements that accumulate in the soil top A-horizon (Ag, Ba, Mn, Na, Nb, Pb, Sn and Zr) were ascribed to the first group according to the ratio of the A-horizon element medians to the median values in the soil parent material (Fig. 4a).

A study of the model soil profile, horizon by horizon, as regards the two subgroups of elements reveals: Zr, Ba, Nb and Na elements that show relatively increases in the eluvial E-horizon; Ag, Mn, Pb and Sn elements that show increases in the top A-horizon, depletions in the eluvial E-horizon and are precipitated in the illuvial B-horizon (Fig. 4b). The first ones are related to the resistant minerals that remain after most other primary minerals have disappeared due to the soil-forming processes (Dixon, 1977). The second ones are anthropogenic and biogenic elements in part and accumulate in the soil organic matter in the top A-horizon and are redistributed downwards with the humus and fine-grained particles (Kabata-Pendias and Pendias, 1993). The variability of the second subgroup elements is noticeably higher (σ3 0.67–0.31 and σ4 0.54–0.26) than of the first group elements (σ3 0.51–0.15 and σ4 0.35–0.13). This indicates that the regional anthropogenic influence of the airborne elements-pollutants on the soil chemistry that was non-avoidable in some sampling sites (Gregorauskienė and Kadūnas, 1998).

The elements that accumulate in the soil illuvial B-horizon (Fe, Li, Al, V, Zn, Ga, Ni, Cu and Rb) were ascribed to the next group according to the ratio of the B-horizon element medians to the median values in the soil parent material (Fig. 5a). Some of the elements (Fe, Li, Al and V) are abundantly precipitated in the B-horizon, while others (Cu, Ni, Ga, Zn and Rb) are less so. The latter ones (also Fe and V) are removed from the eluvial E-horizon and even from the top A-horizon, and have partly accumulated in the B-horizon. The distributions of Zn, Cu and Fe within the soil profile are affected by human activity: these relate to their relatively increased values in the soil top A-horizon and their increased variability (σ3 0.54–0.48). Additionally, the influence of soil texture heterogeneity and of the particular development of the B-horizon (argillic, spodic, calcic and so on) was revealed by analysing the soil profile horizon by horizon, i.e. the variability of Cu, Zn, Fe, Ni and V is moderately high: σ4 0.6–0.3 (Fig. 5b).

The remaining elements (Ca, Mg, U, B, Th, As, Co, Cr, Sr, Y, Mo, La, Sc, Yb, Ti, P and K) were attributed to the group of elements removed from the upper soil horizons by various means (Fig. 6). The most easily removable of these are Ca and

