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Importance of allotigenic accessory elements in factor loading matrix as statistical expression of geochemical composition variation in soils of different age

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The longer duration of weathering and climate changes have caused a relative enrichment of soil by weathering-resistant heavy minerals and allotigenic accessory elements Y, Yb, La, Ti, Zr, Nb (AAE) bound to them. For this study, particular Lithuanian soil regions where soils have been formed on sediments of the last but one glaciation and various deglaciation phases of the last glaciation, and where the highest content of AAE was found were selected. In each region, links between the importance of AAE in the factor loading matrix (AAE importance) and soil age, content of clay based on its content in differently grain-sized soil types and soil anomalousness were evaluated. Analytical results of the <1 mm soil fraction obtained by atomic emission spectrophotometry for the Lithuanian geochemical atlas were used for this study. In each soil region, sandy, sandy-loamy and loamy-clayey soils were studied without classifying them according to the genesis of soil-forming sediments but dividing according to their anomalousness. Factor analysis was applied for primary, anomalous and un-anomalous data. For evaluating AAE importance, only associations of the first three factors with the total percentage of variance more than (or cloze to) 50 were considered. The applied significance level for factor loading was 0.01. The importance of AAE was evaluated taking into account the rank of the factor (according to factor variance percentage), the values of significant AAE loadings on the factor and the proportion of AAE and other trace elements in the group with significant factor loadings. In soils of the Ašmena Highlands, which are the oldest in Lithuania, the importance of AAE is in inverse ratio with clay content in soil. In soils of the Lower Nemunas Plain, which are younger than soils of the Ašmena Highlands, the importance of AAE is in direct ratio with the content of clay and soil anomalousness. With an increase of clay content, the importance of AAE increases both in un-anomalous and in anomalous soils. In soils of the Mūša–Nemunėlis Plain, formed on the youngest soil-forming sediments of Lithuania, both in primary and anomalous soils the first factors are formed by mixed associations of AAE and allotigenic elements (AE), where the importance of AAE decreases with an increase of clay content in soil. Age differences of soils formed on glacial sediments of the last but one and the last glaciation are mostly revealed through links between AAE importance and clay content in soil. The differences of AAE importance in soils formed on sediments of different phases of the last glaciation are mostly related to more distinct changes of the factors with which AAE correlate, and purer AAE associations in soils of the Lower Nemunas Plain than in soils of the Mūša–Nemunėlis Plain.

Key words: allotigenic accessory elements, age of soil-forming sediments, geochemical variation, factor analysis, importance in factor loading matrix

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INTRODUCTION

When natural or anthropogenic changes of the environment or its particular components are investigated, factor analysis is applied for data treatment (Birke et al., 1993; Morsy, 1993; Ramanathan et al., 1996; De Vivo et al., 1997, Gupta, 1998; Bityukova et al., 2000; Heemken et al., 2000; Reimann et al., 2002; Sajn, 2006). To reveal trace element paragenetic associations in soil, the application of factor analysis in Lithuania was started in 1988 at the Geochemical Department of the Institute of Geology (Baltakis, 1993). It was revealed that geochemical peculiarities of natural (uncontaminated) soils are predetermined by two main associations of trace elements related to different carriers. These associations were called lithogenic and clastogenic (Baltakis, 1993; Kadūnas et al., 1999a) or otherwise allotigenic and allotigenic accessory (Kadūnas et al., 1999b). The respective trace elements can be denominated as allotigenic (AE) or allotigenic accessory (AAE).

Allothigenic accessory association is formed by trace elements (Ti, Zr, Nb, Y, Yb, La), which are related to weathering-resistant accessory heavy minerals. They accumulate in different grain-size fractions, although their greater part is found in silt and sand fractions which are enriched in their mineral carriers. Generalisation of AAE into allothigenic accessory association is partly relative, because part of AAE can exist in other modes of occurrence. It is known that the composition of paragenetic associations depends on mineral and grain-size composition, the age and origin of soil-forming sediments (Kadūnas et al., 1999a; 1999b). However, little is known about the reasons that predetermine the variation of the importance of trace element groups according to loadings on factors arranged in descending order of variance. A longer duration of the weathering and climate change predetermines a relative enrichment of soil in weathering-resistant heavy minerals and related AAE. Therefore, the unequal time-span of weathering and climate change in various soil regions should be reflected in the different content of AAE in soil and should lead to their different importance in factor loading matrices.

The aim of this research was to evaluate links between AAE importance in factor loading matrix (AAE importance) and soil age, the content of clay and anomalousness in different soil regions of Lithuania, where soils have been formed on sediments of the last but one glaciation and various deglaciation phases of the last glaciation and where the highest content of AAE was found, without taking into account the origin of soil-forming sediments. In this way, the purpose was to find out the statistical expression of soil geochemical variation. Although there are many factors that simultaneously influence factor analysis results, this research is likely to be a new step in their clarification and will be useful for revealing the regularities of soil geochemical variation.

METHODS

Object. Soil geochemical data stored at the Environmental Geochemistry Department of the Institute of Geology and Geography and obtained for compiling the Geochemical Atlas of Lithuania (Kadūnas et al., 1999a) were used for factor analysis. Positive geochemical anomalies were revealed during the investigation of trace element distribution on the territory of the country (Kadūnas, 1999). From all Lithuanian soil regions, those with the most contrasting multi-element anomalies and one of the highest contents of AAE were selected. Besides, the anomalies were chosen in soil formed on sediments of different age glaciation: in the Ašmena Highlands – of Medininkai (Upper Saalian) glaciation, in the Lower Nemunas Plain and the Mūša–Nemunėlis Plain – of different phases of the Nemunas (Weichselian) glaciation (Mid-Lithuanian phase and North-Lithuanian phase, respectively) (Figure).

