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REGULARITIES OF VERTICAL ELEMENT DISTRIBUTION WITHIN THE SOIL PROFILE IN LITHUANIA

Summary of doctoral dissertation

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INTRODUCTION

Research problem. Vertical distribution of elements in the complete soil profile is being investigated nowadays for several purposes. The modern agricultural recommendations are derived from the last century's scientific researches of soil fertility with the whole depth reached by the plant roots. (Smeck, 1973; Kirby, 1985; Mažvila, 1998). Depletion and redistribution of nutrients is observed in soil after clear–cut down and fire of the forest, as well as after afforestation (Kutiel and Inbar, 1993; Berthelsen ir Steinnes, 1995; Lahdenperä, 1999; Andersen et al., 2002). The recent investigations of soil profile are aimed more and more at the release and immobilization of contaminants added to soil with sewage sludge or fertilizers (Agbenin ir Felix-Henningsen, 2001; Morera et al., 2001; Kaschl et al., 2002). The impact of airborn dust on undisturbed soil and behavior 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. The enrichment of surface soil horizons has been reported: by lead and cadmium in France, and by lead and zinc, as well as by arsenic and cupper, but in lesser extent, in Switzerland (Shotyk et al., 1992; Blaser et al., 2000; Hernandez et al., 2003). Spatial distribution of elements and increase of nickel, iron and chromium in the mineral–humus soil horizons of western Poland has been explained after investigation of the vertical distribution of these partly atmogenic elements (Degorski, 1998). The understanding of location of trace elements in soil profiles also helps to link geochemical maps of trace elements' contents, which are obtained by stream sediment and topsoil analyses (Berrow and Mitchell, 1991).

The relevance of the study. Objective knowledge on vertical distribution of chemical elements in soil profile based on the modern chemical analysis is necessary for assessment of anthropogenic impact on soil and precipitation, filtered through the soil and passed into ground water. This study, based on the analysis and highlight of the vertical element distribution pattern in the complete soil profile, is intended to explain and support the regularity of the spatial element distribution, defined during national geochemical mapping of topsoil and stream sediments. Recognition of the vertical element distribution pattern allows separating the natural and anthropogenic factors during determination of baseline values in the soil surface horizon.

Research object is the soil of Lithuania, formation of which is proceeding on the glacial deposits – the relatively loose parent material, in the temperate-boreal climate with the excess of precipitation, and the alteration of its chemical composition.

The main objective of the study was to estimate the regularities of vertical distribution of chemical elements in soil profile of Lithuania. The following **main tasks** have been undertaken:

1) to identify relation between grain-size composition and chemical composition of soil;
2) to accomplish geochemical analysis of soil parent material, different in origin, and estimate the primary chemical composition of soil parent material;
3) to analyze and define impact of soil forming processes on vertical distribution of chemical elements in soil profile;
4) to highlight the main changes of vertical soil profile chemistry, using comparison of chemical composition of soil parent material (C horizon) versus surficial A horizon, often used in soil geochemical investigations;
5) to compile typical geochemical soil profiles for sand – loamy sand and loam – clay soil, based on genuine geochemical data, obtained from real complete soil profiles, evenly distributed on territory of Lithuania;
6) to model standard soil profile and ascertain regularities of vertical alternation of its chemical composition in Lithuania.

- The solution of these tasks has allowed the formulation of the following **defended statements**: Chemical composition of Lithuanian soil mainly depends on the most abundant sand grain size fraction of soil;
- Values of chemical elements in soil parent material are determined by soil lithology, and lithological factor remains determinative through the complete soil profile
- Dominant soil forming process in Lithuania is depletion and removal down of most of elements through the entire soil profile;
- Character and intensity of chemical element depletion depend the most on the lithological type of soil;
- Elements, related to weathering resistant minerals and anthropogenic–biogenic elements acumulate in the top soil horizon ;

- Elements, related and migrating with clay minerals and hydroxides, accumulate in the illuvial soil horizon.

Originality of the research. Study updates the national sparse knowledges about the peculiarities of the element migration through the multilayered mineral–organic soil cover in the local temperate–boreal climate conditions. For the first time, the behavior of wide set of chemical elements (28 trace elements and 6 major elements), including the rarely investigative, in complete soil profiles have been analysed and characterized. For the first time, the model of the standard soil profile was created, having the master soil horizons A, E, B and C. 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 long-term trend of the regional enrichment of the surface A-horizon by anthropogenic heavy metals also was distinguished. Research data of study, obtained using the standard certified analytical methods, allowed making the internationally calibrated findings. Moreover, the research outcomes were tested in the national and international geochemical mapping projects and applied in a preparation of the methodologies for geochemical and environmental investigation on large areas with different geology, climate, relief and etc.

The history of the present research The research was begun in 1993, in the frames of national geochemical atlas project, and the first scientifical presentation concerning research results was done in 1996. Since this years, the author, working at the former Institute of Geology and at the Lithuanian Geological Survey, participated in the implementation of geochemical mapping of Lithuania at a scale 1:500,000 and many of the geochemical projects in various parts of country. The present research is based on the new geochemical information individually collected by the author during her participation in the national projects and the international low-density multi-element geochemical surveys covering the whole area of Lithuania. Vertical element distribution was analyzed in the 347 soil samples from the 74 complete soil profiles. For the modeling of standard soil profile the 249 soil samples from the 53 complete soil profiles, evenly covered the country area were used. Geochemical analysis was supported by the particle-size analysis determined in the 60 soil samples. Additionally, the chemical composition of the core samples from the 198 boreholes was examined in research of the soil parent material.

Presentation of the research work. Since 1996, the first presentation at a scientific conference, the author has reported the research results at more than 30 international and national scientific conferences. These presentations were made individually or jointly with co-authors. From these presentations, thirty articles, including nine articles in periodicals included in the list of Web of Science of journals of the Institute of Scientific Information (ISI), have been published.

Extent and structure. This dissertation is composed of an introduction, three chapters, conclusions, a list of references (65 sources) and a list of the author's publications (87). The dissertation comprises 109 pages of text, 34 illustrations and 20 tables.

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1. REVIEW OF INVESTIGATIONS

National research of chemical composition of soil profile. Lithuania has long going agricultural traditions, and soil generally is used for plant growing, so most works are concentrated on researches of arable layer and containing nutrients necessary for plants, and major works on chemical composition of the soil are based on agrochemical researches, analyzing influence of the chemical compounds to agricultural productivity. When testing soil profile, most often the plant nutrients are analyzed, e.g. Šleinys and Janušienė in 2001 investigated distribution of chemical elements (SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, P_2O_5, K_2O) in profile of till at weather-beaten heights, and find out that podzoluvization are dominant despite their location on the slope.

Some heavy metals (Cr, Pb, Ni, Cu, Zn, Cd) in loamy sand Albeluvisols at the various anthropogenic impacts were investigated in 1996 by Rimšelis, and together with Greimas and Ignotas he published study on variations of distribution and quantities of such elements in profile of intensely fertilized, limed and contaminated by transport soil in 1997.

Marcinkonis et al., in 2004 also estimated geochemically long-term anthropogenic impact (fertilizing and liming) on various types of arable layer and find out that in the Western and Eastern zones of Lithuania total content of Ca and Sr in arable layer were increased, Zr decreased, Co and Cu also were changed. Impact of liming and fertilizing to Albeluvisols of lowlands of Western Lithuania and Coast, and Heights of Samogitia was evident as differences in total quantities of 15 elements (Al, Fe, Ca, Mg, B, Ba, Co, Cu, Li, Nb, Ni, Sc, Sr, Zn, Zr), and in distinct tillage of 6 elements (Ba, Cr, P, Sr, V, Zn), also in greatly increased quantities of Mn, Ca, Sr, Zr. Immobilization of Sr in arable layer was noticed, caused by increase of Ca due to liming.

Distribution of heavy metals (Cd, Cr, Cu, Pb, Zn, Mn, Fe) in profiles of forest and arable soil was investigated during national monitoring of soil, however samples of soil for such assay are collected from fixed depth instead of naturally formed soil horizons (Vaičys et al., 1998, Mažvila et al., 1996). Mažvila in 2001 study emphasized spatial regional differences of element distribution in topsoil (0-20 cm) instead of vertical variety of elements.

Particular aspects of mobility and migration properties of metals in the soil profile were investigated by Brazauskienė, Sabienė and associates (Brazauskienė et al., 2002 and 2008, Steponkaite et al., 2008). They find out that agility of the metals in the soil is increased by soluble humic compounds, which can be used to purify soil, contaminated with heavy metals or estimate use of treated wastewater to fertilize a soil.

Methodical investigations of heavy metals to find out most suitable methods of dissolving and measuring of soil were published by Motuzas et al., in 2000 and 2003. Also Motuzas and associates published results of methodological educational assay of chemical composition of roadside clay-loam Luvisol profile in 2001 and 2008, which defined that roadside soil along the Vilnius-Kaunas highway is contaminated with Pb and Ni, but quantities of Cr, Zn and Cu do not increases max. allowed concentrations. Also they presented theoretical model of sorption of these elements in soil.

Trimirka continued analogous methodological researches in his dissertation in 2005, where he investigated capability of the finest fraction of Luvisols to absorb and retain heavy metals. They also tried to anticipate possibility of chemical contaminations (Cr, Pb, Ni, Cu, Zn) to migrate in soil profile. Butkus in his dissertation (2008) developed such methodological researches in slightly different direction, investigating saturation of the soil with heavy metals and their impact to the biota of the soil.

Numerous data of the national geological–geochemical investigations often includes upper layer of the soil only, instead of all profile of the soil, so they are not discussed in detail in the study. But it is important to mention studies by Vareikienė 2005 and by Vareikienė and Lehtonen 2004, committed to find conjunctions between mineralogical and chemical composition of the soil, concentrating to chemical analysis of clay minerals and weathering resistant alothigenous minerals and different grain size soil fractions. During the investigation was established, that amount of alothigenous accessory elements (Zr, Ti, La, Y, Yb, Nb) is determined by fine silt fraction, which accumulates heavy minerals, more prevalent as amphibole, epidote, ilmenite, and less, as granate, rutile, hematite, zircon, clinopyroxene and titanite.

Kadūnas et al., 2003 and Vareikienė et al., 2008 in their studies investigated influence of soil age and decay duration to it's chemical and mineralogical composition and find out that soil formed in the region of Ašmena heights during the next-to-last glaciations is enriched with resistant to decay heavy minerals and related to alothigenous accessory trace elements Y, Yb, La, Ti, Zr, Nb, reliably correlates with a soil sand fraction. Whereas, in the planes of Mūša-Nemunėlis, soil was formed on the youngest Lithuanian soil forming sediments and the relation between quantity of such elements and clay amount of the soil is increasing.

Foreign research of chemical composition of soil profile. Foreign researches of chemical composition of the soil profile also are not numerous. Often they do not discloses properties of the soil, but explains distribution of the spatial elements in the soil, or analyses influence of soil quality to the ground water.

Analyzing 22 and 25 soil profiles in Poland, Degorski 1998 and Kabała, Szerszeń 2002 discovered increased quantities of Ni, Cr, Fe and Pb, Cu in the upper hummus layer of the soil and linked that to a capability of the organic substances in the soil to accumulate technogenic elements.

The role of plants in redistributing biophylic elements in soil profile and changing properties of the soil were analyzed by Jobbgy EG. and Jackson RB. in 2001. They stated that regularly cultivated arable layer is constantly homogenized and elements necessary to plants are distributed gradually. But even in 4-20 years if the soil is not cultivated and fertilized, quantities of agile P, K and even Ca were increased in the upper level of the soil, i.e. plants "rises" nourishments in profile and part of them stays on the surface of the soil, together with the decomposing organic remains.

Investigating impact of tillage to quality of the ground water in California, Tanji K. and Valoppi L. in 1989 discovered, that cation form microelements (mostly heavy metals) are immobilized by soil sorption complex and didn't reach ground water. But anion form elements (mostly oxidized), are mobile and accumulates in ground water, even if they are sorbed by clay and hydroxide minerals. If the soil is fertilized with sewage sludge, Cd, Cr, Cu, Ni, Pb, Zr are sobbed by organic substance, clay and hydroxide minerals and accumulated in upper 15 cm layer of the soil.

Tyler, 2004 investigated podzolic soils in Sweden and find out that almost all elements are washed out from E horizon, especially forms which are soluble in HCl acid. Most soluble forms of alkaline elements Na, K, Rb, Cs, Ca, Mg, Sr and Ba, and metals V, Co, Ni, Zn, Cd, Hg, Pb accumulates in upper soil horizon, enriched with organic substances, and forest duff, Fe and Ga accumulates in B1 horizon, Al, Cr, Li, Be, Sc, Si, Th, Zr, Mo – in B2 horizon. The upmost quantities of soluble Yb, La, lanthanides and rare earth elements were discovered in soil parent material. Accumulation of cadmium and lead in upper A1 and A2 horizons are caused by air transferred contamination.

Investigating forest soils in French, Hernandez L., Probst A., Probst J.L. and Ulrich E. in 2003 determined following sequence of accumulating air transferred contamination Cr>Zn>Pb>Ni>Cu>Co>>Cd in the upper layer of soil and decreasing quantities of these anthropogenic elements going deeper in soil profile. Distribution of these elements is controlled by quantities of soil pH, exchanging cations, clay participles, organic substances, iron and aluminium hydroxide. Most of all airborne contamination is visible on Mollic Andosols and Calcaric Cambisols, least on acid soils.

Berrow and Mitchell 1991 analyzed vertical distribution of 21 chemical elements. They performed detailed complex, grain size, mineralogical research of chemical composition of 4 soil profiles and discovered, that: Co, Cu, Li, Mn, Ni, V, Zn, Fe in the soil are related to easy decomposing iron-magnesium minerals and are liable to accumulate in clay and silt fractions; Ti, Zr, La, Y are related to weathering resistant minerals and accumulates in silt and fine sand fractions. Li and Rb accumulates in acid granite weathered crust the silt and clay fractions, while alkaline Ba and Sr accumulates in sand fractions, and are related to feldspars, which are more resistant. Also poor and changeable drainage of the soil increases decay of minerals and transition of Co, Cu, Ni, V, Zn from sand fraction to silt and clay fractions, but migration of these elements down the soil profile is insignificant.

Acostaa et al. 2011 m. investigated and analyzed how quantities of chemical elements are related with grain size and mineral composition of soil in Spain and find out, that largest quantities of Pb, Cd, Cu and Zn accumulates in sand fraction, and soil chemical composition is controlled by chemical and mineral composition of soil parent weathering crust. Pb, Cd, Cu and Zn are associated with aluminium and ferrous minerals, mica, pyroxene, amphibole while Co, Ni and Cr – with magnesium mineral smectite, Ti – with sodium containing plagioclases, albite, andesine.

Investigating quantities of some elements (Cr, Ni, Zn, Rb, Sr, Y, Zr, Pb, Ba, Mn) in eight fractions excluded using x-ray fluorescent method from various soil samples in Hungary, Horváth et al. 2000 m. find out, that most elements are accumulated in the finest fraction. Additionally performed mineralogical analysis allowed to define that microelements are found in three associations: adsorbed at the surface of minerals; in the crystalline lattice of the minerals (e.g. Ti rutile, Zr zirconium); sobbed in the clay minerals.

Author of the study together with Salminen and Tarvainen in 2008 published the results of testing modelling application NORMA, which was created to determine mineralogical composition of Podzols based on chemical composition. The application was tested using chemical composition from ten different soil samples from Northern Europe and was determined, that chemical composition of the soil parent C horizon reflects mineralogical composition of parent rock, and secondary minerals (goethite and hydrous Al-silicate), accumulating in the upper soil horizons, reflects the soil forming processes. But chemical composition of soil parent material controls chemical composition of complete soil profile.

2. METHODS

Scope and structure of chemical investigations. The pedological studies of complete soil profile were carried out in the frames of the project "Geochemical Atlas of Lithuania" (Kadūnas et al. 1999). The 249 soil samples were taken from master horizons A, E, B, BC and C of the 53 complete soil profiles. The selection of sampling sites was based upon an idea to cover the country territory evenly and 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 that the maximum distance to roads, villages, industry and others sources of human activity was guaranteed. Moreover, to confirm or to deny properties of chemical composition of the soil from previous investigations, the data of 13 soil profiles and 59 samples, obtained when preparing European geochemical atlas (Salminen (ed.), 2005; De Vos (ed.), Tarvainen (ed.), 2006) in Lithuanian territory, and data from 8 soil profiles, 39 samples, obtained when performing Vilnius region geochemical mapping (Putys, Gregorauskienė, 2009), were used. Vertical distribution of chemical elements was analysed in 74 complete soil profiles, using total content of 28-34 elements determined in 347 samples from soil master horizons.

To analyze trace element composition of Quaternary soil parent sediments data from chemical analysis of 293 samples from different studies were used (Fig. 2). In addition to 57 soil profiles analysed while developing Lithuanian geochemical atlas, data from 18 soil profiles analysed while proceeding geochemical mapping on the border of the Lithuanian-Polish "Jotvingiai belt" (Lis et al, 1997) and 13 soil profiles analyzed in aforesaid European integrated geochemical mapping (Salminen et al., 1998) were used, to explain distribution of elements in the upper layer of the soil (Gregorauskienė, Kadūnas, 2000). While performing archaeological researches in the ancient settlements of Katra, geochemical description of cultural layer was made using soil parent material characteristics from 20 soil profiles (Gregorauskienė, 1999). Geochemical soil mapping M 1:50 000 was made by Lithuanian Geological Survey in the regions of Molėtai and Biržai, to explain the origin of a geochemical anomaly. The Quaternary core was analyzed from 173 and 16 boreholes respectively (Guobytė, 1995; Gregorauskienė, Putys, 2001).

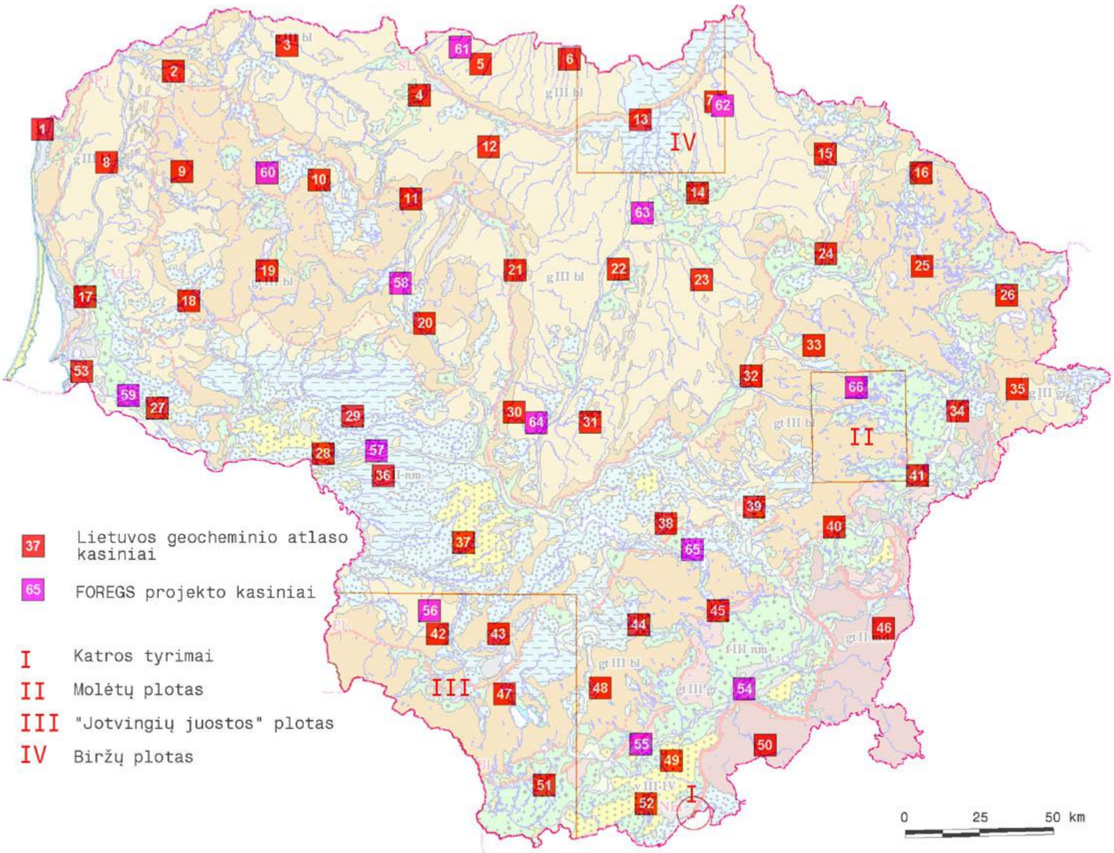


Fig. 1. Scheme of factual data: the complete soil profiles – red squares - of Geochemical Atlas of Lithuania (Kadūnas et al, 1999), pink squares - of [Foregs] Geochemical Atlas of Europe (Salminen et al, 2005), I - Katra area (Gregorauskiene, 1999), II - Molėtai area (Guobytė et al, 1995), III - "Jotvingiai belt" area (Lis et al., 1997), IV - Biržai area (Gregorauskiene, Putys, 2001) [on the background map of Quaternary geology at a scale 1:400 000, Guobytė, 1998)]

During the field work the documentation of terrain and soil profile was made – site coordinates were set, made the pictures of the landscape and soil profile, presented descriptions of local habitat and soil profile, determined grain size composition and depth of carbonates, preliminary determined type of the soil, revised later using the soil maps of Lithuanian districts scaled to 1:50,000.

Analysis of grain-size particles. The description of soil profile texture was made in the field using national soil maps at a scale 1:50 000, and later the grain size classes were revised in selected samples 92 samples by combined sieve and pipette method in laboratory. Samples for grain size analysis from 34 complete soil profiles were selected to correspond representatively all lithogenic soil types (sand loamy sand, loam and clay), all soil regions and all soil master horizons. During sample preparation stage an organic material was removed with peroxide, a carbonates – with hydrochloric acid 5%. The grain-size particles were separated in the four fractions: <0,001 mm – clay fraction using pipette method; 0,001-0,063 mm – silt; 0,063-1 mm – sand; >1 mm – coarse sand and gravel fractions using sieve method. The all fractionated samples (93) were powdered and 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 standard quality control was followed at the all research stages: the sample duplicates were taken in field sampling; the international standards, field and laboratory duplicates were analysed in laboratory; during data treatment only the confidential data sets (30±3 units) were studied using the nonparametric statistical analysis methods.

To assess importance of separate grain size fractions to overall geochemical composition of different types of the soil, average values of grain size fractions (Table 1), and average values of trace elements in fractions (Table 2) were calculated. Hereby importance of each fraction to overall quantities of trace elements was evaluated (Table 3). Analyzing relationship between chemical composition and grain size composition of the soil, 60 samples of mineral soil with all three fractions (clay, silt and sand) were used to interpret the data. According their grain size composition soils are classified to 3 lithological soil groups, with calculated different statistical parameters:

1. 17 sand soil samples with sand fraction no less than 60%, and median quantity – 87%, clay fraction median quantity – 4%, silt – 6%;
2. 19 clay-loam soil samples with clay fraction no less than 40%, and median quantity – 53%, sand fraction median quantity – 21%, silt – 19%;
3. 24 sandy loam soil samples with silt fraction median quantity – 21%, clay – 24%, sand – 44%.

Ratios of accumulation of trace elements in the grain size fractions were calculated dividing element content in separate fraction by element content in unfractionated sample, after that medians for accumulating ratios were calculated to all and separately to sand, loamy sand and clay-loam soils (Fig. 7-10).

Input of trace elements in particular fractions (percentage) to the total content of elements in unfractionated sample, was estimated by multiplying accumulating ratios of each element from separate fraction by percentage of appropriate fraction in the sample (Fig. 11). The reliability or data was verified by estimating overall amount of elements using formula:

$C_{va} = C_m*F_m/100 + C_a*F_a/100 + C_s*F_s/100$, where:

C_{va} – calculated total content in soil sample;

$C_{m, a, s}$ – content of element in clay (m), silt (a) or sand (s) fraction, mg/kg;

$F_{m, a, s}$ – quantity of the fraction in respective sample, %;

and performing correlation of calculated overall quantities in fractionated samples with calculated overall quantities in non fractionated samples. Among both data arrays strong direct Yb, Cr, Cu, Al, V, Ni (r > 0,7), moderate Ti, Sc, Ga, Li, B, La (r – 0,7-0,6), reliable Mo, Mn, Ba, Pb, Co, Sn (r – 0,6-0,5) ir Ag, Zn, Y (r – 0,4-0,3) dependence of elements was established, indicating sufficient representativeness of relatively small data sample. Weak correlation of both arrays Nb – 0,26, Zr – 0,21, P – 0,19 and Sr – -0,05 indicates, that data of both elements must be interpreted reserved.

The all fractionated and unfractionated samples of soil and soil parent material were milled to a powder after homogenization and sieving through 1 mm sieve. The powdered 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. Total content of 6 major (Al, Ca, Fe, K, Mg, Na) and 17 trace elements in the 249 samples from the main 53 soil profiles was determined using a 4-acid digestion (HNO_3-$HClO_4$-HF-HCl) in Acme Analytical Laboratories Ltd. of Canada by ICP-MS to provide internationally comparable data. The loss on ignition (LOI) was calculated after soil burning at a temperature of 450^{o}C, and determination of pH was made using glass electrode in a 1:5 suspension of soil in water. The data of major elements Al, Ca, Fe, K, Mg, Na from Acme Laboratory and data of 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.

Mathematical–statistical data treatment. A set of the whole actual data was separated to the subsets for the master soil horizons A, E, B, BC and C and statistical parameters (median *Md*, arithmetical average *X* and standard deviation *V*) 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 statistical parameters of elements in the master horizons of different texture are shown in table of Appendix and Figures 17 – 19. In reality, not all soil profiles consist of the same sequence of horizons, thus on the basis of actual data the 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 irregular and specific samples, e.g. of the buried organic horizons and the soil layers with the 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 with corresponding texture. Most of the modifications were done for the E–horizon. Medians *Md*, for concentration ratios were calculated ant used representing results of the modeling.