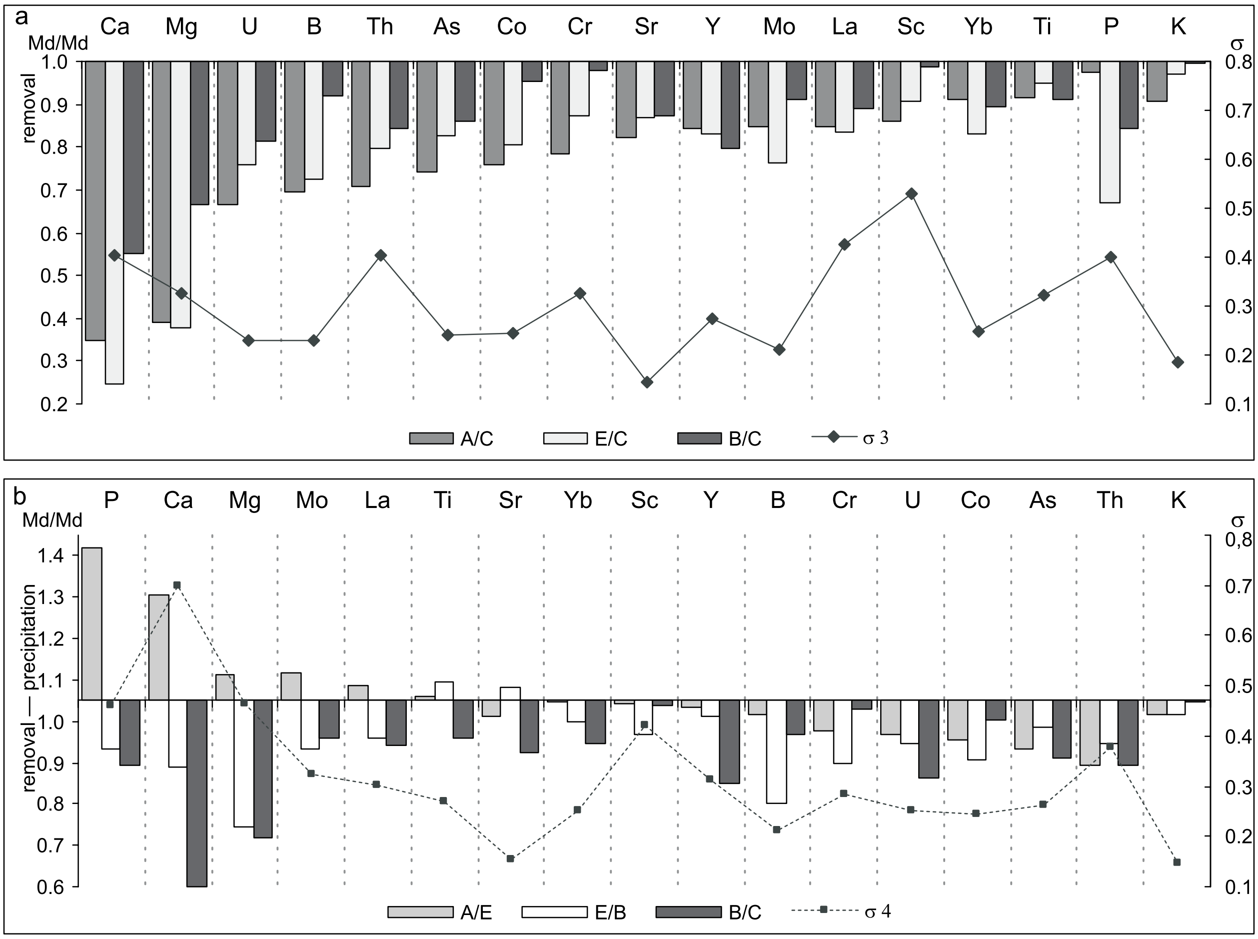

Fig. 6. Elements removed from the upper soil horizons: a — by the ratio of the soil horizon median values to the median value in the soil parent material; b — by the ratio of the median values of contiguous soil horizons

Explanations as on Figure 4

Mg, as components of highly soluble carbonate minerals. As, Co, U, B, Th, Cr and Y are also depleted through the whole soil profile. The variability of Sc, La, Ca and P is moderately high (σ3 >0.4) due to the different behaviour elements of these in the soil profile with respect to different textures (Fig. 6a).

Tracing the movement elements of horizon by horizon the influence of other factors appears: the median values of Ca and Mg in the top A-horizon are increased due to the liming of cultivated sites; the top A-horizon is enriched in P, Mo and La by agricultural fertilization and because of the presence of plant remains; increases of Ti and Sr are observed in the eluvial E-horizon, related to residual resistant minerals (Fig. 6b). The high variability of Ca, Mg, P and Sc (σ4 >0.4) is determined by: different soil textures in the subsets of samples; and calcareous soil parent material.

The variability of elements, i.e. the probability of an element's location in the model soil profile was evaluated using the absolute average deviation calculated in two ways (σ3 and σ4). This enabled discrimination of various soil-forming processes that influence the general patterns of element distribution within the soil profile. The distribution of Ag, Zn, Sc, Ba, Cu, Zr, Fe, La, Th and Ca is most affected by the various soil-forming factors (σ3 >0.4) when compared to the soil parent material, while Sr, Na and K are almost immobile elements (σ3 <0.2) within the soil profile (Fig. 7).