The initial data set from the Ašmena Highlands contains analytical results of 48 soil samples obtained by atomic emission spectrophotometry (16 sandy, 17 sandy-loamy and 15 loamy-clayey samples), from the Mūša–Nemunėlis Plain – of 119 samples (37, 42 and 42, respectively), from the Lower Nemunas Plain – of 152 samples (50, 47 and 55, respectively). The methods of soil sampling and sample preparation for analysis are described in earlier publications (Kadūnas et al., 1999a). The following variables were used in factor analysis: loss on ignition (LOI), pH and the contents of 25 trace elements (Li, B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Nb, Y, La, Yb, Sc, Ba, Sr, Rb).

Data selection and treatment. In each soil region, the primary data sets of sandy, sandy-loamy and loamy-clayey soil were selected without classifying them according to the genesis of soil-forming sediments. They were subdivided into un-anomalous and anomalous subsets. The samples with the content of at least one element exceeding the upper limit $X + 2S$, where X is the mean value and S is the standard deviation of element content in Lithuanian soils, were attributed to the anomalous subset of a soil region. In this way, all samples with an anomalous content of at least one AAE were classified to the subset of anomalous samples. The remaining samples were attributed to the un-anomalous subset of the region. Factor analysis was applied for the primary data set and for un-anomalous and anomalous subsets. Due to the small number of anomalous samples from the Ašmena Highlands, factor analysis for anomalous and un-anomalous subsets of this region was not performed.

For evaluating the accumulation of different AAE in various grain-size types of a soil region, the coefficients of accumulation (Kk) were calculated by dividing the median contents of elements in each grain-size type of soil in the region by respective background values determined in the whole country. For evaluating the accumulation of all AAE in various grain-size types of soil in a region, the coefficient of accumulation of AAE association (Kk_{asoc}) was calculated as the average value of six coefficients of accumulation.

Variation of AAE importance was revealed through paragenetic associations in a sorted factor loading matrix, obtained by principal component analysis with varimax rotation applying the SPSS statistical package. Pearson correlation coefficients were calculated for data logarithms. To simplify the research, several limitations were introduced. Firstly, only the main associations related to the first three factors with cumulative factor variance percentage exceeding or close to 50 were taken into account. So the relation of some AAE to further factors was considered to be of a low relative importance. Secondly, the significance level 0.05 for factor loading was changed to 0.01. The aim was to minimise the overlap of paragenetic associations related to different factors and to reduce the number of elements in associations. When the latter is too great, the prevalence of AE over AAE is more probable. So elements with less significant loadings were considered to be of a low relative importance. The elements that are correlated with the given factor stronger than with the other factors belong to the factor kernel (Zinkutė, 2002). The elements that do not belong to the factor kernel, but are significantly associated with it, in tables below are shown in parentheses. The importance of AAE was evaluated in a complex way: according to rank of the factor predetermined by variance percentage, values of significant AAE loadings on the factor and the proportion of AAE and other trace elements in the group with significant factor loadings.

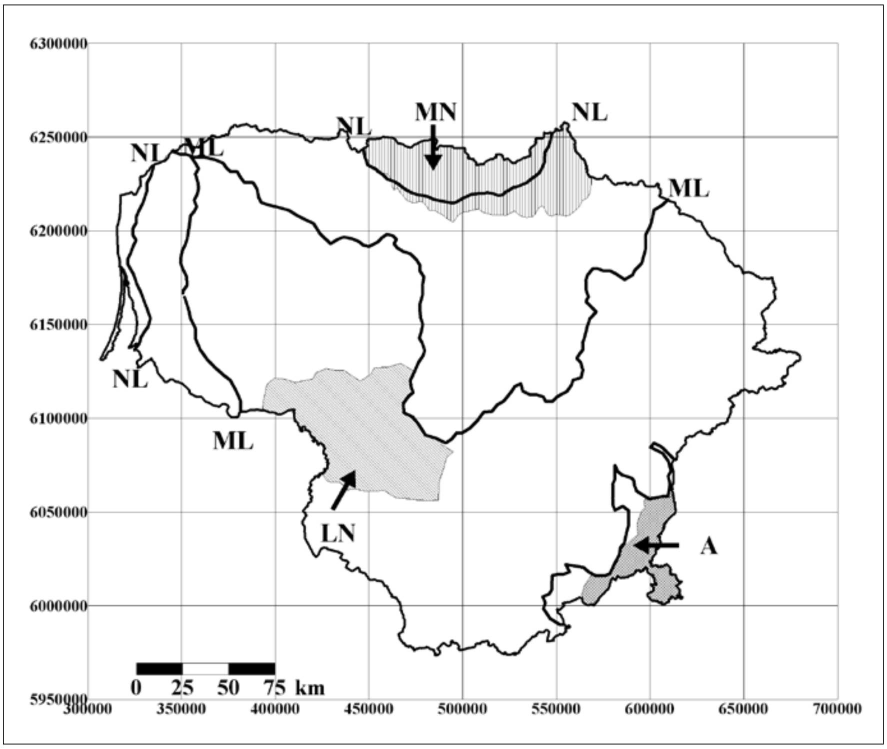

Figure. Areas of the Lithuanian soil regions studied.
Soil regions (after Lietuvos TSR…, 1981): A – the Ašmena Higlands, LN – the Lower Nemunas Plain, MN – the Mūša-Nemunėlis Plain. Limits of some of deglaciation stages of the last (Weichselian, Nemunas) glaciation (after Gaigalas, 2001): GR – Grūda (Brandenburg) stage (or limit of the maximum extention of the last glaciation), ML – Middle-Lithuanian phase, NL – North-Lithuanian phase