On the ultimate expression of data, the absolute average deviation (σ) was used to measure the data variability and to check the probability of location of the element contents within soil profile. Parameter σ was calculated by formula;

$$\bar{\sigma} = \frac{1}{n}\sum x - \bar{x},$$

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

Instead of measured concentrations the several ratios were used to avoid the influence of measurement unit in the (σ) calculations. The several types of σ were applied in order to smooth the unusual fluctuations of element content and reveal the regularities of the element distribution within the soil profile:

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

σ2 shows the variability of elements in the whole model data set (the ratio of element content in the 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 shows the variability of 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 horizon sample to the real element content in the C–horizon (Ax/Cx, Ex/Cx, Bx/Cx,) is used in the calculation);

σ4 shows the variability of elements within model soil profile by the master horizons (horizon by horizon) as the ratio of element content between the contiguous master horizons (Ax/Ex, Ex/Bx, Bx/Cx,) is used..

The author took part in all above mentioned projects, data of which was used in her doctoral dissertation. She arranged methodological part and reports, explanatory notes, was leader of some projects, made all field work and interpretation of the data. The results of the projects were published in numerous (30) scientific articles and presented in many (43) scientific conferences, more than 10 geochemical atlases were published, covering various territories.

3. RESULTS

3.1. Chemical composition of soil grain-size fractions and its importance to the soil total chemical composition

The researches performed with soil and soil parent material in numerous countries shows that with the increasing amount of fine participles in the sediments increases quantities of most microelements (Petuchova, 1987, Kabata-Pendias, Pendias, 1993, Baltakis, 1993). Also, it is known that in various soil fractions different minerals are dominant. They determine overall chemical composition of the soil. This relationship is different for various microelements (Hardy, Cornu, 2006, Berrow, Mitchell, 1991). Depending on the soil type, which is determined by its lithogenous nature, there are different quantities of the grain size fractions and also different influence to amount of microelements in the soil. Assessment of such influence often allows to explain distribution of the microelements and correlation as in natural territories as in areas affected by technological processes, and is especially important when analyzing genesis of geochemical anomalies.

Analyzed types of mineral soil have fairly different grain size composition (Table 1). In the sand soil samples is clearly dominant sand fraction (0.063-1 mm), averages 87.6%. Amounts of participles for clay (<0.001 mm) and silt (0.001-0.063 mm) fractions are quite small (accordingly 3.6% and 5.7%), and these amounts are very variable (variation coefficients in the samples are 88-122%). This is caused by lithogenous diversity of the soil parental sands, including glaciofluvial, glaciolacustrine sands and sand affected by aeolian processes. Loamy sand soil is characterized more even distribution of clay-silt-sand fractions, but sand fraction is still dominant, which amounts 44.4%, also silt fraction has exceptionally high percentage, which averages 20.6%, but average amount of the clay fraction is still higher (24.3%). In the samples of loam-clay soil clay fraction amounts more than half (52.7%) participles, while the rest contains nearly equal parts of silt and sand fractions, accordingly 18.7% and 21.0%, but amounts of all fractions are quite variable, and variation coefficients are 78-55% (Table 1). Such diversity of the clay-loam soil samples probably is caused by variety of lithogenous composition of soil parent material, as this group of samples includes soil formed in the glaciolacustrine clay, as well as in the loam of basal and marginal moraine.

Table 1. Grain size composition of the examined soil, %

Soil type	Statistical parameters	Fractions, mm			
		<0,001	0,001-0,063	0,063-1	>1
Sand n=17	*Md*	3,6	5,7	87,6	0,5
	X	5,9	8,2	83,7	2,2
	Min	0,4	0,8	63,8	0,0
	Max	27,7	23,4	97,3	14,0
	V	122,1	87,7	13,0	180,1
Loamy sand n=24	*Md*	24,3	20,6	44,4	7,9
	X	23,3	25,8	42,1	8,7
	Min	6,0	14,4	11,7	0,5
	Max	37,0	66,6	58,7	22,2
	V	30,3	56,0	29,8	64,6
Clay-loam n=19	*Md*	52,7	18,7	21,0	1,9
	X	55,9	19,4	22,2	2,5
	Min	40,7	6,9	5,2	0,0
	Max	83,0	29,6	37,7	9,9
	V	22,7	31,5	44,0	96,6
All lithological types n=60	*Md*	25,2	18,2	43,8	3,1
	X	28,7	18,8	47,6	4,9
	Min	0,4	0,8	5,2	0,0
	Max	83,0	54,9	97,3	43,1
	V	78,0	57,3	54,5	146,4

Coarse sand-gravel (>1 mm) fraction averages 3% in all analyzed samples. It contains small amounts of microelements, except Ba, Mn ir Sr. Therefore the results from analysis of this fraction henceforth will be rarely used for data interpretation. Also, when routine analysis of soil trace element composition is performed, this fraction usually is ignored (Bloomfield, 1981, Gregorauskiene, Kadunas, 1997).

Average values of chemical elements in the grain-size fractions in sand, loamy sand and loam-clay soil. According to the values of the total element content in the various soil fractions, the trace elements were distributed to four groups, related to the different grain size particles and the dominant minerals in its (Table 2):

elements of the clay fraction – Al, Cu, Mo, Sc, Ti, V; Y, Co, (B, Yb, La);

elements of the both clay and silt fractions – (B, Yb, La), Cr, Ni; Ga, Li, Sn;

of the silt fraction – Ag, Pb, Zn;

of the coarse grained sand and gravel fractions (skeleton of soil) – Mn, Ba, (Sr).

Zr, Nb and P were not attributed to any group, taking into consideration the insufficient data quality of the element analysis of the grain size particles.

Table 2. Average values of trace elements in the soil fractions, mg/kg

	<0,001 mm - clay fraction			0,001-0,063 mm - silt fraction			0,063-1 mm - sand fraction			>1 mm - coarse sand - gravel		
	Md	*X*	*V*	*Md*	*X*	*V*	*Md*	*X*	*V*	*Md*	*X*	*V*
Ag	0,04	0,048	56	0,15	0,301	286	0,07	0,073	32	0,053	0,060	62
Al	9,6	9,8	18	2,3	2,6	58	4,8	5,0	35	7,1	6,6	34
B	50,5	56,4	42	46,0	48,4	35	21,0	27,0	65	14,0	14,6	28
Ba	450	437	25	260	288	50	370	377	37	630	641	58
Co	11	11,0	32	6,8	7,6	49	5	8,3	129	4,6	14,7	130
Cr	68	72	32	74	79	37	26	29	59	15	21	69
Cu	26	32	64	17	23	98	8	8	86	4,5	4,8	61
Ga	15,5	16,2	31	13	13,8	35	4,2	4,8	62	8,0	7,6	28
Y	46	47	44	18	22	74	9,2	20	331	12,5	13,3	36
Yb	3,6	3,5	33	2,2	2,8	72	1,0	1,1	60	1,4	1,3	46
La	52	56	30	34	39	69	11	13	58	18	19	60
Li	17	18	31	20	20	36	12	13	30	12	11	43
Mn	340	407	70	465	502	42	360	681	154	490	1633	148
Mo	2,65	3,07	45	0,71	0,77	39	0,30	0,52	57	0,45	1,20	206
Nb	19,0	17,4	30	16,5	17,2	51	14,0	13,6	31	10,5	9,6	55
Ni	26,5	29,1	39	25	26,9	60	10,0	17,6	128	11	14	57
P	600	769	57	540	603	48	450	503	35	375	545	65
Pb	15,5	22,0	111	23,0	24,1	33	10,0	11,8	65	13	14	53
Sc	14,5	13,9	54	4,8	5,7	90	3,5	4,5	70	6,2	6,9	45
Sn	3	3,0	19	2,9	3,1	44	2,4	2,4	16	2,0	2,1	36
Sr				60	95	167	96	95	37	130	157	60
Ti	8800	8612	26	3100	3156	41	1500	1703	55	1050	1293	38
V	140	159	36	49	54	46	33	38	73	30	35	67
Zn	108	112	49	185	202	79	60	120	119	15	23	73
Zr	275	321	43	310	460	127	230	262	61	145	176	64

Elements of clay fraction, related to the secondary clay minerals, are apparently dominant in this fraction, e.g. median amount of Al in the clay fraction is 4.2 times higher than in the silt fraction and 2 times higher than in the sand fraction, Mo – 3.4 times than in silt and 8.8 times then in sand fraction, Ti – accordingly 2.8 and 5.9 times, Sc – 3.1 and 4.1 times, V – 2.9 and 4.2 times, Y – 2.6 and 5 times, Cu – accordingly 1.5 and 3.3 times, Co – 1.6 and 2.2 times. Considering quite even distribution of these elements (variation coefficient *V* in the clay fraction varies between 18–64%, in the silt fraction – 39–90%, in the sand fraction 35–86%), can be assumed that these elements has strong enough bonds with the clay minerals and are mechanically transferred in the soil profile together with the mineral particles (Table 2, Fig. 2). Attention must be paid, that in the sand fraction Y distinguishes by its high contrast (variation coefficient *V*– 331%), that is probably related with weathering resistant soil primary minerals, and Co (*V* – 331%), which is associated with hydroxides.

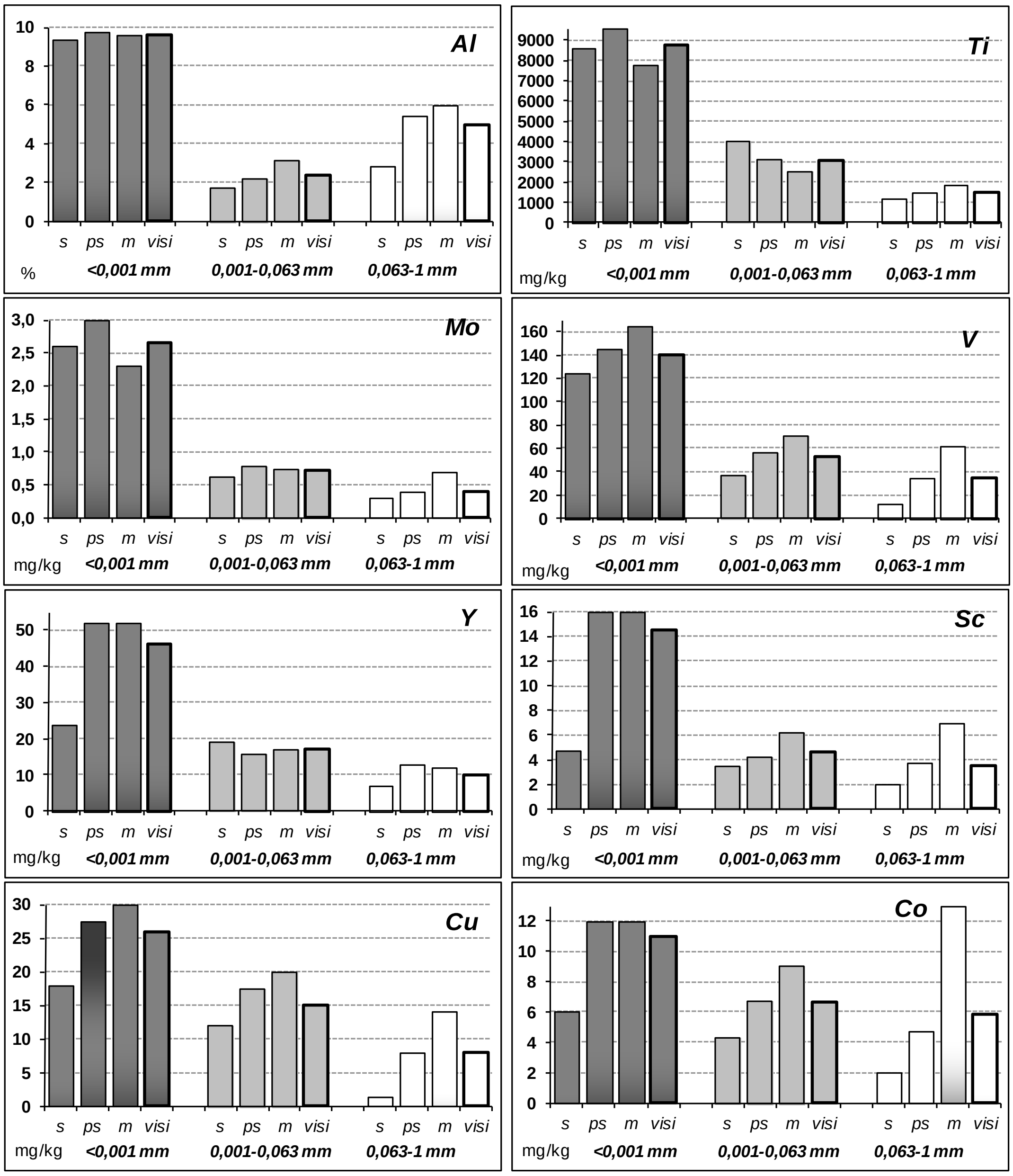


Fig. 2. Median values of the clay fraction elements in clay (<0.001 mm), silt (0.001-0.063 mm) and sand (0.063-1 mm) fractions, examined in the sand (s), sandy loam (ps), loam-clay (m) and the all (visi) analysed samples

Analyzing distribution of these elements in fractions separately in the sand, loamy sand and clay soils, it was evident that smallest amounts of almost all elements (Cu, Co, Y, Sc, V) in <0,001 mm fraction are found in the sand soil, also smallest values of Al, Co, Cu, Sc V contained in 0.001-0.063 mm fraction, also all elements found in 0.063-1 mm fraction, i.e. smallest amount of most elements accumulating in the clay fraction are in the sand soil (Fig. 2).

In both clay and loam fractions highest average amounts has Cr, Ni; Ga, Li, Sn and B, Yb, La, which are absorbed on the surfaces of secondary clay minerals, and also easy associates with primary, more resistant ferrous and magnesium minerals, micas, feldspars (Table 2, Fig. 3).

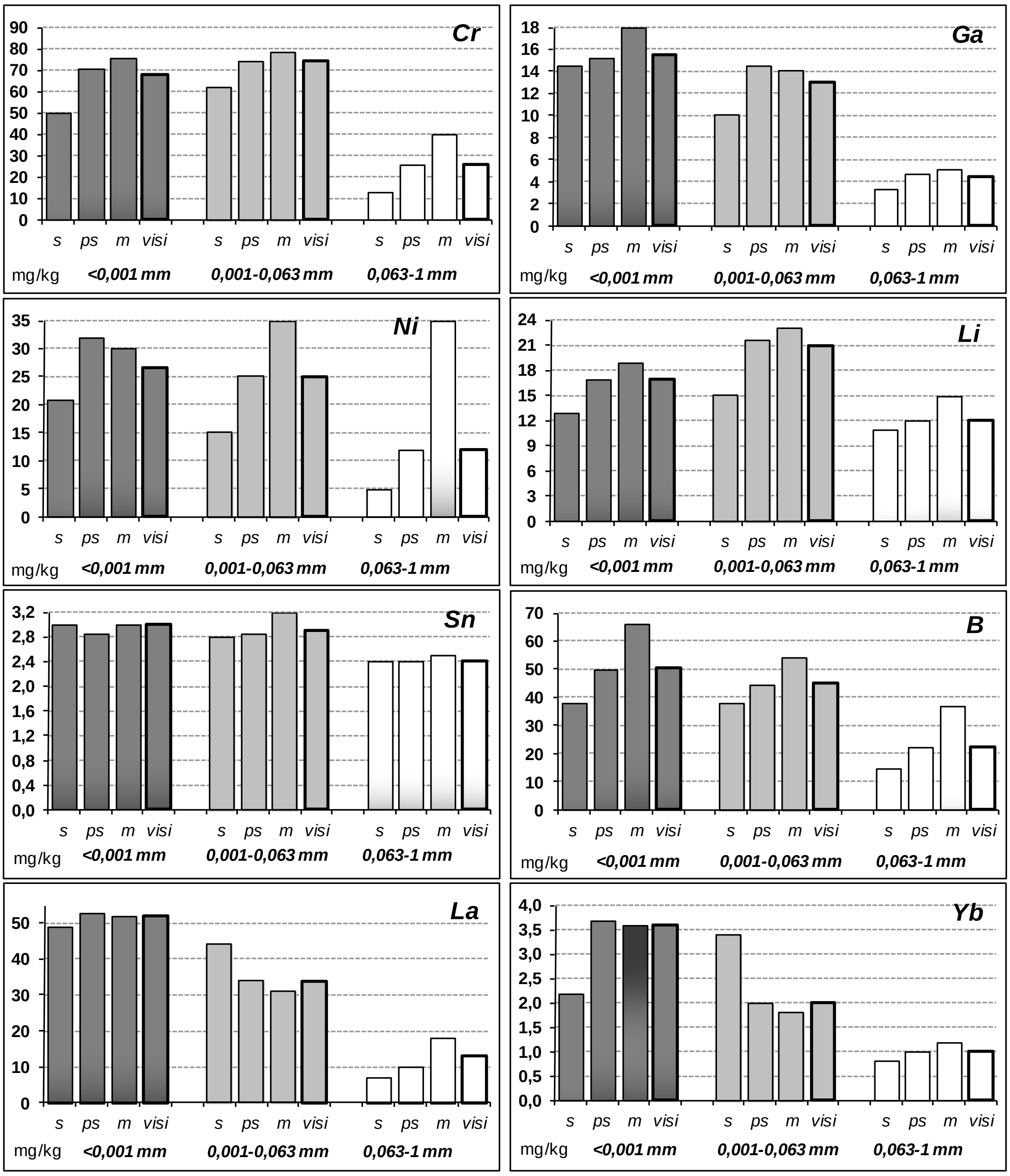


Fig. 3. Median values of the clay and silt fractions elements in clay (<0.001 mm), silt (0.001-0.063 mm) and sand (0.063-1 mm) fractions, examined in the sand (s), sandy loam (ps), loam-clay (m) and the all (visi) analysed samples

Median values of the elements from this group in clay and loam fractions significantly exceeds values in the sand fraction: Cr – accordingly 2.6 and 2.8 times, Ga – 3.7 and 3.1 times, Ni – 2.7 and 2.5 times, Li – 1.4 and 1.7 times, Sn – 1.3 and 1.2 times, B – 2.4 and 2.2 times, Yb – 3.6 and 2.2 times, La – accordingly 4.7 and 3.1 times. The latter three elements (B, Yb, La) can be assigned to the group of clay fraction elements, because their median values in clay fraction significantly exceeds the values in loam fraction – accordingly 1.1, 1.7 and 1.5 times. When elaborating distribution of the total contents of trace elements in different fractions of sand, loamy sand and clay soils it is evident that smallest amounts of all elements from this group in all fractions are found in the sand soil. (Fig. 3).

Dominant in all lithogenous soil types of loam fraction Ag distinguishes by its high contrast (*V* – 286%) and this is caused by characteristics of the element – in the soil it is stronger bound by organic substances than by minerals or sorption ions (Jacobson, 2005). The lowest amount of Ag is in the clay fraction – only one third of loam fraction amount, in sand fraction – only half. Also quantities of element from all fractions are almost the same in the sand, sandy loam and clay-loam soil (Table 2, Fig. 4).

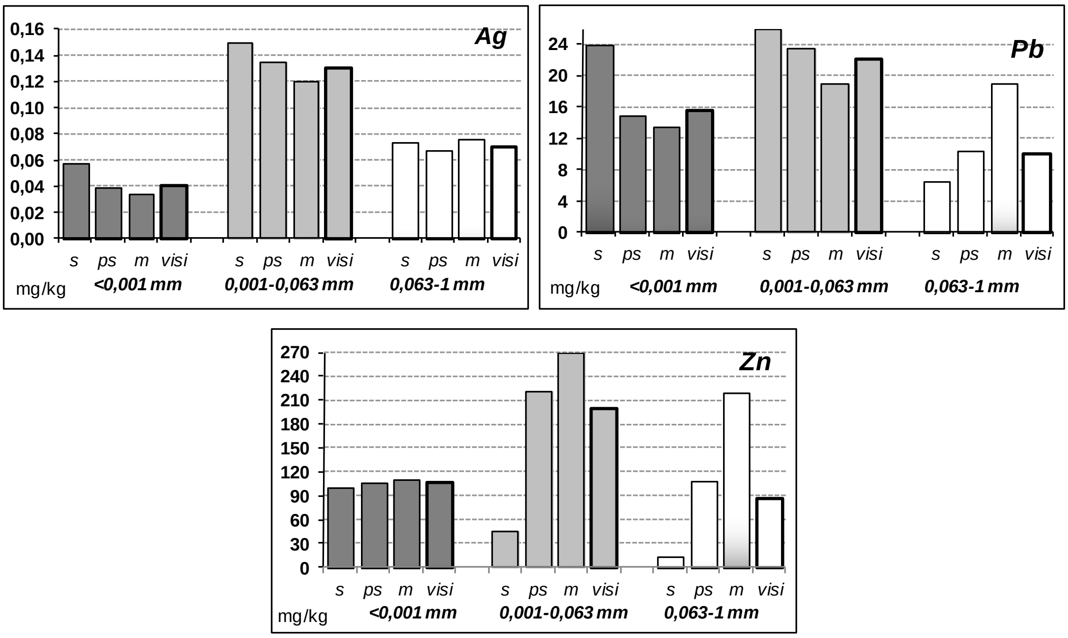


Fig 4. Median values of the silt fraction elements in clay (<0.001 mm), silt (0.001-0.063 mm) and sand (0.063-1 mm) fractions, examined in the sand (s), sandy loam (ps), loam-clay (m) and the all (visi) analysed samples

Zn and Pb can be assigned to the group of silt fraction elements, because their main mineral-bearers in the soil are easy weathering ferrous-magnesium minerals, micas, amphiboles. High diversity of primary minerals in soil with different lithology causes different values of these elements – in clay and silt fractions sand soil is enriched with Pb, while in sand fraction it is clay soil. Largest median values of Zn in loam and sand fractions also were found in the clay soil (Fig. 4).

The highest median amount of Mn was found in sand-gravel fraction, which is eliminated in routine analysis, and ignoring this fraction, Mn can be assigned to elements of loam fraction, associated with clay minerals. But part of element in coarse grained and sand fraction is related with soluble hydroxides and if conditions of migration are changed, they are accumulated in the colmation coatings of large particles of the soil (Fig. 5, 6, Table 2). Existence of several sources for Mn in coarse soil fractions are confirmed by quite high variation coefficient of the element ~150%. In addition to Mn, there were found the highest median amounts of Ba and Sr in the sand-gravel fraction, which are concentrated in carbonaceous soil parent and related resistant to weathering primary minerals (Fig. 5).

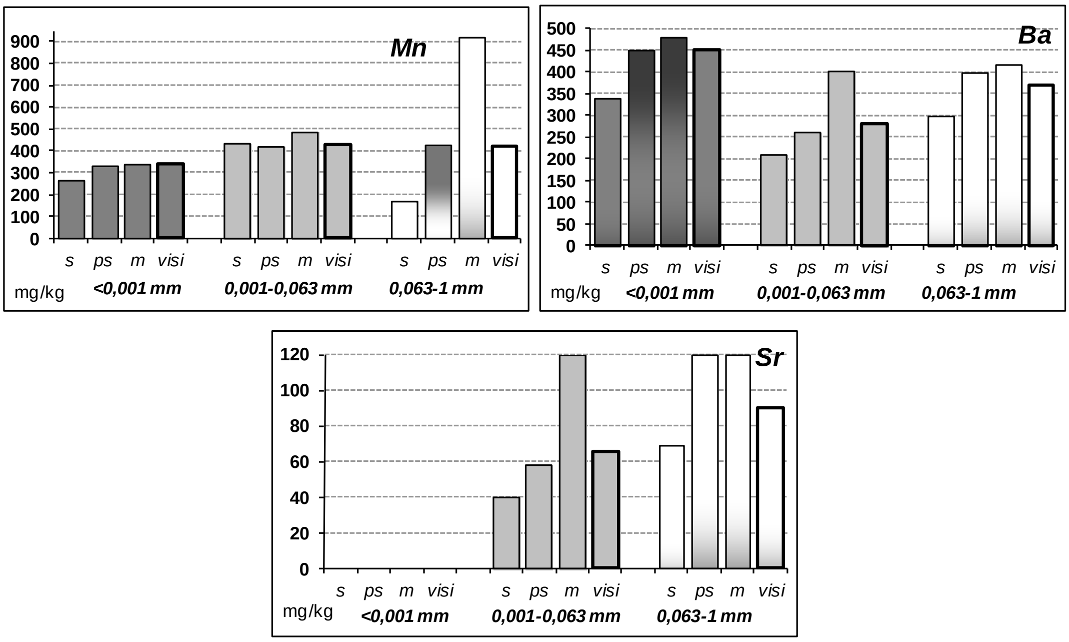


Fig 5. Median values of the coarse sand and gravel fractions elements in clay (<0.001 mm), silt (0.001-0.063 mm) and sand (0.063-1 mm) fractions, examined in the sand (s), sandy loam (ps), loam-clay (m) and the all (visi) analysed samples

Summarizing the results, obtained from chemical analysis of the soil gain size fractions, conclusion can be made that the highest amounts of the trace elements were defined in following soil fractions:

clay fraction (<0.001 mm) – Al, Cu, Mo, Sc, Ti, V; Y, Co, (B, Yb, La);

silt fraction (0.001-0.063 mm) – Ag, Pb, Zn;

clay–silt fractions (<0.001 mm ir 0.001-0.063 mm) nearly evenly distributed – (B, Yb, La), Cr, Ni; Ga, Li, Sn;

sand-gravel (soil skeleton) fraction (> 1 mm) – Mn, Ba, (Sr).

Fig. 6. Accumulation of the iron and manganese hydroxides in the colmation coatings on the calcareous sandstone, Dirvonakiai, Biržai r.

Accumulation coefficients of elements in soil of different lithology. Comparing values of elements, obtained in each fraction of each sample with values of elements in unfractioned sample, accumulation ratios were calculated. That allows to emphasize importance of particular fractions in forming overall chemical composition of the soil, and to indicate elements, quantities of which are regulated not only by lithological composition (Fig. 8–10). Also some bias of laboratory analysis were detected, e.g. while performing grain size analysis in the laboratory, samples probably were contaminated with Zn, as quantities in all lithological soil types of all fractions were 6.7–1.3 times larger than quantity in the non fractional sample, and calculated overall quantity of Zn in non fractioned sample 2,5 exceeded quantity obtained in laboratory. Also likely that contrary to Zn, quantities of Yb in fractions were reduced twice.