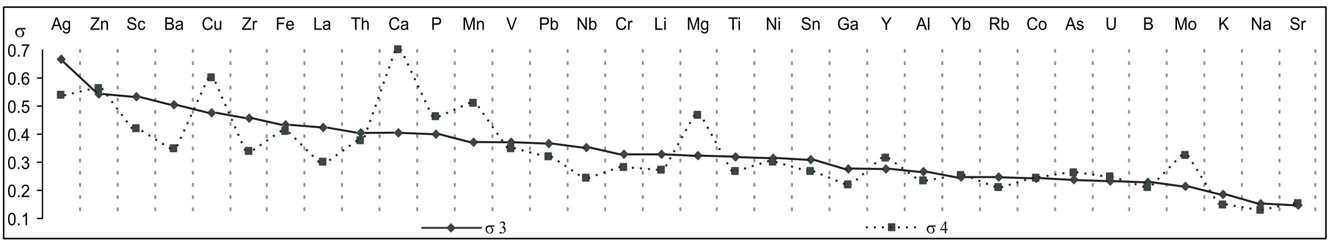

Fig. 7. Variability of the element median values within the model soil profile according to different average deviations: σ3 — in comparison to the real soil parent material; σ4 — by contiguous master horizons

Detailed (horizon by horizon) investigation of element distribution through the soil profile revealed that Ca, Cu, Zn, Ag, Mn, Mg, P, Sc and Fe have the highest variability ($\sigma 4 > 0.4$). In contrast, the lowest variability is of Na, K and Sr again ($\sigma 4 < 0.2$). Consequently, the distribution of Na, K and Sr as well as of B, U, As, Co, Rb and Yb is more or less even within the soil profile, i.e. they are moderately affected by the different soil-forming processes and by human impact.

CONCLUSIONS

Vertical element redistribution within the soil profile, due to different soil-forming processes, is taking place in the soils of Lithuania formed on Late Weichselian and Upper Saalian glacial deposits of variable composition. The most evident soil-forming processes occur in loam-clay soil. Depletion is the dominant process, with most elements being moved from the upper soil horizons or even out of the entire soil profile. Trace elements related to weathering-resistant minerals (Zr, Nb and Ba) and anthropogenic biogenic elements (Ag, Pb, Sn and Mn) accumulate in the surface A-horizon. The elements related to fine soil particles and clay minerals (Fe, Al, Li and V) accumulate in the illuvial B-horizon. The distribution of Na, K and Sr is almost even within the soil profile, whereas of Ca, Cu, Zn, Ag, Mn, Mg, P and Sc are the most mobile elements. Natural factors such as weathering and washout (particularly for Ca, Mg, Mn and Sc), and human impact (on the behaviour of Ag, Cu, Zn, Pb and P) determine the variability of these element contents within the soil profile. Two long-term trends of soil chemistry were distinguished: regional enrichment of the surface A-horizon by anthropogenic heavy metals; and the depletion of bioavailable alkaline elements from the upper soil horizons. These processes within the soil profile influence the regional groundwater quality, mainly by increasing the total dissolved solids, particularly in areas of high agricultural activity.

Further details of these patterns of vertical element distribution should be explored by means of mineralogical analyses. Applications of sequential chemical extraction procedures and of grain-size analyses would also help constrain hypotheses regarding the patterns of element distribution within the soil profile. Furthermore, the samples of soil investigated were collected in the summer, and so the impact of seasonal variability on element variations remains unclear.

REFERENCES

AGBENIN J. O. and FELIX-HENNINGSEN P. (2001) — The status and dynamics of some trace elements in a savannah soil under long-term cultivation. Sc. Total Environ., **277** (1–3): 57–68.