Pav. Tirtų Lietuvos dirvožemių rajonų plotai. Dirvožemio rajonai (pagal Lietuvos TSR…, 1981): A – Ašmenos aukštumos, LN – Nemuno žemupio lygumos, MN – Mūšos-Nemunėlio lygumos. Kai kurių paskutinio (Weichselian, Nemuno) apledėjimo ledyno deglaciacijos stadijų (pagal Gaigalas, 2001) ribos: GR – Grūdos (Brandenburgo) stadija (arba paskutinio apledėjimo maksimali riba), ML – Vidurio Lietuvos fazė, NL – Šiaurės Lietuvos fazė

Table 1. **Accumulation of allothigenic accessory elements in particular soil regions of Lithuania**
1 lentelė. **Alotigeninių akcesorinių mikroelementų kaupimasis atskiruose Lietuvos dirvožemių rajonuose**

Element	Coefficients of accumulation Kk								
	Ašmena Highlands			Mūša–Nemunėlis Plain			Lower Nemunas Plain		
	I	II	III	I	II	III	I	II	III
Y	1.16	0.72	0.73	1.42	1.16	1.07	1.16	1.15	1.20
Yb	1.25	0.93	0.86	1.32	1.26	1.12	1.04	1.17	1.23
La	1.06	0.93	0.85	1.12	1.01	0.90	1.12	1.20	1.14
Nb	1.16	1.13	1.07	0.70	0.87	0.88	1.08	1.09	1.08
Ti	1.24	0.99	0.81	0.91	0.91	0.85	1.36	1.25	1.19
Zr	1.58	1.32	1.18	0.71	0.82	0.80	1.31	1.08	1.15
Kk_{asoc}	1.24	1.00	0.92	1.03	1.00	0.94	1.18	1.16	1.17

Coefficients of accumulation of allothigenic accessory elements in grain-size types of soil: I – sandy, II – sandy loamy, III – loamy-clayey. Kk_{asoc} – coefficient of accumulation of allothigenic accessory element association in soil grain-size types.
Alotigeninių akcesorinių mikroelementų kaupimosi koeficientai dirvožemio mechaninės sudėties tipuose: I – smėlio, II – priesmėlio, III – priemolio-molio. Kk_{asoc} – alotigeninių akcesorinių mikroelementų asociacijos kaupimosi koeficientai dirvožemio mechaninės sudėties tipuose.

RESULTS

In the Ašmena Highlands, the highest coefficients of accumulation (Kk) of all AAE are observed in sandy soils and the lowest in loamy-clayey soils. In the Mūša–Nemunėlis Plain, only Y, Yb and La are characterised by such distribution of Kk with an increase of clay content, while in the Lower Nemunas Plain soil – only Zr and Ti (Table 1).

In all soil regions, the highest value of Kk_{asoc} was observed in sand. In soils of the Ašmena Highlands, the values of Kk_{asoc} considerably decrease, as the content of clay increases. The same tendency, though not so obvious, was observed in soils of the Mūša–Nemunėlis Plain. Meanwhile in soils of the Lower Nemunas Plain the values of Kk_{asoc} in different grain-size types of soil differ insignificantly.

In sandy and sandy-loamy soils from the Ašmena Highlands, AAE have significant loadings on the first factor (Table 2). In sandy soils, also Cr and Mn, while in sandy-loamy soils Mn, Ba, Sr, Rb and Co join them. In loamy-clayey soils there are no AAE in the kernels of the first three factors.

In sandy soils from the Lower Nemunas Plain, all AAE are significantly related to the third factor, in sandy-loamy soils to the second one, and in loamy-clayey soils to the first one (Table 3). In un-anomalous sandy soils, the first factor is mixed: both AE and AAE (Y, Yb, La) as well as pH have significant loadings on it. In un-anomalous sandy-loamy and loamy-clayey

Table 2. **Paragenetic associations of trace elements in soils of the Ašmena Highlands**

2 lentelė. **Mikroelementų paragenetinės asociacijos Ašmenos aukštumos dirvožemiuose**

T	n($r_{0,01}$)	F	FVP	CFVP	Paragenetic associations
Sand	16(0.623)	F1	25.9	52.1	**Yb**–**Y**–**Ti**–**Zr**–**La**–Cr–Mn
		F2	14.6		Ba–Li–Ga
		F3	11.7		V–[P]
Sandy loam	17(0.606)	F1	26.0	61.6	Mn–**Ti**–**La**–Ba–**Y**–Sr–Rb–Co
		F2	22.3		Li–Sn–Pb–Ga–Mo–V
		F3	13.3		(**Y**)–[P]
Loam or clay	15(0.641)	F1	38.4	69.0	Ga–V–Cu–Li–Co–Ni–Cr–Zn–B–Pb–Sn–Rb
		F2	15.8		Ba–Sr–Sc–[P]
		F3	14.8		Ag–Mn–**Nb**

Explanations: T – soil grain-size type; n($r_{0,01}$) – number of samples and the absolute limit value of significant factor loading at 0.01 significance level given in parentheses; F – factor; FVP – factor variance percentage; CFVP – cumulative factor variance percentage. Elements of paragenetic associations are written in descending order of significant at 0.01 level loadings; elements in parentheses do not belong to the factor kernel, but are associated with the factor, elements in brackets have negative loadings on the factor. AAE are indicated in bold.