Sand soil: most intensive accumulation of all elements, except Ag and Zr, is evident in the finest <0,001 mm clay fraction, where V is 8.3 times, Cu – 7.5 times, Ti – 4.4 times more than in all soil (Fig. 7.). In 0.001-0.063 mm loam fraction most intensive accumulates Cu, it quantity is 5 times greater. In 0.063-1 mm sand fraction accumulation of elements is significantly reduced, only Sc, P, Sn and Ba are accumulated, as in this fraction silicon minerals are dominant, but Si wasn't analysed.

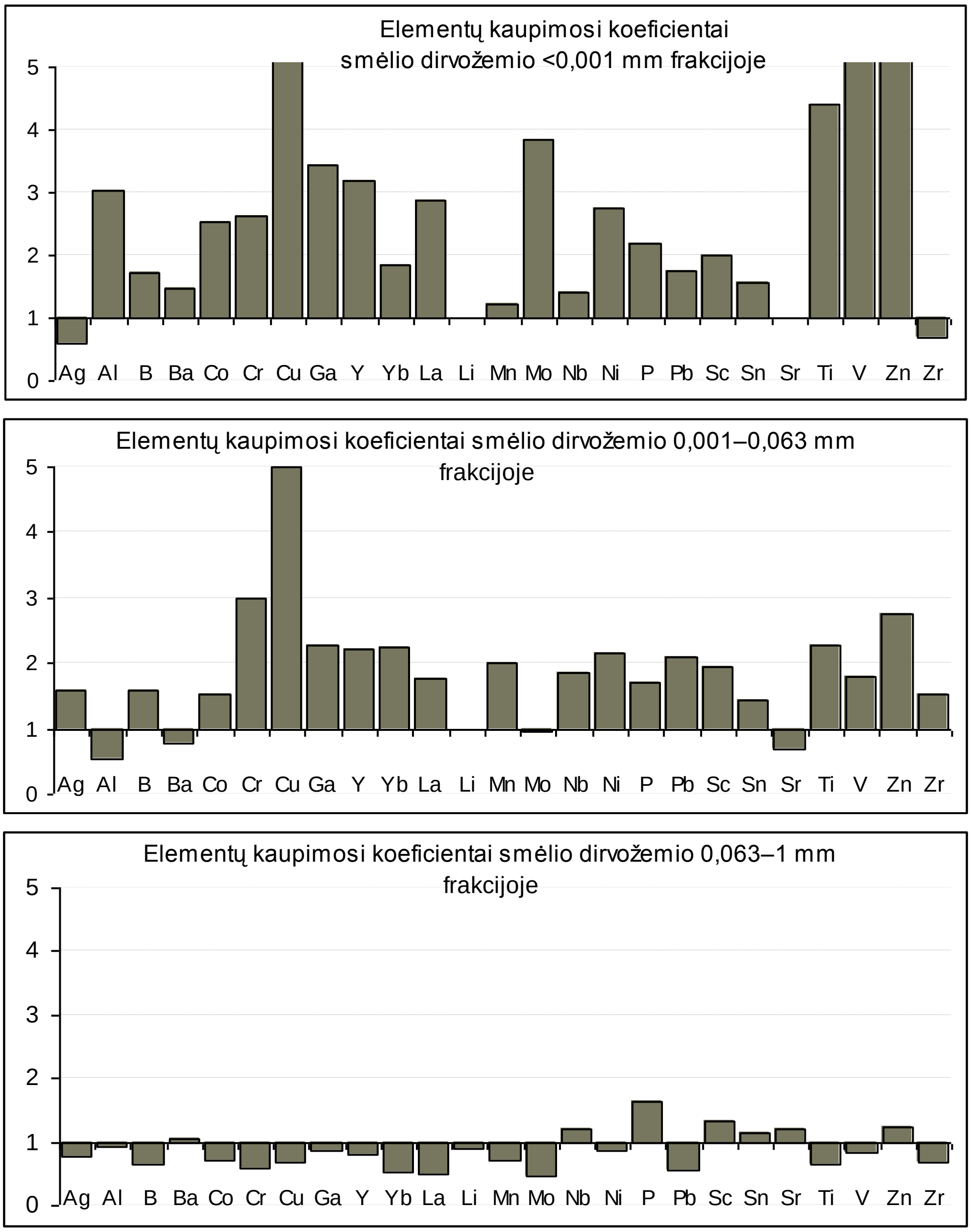


Fig. 7. Accumulation of elements in the different fractions of the sand soil (ratio of element in fraction *vs* in unfractionated soil).

Loamy sand soil: most elements accumulates in the clay fraction, except Ag, Ba, Ba, Co, Y, Li, Mn, Pb, Sn, and most intensive are Mo, V, Al, Ti, Cu, Y, with accumulating rate > 2. The list of elements accumulating in the silt fraction reduces, and accumulating rate reduces – only Ag, B, Cr, Cu, Ga, La, Ni, Pb are accumulated, and in the sand fraction accumulates only Al, Mn, and Sr (Fig. 8).

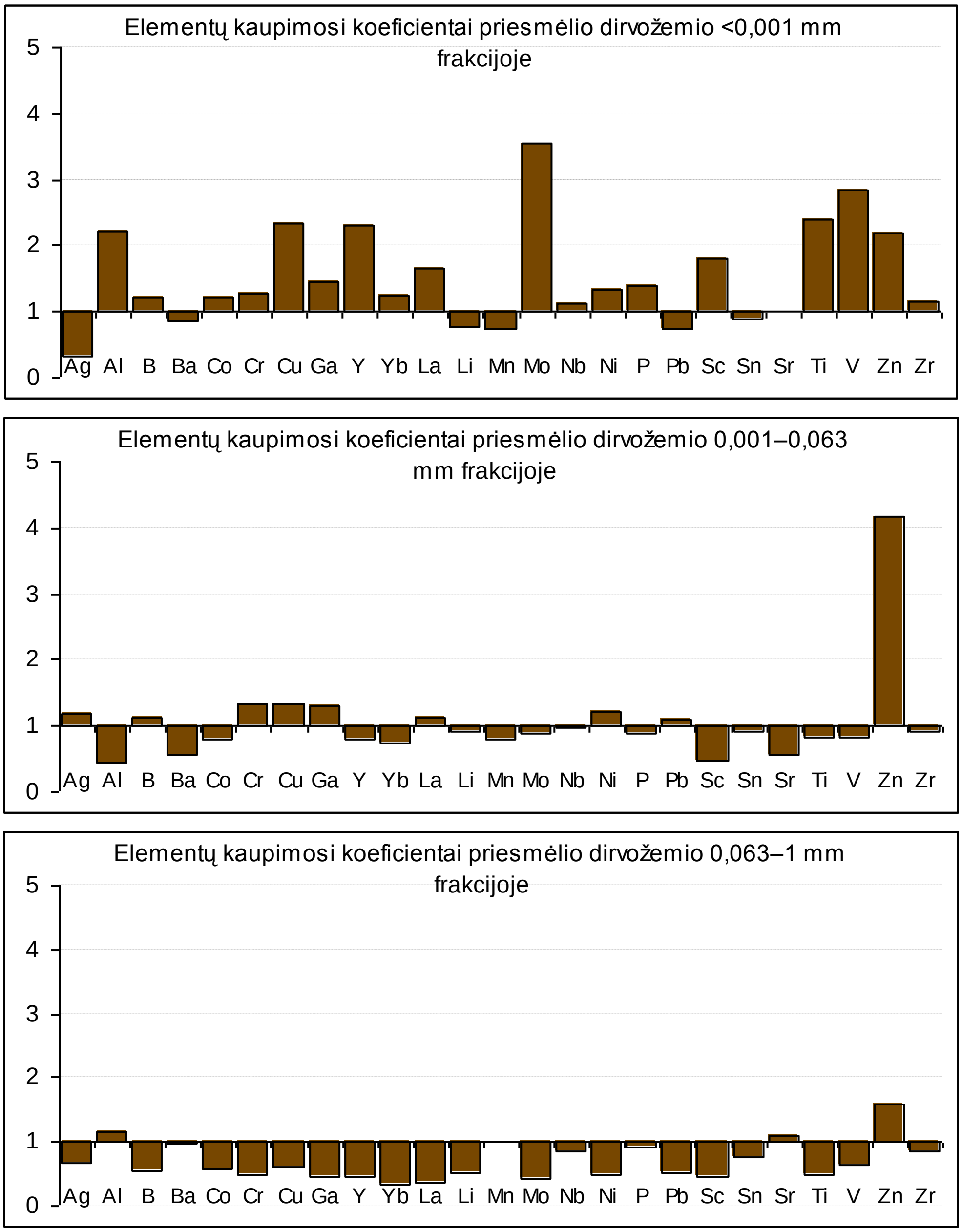


Fig. 8. Accumulation of elements in the different fractions of the loamy sand soil (ratio of element in fraction *vs* in unfractionated soil).

Clay soil: in clay fraction only Cu, Mo, Ti, V, Zn have double quantities comparing to unfractionated soil, while quantities of Ag, Ba, Li, Mn, Pb in this fraction are less than in whole soil. In silt fraction only accumulation of Ag, Cr, Cu, Ga, Pb are significant, in sand fraction accumulates Ag, Co, Mn, Pb, Sr (Fig. 9).

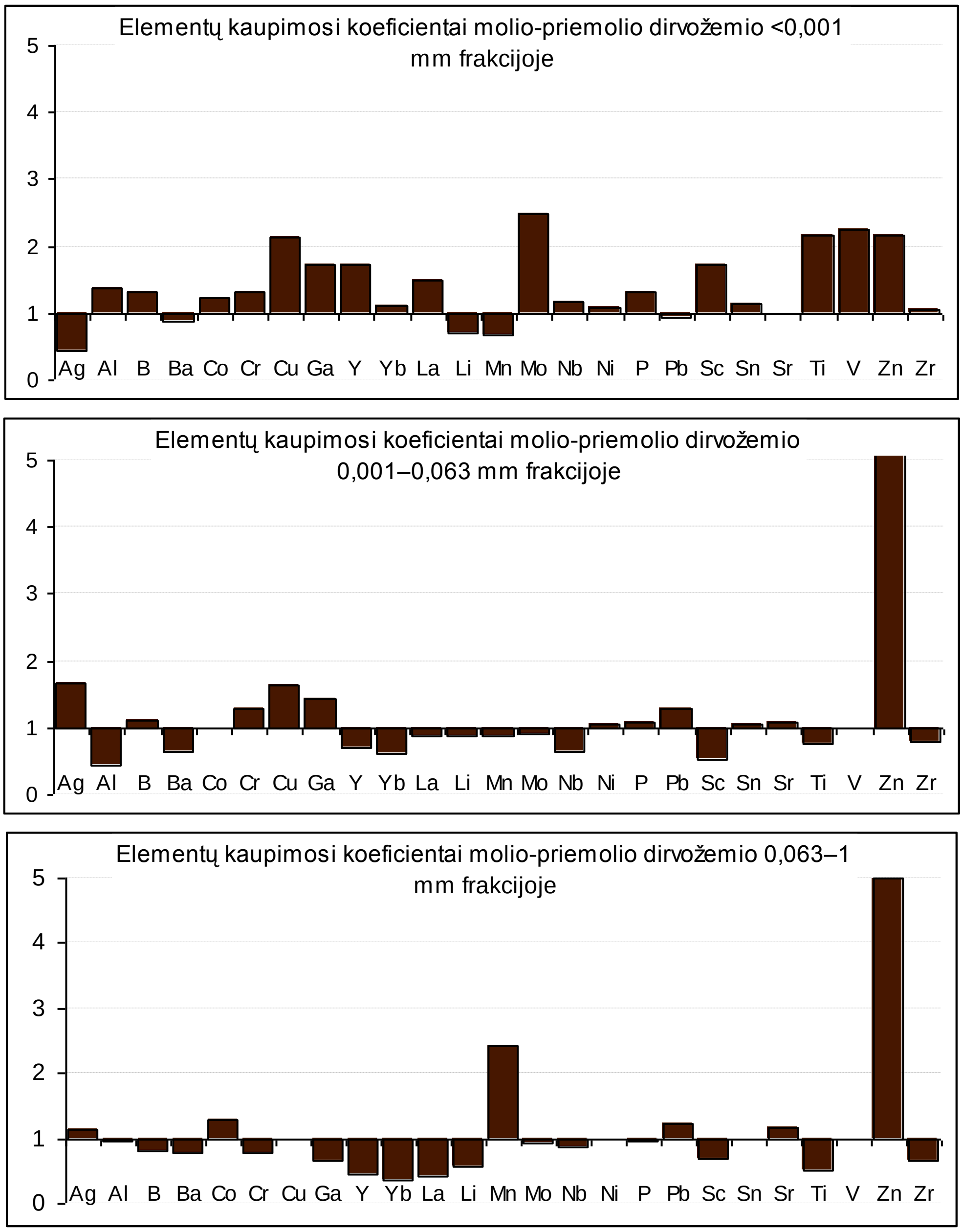


Fig. 9. Accumulation of elements in the different fractions of the loam-clay soil (ratio of element in fraction *vs* in unfractionated soil).

<u>All soils:</u> without splitting to separate lithological groups, trace elements in different grain size fractions are grouped according the accumulation intensity as follows (Fig. 10):

Mo, Cu, V, Ti, Y, Al, La, Sc, Ga, Cr accumulates in the clay fraction, their quantities more than 1,5 times exceeds quantities in whole non fractioned soil;

In silt fraction Zn, Cu, Ga, Ag, Cr, Ni also 1.5 times exceeds quantities in whole unfractioned soil;

In sand fraction only Zn, Sr and Al slightly exceeds quantities in whole non fractioned soil;

Accumulation of all other elements is nearly the same in both clay and silt fractions, only accumulation of B, Co, Yb, P is more intensive in the clay and Mn, Pb is more intensive in the silt fraction.

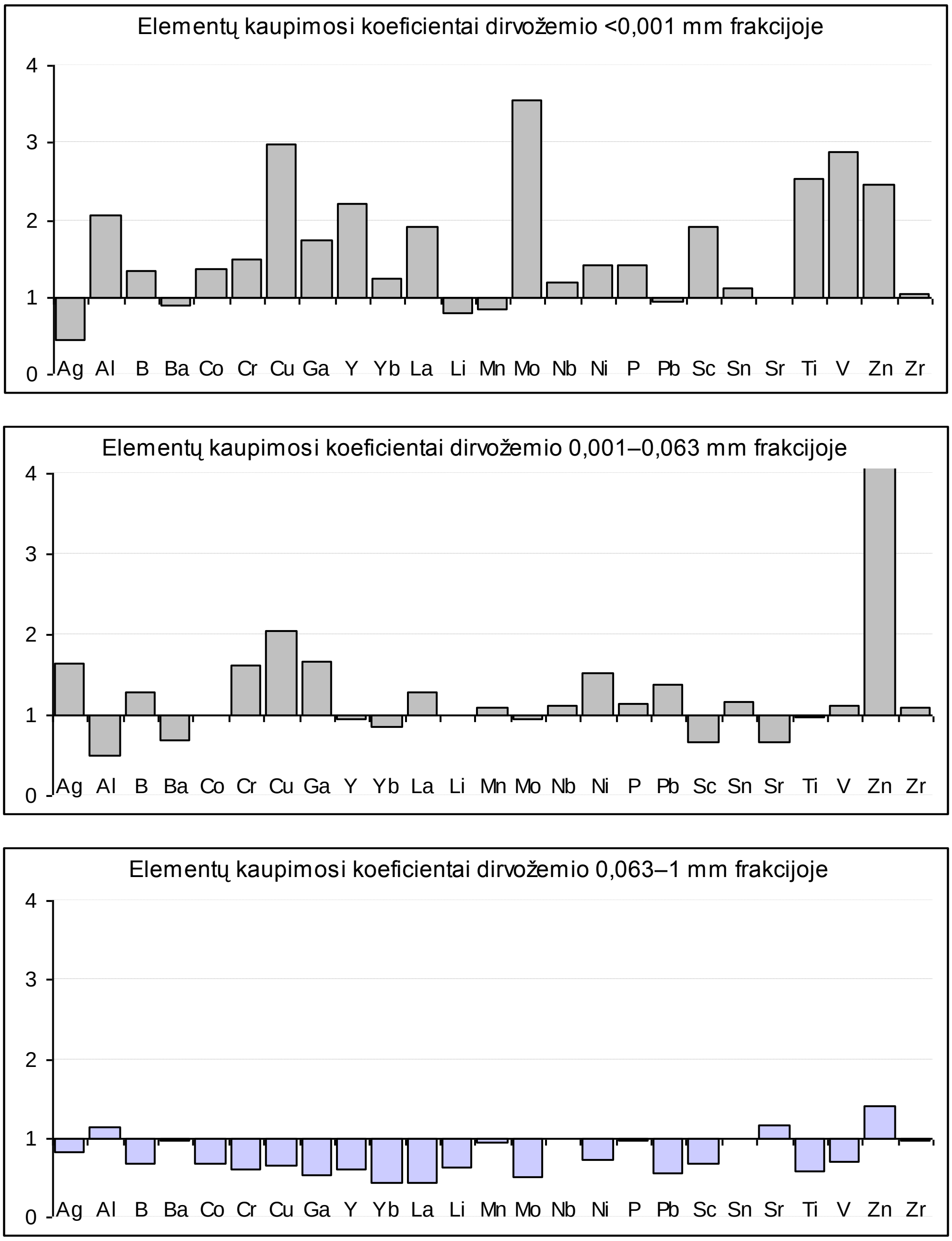
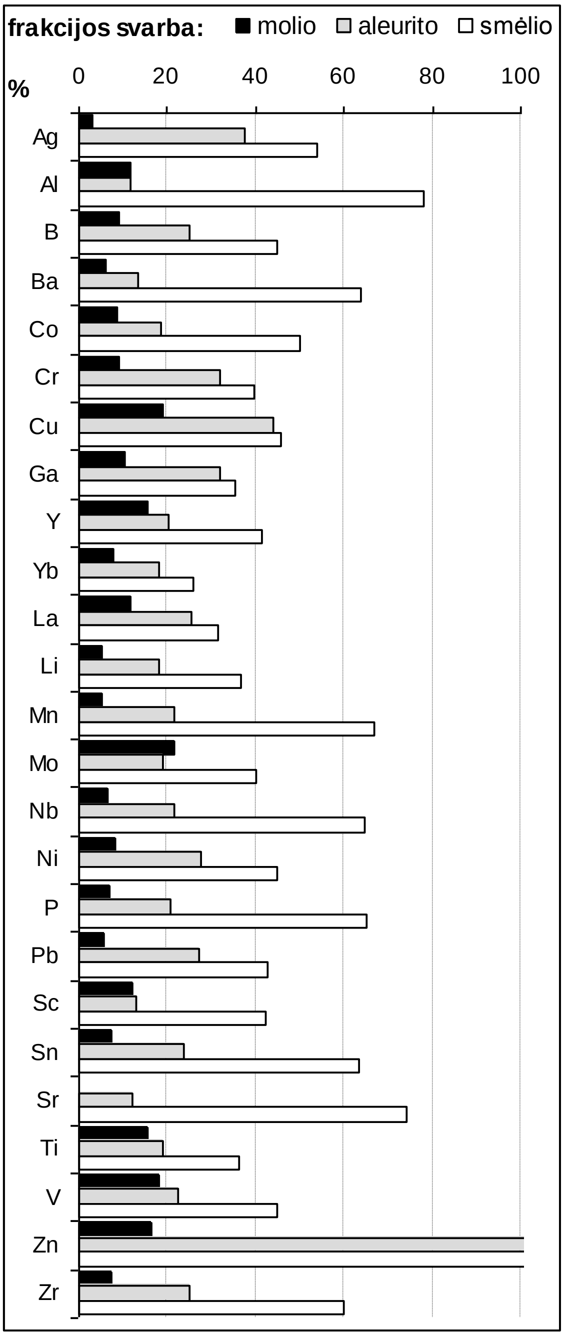


Fig. 10. Accumulation of elements in the different fractions of the all soil samples (ratio of element in fraction *vs* in unfractionated soil).



Assessing accumulation of element in the fraction and amount of fraction in the soil and then comparing it with total content of the element in unfractioned soil, is evident that despite the fact that largest amounts of element were found in the clay fraction, chemical composition of whole Lithuanian soil is formed by the most abundant sand fraction (Fig. 11). Analogous phenomenon was discovered by Berrow and Mitchell in 1991 in soils of Scotland and England, and it was explained by young age of soils and properties of lithological composition of glacial soil parent material – in young soils, formed not *in situ* weathering crust, still dominant coarse sand particles instead of silt, and part of minerals – trace element carriers still are in its primary state, not forming secondary clay minerals.

Fig. 11 Importance of grain size fractions, clay (molio - <0.001 mm), silt (aleurito - 0.001-0.063 mm) and sand (smėlio - 0.063-1 mm) to the total chemical composition of Lithuanian soil, %

Contribution of grain-size fractions to the total chemical composition of soil. Assessing of element values in fractions and amount of fractions in each soil sample, contribution of each fraction to the total chemical composition of soil was obtained in different lithological types of the soil (Table 3).

In the sand soil amount of trace elements unambiguous is dependant on mineral composition of sand fraction. Trace elements contained in clay and silt fractions has no significant influence to total amount, because they amounts less than 25%.

In the loamy sand soil dependence of trace elements from grain size fractions is more complicated. Largest part of Ba, Co, Li, Mn, Nb, P, Sn and Zr is contained in the sand fraction, Zn, Cr and Ga – in silt fraction, while Ti, Mo, Y, Sc and V – in clay fraction. In loamy sand trace elements contained in two fractions often forms the major part of overall quantity: Ag, B, Ni, Pb, contained in silt and sand fractions; La – in clay and silt fractions. Part of Cu is nearly the same in different fractions.

Table 3. Contribution of grain-size fractions to the total chemical composition of soil, %

Frac-tions	Sand soil			Sandy loam soil			Clay-loam soil			All types soil		
	clay	silt	sand	clay	silt	sand	clay	silt	sand	clay	silt	sand
Ag	2,4	11,3	85,3	15,8	37,0	47,4	30,9	36,5	29,6	16,8	34,1	45,7
Al	12,9	4,6	82,3	46,1	8,5	47,2	71,4	8,8	20,9	47,6	7,5	45,9
B	9,2	16,2	73,0	35,4	26,1	31,8	63,3	19,5	13,8	40,2	23,2	33,1
Ba	4,4	3,5	90,2	30,7	14,6	53,5	59,8	16,5	19,3	31,4	13,5	50,8
Co	10,6	6,1	78,6	39,4	23,7	37,9	56,6	16,0	27,7	41,9	16,9	37,5
Cr	11,5	25,2	62,9	33,6	31,9	29,5	64,1	21,8	13,8	40,0	28,1	26,9
Cu	18,7	17,8	48,6	51,0	26,6	19,3	73,0	18,1	10,6	51,9	20,5	19,3
Ga	12,0	14,4	71,5	40,5	32,1	23,3	70,2	21,4	9,7	43,6	26,5	22,9
Y	9,1	14,7	67,7	58,3	16,9	22,7	81,0	9,3	8,2	59,1	14,7	22,4
Yb	6,1	20,7	67,2	52,1	23,7	24,5	76,7	13,1	10,2	52,7	19,1	22,3
La	15,2	23,7	55,1	51,2	26,4	20,2	75,5	13,5	9,0	54,7	22,4	18,6
Li	4,0	7,3	88,3	29,6	30,0	39,4	55,6	23,9	16,3	32,2	24,4	37,7
Mn	6,7	11,5	72,0	23,8	21,9	53,7	34,7	16,9	48,9	24,6	18,8	53,7
Mo	24,5	10,8	62,8	64,2	15,9	19,6	80,9	8,5	8,3	64,6	11,3	18,6
Nb	2,6	10,3	84,1	29,8	19,3	47,1	63,0	15,4	18,9	32,4	17,2	42,9
Ni	11,0	15,8	69,7	38,3	27,5	31,5	53,6	20,4	22,7	39,3	22,7	32,4
P	5,6	4,7	89,0	33,7	26,6	42,8	64,3	15,5	18,3	35,0	18,1	41,4
Pb	10,3	21,0	61,7	24,4	33,5	39,9	47,8	24,0	26,3	29,4	28,6	39,2
Sc	3,7	8,3	78,4	55,0	15,3	25,8	78,8	8,7	11,9	58,0	9,7	23,6
Sn	3,7	9,6	85,5	27,3	24,6	44,1	55,9	19,9	18,4	28,1	20,9	43,5
Sr				0	37,8	62,2	0	100	0		44,4	51,1
Ti	20,3	13,2	62,4	60,4	17,6	21,6	81,7	10,5	9,1	65,4	12,9	19,9
V	22,9	10,1	60,1	57,1	18,0	24,0	77,5	10,7	12,8	58,7	14,2	23,2
Zn	11,1	8,4	60,0	18,1	40,3	28,0	42,0	30,7	28,1	24,6	32,7	37,5
Zr	2,4	15,6	72,2	30,9	19,9	44,5	64,6	16,3	18,8	34,8	17,4	39,2

Values of trace elements, except Ag, Mn and Zn, accumulating in loam-clay soil, forms largest part of the total content, even if the clay fraction isn't dominant. Most important to total content of Zn is silt fraction, Mn – sand fraction. Often parts of trace elements in two fractions are nearly the same: Ag – in silt and sand fractions; Ba, Co, Li, Nb ir Zr – in clay and sand fractions. Part of Pb, contained in different fractions, also Cu in sandy loam, is nearly the same in total quantity.

In conclusion statement can be made, that chemical composition of Lithuanian soil is determined by values of Ti, Mo, Y, V, Sc, La, Yb, Cu, Al, Ga, Co, B, Cr, Ni in clay fraction and values of Mn, Sr, Ba, Al, Ag, Sn, Nb, P, Zr, Pb, Li, Co, Zn in sand fraction. The chemical composition of different lithologic types of soil is formed: in sand soil – by geochemical composition of sand fraction; in loam-clay soil – by geochemical composition of clay fraction, except Ag, Zn, Mn and Pb, since their values are dependent on silt and sand fractions; in loamy sand soil – values of Mo, Ti, Y, V, Sc, Yb, La and Cu in clay fraction, value of Zn in silt fraction, values of Sr, Mn, Ba, Ag, Sn, and Zr in sand fraction.