ANDERSEN M. K., RAULUND-RASMUSSEN K., HANSENA H. C. B. and STROBELA B.W. (2002) — Distribution and fractionation of heavy metals in pairs of arable and afforested soils in Denmark. European J. Soil Sc., **53** (3): 491–502.

BERROW M. L. and MITCHELL R. L. (1991) — Location of trace elements in soil profiles: total contents of particle-size separates. Trans. Royal Soc. Edinburgh. Earth Sc., **82**: 195–209.

BERTHELSEN B. O. and STEINNES E. (1995) — Accumulation patterns of heavy metals in soil profiles as affected by forest clear-cutting. Geoderma, **66** (1): 1–14.

BLASER P., ZIMMERMANN S., LUSTER J. and SHOTYK W. (2000) — Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. Sc. Total Environ., **249** (1–3): 257–280.

DEGORSKI M. (1998) — Spatial and vertical distribution of soil physico-chemical properties and the content of heavy metals in the pedosphere in Poland. In: Proceedings of the International Symposium on Air Pollution and Climate Change Effects on Forest Ecosystems, February 5–9, 1996, Riverside, California: 169–178. USDA Forest Service Gen. Tech. Rep. PSW-GTR-166.

DIXON J. B. (ed) (1977) — Minerals in Soil Environments. SSSA: 78–768. Madison. Wisconsin.

GREGORAUSKIENĖ V. (1997) — Effect of soil formation processes on the distribution of heavy metals in soil profile. In: Abstracts of International Symposium of Applied Geochemistry, Moskow, 1997: 168–169.

GREGORAUSKIENĖ V. and KADŪNAS V. (1998) — The influence of atmospheric transmission of technogenical elements on their background values in Lithuanian soil. Geologija, **26**: 56–60.

GREGORAUSKIENĖ V. and KADŪNAS V. (2000) — Chemical composition of soil and lake sediments — an indicator of geological processes in Lithuania. Geol. Quart., **44** (4): 347–354.

GUOBYTĖ R. (1998) — Quaternary Geological Map of Lithuania. Scale 1:200 000. Geol. Surv. Lithuania. Vilnius.

HERNANDEZ L., PROBST A., PROBST J. L. and ULRICH E. (2003) — Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Sc. Total Environ., **312** (1–3): 195–219.

KABATA-PENDIAS A. and PENDIAS H. (1993) — Biogeochemia pierwiastków śladowych. PWN. Warszawa.

KADŪNAS V. and GREGORAUSKIENĖ V. (1999) — Microelements in soil grain size fractions. Geologija, **28**: 15–22.

KADŪNAS V., BUDAVIČIUS R., GREGORAUSKIENĖ V., KATINAS V., KLIAUGIENĖ E., RADZEVIČIUS A. and TARAŠKEVIČIUS R. (1999) — Lietuvos geocheminis atlasas. Geol. Surv. Lithuania, Geol. Inst.Vilnius.

KASCHL A., RÖMHELD V. and CHEN Y. (2002) — The influence of soluble organic matter from municipal solid waste compost on trace metal leaching in calcareous soils. Sc. Total Environ., **291** (1–3): 45–57.

KUTIEL P. and INBAR M. (1993) — Fire impacts on soil nutrients and soil erosion in Mediterranean pine forest plantation. Catena, **20**: 129–134.

LAHDENPERÄ A. M. (1999) — Geochemistry of afforested and arable soils in Finland. Geol. Surv. Finland. Spec. Pap., **27**: 61–68.

MORERA M. T., ECHEVERRÍA J. C. and GARRIDO J. J. (2001) — Mobility of heavy metals in soils amended with sewage sludge. Can. J. Soil Sc., **81**: 405–414.

SHOTYK W., NESBITT H. W. and FYFE W. S. (1992) — Natural and anthropogenic enrichments of trace metals in peat profiles. Internat. J. Coal Geol., **20**: 49–84.