Paaiškinimai: T – dirvožemio mechaninės sudėties tipas; n($r_{0,01}$) – mėginių skaičius, skliaustuose – absoliuti reikšmingos faktoriaus apkrovos, esant 0,01 reikšmingumo lygmeniui, ribinė vertė; F – faktorius; FVP – faktoriaus dispersijos procentinis kiekis; CFVP – sukauptas faktorių dispersijų procentinis kiekis. Paragenetinių asociacijų elementai, surašyti reikšmingų apkrovų, esant 0,01 reikšmingumo lygmeniui, mažėjimo tvarka; elementai paprastuose skliaustuose nepriklauso faktoriaus branduoliui, bet siejasi su faktoriumi; elementai laužtiniuose skliaustuose turi neigiamas apkrovas faktoriui. AAM išryškinti pajuodintu šriftu.

Table 3. **Paragenetic associations of trace elements in soils of the Lower Nemunas Plain**

3 lentelė. **Mikroelementų paragenetinės asociacijos Nemuno žemupio lygumos dirvožemiuose**

T	DS	n($r_{0,01}$)	F	FVP	CFVP	Paragenetic associations
Sand	1	50(0.361)	F1	21.7	57.2	Rb–Co–Ni–Sc–V–Sr–Mn–(Zn, Ba, **Y**, **La**, Ga, **Yb**)
			F2	18.5		Sn–B–Ga–Li–Ag–**Nb**–Mo–(Cr, Pb, V, Ni, Co, **Ti**)
			F3	17.0		**Zr**–**Yb**–**Ti**–**Y**–**La**–Ba–(**Nb**, Cr)
	2	19(0.575)	F1	33.1	69.2	Ba–Sr–Cr–Sc–**Y**–**Yb**–**La**–pH
			F2	20.1		Ni–Rb–Co–V–Zn–Pb–Mn–Ga
			F3	16.0		LOI–Li–Ag–Sn
	3	31(0.456)	F1	19.8	57.2	pH–Ni–Cu–Zn–Co–V–Sc–(Ga, Cr, Rb, **La**)
			F2	19.5		**Yb**–**Zr**–**Y**–Ba–**La**–(**Ti, Nb**)
			F3	17.9		B–Mo–**Nb**–**Ti**–Ga–Sn–Cr–(Pb, Ag, Co)
Sandy loam	1	47(0.372)	F1	25.1	54.0	Ga–V–Cr–B–Ni–Pb–Li–Co–Mo–(**Ti**, **Yb**, **Nb**, Sn, Sc)
			F2	16.5		**Zr**–**Y**–**La**–**Yb**–**Ti**–**Nb**–(Ba)
			F3	12.4		Zn–Cu–Ag–Mn–Sn–(Mo)
	2	28(0.478)	F1	25.1	56.2	Ni–Co–pH–Sc–V–Ga–B–Cr–Sn–(Ba, Cu)
			F2	18.3		**Y**–**La**–**Zr**–**Ti**–**Yb**–(**Nb**)
			F3	12.7		Mo–Pb–Ag
	3	19(0.575)	F1	28.8	57.1	Cr–V–Ni–Ga–**Yb**–**Ti**–B–**Nb**–Sr–Li–Co
			F2	15.0		P–Mn–Cu–Ag–Pb–[Ba]
			F3	13.2		Sc–Rb–LOI
Loam or clay	1	55(0.345)	F1	18.9	48.7	**Y**–**Yb**–**Ti**–**Zr**–**La**–**Nb**–Sr–(Ga, P)–[Sn]
			F2	17.5		V–Ni–B–Co–Cu–Cr–(Ga, Li, Mo)
			F3	12.2		Pb–Ag–Ga–Zn–(P, Mo, **Nb**)–[Rb, Sc]
	2	26(0.496)	F1	23.6	53.5	Co–V–Ni–B–Zn–Sn–Cu–Cr–Mo
			F2	20.6		**Yb**–**Ti**–**Zr**–**Nb**–**La**–**Y**–Ba–Sc
			F3	9.3		pH–Ga–Ag
	3	29(0.471)	F1	20.0	50.5	**Y**–**Yb**–**Ti**–**Zr**–**Nb**–**La**–(Sr)
			F2	15.8		Pb–Ag–P–Sc–Mo–Ga–Rb–(**Nb**)
			F3	14.7		Cu–Co–Ni–pH–Cr–(V, Ga)

Main explanations are given in Table 2. DS – data sets: *1* – primary samples, *2* – un-anomalous samples, *3* – anomalous samples.