3.2. Chemical peculiarities of soil parent material and its significance to the soil chemical composition

The all minerogenic soil in Lithuania are formed on the glacial Quaternary sediments of different age – sandy loam and loam till, glaciolacustrine clay and sand, glaciofluvial sand and gravel (Guobytė, 1998). Part of sediments were transposed by the posterior aeolian and fluvial processes, part was covered by the organic peat material. (Guobytė 1998). The geochemical methods were applied in solving the issues of stratigraphy of moraines (Bitinas, Baltrūnas, 1995). Comparative analysis of chemical composition (including trace elements) of soil parent material (horizon C) and surface layer (horizon A) has been recently widely used in identifying the natural and anthropogenic nature of anomalies in weakly polluted territories. The principle of comparison lies at the basis of the geochemical mapping of arable soils in ten countries of the Baltic Sea basin and the integrated geochemical baseline mapping of the European countries initiated by the FOREGS (Reimann et al., 2000, Salminen et al., 1998). Comparative method also was used in this study, trying to generalize the primary spatial distribution of geochemical properties of the soil parent material in Lithuania, and to highlight on this background the secondary soil alteration features due to soil forming processes.

Values and distribution of chemical elements in soil parent material of different lithology. The concentration and distribution of trace elements in the soil parent material, first of all, is predetermined by the lithological composition of deposits (Table 4). The lowest concentrations of almost all trace elements, except Nb, occur in sand, amounts of Ag, Mo, P, Pb, Sn, Sr and Zr are more or less at the same levels in all lithological types of the soil parent material. The highest concentrations of the rest trace elements occur in clays.

Table 4. The content of trace elements in the various types of Quaternary soil parent material, mg/kg

	all types n=294			sand n=98			gravel n=28		
	Md	*X*	*V*	*Md*	*X*	*V*	*Md*	*X*	*V*
Ag	0,050	0,055	40	0,050	0,058	39	0,050	0,052	17
B	39	42	52	20	23	40	24	25	16
Ba	280	303	45	180	213	37	200	210	31
Co	4,80	5,44	62	2,59	2,81	55	3,20	3,34	45
Cr	32,0	34,1	62	14,0	17,7	60	17,0	17,8	37
Cu	8,7	9,1	60	5,0	5,3	63	7,0	6,9	59
Ga	5,00	6,15	60	3,00	3,59	59	3,40	4,11	47
La	24,4	26,8	55	12,0	13,3	53	20,9	24,0	39
Li	13,0	15,0	50	9,5	10,4	31	8,5	10,1	27
Mn	400	414	45	278	298	55	390	423	33
Mo	0,70	0,79	30	0,70	0,64	24	0,70	0,77	19
Nb	13,7	13,4	38	15,0	16,0	33	10,0	9,9	51
Ni	15,0	16,5	63	7,4	8,6	54	10,0	10,0	25
P	539	631	54	498	548	40	740	810	46
Pb	9,7	10,7	45	7,6	8,9	48	8,3	9,3	40
Sc	5,0	5,5	66	2,0	2,4	57	2,0	2,9	40
Sn	1,8	2,0	34	1,5	1,7	21	1,5	1,6	19
Sr	100	105	26	80	91	25	120	122	25
Ti	1894	2165	59	1247	1406	48	840	1005	48
V	28,0	35,6	74	13,0	15,8	71	14,0	17,4	41
Y	15,0	16,0	59	8,4	9,3	64	11,9	12,1	48
Yb	1,39	1,72	61	0,90	1,02	67	0,90	1,01	48
Zn	25,0	29,1	50	25,0	20,6	45	25,0	25,3	28
Zr	194	211	49	192	218	60	129	150	55

The concentrations of V and Sc in clays are even five times higher than as in sands; Co, Cr, La, Ni – four times; Ba, Cu, Ga, Ti, Y, Yb – three times. The trace element composition of the loam is ‘poorer’ than that of the clay, whereas the loamy sand is, respectively, 'poorer' than loam. The content of the fine-grained size fraction in the soil-forming deposits is the main cause of the described distribution pattern – the concentrations of elements related to the silt and clay fractions increase in proportion to the content of the fine-grained size fractions (Kadūnas, Gregorauskienė, 1999).

Table 4:extention. The content of trace elements in the various types of the Quaternary soil parent material, mg/kg

	loamy sand n=74			loam n=69			clay n=25		
	Md	*X*	*V*	*Md*	*X*	*V*	*Md*	*X*	*V*
Ag	0,050	0,054	40	0,050	0,058	46	0,050	0,048	27
B	35	37	27	48	51	31	66	72	42
Ba	300	331	43	369	373	31	480	472	19
Co	5,40	5,82	36	8,15	8,35	35	10,15	9,85	31
Cr	36,0	37,9	30	51,8	53,3	36	54,0	56,5	30
Cu	10,5	10,8	34	12,0	12,2	50	15,0	14,0	41
Ga	5,80	6,21	41	9,21	9,38	35	9,67	10,29	37
La	26,0	28,8	34	31,5	31,9	38	47,5	44,6	36
Li	15,5	15,8	43	19,5	20,5	38	24,3	22,0	35
Mn	430	467	38	450	487	35	520	530	22
Mo	0,70	0,82	21	0,84	0,90	33	0,95	0,96	25
Nb	13,3	11,9	28	13,7	13,2	38	10,0	11,0	32
Ni	17,0	18,1	32	23,9	25,3	42	28,0	28,6	36
P	591	600	44	566	711	64	580	615	31
Pb	9,0	10,7	39	13,0	13,8	39	12,0	12,9	25
Sc	6,0	6,3	39	8,2	8,7	34	11,0	10,1	33
Sn	2,0	2,0	32	2,3	2,3	29	2,2	2,6	42
Sr	120	112	19	104	106	29	120	120	17
Ti	2175	2215	31	2919	2908	36	4500	4167	35
V	33,5	37,4	46	55,7	58,9	38	63,8	68,1	43
Y	16,8	17,0	46	19,6	21,8	41	25,0	25,5	29
Yb	1,50	1,83	48	2,57	2,48	37	2,80	2,65	37
Zn	25,0	27,9	30	33,7	38,2	43	45,0	46,6	40
Zr	210	226	35	196	204	31	200	205	24

The content of fine-grained material influences the composition of the soil-forming deposits also indirectly – through the genesis. The roughly sorted and less washed out the glaciofluvial sand of variable grain-size in Molėtai area is more enriched by the trace elements than the well washed out glaciolacustrine fine-grained sand of Katra area, redeposit by the later aeolian processes. The concentrations of elements related to clay fraction – Co, Cr, Cu, Mo, Ni, V, Y – in the glaciolacustrine Katra sand are half the values of glaciofluvial sand in Molėtai, whereas the concentration of La, Sc and Zn in most cases are below the detection limit. Yet, it displays considerably higher concentrations of Zr and Nb, i.e., elements related to the weathering resistant minerals.

Table 5. The content of trace elements in the Quaternary sand of soil parent material, mg/kg

	sand of various genesis *, n=15			glaciofluvial sand, (III), n=60			glaciolacustrine sand, (I), n=20		
	Md	*min*	*max*	*Md*	*min*	*max*	*Md*	*min*	*max*
Ag	0,069	0,035	0,169	0,050	0,050	0,090	0,043	0,030	0,050
B	22,8	15,9	60,8				18,0	13,0	26,0
Ba	239	119	529	180	180	600	200	150	340
Co	3,39	1,79	10,29	3,00	0,80	6,40	1,60	1,30	2,10
Cr	19,9	11,0	78,4	17,0	2,3	45,0	9,4	8,0	13,0
Cu	5,0	1,0	10,8	7,0	2,0	14,0	1,2	0,8	2,0
Ga	6,0	2,2	18,6	3,1	1,6	6,2	2,4	1,6	3,1
La	18,9	8,9	37,2				7	10	15
Li	12,9	9,9	22,5	10,0	8,0	21,0	8,2	5,2	13
Mn	296	160	549	330	150	1000	105	80	140
Mo	0,66	0,40	0,92	0,70	0,70	1,00	0,30	0,43	0,66
Nb	12,9	5,6	21,0				20,0	9,0	28,0
Ni	7,0	4,5	28,4	9,0	3,0	23,0	3,9	3,4	10,0
P	448	297	882				500	300	900
Pb	12,9	6,9	33,3	7,6	5,0	12,0	6,8	5,4	28,0
Sc	2,3	0,8	6,7	2,0	2,0	7,5	1,5	0,0	0,0
Sn	1,9	1,4	3,0	1,5	1,5	2,5	2,0	1,4	3,0
Sr	64	43	102	100	80	150	86	62	120
Ti	1485	771	4312	1300	430	4400	1050	800	1800
V	17,9	9,4	78,4	14,0	6,0	47,0	7,8	5,0	10,0
Y	11,0	5,0	31,9	8,7	4,0	22,0	0,6	0,4	0,8
Yb	1,4	0,5	5,3	0,7	0,4	2,5	1,0	0,7	1,2
Zn	11,0	9,9	62,7	25,0	25,0	35,0	8,0	0,0	0,0
Zr	149	89	548	175	43	620	275	90	580

* - complete soil profiles of the Geochemical atlas of Lithuania and Foregs atlas
I - Katra area (Gregorauskiene, 1999)
II - Molėtai area (Guobytė et al, 1995)

The genesis of sediments in the trace element composition of the loamy sand till is not so well expressed as in the sand (Table 6). Comparison of loamy sand till of different genesis and different glaciation phases shows that the till of marginal formations of the South Lithuanian phase of the Baltic stage is richest in trace elements. It contains the highest average concentrations of many elements – Ag, B, Co, Cr, Cu, Ga, La, Li, Nb, Ni, P, Sc, Sn, Ti, V, Zn. The loamy basal till of the North and Middle

Lithuanian phases in the Biržai area contains the highest average concentrations of Ba, Sr, La, Mn, Mo, Y, and Zr, what may be taken as an implication of the stronger influence of calcareous coarse fragments in these deposits on the trace element composition.

Table 6. The content of trace elements in the soil parent material of the Quaternary loamy sand till, mg/kg

	loamy sand of various genesis*, n=10			loamy sand of basal till, (IV), n=17			loamy sand of marginal till, (II), n=44		
	Md	*min*	*max*	*Md*	*min*	*max*	*Md*	*min*	*max*
Ag	0,074	0,039	0,136	0,030	0,020	0,054	0,050	0,050	0,090
B	40,4	24,7	52,6	33,0	23,0	56,0			
Ba	427	146	1079	400	90	500	300	180	660
Co	9,64	6,70	11,69	5,60	4,30	7,40	4,90	1,30	12,00
Cr	51,6	34,4	81,5	37	27	50	34	16	52
Cu	13,1	9,8	19,4	6	2	8	12	3,5	20
Ga	9,6	6,7	14,1	7,4	5	9,2	4,5	2,4	8,2
La	30,4	21,4	52,4	26,0	18,0	30,0			
Li	21,9	10,8	32,4	16,0	9,0	27,0	12,5	8,0	40,0
Mn	540	344	1169	460	400	660	400	270	1400
Mo	0,92	0,60	1,36	0,92	0,80	1,25	0,70	0,70	1,20
Nb	14,1	10,7	16,8	9,0	4,5	15,0			
Ni	22,4	14,8	39,0	16,0	11,0	17,0	16,0	9,0	32,0
P	483	263	1380	600	350	700			
Pb	16,5	10,8	27,2	11,8	11,0	16,0	8,1	6,0	15,0
Sc	6,7	4,9	13,6	7,3	4,0	8,4	5,8	2,0	12,0
Sn	2,6	1,5	4,3	1,4	1,1	1,7	2,0	1,5	4,0
Sr	80	69	111	110	100	150	120	80	160
Ti	2965	2366	5043	2300	1600	2700	1900	900	3600
V	68,0	30,4	89,6	35,0	24,0	40,0	30,5	12,0	68,0
Y	17,6	2,3	54,3	23,0	21,0	30,0	15,0	7,0	28,0
Yb	2,6	2,2	4,7	2,5	1,2	3,5	1,2	0,7	2,9
Zn	36,0	19,4	62,4	25,0	15,0	30,0	25,0	25,0	45,0
Zr	220	175	331	220	120	540	210	130	420

* - complete soil profiles of the Geochemical atlas of Lithuania and Foregs atlas
II - Molėtai area (Guobytė et al, 1995)
IV - Biržai area (Gregorauskiene, Putys, 2001)

The loamy till of marginal formations of Baltic stage in Molėtai area contains considerably lower concentrations of TE than the younger loamy till in Biržai area and the loamy till of similar age on the Lithuanian–Polish border zone. Especially high differences are seen in the concentrations of elements – Co, Ga, Li, V, and Zn – associated with the clay fraction. Their concentrations in the loamy till of Molėtai area are half the concentrations in loamy till of Lithuanian–Polish border zone, which is of the same genesis and, partly, of the same time. The differences of the lithological composition of loamy tills in the mentioned areas account for the mentioned values: the loamy till of Molėtai' marginal formations contain a greater portion of sand, Biržai' loamy till – a greater portion of silt, and loamy till in the Lithuanian–Polish border zone – a greater portion of clay..

Table 7. The content of trace elements in the soil parent material of the Quaternary loam till, mg/kg

	loam of various genesis*, n=36			loam of basal till, (IV), n=7			loam of marginal till, (III), n=11			loam of marginal till, (II), n=15		
	Md	*min*	*max*	*Md*	*min*	*max*	*Md*	*min*	*max*	*Md*	*min*	*max*
Ag	0,069	0,030	0,206	0,043	0,034	0,054	0,056	0,038	0,067	0,05	0,05	0,07
B	40,4	21,8	94,4	42	35	68	48	25	96			
Ba	437	187	614	500	290	580	428	213	528	340	200	700
Co	10,1	4,7	17,2	8	5,4	10	8,6	5,3	13,5	4,7	3	11
Cr	52,9	27,7	153,3	50	40	69	55	30	83	35	27	52
Cu	12,6	5,8	49,8	6	3	14	9,8	6,8	21,1	11	7	15
Ga	9,6	6,1	18,7	9	7,4	11,5	12,4	6,5	16,3	5,2	3,5	6,6
La	35,4	2,9	67,1	39	23	56	21,3	14,6	44,8			
Li	22,4	9,3	44,5	18	14	27	22,4	12,7	35,6	14	8	25
Mn	556	262	1423	620	530	680	428	332	461	360	280	760
Mo	0,9	0,6	2,2	1,05	0,92	1,3	0,65	0,51	0,9	0,7	0,7	1,1
Nb	14,1	4,9	31,6	9	5	11	14	11	16			
Ni	23,7	10,4	80,5	20	15	29	27,9	16,6	40,4	17	14	28
P	483	216	2408	500	400	700	642	293	2114			
Pb	14,1	9,8	34,7	14	12	16	14	9	23	8	6	11
Sc	8,5	3,4	17,3	9,4	7	12	9,7	4,2	14	7	3	9,5
Sn	2,6	1,1	4,4	1,65	1,4	2,8	2,6	1,5	3,1	2	1,5	3,5
Sr	80,3	38,2	172,0	135	110	165				120	80	160
Ti	3081	1879	7193	3000	2500	4300	3171	399	4192	1900	1500	4000
V	68,0	18,8	115,0	46	38	80	61	36	103	33	21	66
Y	17,6	11,6	49,1	23	19	25	19,5	10,7	40,1	13	8	30
Yb	2,9	1,4	4,5	2,6	2,2	3,6	2,6	1,6	4,3	1,2	0,7	2
Zn	37,6	9,9	88,4	36	20	70	52	19	59	25	25	33
Zr	217	66	403	230	180	300	191	125	233	190	120	300

* - complete soil profiles of the Geochemical atlas of Lithuania and Foregs atlas
II - Molėtai area (Guobytė et al, 1995), III - "Jotvingiai belt" area (Lis et al., 1997)
IV - Biržai area (Gregorauskiene, Putys, 2001)

The glaciolacustrine clays of North and Middle Lithuanian phases in the Biržai area are characterized by higher average concentrations of many trace elements – Co, Cr, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Sc, Sn, Ti, V, Yb, and Zn – than the clay of the Baltic stage in Molėtai area, that with a higher portion of sand. Only the average concentrations of Ag, Cu, Cr, Y, and Zr – related to the increased amount of sand fraction in the latter, are higher than in the Biržai area.

Table 8. The content of trace elements in the soil parent material of the Quaternary glaciolacustrine clay, mg/kg

	clay of various genesis *, n=5			glaciolacustrine clay, (IV), n=10			glaciolacustrine clay, (II), n=10		
	Md	*min*	*max*	*Md*	*min*	*max*	*Md*	*min*	*max*
Ag	0,055	0,039	0,064	0,038	0,025	0,048	0,050	0,050	0,090
B	64,4	54,1	66,0	91,0	31,0	125,0			
Ba	503	312	580	490	400	580	460	280	660
Co	11,1	10,2	14,1	11,3	5,8	14,0	9,2	4,3	16,0
Cr	55,1	44,9	66,0	73,0	32,0	88,0	53,5	32,0	94,0
Cu	14,5	7,7	22,3	13,5	4,0	17,0	16,0	7,0	30,0
Ga	10,7	9,7	16,5	13,5	6,2	15,0	8,2	4,6	16,0
La	38,8	32,8	58,0	55,0	14,0	62,0			
Li	25,1	18,5	27,1	29,0	13,0	36,0	16,5	8,0	26,0
Mn	513	387	582	640	490	680	480	320	760
Mo	0,95	0,78	0,97	1,13	0,80	1,50	0,70	0,70	1,10
Nb	14,5	6,8	16,5	10,0	5,4	14,0			
Ni	32,8	24,4	38,0	37,0	13,0	45,0	27,0	13,0	48,0
P	570	386	776	700	350	900			
Pb	10,7	9,7	16,5	14,5	10,0	19,0	12,0	8,0	20,0
Sc	10,6	1,1	15,7	11,5	5,0	14,5	11,0	6,0	13,0
Sn	1,9	1,7	3,0	3,0	1,4	5,5	2,0	1,5	4,0
Sr	125	104	151	113	94	165	115	100	140
Ti	4637	3705	6270	4700	1750	5300	4150	1600	7200
V	72,2	61,8	116,4	94,0	33,0	120,0	55,0	21,0	100,0
Y	29,9	25,1	42,8	24,0	18,0	26,0	25,5	10,0	34,0
Yb	2,9	2,6	5,7	2,9	1,4	3,5	2,3	0,8	3,7
Zn	62,4	24,2	76,0	48,0	24,0	76,0	40,0	25,0	80,0
Zr	242	176	304	170	130	290	205	150	280

* - complete soil profiles of the Geochemical atlas of Lithuania and Foregs atlas
II - Molėtai area (Guobytė et al, 1995) IV - Biržai area (Gregorauskienė, Putys, 2001)

Element associations in the different lithological types of soil parent material. Soil parent material of different lithological compositions has unique associations of elements linked of different strengths of relationship.

In soil parent sand material of various genesis, the main association comprised of elements, related to clay and silt fractions, and its core consist of elements, related to clay minerals – Li-Ni-Zn-V-Cr-Cu-Ga-Co-Yb-Ti (Fig. 12).

Association core elements with very strong positive relationship (correlation coefficients r = 0.9–0.8), Sc-Mn-Y-La-B correlates quite strong with core elements and between each other (r > 0.7). Moderately correlated silt fraction elements (r = 0.5–0.4) aggregates to separate association Pb-Mo-Ag, behalf its strong bonds to Pb, Sn also joins this association. Ba has weak but positive relations to all elements of both associations and forms its “own association”. Sr-P and Zr-Nb from coarse grained fraction are moderately related between each other and has negative correlative relations with most elements from former three associations, so they forms separate association with negative factor load.

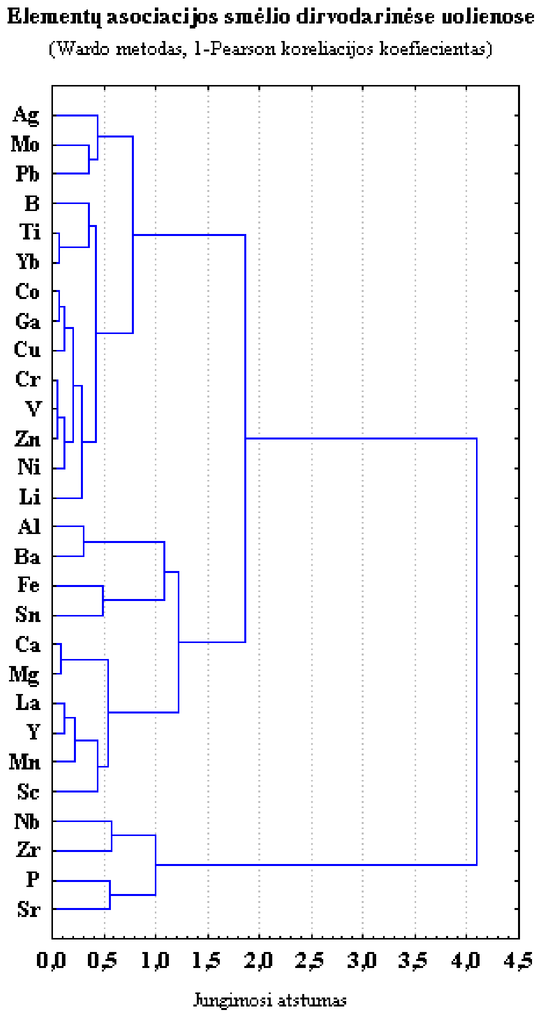


Fig. 12. Dendrogram of the element associations in the soil parent sand material.

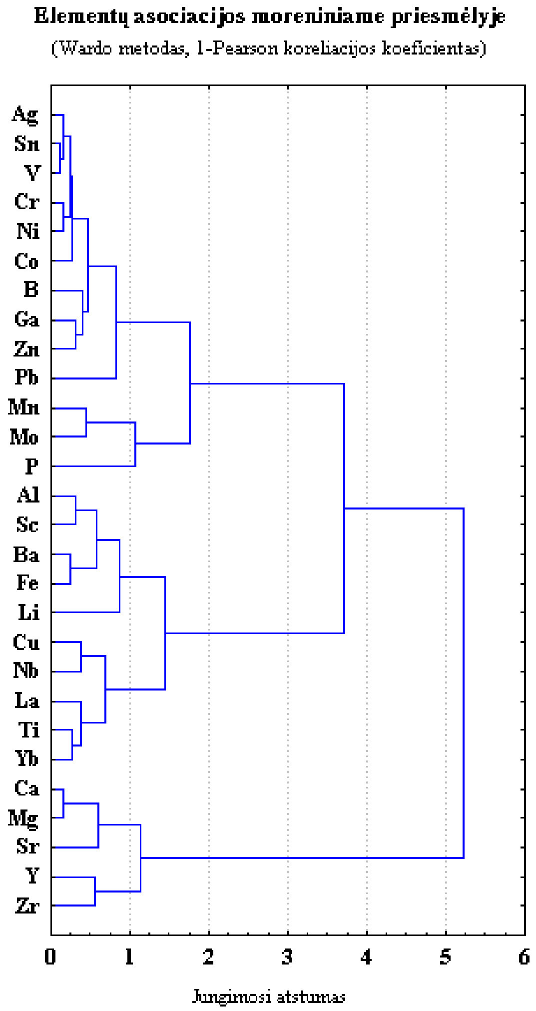


Fig. 13. Dendrogram of the element associations in the soil parent loamy sand.

In the loamy sand correlation among trace elements is considerably weaker, associations of elements are dissimilated. Elements with quite strong relations (r = 0.7) Zn-Ga-B-Co-Ni-Cr-V-Sn-Ag forms association of silt-clay fractions (Fig. 13). Pb has moderate correlation to this fraction and with association elements of clay fraction Yb-Ti-La-Nb-Cu-Li-Sc-Ba, which relations between each other and with the first association varies from weak to moderate (r = 0.6–0.3).

Barium, same like in the sand soil parent, has weak correlation relations with elements of both associations, except Sc. Zr-Y-Sr and P-Mo-Mn has negative correlation with most elements and forms two slightly related associations of the sand and coarse sand. In the loamy sand lithological heterogeneity, absence of one distinctly dominant fraction, is evident by weak relationships between trace elements and undistinguished associations of elements.

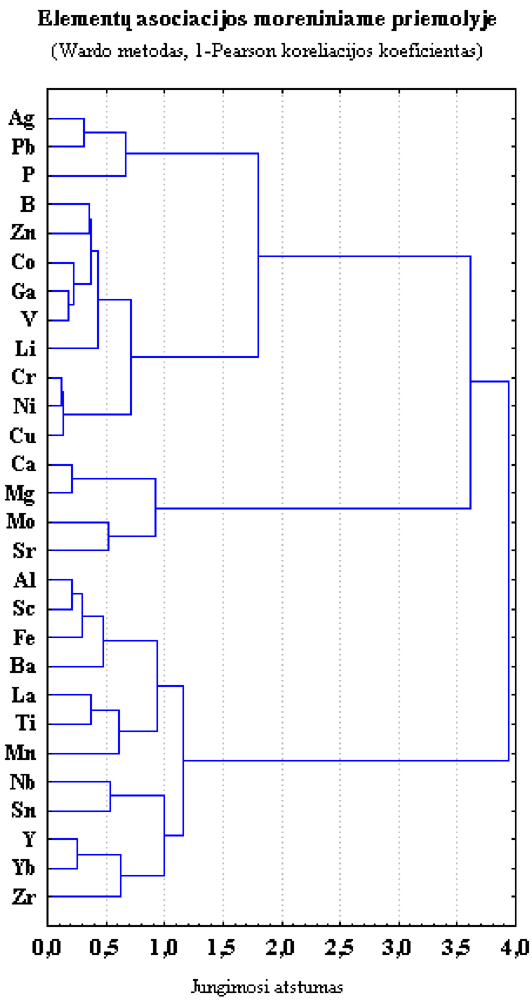


Fig. 14. Dendrogram of the element associations in the loam till soil

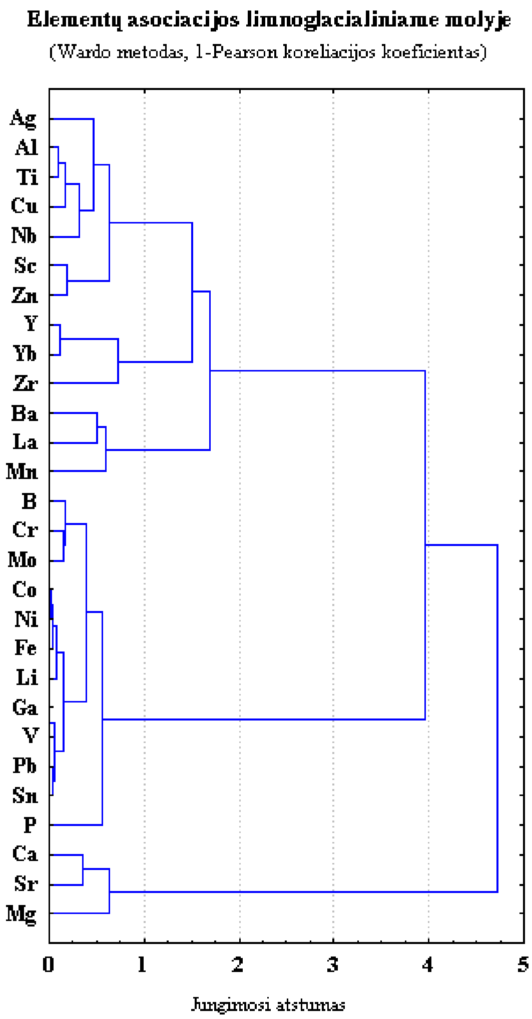


Fig. 15. Dendrogram of the element associations in the glaciolacustrine clay.