Pagrindinius paaiškinimus žr. 2 lentelėje. DS – duomenų aibės: *1* – pirminiai duomenys, *2* – neanomalūs ėminiai, *3* – anomalūs ėminiai.

soils, significant loadings of AAE are found in the second factors. In anomalous sandy soils, AAE are in the kernel of the second factor or associated with it, also Ba is in the kernel of this factor. In anomalous sandy-loamy soils, part of AAE (Ti, Yb, Nb) joins the AE according to significant loadings on the first factor. In anomalous loamy-clayey soils, AAE are significantly correlated with the first factor.

In primary sets of all soil types from the Mūša–Nemunėlis Plain, a mixed association of AAE and AE is related to the first factor (Table 4). The importance of AAE in this factor decreases as the content of clay increases, although the number of AAE remains the same in sandy and sandy-loamy soils and slightly increases in loamy-clayey soils: in sand there are 4 AE and 5 AAE, in sandy loam 9 and 5, while in loamy-clay 12 and 6, respectively. Like in the first factors, the composition of variable groups significantly related to the second and third factors in different soil grain-size types is rather mixed due to various modes of occurrence of elements. However, unlike in the first factors, the number of AAE with significant loadings on the next two factors is lower and AAE do not belong to factor kernels: they are associated with the second factor in sandy-loamy and loamy-clayey soils and with the third factor in loamy-clayey soils. In un-anomalous sandy soils, Y and Yb as well as LOI are significantly related to the first factor, while in anomalous soils the first factor is formed by a mixed association of AAE and AE, besides, almost all AAE, except Nb, are present in its kernel. In un-anomalous sandy-loamy soils, AAE and AE form a mixed association related to the first factor, while in un-anomalous loamy-clayey soils four AAE are present in the kernel of the second factor and form a pure association. In anomalous sandy-loamy soils, AAE with AE have significant loadings on the second factor, while in anomalous loamy-clayey soils four AAE and seven other elements are significantly correlated with the first factor.

DISCUSSION

To evaluate the variation of AAE importance, it is substantial to relate it with the coefficients of accumulation of these elements, which in natural soils depend on natural processes (weathering, soil formation, formation of geochemical barriers), their duration and intensity, also on the properties of soil-forming sediments and elements themselves. The main mineral-carrier of Zr, which is considered to be a little mobile trace element in soil, is zircon which is attributed to the most weathering-resistant minerals (Morton, 1986; Lång, 2000). Therefore, the variation of Zr content in soil reflects well the duration of weathering and climate change. In all soil grain-size types from the Ašmena Highlands where soils have been formed on older sediments compared to the rest of the territory of Lithuania, Zr is characterised by the highest Kk values in comparison with the other regions. They are lower in soils from the Lower Nemunas Plain, which have been formed on the Mid-Lithuanian phase of Nemunas (Weichselian) glaciation, and the lowest – in soils from the Mūša–Nemunėlis Plain, which have been formed on the sediments of the latest phase of the last glaciation.

The values of Kk_{asoc} reveal the general peculiarities of soil AAE contents. In all the soil regions investigated, the highest Kk_{asoc} values were found in sandy soils (Table 1). In soils from the Ašmena Highlands, the values of Kk_{asoc} markedly decrease with an increase of soil clay content. The same tendency, though less pronounced, is observed also in soils from the Mūša–Nemunėlis Plain. The differences among the Kk_{asoc} values in soil from the Lower Nemunas Plain are negligible. The longer duration of weathering and soil-forming processes in the Ašmena Highlands compared to the rest of Lithuanian territory influenced trace element contents in soils. This circumstance predetermined a more intensive redistribution of trace elements, which is confirmed by the values of general geochemical indices. According to them, soils of this region can be clearly distinguished from other soil regions: the coefficient of geochemical contrast is the highest among all soil regions, while the additive geochemical index is the lowest (Kadūnas, 2000). This peculiarity indicates the prevailing tendency of trace element leaching from soil and at the same time the rise of a distinct contrast among the contents of trace elements: for some of them (P, Mn, Ag, Zr, Nb, Y) they increased several times, for others (Cr, Co, Ni, V, Sc) they decreased (Kadūnas, 2000). For these reasons, the values of Kk_{asoc} in sandy and loamy-clayey soils from the Ašmena Highlands differ significantly, while in soils from the other regions the differences among Kk_{asoc} values are insignificant.

In the oldest soils of the Ašmena Highlands, the importance of AAE is in inverse ratio with soil clay content, i.e. AAE importance decreases as the content of clay increases (Table 2). Such relationship, as well as obvious decrease of Kk_{asoc} values with the growth of clay content was predetermined by a longer than in other parts of Lithuania duration of weathering and forming of soils and their elemental composition in the Ašmena Highlands resulting in a more intensive redistribution of AAE and other trace elements in the soil profile. A detailed chemical-mineralogical research of sandy-loamy soils from the Ašmena Highlands has shown that the contribution of AAE related to heavy minerals in the fine silt fraction (0.063–0.005 mm) makes up more than 90% of the total content in soil for Zr and Nb, about 70% for Y and about 50% for Ti and Yb (Vareikienė, 2005). This fact implies that the redistribution of AAE in sandy soils can be preconditioned by an even more intensive relative accumulation of heavy minerals in comparison with sandy-loamy and loamy-clayey soils. Therefore, in sandy soils there are more AAE significantly related to the first factor, meanwhile in sandy-loamy soils their number markedly decreases and in loamy-clayey soils almost vanishes.

In soils of the Lower Nemunas Plain, the anomalies of AAE are especially typical. In soils of this region unclassified according to grain-size type, the most abundant anomalies of Ti, Y, Yb, La and Nb were revealed in comparison with the other soil regions, while the anomalousness of Zr is higher only in the Ašmena Highlands (Kadūnas, 2000). An obvious direct relationship among the importance of AAE, soil clay content and soil anomalousness was observed in the soil of this plain (Table 3). Both in anomalous and in un-anomalous data subsets, the importance of AAE increased with an increase of soil clay content. These soils were formed on sediments of the Jūra–Šešupė glaciolacustrine basin with a characteristic lamination of clay and a higher silt content in the clay series (Kazakauskas, 2000). Enrichment of soil-forming sediments with AAE can be related to the hydrodynamic differentiation of sedimentary material

Table 4. **Paragenetic associations of trace elements in soils of the Mūša–Nemunėlis Plain**
4 lentelė. **Mikroelementų paragenetinės asociacijos Mūšos-Nemunėlio lygumos dirvožemiuose**

T	DS	$n(r_{0,01})$	F	FVP	CFVP	Paragenetic associations
Sand	1	37(0.418)	F1	33.1	60.7	**Yb**–**Y**–Ba–**Zr**–Sc–**Ti**–Cr–**La**–Co–(Ni, Li, Rb)
			F2	17.6		Cu–LOI–Pb–Ni–V–Zn–(Mo)–[pH]
			F3	10.1		B–Ag–Mo–Sn
	2	14(0.661)	F1	30.2	61.1	LOI–**Y**–**Yb**
			F2	16.7		Cu–Zn–Mn
			F3	14.2		Pb–Ga
	3	23(0.526)	F1	37.8	66.7	**Y**–**Yb**–**Ti**–V–**Zr**–**La**–Cr–Co–Sc–Ba–Ni
			F2	18.1		Kn–Pb–Cu–[pH, Rb]
			F3	10.9		Zn–Mo–Ag–Sn–[B]
Sandy loam	1	42(0.393)	F1	41.4	62.5	Co–**Ti**–V–B–Ga–Rb–Cr–**La**–**Y**–Zn–Ni–**Zr**–**Yb**–Li–(**Nb**, Sc)
			F2	12.6		Ba–Sc–Sn–(**Zr**, **Yb**, **Y**, Li, Cr, Ag)
			F3	8.5		pH–Mo–(Mn, P)–[LOI]
	2	30(0.463)	F1	39.4	63.2	Sc–**Y**–**Zr**–Ba–**Yb**–**Ti**–Cr–Co–Ga–Li–**La**–(**Nb**, Ag)
			F2	14.0		Mn–Pb–Mo–Ag–(P, pH)
			F3	9.8		Sr–**Nb**–P
	3	12(0.708)	F1	39.6	70.4	Co–Ga–B–V–Pb–Ni–Mn
			F2	17.6		**Zr**–Sn–Sc–**Yb**
			F3	13.3		pH–[LOI]
Loam or clay	1	42(0.393)	F1	47.5	67.0	Ni–V–Cr–Ga–B–Co–Li–**Ti**–**La**–Rb–Sn–Zn–Cu–**Yb**–**Y**–Pb–**Zr**–**Nb**–(Mn)
			F2	11.6		P–(Zn, **Y, La**, Pb, **Nb**, LOI, **Ti, Zr**, Mo)
			F3	7.9		Ba–Sc–(**Yb**)
	2	26(0.496)	F1	27.7	54.6	B–Ni–Co–Cr–Li–Ga–V–Rb–Sr–[P]
			F2	15.8		**Y**–**Zr**–**Ti**–**La**–(V)
			F3	11.1		Ag–Zn–Sn–Mo–Pb–(Li)–[LOI, Rb]
	3	16(0.623)	F1	49.6	74.0	**Y**–Ag–**Yb**–Zn–**La**–Li–P–**Zr**–Sn–Pb–Ga
			F2	13.7		B–Mn–V–Co
			F3	10.8		Sr–Cu–Rb–Ni

Main explanations are given in Table 2. DS – data sets: *1* – primary samples, *2* – un-anomalous samples, *3* – anomalous samples.
Pagrindinius paaiškinimus žr. 2 lentelėje. DS – duomenų aibės: *1* – pirminiai duomenys, *2* – neanomalūs ėminiai, *3* – anomalūs ėminiai.

within the glaciolacustrine basin: in sandy sediments this accumulation can be explained by formation of heavy mineral concentrates in particular near-shore zones of the basin, while in loamy-clayey sediments – by the transportation of silt to deeper zones of the glaciolacustrine basin, leading to a higher silt admixture in clay and therefore a higher content of heavy minerals from silt fraction. In loamy-clayey soil, the highest content of heavy minerals was determined mainly in the fine silt fraction (Vareikienė, 2005). The greatest importance of AAE in loamy-clayey soil can be explained by the above-mentioned reason.