In the loam till relations between elements, related to clay minerals, are stronger and they forms main association, with two cores Cu-Ni-Cr and Li-V-Ga-Co-Zn-B (Fig. 14). Elements related with sand and coarse grained material forms appropriate associations Sn-Nb-Mn-Ti-La and Zr-Yb-Y-Sc-Ba, members of which has quite strong bonds between each other (0.7–0.5) and moderate bonds (0.6–0.3) to elements of clay fraction. Elements Sr-Mo-P-Pb-Ag, which are related to silt fraction and have especially weak and negative correlation with most elements, forms separate association.

In the glaciolacustrine clay are dominant trace elements, related to clay fraction. Core of the association is formed of Sn-Pb-V-Ga-Ni-Co, which are especially strong correlated (correlation coefficients = 0.99–0.97) and they are strongly related (0,9–0,8) to other members of association Li-Cr-Mo-B (Fig. 15). Zn-Sc-Nb-Ti-Cu elements are also related to clay fraction, but they have more fragile relations between each other and to elements from core of association (0.6–0.7), so they form separate association. Mn-La-Ba association comprised of elements, that are related to sand fraction and has weak but positive relations with elements from clay fraction associations. Bonds between elements related to silt fraction Sr-Zr-Yb-Y-Ag are moderate (r = 0.8–0.4), but they are often negative to other elements.

3.3. Impact of natural and anthropogenic processes on the soil profile chemical alteration

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. more or less uniform parent material In fact, not only vertical but also horizontal (spatial) variation of chemical elements of soils is apparent and it means that variations should also be interpreted in the light of pedochemical processes like podzolization, lessivage, gleyfication and humification (Gregorauskiene, 1997).

The element depletion and podzolization at the same time are apparently observed in the soil profiles developed on the marginal till formations of different age on the East Baltic and Žemaitija Highlands. The element depletion in the freely drained cultivated Albic Luvisol, developed on the marginal till of the Baltic stage of last Weichselian glaciation, in East Lithuania, is also recognized by pH_{H2O} values. The latter values indicate that very alkaline conditions are in the parent material, while neutral-subacid conditions are in the upper part of soil profile (Table 9). 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.

Table 9. Total contents of some elements and parameters in soil profile No. 33, (*Albic Luvisol*)

Horizon depth, cm	Tex-ture	pH	LOI %	Fe %	U ppm	Ba ppm	As ppm	Sc ppm	Cu ppm	Co ppm	Mn ppm
A_p 0-27	ps	6.7	4	1.07	2.6	317	2.6	4.80	7,68	5,95	461
AE 27-35	p_1	6.35	1.6	1.56	2.2	443	3.6	6.40	13,8	6,89	315
B_s 35-64	p_2	6.65	3	2.64	3.0	543	4.7	8.73	33,0	11,64	563
C_k 64-100	p_2	8.7	1.8	1.54	2.8	196	4.1	5.50	25,5	13,26	511

Podzolization and gleyfication simultaneously are reflected in the soil profile of Carbi-Gleyic Podzol, formed on the binary glaciolacustrine sand of the South Lithuania stage of Late Weichselian glaciation. Under sand, at the depth of 80 cm, is layer of the gleyed till with the weathered micas, granites and the bullet–like hard iron concretions. Layer was characterized as a soil BC_{sg} horizon. In soil profile is clearly seen the primary lamination of the glaciolacustrine soil parent material, which is accentuated even more because of an unstable soil moisture regime, consequent on the seasonal Nemunas River floods. The floods change the level of ground water in soil and oxidizing–reducing conditions, and respectively, the vertical redistribution of chemical elements and soil organic material within soil profile is proceeding. E.g., the illuvial soil B horizon, underlying the arable layer, is the strip of 7 cm thickness, cemented with iron and organic compounds (concentration of Mn is higher in 1.5 and of Fe in 3 times, than in arable A horizon), and marks the highest level of ground water (Table 10). Deeper, on the oxidation–reduction and mechanical geochemical barriers of BC_{sg} horizon, accumulation of elements is even more active – values of Mn and Fe increase there in 4 times, amounts of elements bind to clay minerals (Co, Cr, Cu, Li, Sc and etc.) – from 2 to 8 times. The surface arable A horizon is enriched with Zr, Y, Ti and Yb – elements related to the weathering resistant minerals, amount of which evenly decreases downward the sand soil profile.

Table 10. Total contents of some elements and parameters in soil profile No. 59, (*Carbi-Gleyic Podzol*)

Horizon depth, cm	Tex-ture	pH	LOI %	Zr ppm	Y ppm	Co ppm	Cr ppm	Cu ppm	Li ppm	Sc ppm	Mn ppm	Fe %
A_p 0-28	ps	6,5	5,93	488	28,2	3,6	37,6	3,8	8,5	1,9	216	0,85
B_s 28-35	s	6,8	4,21	227	15,3	4,6	36,4	2,9	12,5	1,7	354	2,49
B2 35-50	s	6,6	2,21	276	13,7	4,6	31,3	2,9	11,7	1,3	264	1,37
B3 50-65	s	6,8	1,69	210	12,8	5,5	30,5	2,9	12,8	1,3	344	1,67
BC_{sg} 80-100	p_2	7,2	5,52	266	49,1	11,8	62,4	12,3	23,6	16,1	831	3,87

Analogous to the above mentioned element distribution was observed in other Carbi-Gleyic Podzol, formed on the glaciolacustrine sand of the Middle Lithuania stage of Late Weichselian glaciation investigated during Foregs project. The bullet–like hard iron concretions were found at the depth of 51–64 cm in the illuvial B2sh horizon. Amount of Mn in this horizon reaches 804 ppm, and is 3 times higher than its amount in the above situated illuvial Bsh horizon (Table 11).

Taking into account, that the highest concentration of Mn was determined in the coarse sand–gravel fraction (Table 2), and the highest values of element were found in the illuvial Bsh horizon with the iron concretions, could be concluded, that in the podzol soil, in the changeable oxidizing–reducing conditions, the manganese accumulates in the soil skeleton, on its colmation coatings. Most probably, on the surface of the colmating iron and manganese hydroxides Al, Zn, Sc, Pb and Cu are also adsorbed, as their values were degreased in soil samples from Bsh ir B2sh horizons, analysed after elimination of soil fraction >1mm.

Table 11. Total contents of some elements and parameters in the soil profile No. 61, *Carbi-Gleyic Podzol* profile.

Horizon depth, cm	Tex-ture	pH	LOI %	Ca %	Fe %	Mn ppm	Zn ppm	Sc ppm	Pb %	Cu ppm	Al %
A_p 0-31	ps	7,4	5,28	0,64	1,42	313	3,22	3,2	15,2	6,6	5,87
B_{sh} 31-51	s1	8,0	4,17	0,53	1,20	259	1,72	1,4	10,5	2,9	5,37
$B2_{sh}$ 51-64	s1	7,6	2,01	0,53	1,27	804	1,96	1,4	9,8	2,9	5,10
B3 64-76	s	7,6	0,78	0,54	1,29	228	2,18	1,6	10,9	4,0	5,36
BC_{sg} 76-92	da	7,7	2,94	0,72	2,43	417	4,08	11,2	18,0	8,7	5,44
C_g 92-110	s1	8,5	0,2	4,29	1,40	379	3,39	5,2	15,5	7,0	5,79

The effect of podzolization can 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. Almost equal element depletion is observed in the moderately drained cultivated Gleyic Podzoluvisol developed on the marginal till of the oldest stage of Late Weichselian glaciation (Table 12). Carbonates are leached up to the depth of 75cm and Ca value in the BC_{kg} 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 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.

Table 12. Total contents of some elements and parameters in soil profile No. 35, (*Gleyic Podzoluvisol*)

Horizon depth, cm	Tex-ture	pH	LOI %	Ca %	Zr ppm	V ppm	Ga ppm	Li ppm	Ni ppm	Cu ppm	Fe ppm
A_p 0-26	ps	7.35	4.2	0.49	316	40	6.5	14.4	12,0	9,58	1,34
AE 26-40	p	6.9	2.6	0.37	351	51	6.8	15.6	12,2	9,74	1,64
E 40-44	p	7.05	2.3	0.36	352	55	6.6	12.7	13,7	7,82	2,35
B_t 44-75	dp_2	7.45	3.5	0.42	270	71	10.1	20.3	23,2	17,4	3,51
BC_{kg} 75-105	p_2	8.65	3.0	1.91	243	116	16.5	24.3	34,9	22,3	3,14

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 13). These trace elements are leached from the overlying water-saturated Ej-horizon when changing from oxidizing to reducing conditions and *vice versa* and accumulated in the underlying Bt-horizon enriched in clay and silt particles. Notable is the distinct change of texture of the soil illuvial Bt horizon (amount of clay fraction increases twice – from 8% up 15%) and the high amount of organic material indicate more the binarity of soil parent material due to the rapid changes of the glacial facies and less – soil forming processes (Bitinas et al. 1997). Increased values of phosphorus in this horizon give an evidence of accumulation or fertilizer products on the soil carbonate geochemical barrier, present in the soil parent Ck horizon.

Table 13. Total contents of some elements and parameters in soil profile No. 8, (*Stagnic Luviso)l*

Horizon depth, cm	Tex-ture	pH	LOI %	Nb ppm	Co ppm	B ppm	Ni ppm	Cr ppm	Pb ppm	Ti ppm	V ppm	P ppm
Ap 0-30	ps	7.2	9.2	15.4	6.9	27	15	38	22,7	3450	36	763
E 30-53	sp	7.4	2.5	21.5	8.8	35	24	60	25,4	2925	57	341
E_j 53-65	sp_2	7.8	3.8	21.2	8.7	30	20	58	22,1	3175	40	414
B_t 65-76	p_2	8.4	3.7	23.1	14.4	58	48	106	33,7	5200	96	1348
C_k 76-100	p_2	8.5	3.3	10.6	12.6	45	37	64	19,3	4061	77	484

A similar mobility of trace elements is noticed in the Carbi-Gleyic Podzol formed on the glaciolacustrine sand of the South Lithuanian phase (Table 14). 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 acts as biogenic geochemical barrier (partly mineralized roots and peat) and 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.

Table 14. Total contents of some elements and parameters in soil profile No. 37, (*Carbi-Gleyic Podzol*)

Horizon depth, cm	Tex-ture	pH	LOI %	P ppm	Mn ppm	La ppm	Y ppm	Zn ppm	Sn ppm	Ag ppm	B ppm
A_p 0-25	s_1	6.6	4.5	573	191	25.8	11.5	11.5	2,2	0,143	16,5
O_b 25-35	d	5.05	34.1	1188	73	19.1	9.9	7.9	0,92	0,066	30,6
E 25-45	s_1	5.55	2.1	490	142	10.8	5.9	9.8	1,76	0,098	26,4
B_h 45-50	s_1	5.75	1.9	324	157	16.7	8.4	9.8	1,96	0,078	27,5
B_s 50-68	s_1	5.85	1.4	325	148	17.7	7.5	9.9	1,58	0,059	25,6
BC 68-106	s_1	5.9	0.3	319	160	18.9	10.0	11.0	1,5	0,100	25,9
C_r 106-136	s_1	5.85	0.3	299	189	35.9	12.0	12.0	2,09	0,120	29,9

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 15). 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 (Fig.16).

Table 15. Total contents of some elements and parameters in soil profile No. 43, (*Anthric Histosol*)

Horizon depth, cm	Tex-ture	pH	LOI %	Ag ppm	Pb ppm	Sn ppm	Mo ppm	Zn ppm	V ppm	Cr ppm
H_p 0-16	d	7.35	46.0	0.130	36.7	3.24	1.73	151	108	48,6
H_b 16-44	d	7	49.5	0.076	5.1	1.16	1.31	40	58,1	19,7
BC_g 44-62	p_2	8.15	4.0	0.054	13.4	1.82	0.67	59	76,8	38,4
C_g 62-82	p_2	8.55	4.5	0.048	10.5	1.81	0.90	38	66,9	45,84

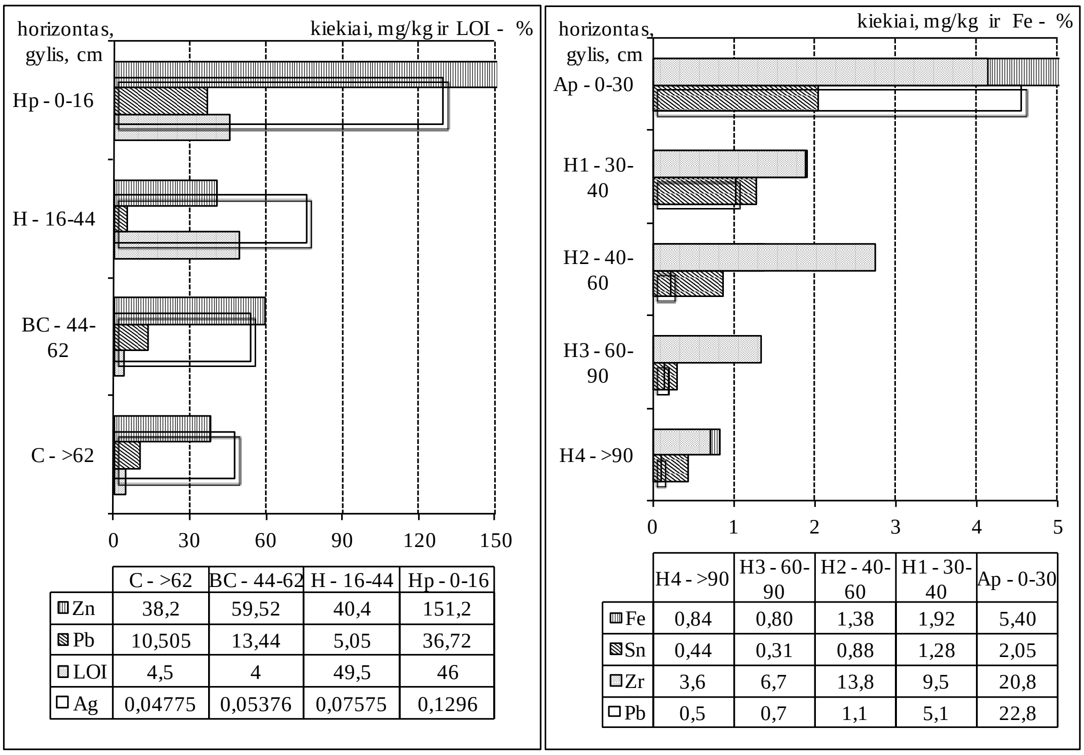
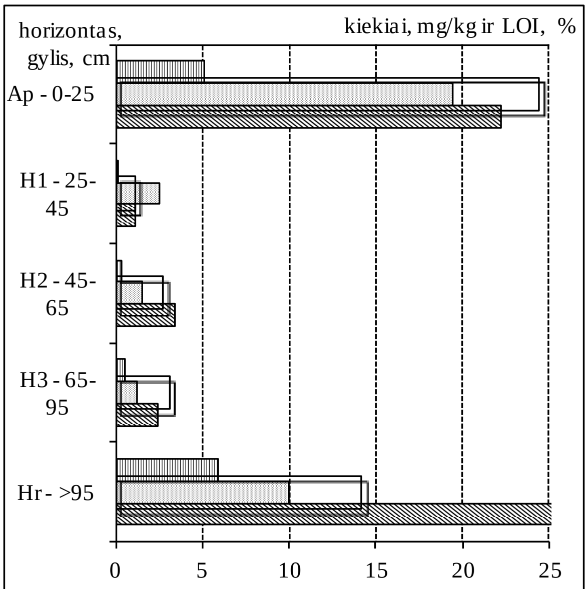


Fig. 16. Distribution of some elements and parameters in the Anthric Histosol profile No. 43 and the Terric Histosol (Glitiškės, Vilnius r.)

The similar element distribution was observed in the Terric Histosol situated in Glitiškės, Vilnius region, on the drained re-naturalized grazing land, the arable surface A horizon of which *versus* the lower histic H1 horizon is enriched in several times with Sn, Sc, Pb, La, Cr, Yb, Nb, Fe, Zr (Table 16, Fig. 16). Part of elements (Yb, Zr, La, Nb) was contributed to the soil surface with liming and phosphorous fertilizing, part of element amounts (Fe, Sc, Sn) increased due to the activated peat mineralization after the peatland was drained.

Table 16. Total contents of some elements and parameters in the *Terric Histosol* profile, Glitiškės, Vilnius r.

Horizon depth, cm	Tex-ture	LOI %	Ca %	Sn ppm	Sc ppm	Pb ppm	Sr ppm	La ppm	Cr ppm	Yb ppm	Nb ppm
A_p 0-30	d	79,25	2,18	2,05	4,15	22,8	249	8,3	4,15	1,3	1,25
H_1 30-40	d	87,22	2,04	1,28	1,92	5,11	230	1,8	1,92	0,2	0,26
H_2 40-60	d	87,5	1,63	0,88	2,63	1,13	175	0,6	2,63	0,3	0,25
H_3 60-90	d	90,44	1,91	0,31	1,05	0,72	82,2	0,5	1,05	0,5	0,14
H_4 >90	d	91,16	1,68	0,44	0,8	0,53	88,4	0,4	0,8	1,2	0,13



	Hr - >95	H3 - 65-95	H2 - 45-65	H1 - 25-45	Ap - 0-25
Sc	5,91	0,52	0,34	0,18	5,10
Pb	10,0	1,3	1,6	2,6	19,5
Cr	25,4	2,5	3,4	1,2	22,3
Zr	79,8	17,4	15,5	6,5	136,9

Fig. 17. Total contents of some elements and parameters in the *Terric Histosol* profile , Verusava, Vilnius r.

The Terric Histosol profile, situated in Verusava, Vilnius region, on the drained re-naturalized grazing land, reflects traces of the intensive fertilization using phosphoric fertilizers. Y, La, Zr, Yb, Ti are elements related to the rare Earth minerals – tailing components of apatite's, i.e. raw material from which phosphoric fertilizers were produced. Accordingly, they increased values were found in the arable surface Ap horizon, as well as in the bottom of pit – the permanently waterlogged Hr horizon, and indicates free migration of these elements, weakly bind to soil organic material. (Table 17, Fig. 17).

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 18). 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^o 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.

Table 17. Total contents of some elements and parameters in *Terric Histosol* profile Verusava, Vilnius r.

Horizon depth, cm	Tex-ture	LOI %	Sn ppm	Sc ppm	Pb ppm	Y ppm	La ppm	Zr ppm	Yb ppm	Ti ppm
A_p 0-20	d	53,6	1,39	5,1	19,5	16,2	16	137	16,2	1299
H_1 30-40	d	86,47	0,2	0,18	2,57	2,3	0,4	6,49	2,3	111
H_2 50-60	d	84,47	0,19	0,34	1,55	2,64	0,8	15,5	2,64	326
H_3 70-80	d	87,09	0,15	0,52	1,29	4,91	0,9	17,4	4,91	245
H_r >95	d	70,46	1,45	5,91	10	20,7	7,7	79,8	20,7	960

Normally, calcification/salinization (accumulation of salts of Na and Ca) is observed in soil of aridic environment, but here, in temperate-boreal climate this process is limited by the glacial soil parent material strongly enriched with calcareous material, and accumulation of its secondary salts stimulates the changeable moisture regime of the soil. Accumulation of the secondary carbonates on the upper boundary of permanently wet BCg horizon reaches up to 16 % (Table 18). Distribution of Mg is less contrast, as element present mainly in the less soluble dolomite, and accumulates not so much in the illuvial Bt horizon, in contrary to Al, Fe, Zn, Na, related to the clay minerals.

Table 18. Total contents of some elements and parameters in soil profile No. 3, (*Stagni-Calcaric Cambisol*)

Horizon depth, cm	Tex-ture	pH	LOI %	Ca %	Mg %	Ti %	Al %	Na %	Fe %	Zn ppm
A_p 0-20	p_1	7.25	7.0	0.76	0.62	0.298	4.38	2,12	1,98	27,9
B_t 20-36	p_2	8.05	7.5	0.71	1.83	0.278	8.34	3,55	4,98	70,3
B_{gk} 36-60	p_2	8.8	5.5	7.66	2.35	0.406	6.78	3,11	3,7	37,8
B_k 60-62	p_1	8.85	5.3	16.29	1.92	0.218	4.35	2,09	2,2	47,4
BC_g 62-98	p_2	8.9	4.2	4.16	2.11	0.326	5.22	2,3	3,15	57,5

Similar accumulations of secondary carbonates also were found in the freely aerated calcareous sediments of coarse texture, in the soil pit of Gelžė gravel quarry (Fig. 18).

Content of secondary Ca reaches there up to 17 % in the accumulations on the biomorfic voids of this soil.

Fig. 18. Accumulation of secondary carbonates in the multilayered gravel sediments of came formation near the Luokė, Telšiai r.

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 more homogenous texture(Table 19).

Table 19. Total contents of some elements and parameters in soil profile No. 49, (*Haplic Arenosol*)

Horizon depth, cm	Tex-ture	pH	LOI %	Al %	Pb ppm	Ag ppm	Sr ppm	Zr ppm	Sn ppm	Mn ppm
A 5-23	s	5,4	1	1,35	10,4	0,089	46	257	1,88	366
E 23-44	s	5,45	0,2	1,43	7,0	0,050	48	210	1,60	250
B 44-70	s	5,75	0,2	1,44	8,0	0,060	43	135	1,60	240
BC 70-120	s	5,75	0,2	1,55	8,0	0,060	64	110	1,40	230

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 Haplic Arenosol on the glaciofluvial sand (remade by aeolian 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 accumulated by the forest litter of the surface mineral A-horizon (Table 19).

3.4. Vertical distribution of chemical elements in the standard soil profile

Changes of element contents in the standard sand and loam-clay soil profiles. Each genetic horizon of every soil (A, E, B, C etc.) has its own specific diagnostic features (calcaric, gleyic, stagnic, mollic, etc.) and corresponding geochemical features. Present study is attempting to generalize geochemical features and ascertain the dominant ones in soil of Lithuania. On purpose to get correct results, two lithological types of soil were standardized: the sand soil developed on soil parent sand and gravel of various geneses; loam-clay soil developed on soil parent sandy loam, loam till and glaciolacustrine clay. Median values were used to create standard soil profiles of both types and investigate vertical distribution of elements in soil profiles (Fig. 19–21).

The loam clay soil in comparison to the sand soil contains double amounts of elements related to clay and silt soil fractions (Li, Ga, Sc, Al, Mo, Cu, Ni, Pb, Zn, Cr, V) and alternation of its values within soil profile is markedly contrasting (Fig. 19). The sand soil contains only 43% of these elements in comparison to loam-clay soil, and they are removed from the upper A and eluvial E horizons. Zn and V related to silt fraction slightly accumulate in illuvial B horizon, Li and Ga related to clay fraction are transported a little bit deeper, to BC horizon. Values of all above mentioned elements increase again in the bottom of soil profile, in the permanently wet G horizon, that indicates transportation of elements throughout soil profile into ground water. Similar pattern of element distribution was observed in the loam-clay soil profile, only accumulation of elements in illuvial B horizon is more distinct and transportation of V, Al, Ni and Cu to the waterlogged G horizon is less observable.

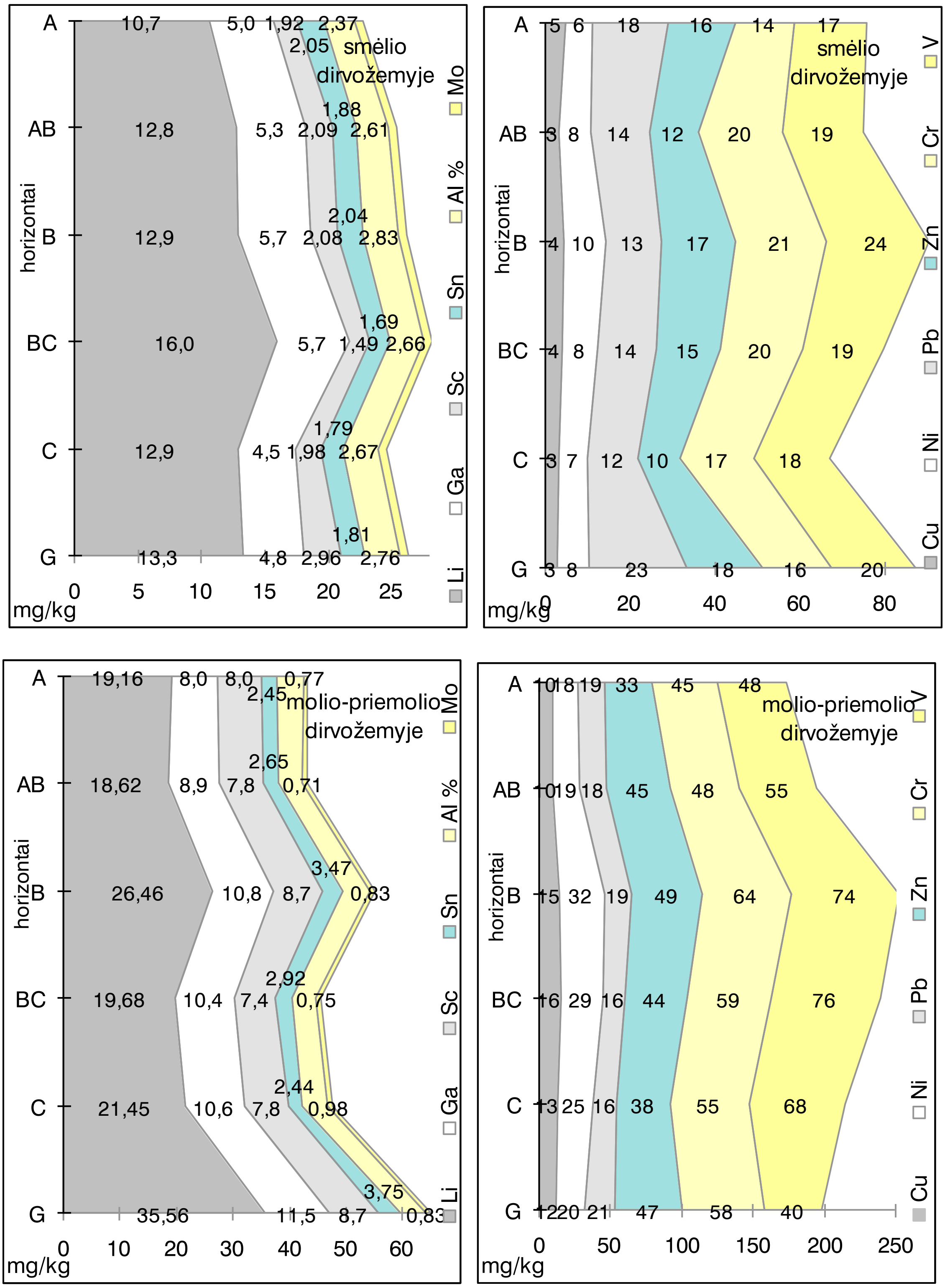


Fig. 19. The distribution of the median element values in the standard sand (uppermost) and loam–clay (bottom figures) soil profiles. Analytical method - DC Arc ES – real total contents.

Values of Zr, Sr, Ba, Mn, La and of Ag, P, related to sand and partly to silt fractions, in the sand soil are prominent, but on the average contains only 64% of values in loam-clay soil (Fig. 20).

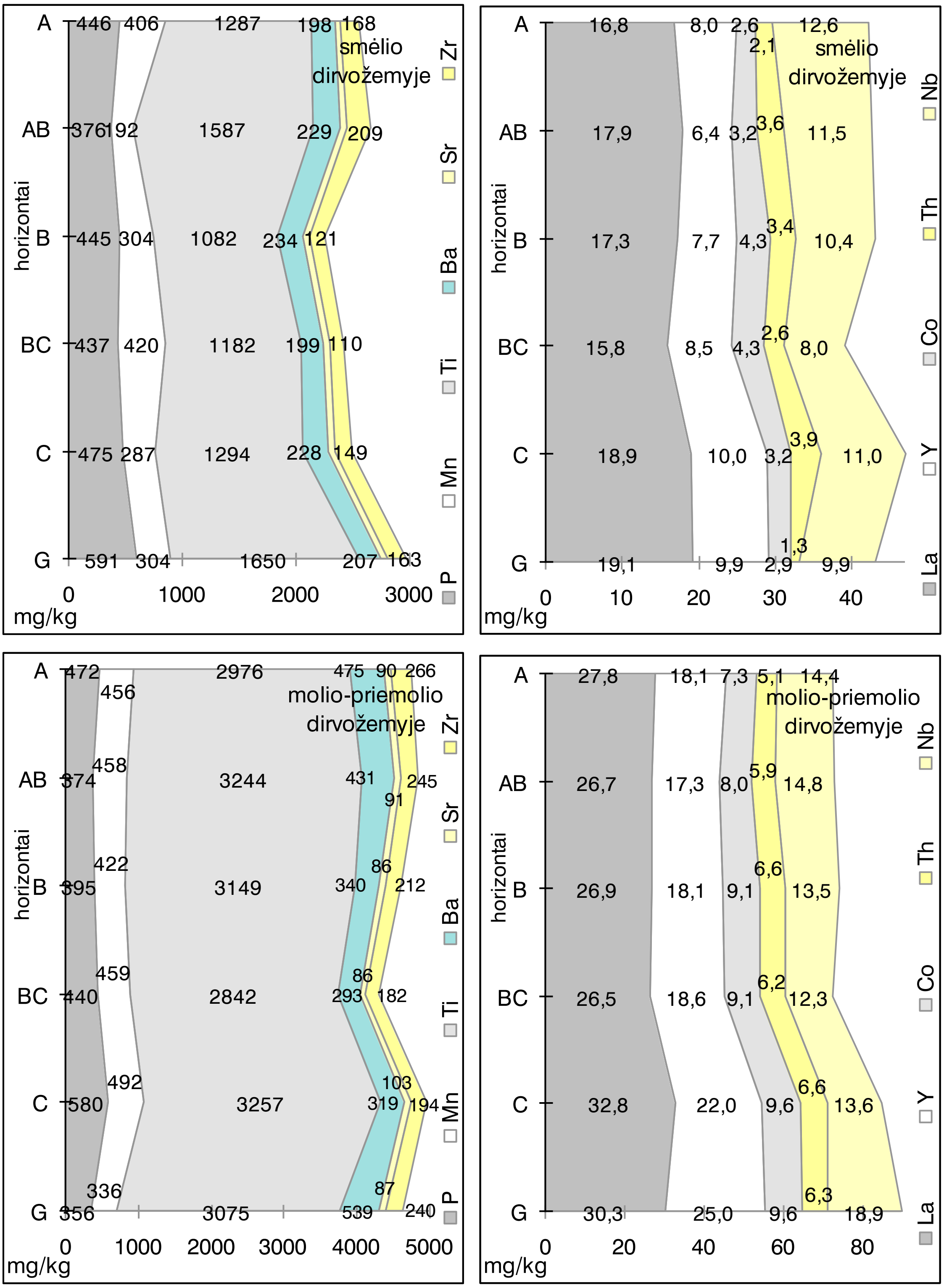


Fig. 20. The distribution of the median element values in the standard sand (uppermost) and loam–clay (bottom figures) soil profiles. Analytical method - DC Arc ES – real total content.

Vertical distribution of elements in the sand soil profile seems to be complicated with lateral inflow of ground water, possibly transporting La, Ba, P and Ti, related to weathering resistant minerals of silt fraction and accumulations of which in the waterlogged G horizon were observed (Fig. 20). The highest values of Mn and Nb are present in the top A and soil parent C and BC horizons, of Zr related to weathering resistant minerals – in the eluvial E (AB) horizon of the sand soil. In the loam-clay soil the highest values of the majority of elements is observed in the soil parent C horizon, except Zr, values of which relatively increase in depleted eluvial E horizon.

On the average, values of major elements (Ca, Mg, Na, K, Fe, Al) in the sand soil contain only 38% of values in the loam-clay soil. The latter elements accumulate negligibly in the illuvial B horizon of the sand soil, while in the parent C horizon of the loam-clay soil the highest values of Ca are observed (Fig. 21).

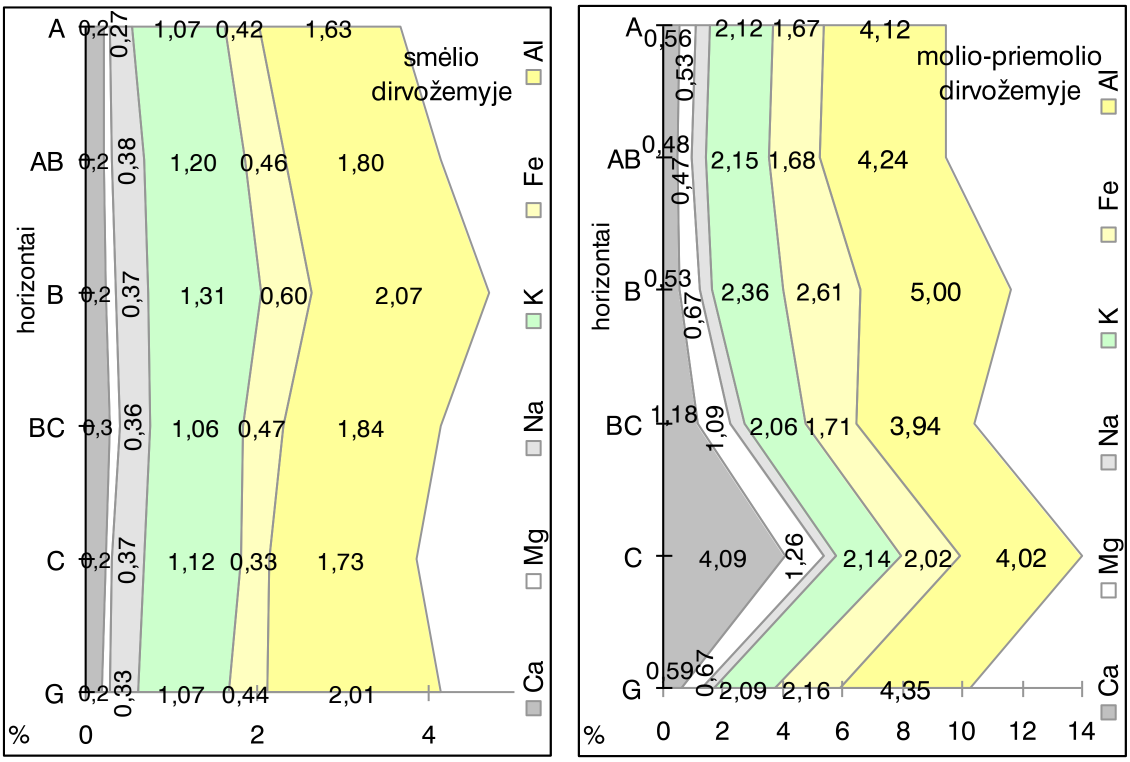


Fig. 21. The distribution of the median element values in the standard sand (left) and loam–clay right figure) soil profiles. Analytical method – ICP-MS, total content in strong 4-acid digestion.

On the average, values of trace elements in the sand soil contain only 54% of values in the loam-clay soil. Moreover, vertical element distribution in the sand soil of the coarser texture is more smoothed, and many elements migrate throughout soil profile down to the waterlogged horizon and accumulate therein. In the illuvial B horizon of the loam-clay soil markedly accumulate trace elements, related to fine grained soil particles.

Changes of element contents in the soil parent C horizon *versus* upper A horizon. 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. Reasons of this phenomenon are mainly natural: cool climate, high amount of precipitations, relatively loose glacial soil parent material, where easy migrates soluble elements (Ca, Mg) and with the fine clay particle related elements (Fig. 22).

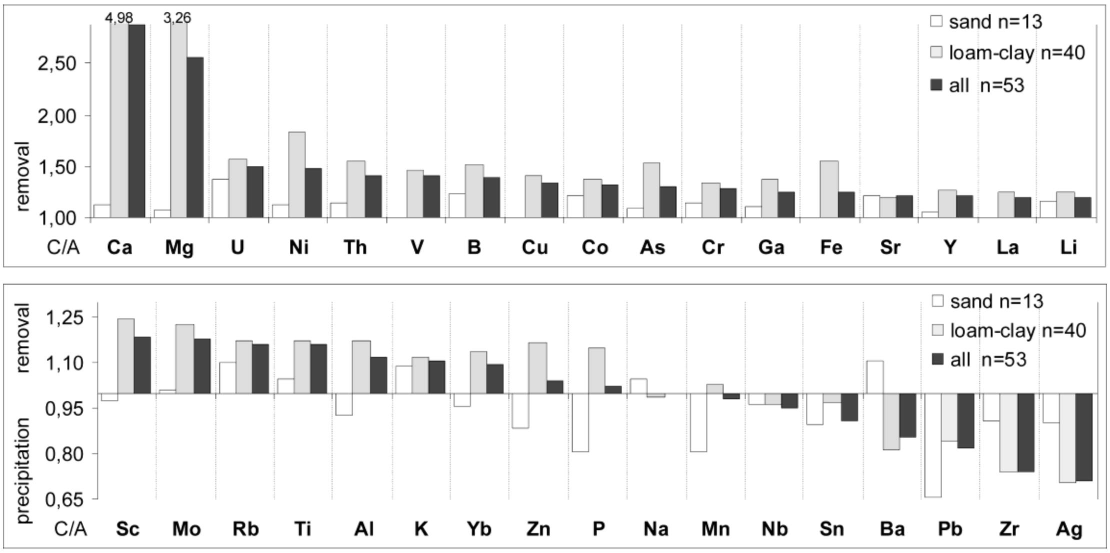


Fig. **22.** Ratio of median values of elements in soil parent material (C-horizon) and topsoil (A-horizon) of soil with different texture, n - number of samples

The character and intensity of the depletion process depends also on the soil profile texture. Berrow and Mitchell 1991 have 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). 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 camouflaged by an active depletion of the weathered non-silicate primary minerals. 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. Part of Zr also is agrogenic in origin and was imported from Kola peninsula (Russia) together with phosphorous fertilizers, enriched with resistant to weathering mineral zirconium. Anomalies of Zr (ratio of values in topsoil *vs* subsoil reach 1.8) in agricultural areas of Lithuania and Latvia were found during European geochemical mapping of soil (De Vos et al., 2006).

Element depletion in the sandy soil is less visible, as geochemical soil profile is composed mainly from chemically and physically passive silicates Removal of Ca and Mg also is weak, because soil forming sandy material is mainly non calcareous. For similar reasons weakly leached are elements related to clay minerals. Conversely, in topsoil A horizon of sandy soil is observed more distinct accumulation of above mentioned Ag, Pb, Sn, Zr, Ba, Nb and Na, as well as biogenic and fixed in soil organic matter of P and Mn, and due to anthropogenic activity – of Al, Yb, Sc and Zn. Concluding, the sandy soil profile reflects primary lithological-mineralogical-geochemical composition of soil parent material and obvious anthropogenic impact on the topsoil. In the loam-clay soil this impact is shaded with weathering of the primary hydrous Al-silicates (ilite, montmorillonite) and removal of elements related to them.

Element correlation and associations in different soil master horizons. The core of main element association in soil parent material (C horizon) is comprised of lithogenic elements related to clay minerals Li-Cu-Ni-Cr-B-Ga-Co-V-Zn, with very strong positive relationship (Pearson correlation coefficient r = 0.9–0.8), as well of strong related (r = 0.9–0.6) elements of clay and silt fractions Sc-K-Fe-Al-Rb-Ba-(Ti-Y-Yb-La). Separate association is comprised of elements of silt fraction Pb-Ag-Sn-Zr-Nb, correlation of which is rather moderate (r = 0.5–0.3). Moderately correlated (r = 0,5–0,3) are elements of the third association Ca-Mg-Th-Sr-U, also related to soil pH and soil calcareous material (Fig. 23).

Paragenetic associations of elements in the topsoil A horizon are changed due to various soil forming processes, and its correlation is weakened (Fig. 23). Very strong positive relationship is left only among elements related to clay minerals B-V-Ni-Ga-Cr-Co-Cu-Zn-Mo (r = 0.9–0.7), as well as among elements of the both silt and clay fractions (r = 0.9–0.6) K-Al-Rb-Fe-Sc-Ba, and among elements of sil fraction Ti-La-Y-Yb. Moderately correlated Na-Sr-As – elements inactive in soil forming processes, and Th-U (r > 0.3). P and Pb are strongly related to soil organic material (r = 0.5), which plays important role in the redistribution of these elements in soil profile.

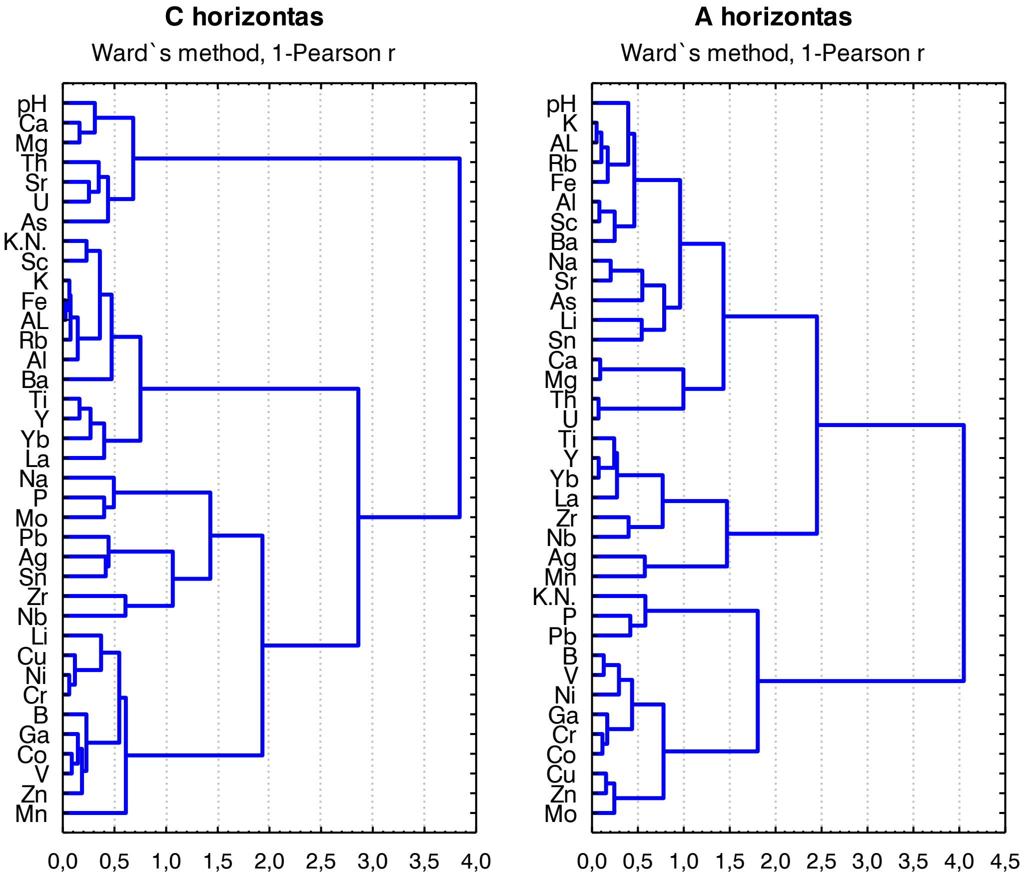


Fig. 23. Dendrograms of the element associations in the soil parent C–horizon and the surface A–horizon

Many of elements in the eluvial E (AB) horizon correlate even stronger than in soil parent C horizon, due to strongly dominant soil forming processes, and two distinct element associations are distinguished (Fig. 24). Trace elements related to secondary clay minerals Li-Ga-Sn-Pb-B-Cu-Ni-Cr-V-Zn-Co separate and K-Fe-Al-(Rb-Sc-Ba) interlink into one association with very strong positive relationship (r = 0.9–0.7). Other element association also consists of two nuts: Ti-Y-Yb-Zr-Nb and Na-Sr-La, comprised of elements related to weathering resistant minerals, present in the coarse soil fraction and very strong correlated (r = 0.8–0.6). Rest of elements do not create any association, but some of them (Ca, Mg, As, Mn) are strongly related to soil pH (r > 0.6).

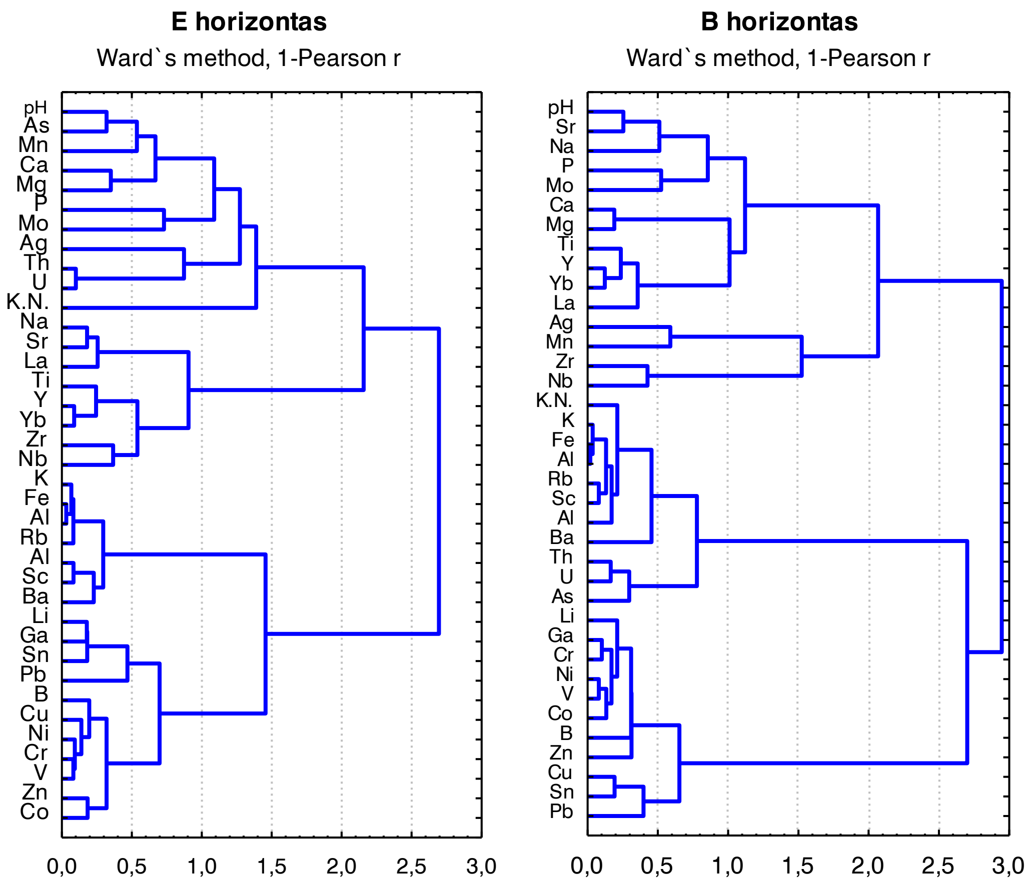


Fig. 24. Dendrograms of the element associations in the eluvial E–horizon and the illuvial B–horizon

Element associations in the illuvial B horizon remain the similar as in E horizon, just correlation becomes stronger (r = 0.9–0.8) among elements of association nuts K-Fe-Al-Rb-Sc and Li-Ga-Cr-Ni-V-Co-B, as well as with elements related to secondary clay minerals (Fig. 24). B, Zn, Cu, Sn, Pb, Th, U, As and To, related to silt fraction also join strongly (r >0,6) to this association. In the association of elements related to weathering resistant minerals remain only Ti-Y-Yb-La, as well Ca and Mg (r > 0.5), related to accumulations of secondary carbonates in this horizon.

3.5. Model of vertical element distribution within the soil profile in Lithuania

On the base of original geochemical data of 249 soil samples from 53 complete soil profiles the 53 model soil profiles were created, each having the master soil horizons

A surface, E eluvial, B illuvial and C parent (altogether 212 soil samples) (Table 20).

Table 20. Median values of elements of the soil master horizons in the soil of different lithology: s – sand, ps – sandy loam, p/m – loam-clay, visi – all types.

Elements	A horizon				E horizon				B horizon				C horizon		
	s	ps	p/m	visi	s	ps	p/m	visi	s	ps	p/m	visi	s	p/m	visi
	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
mg/kg															
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

Median values of elements in the master horizons of different texture were used in place of missing samples, while aberrant samples from specific diagnostic horizons were discarded. These 53 model soil profiles were used to create the standard soil profile and to reveal regularities of vertical alteration of geochemical composition of soil (Table 20).

The variability in element contents in the whole dataset of the 53 model soil profiles has been analysed. High 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. But, the variability in Fe, Ni, Sc, U and Th related to the particular development of the illuvial 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 particular 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. (Fig. 25).

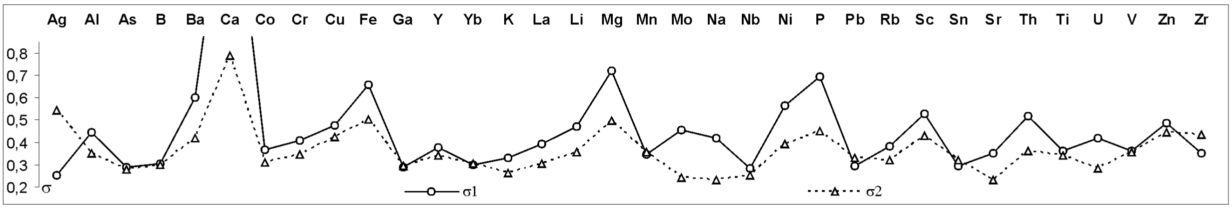


Fig. 25. Variability of element contents in the whole real dataset (*σ_1*) and in the whole dataset of the 53 model soil profiles (*σ_2*).

Cumulative elements in the upper soil A horizon. 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 *versus* the median values in the soil parent material (Fig. 26a).

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).

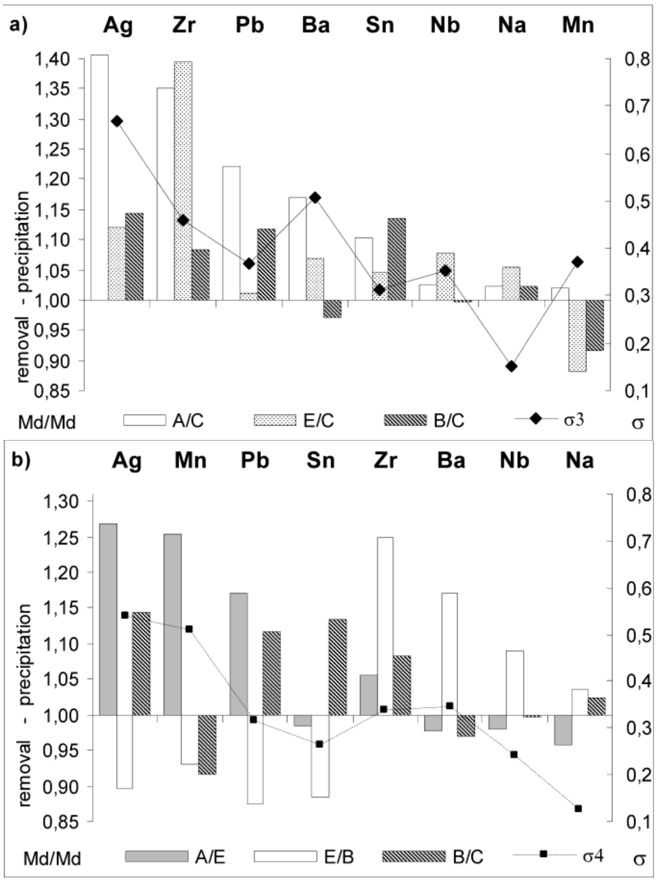


Fig. 26. Accumulative elements in the topsoil A horizon: a – by the ratio of the soil horizon medians to the median value in the soil parent material; b – by the ratio of the median values of contiguous soil horizons

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 (σ_3 0.67–0.31 and σ_4 0.54–0.26) than of the first group elements (σ_3 0.51–0.15 ir σ_4 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).