In soils of the Mūša–Nemunėlis Plain, which have been formed on the North-Lithuanian phase of the Nemunas (Weichselian) glaciation, the importance of AAE could be predetermined not only by their age, but also by chemical and mineral composition of soil-forming sediments and soils: the bedrock of carbonate rocks lying not deep from the Earth's surface predetermined the highest median pH value among all soil regions, and such alkaline reaction of soil favoured the accumulation of some of AE. Therefore, in all grain-size types of soils, the main factor indicates a mixed association of AAE and AE (Table 4). The importance of AAE is predetermined by the proportion of the number of AAE and the number of other trace elements having significant loadings on the first factor, as well as by the values of the loadings on this factor. A more intensive leaching of carbonates from sandy soils compared to sandy-loamy or loamy-clayey soils during weathering and soil-forming processes lead to a greater importance of AAE according to the ratio of their number and the number of AE in the main factor. This importance decreases as soil clay content increases. Different AAE are redistributed in the factor loading matrix with significant loadings both on the first factor and on the other factors. In un-anomalous soils, the importance of AAE also decreases with the growth of soil clay content: in un-anomalous sandy soils two AAE (together with loss on ignition) have significant loadings on the first factor, in un-anomalous sandy-loamy soils AAE and AE form a mixed association related to the first factor, while in un-anomalous loamy-clayey soils the AAE association is found in the kernel of the second factor. Meanwhile, in anomalous soils from the Mūša–Nemunėlis Plain the tendency is slightly different: the lowest importance of AAE is observed in sandy-loamy soils, it grows both with an increase of clay content and with an increase of sand content. Such a different tendency can be explained by the variation of distribution of heavy minerals in fractions and the proportions between different modes of AAE occurrence. Both in anomalous sandy and in anomalous loamy-clayey soils of this region, mixed AAE and AE associations are related to the first factors, however, in the first case they contain more AAE and have relatively higher loadings. This suggests that in anomalous sandy soils AAE are probably bound to a crystalline mode of occurrence and in anomalous loamy-clayey soils to other modes of occurrence. High loadings of Y, Yb and La in the latter case lead to a speculation that AAE can be bound to amorphous forms of carbonates or Fe and Mn hydroxides (Zhu et al., 1992).

CONCLUSIONS

In soils of the Ašmena Highlands considered to be the oldest in Lithuania, the importance of AAE is in a direct relation with the coefficient of accumulation of the AAE association and in an inverse relation with clay content in soil. Only sandy soils are characterised by a purer AAE association.

In soils of the Lower Nemunas Plain, which are younger than soils of the Ašmena Highlands, the importance of AAE is directly related with soil clay content and soil anomalousness. With an increase of soil clay content, the importance of AAE increases both in un-anomalous and anomalous soils. In each grain-size type of soil AAE are significantly correlated with a single factor and form pure complete paragenetic associations; the same concerns anomalous sandy and loamy-clayey soils. In un-anomalous soils of all grain-size types and in anomalous sandy-loamy soils, AAE and other trace elements form mixed associations related to factors.

In soils of the Mūša–Nemunėlis Plain, formed on the youngest soil-forming sediments of Lithuania, both in primary and anomalous soils the first factors are formed by a mixed AAE and AE association in which the importance of AAE decreases with an increase of clay content in soil both in the primary set and in the un-anomalous subset of samples. Meanwhile in the anomalous subset of samples from the region the tendency is slightly different: the lowest importance of AAE is observed in sandy-loamy soils; it grows with an increase in both clay and sand contents.

Age differences manifested through the unequal duration of the weathering of soil-forming sediments are most obvious when comparing soils formed on sediments of the last but one and the last glaciation. In the Ašmena Highlands, the AAE importance is in inverse ratio with the clay content in soil, meanwhile in the Lower Nemunas Plain is in direct ratio. Although in soils from the Mūša–Nemunėlis Plain, which are the youngest in Lithuania, there is also a reverse relationship between the importance of AAE and soil clay content, like in the oldest soils of the Ašmena Highlands, sandy soils of the latter region, unlike the Mūša–Nemunėlis Plain, are characterised by a purer AAE association.

Despite smaller age differences between soils of the Lower Nemunas Plain and the Mūša–Nemunėlis Plain, which were formed on sediments of various phases of the same last glaciation, the importance of AAE in soils of these regions is different. Unlike in the Mūša–Nemunėlis Plain, soils in the Lower Nemunas Plain are characterised by more pronounced changes in AAE correlation with different factors arranged in descending order of their variance and purer AAE associations related to these factors.

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ALOTIGENINIŲ AKCESORINIŲ MIKROELEMENTŲ SVARBA FAKTORINIŲ APKROVŲ MATRICOJE – SKIRTINGO AMŽIAUS DIRVOŽEMIŲ GEOCHEMINĖS KAITOS STATISTINĖ IŠRAIŠKA