A study of spatial distribution of the accumulative elements on the territory of Lithuania reveals the trend of topsoil enrichment with silver – average of ratio of element content in topsoil *versus* subsoil Ahor/Chor is 1.4 (Fig. 27). The most intensive accumulation of silver in the topsoil was observed in the industrial regions and vicinities of thermo-power stations, these use heavy oil and used in the past coal – in Middle Lithuania, Vilnius region and Suvalkija. Part of silver in the arable surface A horizon is, most probably, agrogenic in origin, as intensive agriculture is developed in the above mentioned regions.

Lead accumulates in the topsoil a little bit weaker than silver – average of ratio of element content in topsoil *versus* subsoil Ahor/Chor is 1.25, and shape of the most intensive anomalies elongated downwind of the dominant southwest winds in the country indicates the partly airborn origin of lead in soil. (Fig. 27). The evidences, that part of Pb arrives into soil of Lithuania via air, were found during geochemical mapping of terrestrial moss and humus layer of forest in Baltic countries (Salminen et al., 2011). Pending geochemical mapping of soil in Lithuania (Kadūnas et al., 1999) the most significant accumulation of Pb were observed in soil of Western Lithuania, in area with the highest amount of precipitations. Anomalies of Pb in organic soil and snow dust also confirm partly airborn origin of lead.

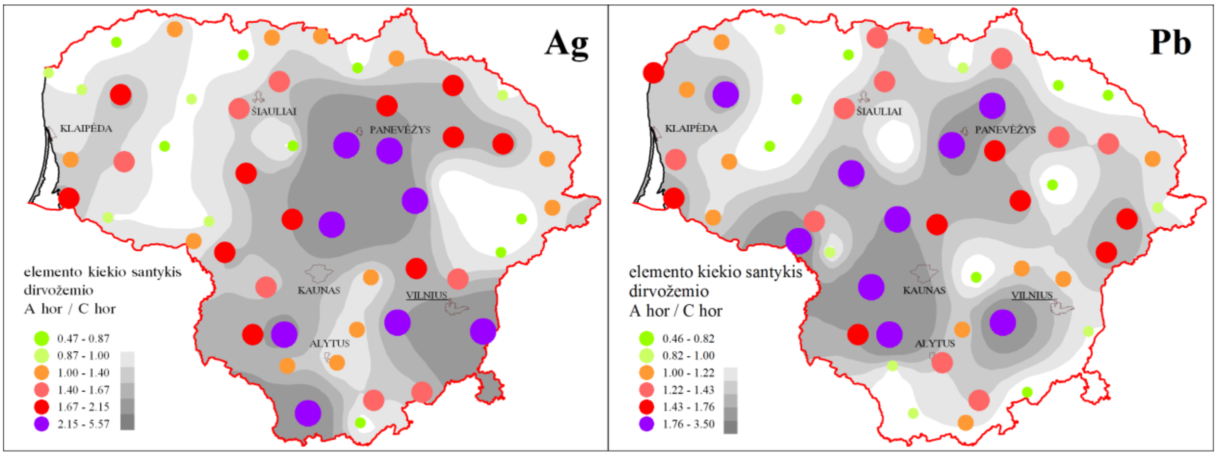


Fig. 27. The spatial soil enrichment with Ag and Pb according ratio of element in topsoil *vs* subsoil

Spatial distribution of zirconium anomalies with average ratio of element content in topsoil *versus* subsoil Ahor/Chor 1.4 differs from of Pb and Ag (Fig. 27). The distinct anomalies of element was observed in the topsoil of the main agricultural areas of the Middle and North Lithuania, but the most significant accumulation was found in the South East Lithuania, in soil formed on sediments of penultimate glaciation and glaciofluvial sand.

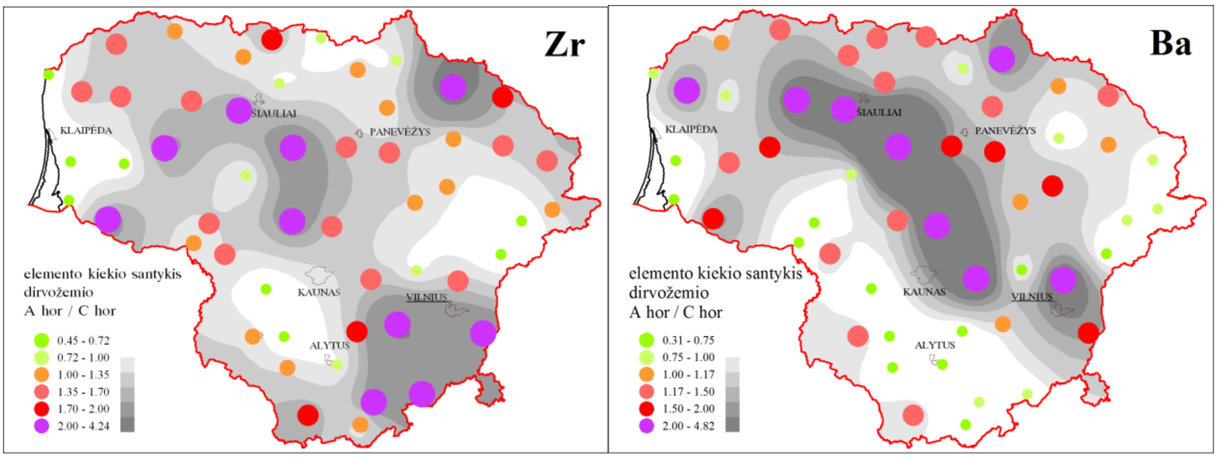


Fig. 28. The spatial soil enrichment with Zr and Ba according ratio of element in topsoil *vs* subsoil

Values of Zr in topsoil here are relatively supplemented with amounts of element related to weathering resistant minerals. Content of barium in topsoil of Lithuania is higher 1.17 times, than in soil parent C horizon, the most significant accumulation was observed in loam–clay soil in the Middle and North Lithuania, and linked to the primary weathering resistant clay minerals, immobile and insoluble in the alkaline environment. (Fig. 28)

Cumulative elements in the illuvial soil B horizon. 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. 29a). 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: this prelate to their relatively increased values in the soil top A horizon and their increased variability (σ3 – 0.54-0.48).

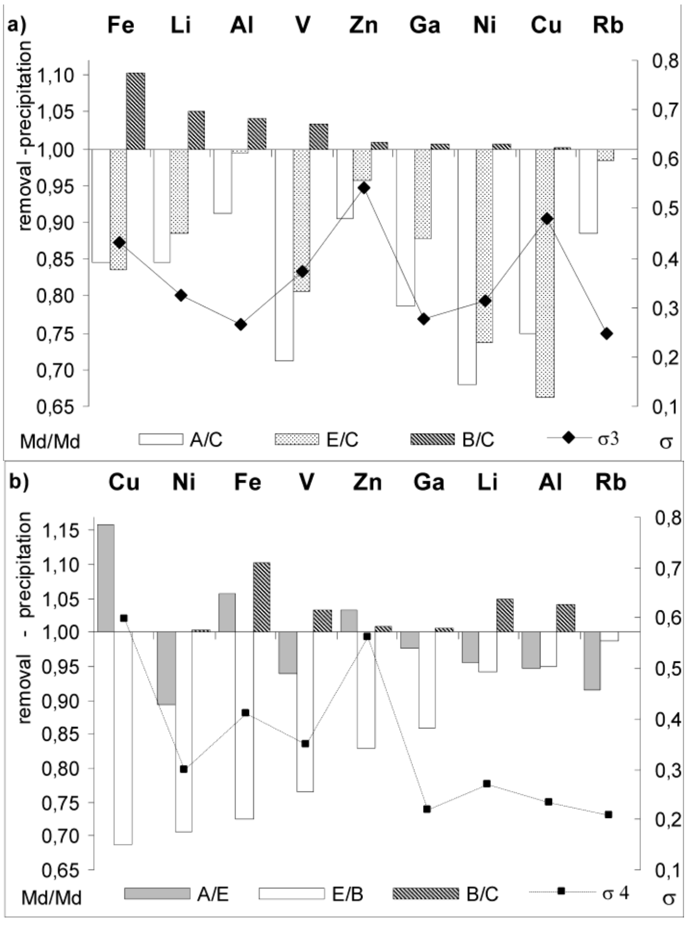


Fig. 29. Accumulative elements in the soil illuvial B-horizon: a – by the ratio of the soil horizon medians to the median value in the soil parent material; b – by the ratio of the median values of contiguous soil horizons

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 analyzing the soil profile horizon by horizon, i.e. the variability of Cu, Zn, Fe, Ni and V is moderately (σ4 – 0.6-0.3) (Fig. 29b).

Elements, depleted from the entire soil profile. 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. 30a, 30b). The most easily removable of these are Ca and 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 behavior elements of these in the soil profile with respect to different textures (Fig. 30a).

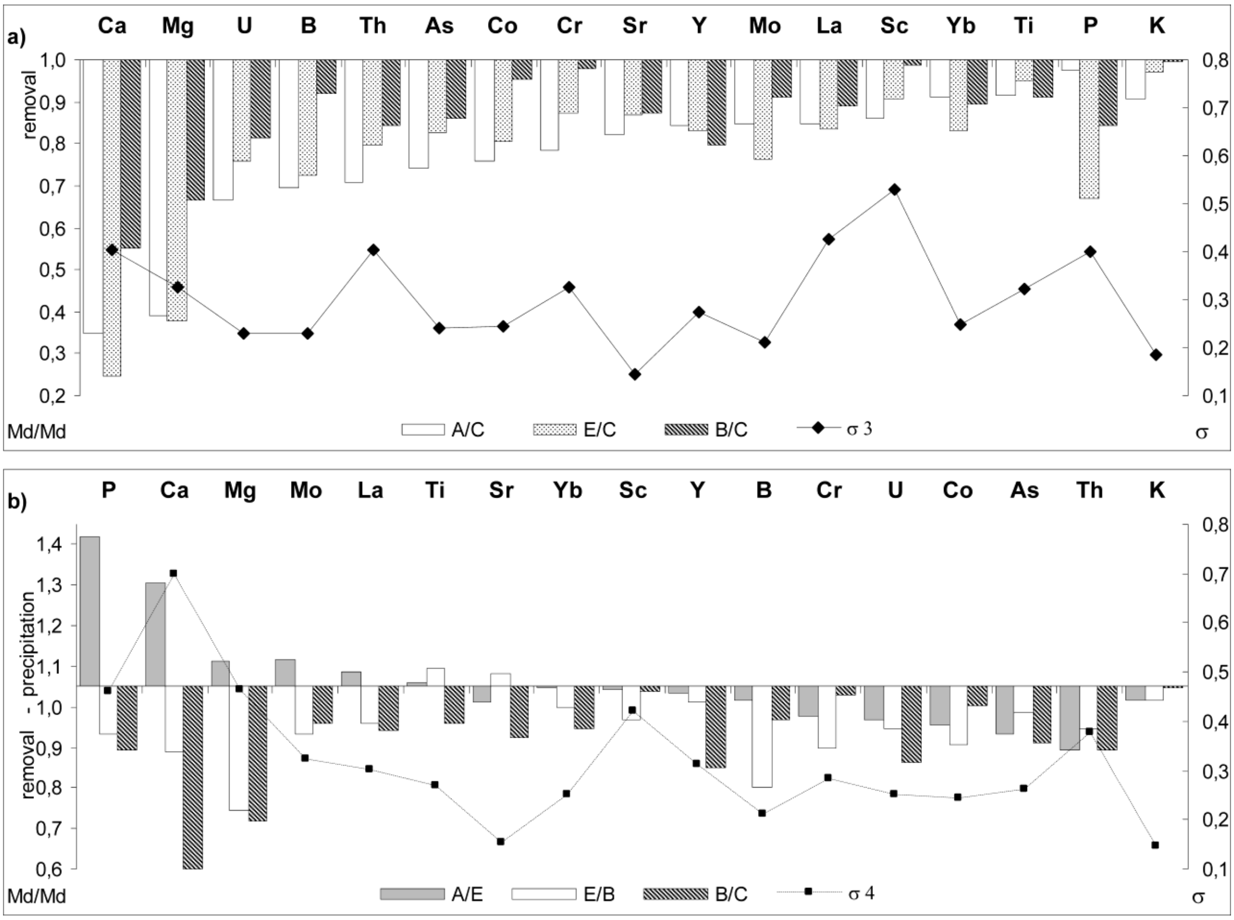


Fig. 30. Elements removed from the upper soil horizons: a – by the ratio of the soil horizon median values to the median value in the soil parent material; b – by the ratio of the median values of contiguous soil horizons

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. 30b). The high variability of Ca, Mg, P and Sc ($\sigma 4 > 0.4$) is determined by: different soil textures in the subsets of samples; and calcareous soil parent material.

Character and intensity of element depletion depends on the soil composition – the most significant is depletion of Ca and Mg in the calcareous soil of Middle and Northern Lithuania (Fig. 31). The main minerals–bearers of Ca and Mg are different, respectively carbonate and dolomite, consequently disagree the areas with the greatest losses of these elements. On the average, in topsoil of Lithuania only 1/3 part of Ca and Mg was left from the primary soil parent material, ratio of element content in topsoil *vs* in subsoil Ahor/Chor are 0.35 and 0.39 respectively.

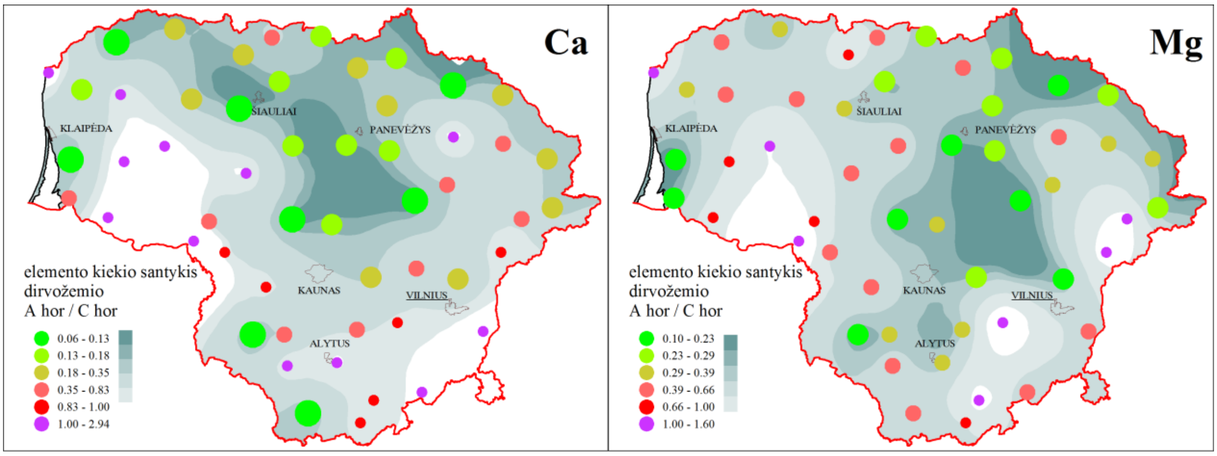


Fig. 31. The spatial soil depletion of Ca and Mg according ratio of element in topsoil *vs* subsoil

Elements related to clay minerals As, Co, U, B, Th and Cr are easily removed from surface soil horizons, and this process the most significant is in loamy soil of the Žemaitija highland, particularly on the its western slopes, these receive maximum of precipitations (Fig. 32). Rather significant removal is observed on the western slopes of Baltija highland, also with similarly high amount of precipitations and the soil erosion related to it. Ratio of cobalt content in topsoil *vs* in subsoil Ahor/Chor is 0.76, of boron – 0.69.

Uranium is much stronger depleted from the top A horizon – ratio of element content in topsoil *vs* subsoil Ahor/Chor is 0.67, as element in soil most often is adsorbed on clay minerals, iron and aluminium hydroxides, and easy migrates in the both acid and alkaline environments, as well in oxidation medium. Most significant depletion is in the north western part of country and could be explained with presence of soil parent material rich in uranium (Geochemical Atlas of Lithuania indicates in this area the largest anomaly of uranium in mineral soils (Kadūnas et al., 1999), and with highest amount of precipitation overall country (Fig. 33).

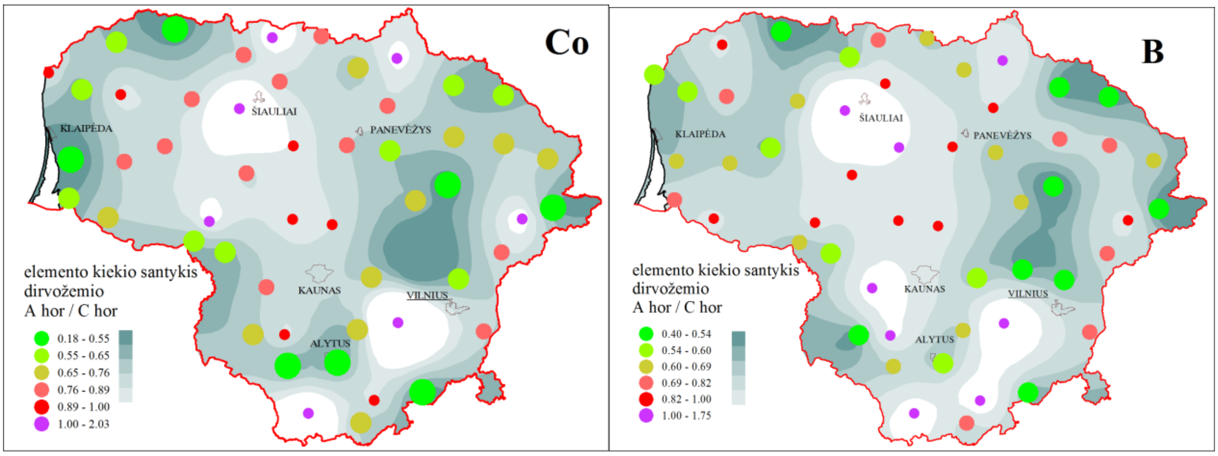


Fig. 32. The spatial soil depletion of Co and B according ratio of element in topsoil *vs* subsoil

Trend of potassium depletion out of the top A horizon was observed in soil of the intensive agricultural areas, where soils are developed on the loamy sand till of coarser texture – Alytus, Panevėžys, districts and Klaipėda region (Fig. 33). Deficiency of element is not very distinct, ratio of element content in topsoil *vs* in subsoil Ahor/Chor is 0.91, and points out, that potassium is in not very soluble compounds and partly replaced with fertilizers.

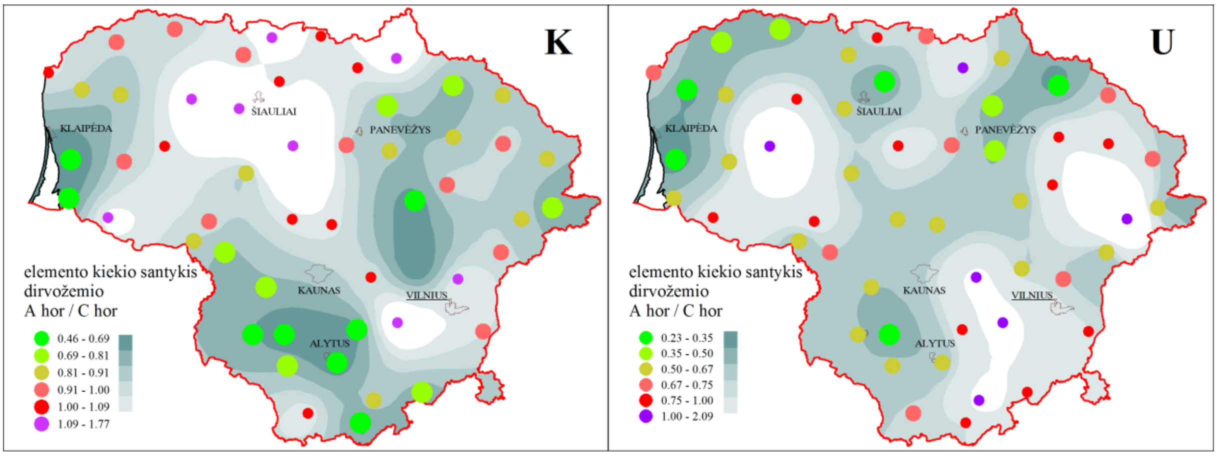


Fig. 33. The spatial soil depletion of K and U according ratio of element in topsoil *vs* subsoil

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 ir 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. 34).

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 (σ4 >0.4). In contrast, the lowest variability is of Na, K and Sr again (σ4 <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.

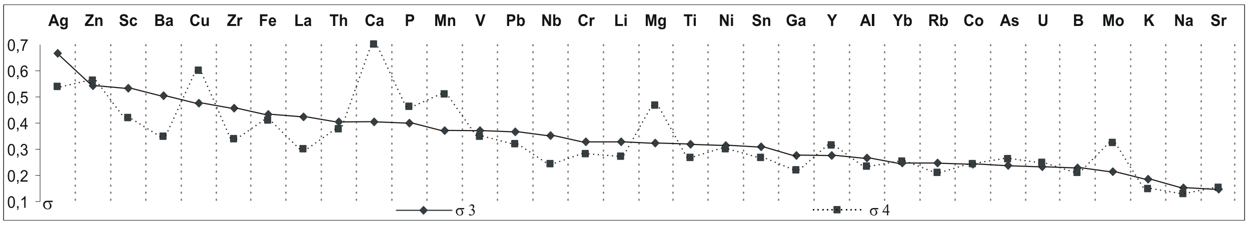


Fig. 34. Variability of the element median values within the model soil profile according to different average deviations: σ_3 – in comparison to the real soil parent material; σ_4 – by contiguous master horizons.

CONCLUSIONS

●Regardless of the fact, that the most of elements are concentrated in the finest grain particles of soil – clay fraction (<0,001 mm) and the both clay and silt fractions (0,001-0,0063 mm), the chemical composition of soil in Lithuania is mainly impacted of the most abundant sand fraction.

● Chemical and lithological composition of the soil parent material is the main primary factor determinating the posterior element distribution in soil profile. The lowest values of all elements, except Nb, were found in the sand soil parent material. Values of B were the highest in organic peat material, values of Ag, Mo, P, Pb, Sn, Sr and Zr are more or less similar in the all lithological types of the soil parent material. The highest values of rest elements were fixed in the clay material.

• Vertical redistribution of chemical elements in the soil profile depends on the podzolization, lessivage, calcification, humification, gleyification soil forming processes, these remain under control of the primary lithological composition. Alternation of chemical element values is the most distinct in the profile of the loam and clay soil. Element distribution in the sand soil profile of coarse texture is much more even.

• The most fluctuative values in soil profile are of Ag, Zn, Sc, Ba, Cu, Zr, Fe La, Th and Ca – elements, composing the soluble compounds or related to the secondary clay minerals of the silt fraction. The most inactive, i.e. more or less evenly distributed in the soil profile are Na, K and Sr, related to the primary weathering resistant minerals of sand fraction.

●The element depletion from the upper soil horizons and removal from the all soil profile is the dominant geochemical process in the soil of Lithuania, as a result of relatively loose soil material and temperate–boreal climate with excess of precipitations.

●Character and intensity of element depletion depends on the lithological type of soil, and the most distinct is in the upper horizons of the loam-clay soil, which loses 18% of trace elements and 34% of major elements in average. The most mobile and easily leachable are the alkaline elements (Ca and Mg) and related to clay minerals and hydroxides. Many elements in the sand soil, hydromorphic in particular, are depleted through the whole soil to the ground water.

●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, adsorbed by soil organic material.

●The elements related to fine soil particles and clay minerals (Fe, Al, Li and V, to less degree Cu, Ni, Ga, Zn and Rb) accumulate in the illuvial B-horizon.

Practical conclusions

●Soil in Lithuania is impoverishing due to dominant depletion process and removal of chemical elements, plant nutrients as well. Therefore, soil of arable lands, which is using for agriculture, needs additional permanent fertilizing.

●Soil in Lithuania, particularly of the coarse texture, is in general permeable to contamination and is not able to protect ground water sufficiently.

●The coarse soil particles (> 2mm), which are eliminated during routine chemical analysis of soil, contains chemical elements available for plants, and significant for assessment of agrochemical quality of soil.

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SANTRAUKA

Vertikalus cheminių elementų pasiskirstymas įvairių šalių dirvožemio profilyje yra gana retai tiriamas. Tyrimų rezultatai taip pat dažnai yra sunkiai palyginami, nes atliekami taikant skirtingus tyrimų metodus, pritaikytus įvairių uždavinių (agrocheminių, aplinkosauginių, naudingų iškasenų paieškų ir kt.) sprendimui. Nustatant antropogeninio poveikio mąstą dirvožemiams bei per juos besifiltruojantiems krituliams, patenkantiems į gruntinį vandenį, yra būtini objektyvūs ir patikimi duomenys apie Lietuvos dirvožemių cheminės sudėties vertikaliąją kaitą bei ją formuojančius procesus.

Tyrimų objektas apėmė visą Lietuvos teritoriją ir visus dirvožeminius rajonus reprezentuojančius dirvožemius. Pagrindinis darbo tikslas buvo nustatyti cheminių elementų vertikalaus pasiskirstymo dėsningumus Lietuvos dirvožemyje. Darbe pateiktos išvados yra pagrįstos panaudojus 74 kasinių pagrindinių horizontų 347 mėginiuose akredituotose laboratorijose nustatytais 28 mikroelementų ir 6 makroelementų visuminiais kiekiais, 293 dirvodarinių uolienų kerno geocheminės sudėties duomenimis bei 92 mineralinio dirvožemio bandinių iš 34 kasinių granuliometrinių tyrimų ir jų metu išskirtų granuliometrinių frakcijų cheminių tyrimų rezultatais.

Tai leido objektyviai pagrįsti vertikalaus cheminių elementų pasiskirstymo dirvožemyje bendrus dėsningumus ir išryškinti Lietuvos dirvožemio vertikalios geocheminės sudėties specifiką tarptautiniame kontekste. Dirvožemio granuliometrinės sudėties ir išskirtų frakcijų cheminės sudėties analizė atskleidė sąsajas tarp dirvožemio granuliometrinės ir cheminės sudėties. Disertacijoje pateiktos nustatytos dirvodarinių uolienų bei atskirų jų litologinių tipų pirminės cheminės sudėties savybės ir šių savybių vaidmuo dirvožemio profilio formavimesi.

Apžvelgiant geocheminės sudėties kaitą atskiruose dirvožemio profiliuose, atskleista įvairių dirvodaros procesų bei žmogaus veiklos įtaka vertikaliam elementų persiskirstymui dirvožemyje. Lietuvos teritorijoje tolygiai išdėstytų dirvožemio kasinių geocheminių tyrimų duomenys leido korektiškai suformuoti tipinius smėlio–priesmėlio ir molio–priemolio dirvožemio geocheminius profilius ir atskleisti jų būdingąsias savybes. Realių duomenų pagrindu sudarytas tipinio Lietuvos dirvožemio geocheminio profilio modelis leido apibendrinti bei išryškinti esminius dirvožemio vertikalios geocheminės sudėties bruožus.

Apibendrinus tyrimų, tame tarpe ir autorės atliktų, rezultatus galima teigti, kad nors didžiausi daugumos elementų kiekiai yra susikaupę smulkožemyje – molio (<0,001 mm) ir molio–aleurito (0,001-0,0063 mm) frakcijose, tačiau dėl glacigeninių dirvodarinių nuogulų ypatybių viso Lietuvos dirvožemio cheminę sudėtį labiausiai įtakoja jo gausiausia smėlio (0,0063-1 mm) frakcija

Dirvodarinių nuogulų cheminė ir litologinė sudėtis yra lemiamas faktorius, apsprendžiantis vėlesnį cheminių elementų pasiskirstymą dirvožemio profilyje veikiant dirvodaros procesams. Beveik visų mikroelementų, išskyrus Nb, mažiausi kiekiai yra dirvodariniame smėlyje, B daugiausia durpėse, o Ag, Mo, P, Pb, Sn, Sr ir Zr kiekiai gana panašūs visose litologinėse dirvodarinių uolienų atmainose. Visų kitų mikroelementų didžiausi kiekiai randami molyje.

Lietuvos dirvožemių profilių cheminės sudėties elementų vertikalų persiskirstymą nulemia jaurėjimo, lesivažo, kalcifikacijos, humifikacijos, išmolėjimo bei glėjėjimo procesai, tačiau visi šie procesai yra priklausomi nuo pirminės dirvožemio litologinės sudėties. Vertikali cheminių elementų kiekių kaita dėl pastarųjų procesų suformuotų geocheminių barjerų yra ryškiausia priemolio ir molio dirvožemyje. Rupesnės sudėties smėlio dirvožemio profilyje elementų pasiskirstymas yra žymiai tolygesnis.

Didžiausia kiekių kaita dirvožemio profilyje pasižymi elementai – Ag, Zn, Sc, Ba, Cu, Zr, Fe La, Th ir Ca, sudarantys tirpius junginius arba susiję su aleurito frakcijos antriniais molio mineralais. Inertiškiausi, t.y. daugiau ar mažiau tolygiai pasiskirstę dirvožemio profilyje, yra Na, K ir Sr, susiję su pirminiais dūlėjimui atspariais smėlio frakcijos mineralais.

Lietuvos dirvožemyje dėl teigiamo drėkinimo koeficiento ir palyginti purių glacigeninių dirvodarinių uolienų vyrauja daugumos elementų išplovimas iš viršutinių dirvožemio horizontų ir išnešimas žemyn, už dirvožemio profilio ribų.

Elementų išnešimo pobūdis ir intensyvumas priklauso nuo dirvožemio litologinio tipo ir ryškiausias yra molio–priemolio dirvožemio viršutiniuose horizontuose, kurie vidutiniškai netenka 18% mikroelementų ir 34% makroelementų kiekio. Judriausi ir lengviausiai išnešami yra šarminiai elementai (Ca ir Mg), taip pat su molio mineralais ir hidroksidais susiję elementai (U, B, Th, As, Co, Cr, Sr, Y, Mo, La, Sc, Yb, Ti, P ir K). Smėlio dirvožemyje, ypač hidromofiniame, vyksta daugelio elementų išnešimas per visą profilį į gruntinį vandenį.

Viršutiniame dirvožemio A horizonte kaupiasi elementai – žmogaus ūkinės veiklos produktai (Ag, Pb, Sn, Mn), kuriuos sorbuoja ir imobilizuoja čia besikaupianti dirvožemio organinė medžiaga. Be to, dėl gamtinio dūlėjimo dirvožemio profilio viršutinėje dalyje santykinai didėja su dūlėjimui atspariais mineralais susijusių mikroelementų Zr ir Nb bei Na kiekiai.

Iliuviniame B horizonte kaupiasi elementai, susiję su smulkiąja dirvožemio frakcija transportuojamais molio mineralais ir hidroksidais (Fe, Al, Li, V, kiek silpniau – Cu, Ni, Ga, Zn, Rb).

Darbas iliustruotas 20 lentelių ir 34 paveikslais ir pridedama lentelė, kurioje pateikiami dirvožemio profilio cheminės sudėties tyrime naudotų mikroelementų visuminių kiekių pasiskirstymo parametrai.

APPENDIX

Table. Statistical parameters of data from 53 individual complete soil profiles, used in modeling of the standard geochemical soil profile of the sand and loam-clay soil (DC Arc ES analysis, total contents)

	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
sand soil, top A horizon, n=9																												
Md	0,088	2,0	22	198	2,6	13,9	4,9	5,0	8,0	1,3	16,8	10,7	406	0,65	12,6	6,3	446	17,7	31	1,9	2,05	54	2,1	1287	1,3	17	15,8	168
X	0,092	1,9	22	196	3,2	18,6	4,0	4,9	8,2	1,2	17,7	11,1	410	0,65	11,5	7,6	570	17,7	37	1,9	2,05	53	2,9	1535	1,6	21	19,6	169
Min	0,056	1,0	10	85	1,1	7,9	1,0	1,7	3,0	0,7	8,5	7,3	182	0,39	5,6	3,9	186	10,4	20	1,0	1,69	33	1,1	846	1,0	11	9,9	86
Max	0,143	3,5	36	286	7,1	47,3	7,9	9,7	15,8	2,1	26,6	20,6	706	0,78	14,3	17,7	1533	28,7	64	3,0	2,37	74	6,3	2662	2,5	47	39,4	257
V	34	48	38	35	55	63	66	48	50	43	32	34	47	17	22	55	68	32	41	38	12	25	67	44	39	54	50	33
sand soil, eluvial E (AB) horizon, n=18																												
Md	0,079	2,4	25	229	3,2	19,7	3,0	5,3	6,4	1,1	17,9	12,8	192	0,62	11,5	7,5	376	13,9	45	2,1	1,88	61	3,6	1587	2,0	19	11,8	209
X	0,080	2,4	25	237	4,2	24,8	4,2	5,3	9,4	1,4	17,8	13,3	261	0,63	11,8	9,7	404	14,1	45	2,6	2,07	58	3,3	1711	1,9	25	16,7	208
Min	0,050	1,0	13	92	1,4	10,5	1,0	2,4	3,5	0,5	7,0	7,2	114	0,40	5,9	4,0	243	7,0	22	0,7	1,58	37	1,0	757	1,0	9	7,9	90
Max	0,129	4,9	42	346	14,7	57,0	11,8	9,6	24,8	3,5	31,6	21,9	570	0,85	17,8	25,6	753	23,6	66	6,9	2,95	80	6,6	3366	3,9	69	40,3	347
V	24	37	31	33	77	54	79	40	65	65	34	32	55	18	27	61	29	30	26	72	20	23	55	47	41	66	58	40
sand soil, illuvial B horizon, n=16																												
Md	0,076	2,5	26	234	4,3	21,3	4,5	5,7	7,7	1,3	17,3	12,9	304	0,67	10,4	9,7	445	13,2	39	2,1	2,04	61	3,4	1082	1,8	24	17,4	121
X	0,104	2,5	28	229	4,2	24,2	5,1	5,9	9,1	1,3	17,7	13,7	466	0,68	10,3	11,4	451	14,0	45	2,4	2,04	63	3,6	1277	1,8	28	19,8	186
Min	0,059	1,0	13	119	1,7	12,3	1,0	2,8	2,9	0,5	7,9	8,9	128	0,40	6,5	4,0	238	8,0	29	1,0	1,57	43	1,2	619	1,0	9	9,8	79
Max	0,299	4,8	52	353	8,7	49,2	13,8	9,8	19,6	2,3	27,8	22,7	2495	0,90	14,9	25,6	699	22,6	64	5,8	2,97	104	7,3	2256	3,1	73	44,2	589
V	68	47	35	27	47	47	69	40	53	41	34	27	122	19	27	60	33	31	28	59	21	28	55	43	40	63	53	85
sand soil, BC horizon, n=9																												
Md	0,070	2,8	23	199	4,3	19,7	4,0	5,7	8,5	1,2	15,8	16,0	420	0,66	8,0	8,2	437	14,0	43	1,5	1,69	68	2,6	1182	1,6	19	14,9	110
X	0,082	2,9	25	216	3,9	21,3	3,9	5,9	10,0	1,3	15,5	14,9	394	0,69	8,8	9,7	464	13,6	42	2,1	1,94	67	2,8	1254	1,7	23	18,5	131
Min	0,049	1,1	13	99	2,1	12,9	1,0	3,6	3,5	0,6	8,9	8,9	139	0,40	5,9	4,0	327	9,8	21	0,9	0,99	44	1,0	539	1,1	9	9,8	71
Max	0,129	4,6	39	354	5,3	35,5	6,9	7,9	18,0	2,0	20,7	19,7	845	0,99	13,0	17,3	596	16,3	56	4,9	3,34	93	5,5	1980	2,7	49	39,4	199
V	37	43	37	37	27	40	56	22	55	36	23	22	56	28	23	47	21	17	24	68	37	23	62	40	36	56	55	36
sand soil, parent C horizon, n=13																												
Md	0,077	2,4	23	228	3,2	17,4	3,0	4,5	10,0	1,4	18,9	12,9	287	0,68	11,0	7,0	475	12,0	36	2,0	1,79	64	3,9	1294	2,2	18	10,0	149
X	0,090	2,4	28	227	3,9	23,7	4,3	5,9	11,3	1,6	18,5	13,3	310	0,66	11,0	10,3	496	13,9	42	2,4	1,87	70	3,6	1526	2,2	25	17,3	205
Min	0,035	1,3	16	109	1,8	11,0	1,0	2,2	5,0	0,5	8,9	9,9	160	0,40	6,9	4,5	297	6,9	30	1,0	1,09	48	1,3	749	1,1	9	9,9	89
Max	0,169	3,3	61	379	10,3	78,4	10,8	18,6	24,5	5,3	37,2	22,5	549	0,92	15,0	28,4	882	33,3	70	6,7	2,96	102	5,4	4312	3,3	78	62,7	548
V	47	25	45	39	57	81	72	73	51	77	37	26	41	22	27	74	32	51	28	66	31	23	34	62	26	84	95	69

	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
sand soil, buried organic H horizon, n=3																												
Md	0,095	1,4	17	207	2,9	16,2	2,9	4,8	9,9	1,0	19,1	13,3	304	0,72	9,9	7,6	591	22,8	37	3,0	1,81	54	1,3	1650	1,4	20	18,1	163
X	0,093	2,2	24	206	3,8	25,2	4,6	6,9	9,1	1,2	17,7	12,1	388	0,59	10,7	9,9	688	21,5	34	2,7	1,99	66	1,7	1686	1,7	25	27,0	231
Min	0,066	1,3	17	145	1,1	13,2	2,0	2,2	6,7	1,0	14,3	5,3	73	0,26	9,5	3,3	285	15,2	10	1,9	0,92	50	1,0	1045	1,0	11	7,9	133
Max	0,118	3,8	39	266	7,6	46,3	8,9	13,8	10,8	1,7	19,7	17,7	788	0,79	12,8	18,7	1188	26,6	54	3,3	3,25	94	2,8	2364	2,7	43	55,2	396
V	28	65	54	29	88	73	82	88	24	31	17	52	94	48	17	81	67	27	66	27	59	37	57	39	52	69	92	63
sand soil, watterlogged G horizon, n=3																												
Md	0,100	2,4	33	449	4,7	42,7	7,9	5,2	9,9	2,3	35,9	10,0	427	0,66	15,0	8,3	581	11,0	42	2,6	2,78	80	4,0	3154	2,3	25	26,8	278
X	0,096	3,2	36	559	5,9	40,9	7,8	5,8	8,1	2,4	32,0	13,6	388	0,75	15,4	13,3	558	12,5	58	4,8	2,65	81	4,4	3107	2,8	42	31,7	404
Min	0,071	2,4	30	149	3,2	26,9	3,0	3,9	2,3	1,6	16,9	6,0	189	0,60	13,3	6,6	299	10,8	39	2,0	2,09	67	2,5	2792	1,5	18	12,0	216
Max	0,116	4,8	45	1079	10,0	53,1	12,5	8,3	12,0	3,3	43,2	24,9	548	1,00	17,9	24,9	794	15,9	94	10,0	3,07	97	6,8	3376	4,7	83	56,4	718
V	24	43	22	85	60	32	61	39	63	36	42	73	47	29	15	76	45	23	53	92	19	18	49	9	59	85	71	68
loam-clay soil, top A horizon, n=15																												
Md	0,089	4,1	36	475	7,3	45,4	9,5	8,0	18,1	2,5	27,8	19,2	456	0,77	14,4	17,9	472	18,5	75	8,0	2,45	90	5,1	2976	2,6	48	33,3	266
X	0,100	3,8	37	451	7,3	44,7	9,6	8,0	17,2	2,5	27,7	19,7	467	0,79	14,0	17,7	550	16,8	81	7,8	2,49	94	5,0	3096	2,6	49	34,7	286
Min	0,038	2,3	27	156	5,3	31,1	7,5	6,1	8,8	1,6	18,9	11,7	335	0,57	10,5	12,0	230	9,5	53	3,5	1,98	66	2,1	1888	1,3	36	12,5	160
Max	0,311	5,2	48	714	9,5	57,5	12,4	9,6	24,7	3,8	37,7	28,2	671	1,24	17,3	24,9	1038	21,7	131	13,2	3,07	131	9,1	4416	4,9	71	51,8	528
V	66	26	18	34	13	15	18	12	26	24	22	23	21	19	13	22	48	22	27	33	15	22	36	21	31	19	31	33
loam-clay soil, eluvial E (AB) horizon, n=21																												
Md	0,088	4,1	37	431	8,0	48,2	9,6	8,9	17,3	2,4	26,7	18,6	458	0,71	14,8	19,1	374	18,1	89	7,8	2,65	91	5,9	3244	2,6	55	44,9	245
X	0,088	4,2	39	443	8,2	52,0	10,9	9,5	18,7	2,7	30,0	22,5	466	0,80	14,9	22,7	426	17,5	91	7,9	2,97	94	6,3	3266	2,9	58	44,9	271
Min	0,048	2,7	26	208	5,7	29,0	4,9	6,6	11,3	2,0	20,7	11,6	285	0,10	8,7	12,2	195	8,8	57	1,9	1,44	64	2,6	1881	1,5	40	23,4	120
Max	0,176	5,3	65	726	12,0	104,9	30,5	16,6	26,1	3,9	60,0	40,1	877	1,43	21,5	55,5	1160	25,4	160	13,9	5,46	143	10,5	4382	5,3	100	70,3	488
V	41	19	24	29	19	34	55	29	20	22	34	40	30	35	24	47	48	25	27	33	36	20	39	22	36	26	27	38
loam-clay soil, illuvial B horizon, n=27																												
Md	0,073	4,0	51	340	9,1	63,6	14,7	10,8	18,1	2,6	26,9	26,5	422	0,83	13,5	31,8	395	18,6	87	8,7	3,47	86	6,6	3149	3,0	74	48,8	212
X	0,108	4,0	53	383	9,5	67,5	14,8	11,4	18,8	2,6	28,9	26,7	423	0,94	13,7	31,0	478	18,6	92	8,7	3,43	89	6,6	3042	3,2	76	50,2	222
Min	0,030	2,1	29	145	5,4	44,8	6,8	7,6	9,6	1,8	17,3	14,4	185	0,63	9,0	17,5	232	8,2	62	4,8	1,69	69	3,3	1828	2,0	55	25,3	106
Max	0,385	6,3	92	684	14,4	110,9	33,0	16,4	35,6	4,2	67,4	40,4	718	1,73	23,1	48,2	1348	33,7	132	15,4	5,21	145	10,7	5200	4,4	116	77,0	421
V	74	23	29	40	20	27	38	21	29	21	34	27	27	32	22	28	56	32	23	30	25	19	31	23	21	20	27	34

	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
loam-clay soil, BC horizon, n=13																												
Md	0,088	4,3	50	293	9,1	59,0	15,6	10,4	18,6	2,5	26,5	19,7	459	0,75	12,3	28,8	440	16,1	79	7,4	2,92	86	6,2	2842	2,9	76	43,7	182
X	0,089	4,2	52	368	9,0	60,7	14,0	10,5	18,2	2,7	27,4	23,0	476	0,81	12,1	29,4	519	17,8	84	7,8	2,82	89	6,3	2834	3,0	70	47,3	213
Min	0,035	3,3	34	192	4,7	38,4	5,8	6,8	11,7	2,1	20,5	15,4	265	0,10	6,8	15,1	276	13,2	54	3,9	1,56	72	4,2	1862	2,1	46	27,4	86
Max	0,155	5,2	94	721	12,2	89,2	19,5	15,6	24,7	4,0	34,9	42,7	666	1,46	15,8	48,7	980	29,3	127	12,8	4,17	107	8,7	3591	4,0	107	77,8	416
V	41	13	30	45	19	26	33	21	21	19	21	35	25	40	25	30	38	26	24	34	30	14	21	17	19	27	31	43
loam-clay soil, parent C horizon, n=45																												
Md	0,064	4,5	50	319	9,6	55,1	12,7	10,6	22,0	2,9	32,8	21,5	492	0,98	13,6	25,4	580	15,6	82	7,8	2,44	103	6,6	3257	3,7	68	38,2	194
X	0,076	4,5	52	340	9,9	59,8	13,9	11,2	22,6	2,9	34,0	23,4	522	1,05	13,0	29,7	677	16,9	84	8,3	2,52	104	6,8	3411	3,6	69	44,1	212
Min	0,030	1,0	28	146	6,7	34,4	5,8	6,7	11,6	1,4	2,9	9,3	262	0,66	4,9	14,7	216	9,7	48	1,1	1,07	65	1,2	2066	1,8	30	9,9	66
Max	0,243	8,4	94	580	17,2	153,3	49,8	18,7	42,8	5,7	67,1	44,5	1169	2,21	31,6	80,5	2408	34,7	127	17,3	4,46	172	10,5	7193	5,1	116	88,4	403
V	57	25	23	31	23	33	51	26	31	27	34	35	31	30	40	37	61	34	22	36	34	23	35	32	22	32	43	33
loam-clay soil, watterlogged G horizon, n=3																												
Md	0,115	3,8	31	539	9,6	57,7	11,5	11,5	25,0	3,1	30,3	35,6	336	0,83	18,9	20,2	356	21,1	80	8,7	3,75	87	6,3	3075	3,0	40	47,4	240
X	0,110	4,0	39	576	9,6	64,2	12,3	9,9	23,6	2,8	29,0	31,9	316	0,73	17,2	24,6	345	17,4	86	9,6	3,20	116	6,6	2809	3,1	55	47,2	224
Min	0,043	2,8	30	432	8,7	42,6	7,1	5,2	20,8	1,9	23,1	19,9	275	0,47	11,5	17,0	265	9,0	76	8,6	1,52	84	4,4	2178	2,2	33	46,2	123
Max	0,173	5,4	56	758	10,4	92,3	18,3	13,0	25,0	3,6	33,7	40,4	337	0,90	21,2	36,5	414	22,1	101	11,4	4,32	177	9,0	3175	4,0	90	48,1	308
V	59	33	37	29	9	40	46	42	10	30	19	34	11	31	29	43	22	42	16	16	46	46	35	20	29	57	2	42

Table extention: Statistical parameters of data from 53 individual complete soil profiles, used in modeling of the standard geochemical soil profile of the sand and loam-clay soil (ICP-MS analysis, total contents)

	Al	Ca	Fe	K	Mg	Na	LOI	pH
sand soil, top A horizon, n=9								
Md	2,37	0,21	0,42	1,07	0,06	0,27	2,4	5,5
X	2,39	0,25	0,50	1,11	0,09	0,31	7,0	5,9
Min	1,69	0,13	0,25	0,88	0,04	0,23	1,0	5,2
Max	3,14	0,47	1,01	1,80	0,25	0,46	43,6	6,8
V	19	49	47	25	72	27	197	11
sand soil, eluvial E (AB) horizon, n=18								
Md	2,61	0,21	0,46	1,20	0,09	0,38	1,0	6,6
X	2,74	0,23	0,53	1,27	0,12	0,35	2,9	6,3
Min	1,51	0,11	0,13	0,90	0,03	0,21	0,2	4,8
Max	4,52	0,64	1,43	1,78	0,31	0,47	34,3	7,1
V	33	54	61	23	68	24	269	11

	Al	Ca	Fe	K	Mg	Na	LOI	pH
loam-clay soil, top A horizon, n=15								
Md	4,81	0,56	1,67	2,12	0,53	0,46	5,0	7,5
X	4,82	0,89	1,74	2,12	0,54	0,47	4,6	7,5
Min	3,12	0,31	0,66	1,33	0,15	0,35	2,4	6,5
Max	6,34	3,20	3,06	2,95	1,19	0,64	7,0	8,4
V	18	83	34	19	51	17	28	7
loam-clay soil, eluvial E (AB) horizon, n=21								
Md	4,43	0,48	1,68	2,15	0,47	0,46	2,6	7,2
X	4,81	1,23	2,00	2,28	0,68	0,49	3,0	7,4
Min	2,18	0,28	1,12	1,88	0,29	0,36	1,0	6,0
Max	7,64	6,80	4,98	3,55	2,13	0,79	7,5	8,8
V	29	159	48	18	80	26	49	9

	Al	Ca	Fe	K	Mg	Na	LOI	pH
sand soil, illuvial B horizon, n=16								
Md	2,83	0,23	0,60	1,31	0,13	0,37	0,9	6,5
X	2,73	0,52	0,63	1,27	0,23	0,38	1,0	6,5
Min	1,69	0,13	0,23	0,90	0,04	0,26	0,1	5,2
Max	3,28	3,93	1,15	1,85	1,73	0,56	2,0	8,6
V	19	180	51	21	178	22	68	14
sand soil, BC horizon, n=9								
Md	2,66	0,28	0,47	1,06	0,12	0,36	0,7	6,9
X	2,43	0,94	0,49	1,20	0,28	0,38	0,9	6,9
Min	1,29	0,16	0,18	0,99	0,04	0,31	0,1	5,8
Max	3,35	4,00	0,74	1,60	1,42	0,47	1,7	8,7
V	26	152	34	19	159	17	68	14
sand soil, parent C horizon, n=13								
Md	2,67	0,23	0,33	1,12	0,08	0,37	0,7	6,7
X	2,59	1,10	0,49	1,26	0,31	0,37	0,8	7,0
Min	1,59	0,13	0,27	0,92	0,05	0,24	0,2	5,8
Max	3,29	4,20	1,27	2,21	1,31	0,58	2,0	8,7
V	22	129	64	28	137	22	64	16
sand soil, buried organic H horizon, n=3								
Md	2,76	0,19	0,44	1,07	0,08	0,33	5,0	5,1
X	2,67	0,56	0,53	1,12	0,20	0,30	13,5	5,8
Min	1,81	0,17	0,22	0,67	0,04	0,15	1,5	4,8
Max	3,43	1,33	0,94	1,61	0,48	0,43	34,0	7,5
V	31	118	69	42	122	47	132	26
sand soil, watterlogged G horizon, n=3								
Md	3,89	0,34	0,66	1,69	0,12	0,38	0,7	7,0
X	4,07	0,62	1,92	1,65	0,39	0,38	6,0	6,7
Min	1,69	0,27	0,39	0,96	0,10	0,33	0,3	5,9
Max	6,64	1,26	4,70	2,31	0,94	0,42	17,0	7,2
V	61	89	126	41	124	12	159	11

	Al	Ca	Fe	K	Mg	Na	LOI	pH
loam-clay soil, illuvial B horizon, n=27								
Md	4,75	0,53	2,61	2,36	0,67	0,43	3,0	7,4
X	4,91	1,12	2,57	2,41	0,81	0,46	3,1	7,5
Min	3,02	0,25	1,41	1,71	0,32	0,25	0,5	5,7
Max	8,00	7,66	4,47	3,34	2,35	0,86	5,5	8,8
V	29	142	32	17	60	26	38	10
loam-clay soil, BC horizon, n=13								
Md	4,18	1,18	1,71	2,06	1,09	0,42	2,4	7,8
X	4,45	2,16	2,01	2,17	1,14	0,43	2,9	7,9
Min	3,04	0,37	1,37	1,65	0,38	0,33	1,4	7,1
Max	6,64	6,10	3,55	3,00	2,55	0,58	5,5	9,0
V	26	98	31	17	60	17	45	7
loam-clay soil, parent C horizon, n=45								
Md	4,41	4,09	2,02	2,14	1,26	0,44	2,6	8,4
X	4,73	3,62	2,08	2,23	1,28	0,45	2,7	8,0
Min	2,17	0,29	0,72	1,56	0,38	0,27	0,6	5,6
Max	8,63	8,47	3,81	3,46	2,82	0,91	5,0	9,0
V	30	78	33	16	51	26	37	11
loam-clay soil, watterlogged G horizon, n=3								
Md	4,61	0,59	2,16	2,09	0,67	0,42	3,9	7,8
X	4,59	5,79	2,02	2,22	1,00	0,47	4,3	8,0
Min	4,55	0,48	1,71	2,02	0,41	0,36	3,8	7,3
Max	4,62	16,29	2,20	2,55	1,92	0,63	5,3	8,9
V	1	157	13	13	81	30	19	10