Santrauka

Ilgesnė dūlėjimo trukmė ir klimato kaita lemia dirvožemio santykinį praturtinimą atspariais dūlėjimui sunkiaisiais mineralais ir su jais susijusiais alotigeniniais akcesoriniais mikroelementais Y, Yb, La, Ti, Zr, Nb (AAM). Lietuvos dirvožemių rajonuose, kurių dirvožemiai susiformavę ant priešpaskutinio ir paskutinio apledėjimo skirtingų fazių nuogulų ir kuriuose nustatyti didžiausi AAM kiekiai, įvertinti ryšiai tarp AAM svarbos faktorinių apkrovų matricoje (AAM svarbos) ir dirvožemio amžiaus, molingumo (molingos dalies kiekio skirtingos mechaninės sudėties dirvožemiuose) ir anomalingumo nediferencijuojant dirvožemių pagal jų dirvodarinių nuogulų genezę. Darbe panaudoti Lietuvos geocheminio atlaso duomenys, nustatyti dirvožemio <1 mm frakcijoje atominės emisinės spektrofotometrinės analizės metodu. Kiekviename rajone analizuoti smėlio, priesmėlio ir priemolio-molio dirvožemiai. Faktorinei analizei pasirinkti pradinių, neanomalių ir anomalių ėminių masyvai, kuriuose AAM svarbos kaita išryškinta atsižvelgiant tik į pirmųjų trijų faktorių, kurių suminė dispersija viršija arba artima 50%, asociacijas. Faktorinėms apkrovoms pasirinktas reikšmingumo lygmuo 0,01. AAM svarba vertinta atsižvelgiant į faktoriaus rangą pagal jo dispersijos procentą, AAM reikšmingų apkrovų faktoriui dydį ir AAM bei kitų mikroelementų skaičiaus santykį reikšmingų faktoriaus apkrovų grupėje. Seniausiuose pagal amžių Ašmenos aukštumos dirvožemiuose AAM svarba su dirvožemio molingumu susijusi atvirkštiniu ryšiu. Jaunesniuose Nemuno žemupio lygumos dirvožemiuose AAM svarba didėja didėjant dirvožemio molingumui ir anomalingumui. Didėjant molingumui ji didėja tiek neanomaliuose, tiek anomaliuose dirvožemiuose. Mūšos-Nemunėlio lygumos dirvožemiuose, susiformavusiuose jauniausiose Lietuvos dirvodarinėse nuogulose, tiek bendrų, tiek ir anomalių dirvožemių pirmąjį faktorių formuoja mišri alotigeninių mikroelementų ir AAM asociacija, kurios AAM svarba mažėja didėjant dirvožemio molingumui. Dirvožemių amžiaus skirtumai daugiausia išryškėja priešpaskutinio ir paskutinio apledėjimo nuogulose suformuotų dirvožemių AAM svarbos ir dirvožemio molingumo ryšiuose. Dirvožemiuose, susiformavusiuose to paties apledėjimo skirtingų fazių nuogulose, AAM svarbos skirtumai susiję su ryškesne faktorių, su kuriais koreliuoja AAM, kaita augant molingumui ir grynesnėmis AAM asociacijomis Nemuno žemupio lygumos dirvožemiuose nei Mūšos-Nemunėlio.

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ВАЖНОСТЬ АЛЛОТИГЕННЫХ АКЦЕССОРНЫХ МИКРОЭЛЕМЕНТОВ В МАТРИЦЕ ФАКТОРНЫХ НАГРУЗОК КАК СТАТИСТИЧЕСКОЕ ВЫРАЖЕНИЕ ГЕОХИМИЧЕСКОЙ ИЗМЕНЧИВОСТИ ПОЧВ РАЗЛИЧНОГО ВОЗРАСТА

Резюме

Более продолжительная длительность выветривания и изменение климата обусловили относительное обогащение верхних слоев почв устойчивыми к выветриванию тяжёлыми минералами и связанными с ними аллотигенными акцессорными микроэлементами Y, Yb, La, Ti, Zr, Nb (AAM). В почвенных районах Литвы, в которых почвы сформировались на отложениях предпоследнего и различных фазах последнего оледенения и в которых найдено наивысшее содержание AAM, установлены связи между важностью распределения AAM в матрице факторных нагрузок (важностью AAM) и возрастом почв, их глинистостью (количеством глинистой части в почвах разного механического состава) и аномальностью, без подразделения почвы по генезису почвообразующих пород. В работе использованы данные Геохимического атласа Литвы, полученные атомным эмиссионным спектрофотометрическим анализом фракции почв <1 мм. В каждом почвенном районе исследованы песчаные, супесчаные и суглинисто-глинистые почвы. Для факторного анализа выбраны массивы первичных, неаномальных и аномальных данных, в которых важность AAM определена по ассоциациям первых трёх факторов, для которых суммарный процент дисперсии больше или близок 50. Для факторных нагрузок использовался уровень значимости 0,01. Важность AAM определена на основании ранга фактора по проценту его дисперсии, величин значимых нагрузок AAM на фактор и соотношению числа AAM и других микроэлементов в группе со значимыми нагрузками на фактор. В древнейших почвах Ашмянской возвышенности важность AAM связана со степенью глинистости почв обратной связью. В более молодых, чем в Ашмянской возвышенности, почвах Нижненямунской равнины важность AAM увеличивается при возрастании глинистости и аномальности почвы. При возрастании глинистости важность AAM увеличивается, как в неаномальных, так и в аномальных почвах. В почвах равнины Муши и Нямунелиса, сформировавшихся на самых молодых почвообразующих породах Литвы, как в первичных, так и в аномальных почвах первый фактор формирует смешанная ассоциация из AAM и аллотигенных микроэлементов, в которой важность AAM уменьшается при возрастании глинистости почвы. Разница в возрасте почв, сформировавшихся на отложениях предпоследнего и последнего оледенения, наиболее ярко выражается в связях между важностью AAM и глинистостью почв. В почвах, сформировавшихся на отложениях различных фаз последнего оледенения, различия в важности AAM проявляются в более выявленной изменчивости факторов, с которыми существенно коррелируют AAM, при возрастании глинистости и более чистом составе ассоциаций AAM в почвах Нижненямунской равнины по сравнению с равниной Муши и Нямунелиса.