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## **Long-term agrogenic impact on agricultural soil geochemistry in East and West Lithuania**

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Direct and indirect impacts of different anthropogenic load on element distribution and redistribution were investigated in agricultural soils. The atomic absorption spectrophotometry method and radiofluorescence analysis showed that the soils were affected by agrogenic agricultural activities.

Total soil concentrations of some elements were found to be enhanced by agrogenic activities, but for some elements these enhancements were not statistically significant, and for other elements the concentrations are enhanced at some sites but diminished at others. As compared to the background levels of the elements studied, the anthropogenic agrogenic impact in Albeluvisols of Western Lithuania was revealed in statistically reliable deviations of 11 elements (Al, Ca, Fe, Mg, B, Ba, Co, Cu, Ni, Sr, Zn), while in Eastern Lithuanian Luvisols only four elements (Ca, Co, Cu, Sr) showed such deviations. Regarding the anthropogenic impact, significant changes  $(>2$ versus the background levels) in the Western zone were shown only by Ca and Sr and in the Eastern zone only by Ca. The mean soil concentrations reported were all substantially lower than the maximum permitted concentrations.

**Key words**: long-term field experiments, fertilisation, liming, trace and rare earth elements, Lithuania

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### **INTRODUCTION**

In soils, the content of chemical elements depends on the type and genetic properties of pedogenic sediments, their texture, the trend of the pedogenic

process, the chemical and physical characteristics of soil, anthropogenic load, etc. (Pauliukevièius, 1986; Kadûnas, 1998; Kadûnas et al. 1999; Maþvila & Adomaitis, 2001, Maþvila et al., 2001). The antropogenic impact on soil evokes new elementary processes in natural pedogenesis, induces transformation of soil morphological traits, modifies the dynamics of soil composition and properties as well as its macro- and microstructure (Seredina et al., 2003). There are numerous studies to document the fact that agricultural activities change the total and mobile content of elements in soil, resulting in formation of their new associations, and exert effects on the basic chemical characteristics of soil (Сапрыкин, 1984; Baltakis, 1993; Kadûnas et al. 1996; Murray et al. 2004). In this way the objects close in the geographic or agronomic respects acquire different geochemical properties.

The anthropogenic impact of agriculture can be differentiated into agrotechnical and agrogenic. The agrotechnical impact is induced by mechanical soil cultivation when Mn, Ni, Cr, Fe, Co, V and Pb get into it. The agrogenic impact directly follows from agricultural activities such as soil fertilization with various mineral (nitrogen, potassium, phosphorus) and organic fertilizers, liming (Vareikienë, 1998). Commercial fertilizers in Lithuania have been intensively used for decades since 60ties. Hence, even low annual accumulations may finally build up undesired concentrations in soil, especially where fertilizers with high heavy metal or rare earth element concentrations are used (Mortvedt, 1987). It has been noted that phosphorous fertilizers produced from apatite (or from concentrated phosphate) introduce a particularly abundant association of chemical compounds (Ba, Mn, Ni, Cu, Zn, Sr, V, Y, Zr et al.) as soil admixtures (Сает, 1990; Todorova, 1995; Rutherford et al. 1996; Mortvedt & Beaton, 1996). The most distinct soil geochemical anomalies are formed by element impurities including rare-earth elements from phosphate raw materials (Abdel-Haleem et al., 2001). These elements are absorbed by plants and some are contaminants, which might become hazardous to the environment and health (Lavado et al., 1999). In contrast, other authors concluded that there were no discernible changes in the masses of trace elements that could be unambiguously associated with the application of phosphate fertilizers for 50 years (Agbenin & Felix-Henningsen, 2001). However, some authors like to stress that the major contribution of heavy metals arises from the use of organic fertilizers (Dach & Starmans, 2005).

Studies of trace element dynamics in long-term field experiments have shown to be a useful complementary tool to assess soil accumulation (Jones et al., 1987). Because of their indefinite residence time in soils, the input of heavy metals and other trace elements to agricultural lands with soil amendments may pose the greatest (albeit undetermined) longterm threat (Hesterberg, 1998).

With regard to agrogenic load, the West Lithuanian and East Lithuanian zones can be urgent on the territory of Lithuania. In West Lithuania, originally con-

ditionally acid (pHKCl 5.5 and <) soils comprise 66.3% and in East Lithuania 51.9% (Maþvila, 1998). These soils in the period 1950–1970 till 1990 were intensively limed, and in that period they underwent at least three rounds of liming (Švedas, 1997). Element diversity in these soils results not only from mineral and organic fertilization, but also from the liming materials. A series of field trials were established to investigate the combined effect of liming and fertilization on these soils on a local scale and to assess the status of the agroecosystems in 1947–1982. In these trials, seven of this series, in separate treatments the chemical composition of soil was investigated. Eighteen elements important with respect to agronomical, nutritional or environmental pollution were studied. We determined the total percentage of the elements abundant in soil, such as Al, Fe, Ca, K or somewhat less abundant Mg, whose mobility in soil strongly depends on liming. With regard to the national hygiene norms, the soil levels of Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn were assessed (Council Directive 86/278/EEC, 1986). Soil Sr was also tested.

The arable soil layer was chosen as the study object as the most significant part of soil most strongly exposed to agrogenic impact. The purpose of the current study was to determine the chemical composition of agricultural soils, element distribution and redistribution under different type antropogenic load of various intensity in East and West Lithuania.

#### **METHODS**

Soil samples were taken from seven long-term field trials in two Lithuanian soil zones (four in Western and three in Eastern Lithuania, Fig. 1). The trials had a randomized block design, with 3–5 replications of



**Fig. 1.** Location map of soil sampling **1 pav.** Tirtø pavyzdþiø lokalizacija

Element	Ag	В	Ba	Co	Cr	Cu	Ga	La		Mn	Mo
Limit of detection mg $kg^{-1}$	$\vert 0.03 \vert$		30		റ ∼	$\overline{v}$			10	10	0.5
Element	Nb	Ni	D	P <sub>b</sub>	Sc	Sn	Ti				
Limit of detection mg $kg^{-1}$	3	$\Omega$	300				10			0.3	

Table 1. **Limits of detection of AAS analytic technique for chemical elements** 1 lentelë. **Analizuotø elementø AAS metodo jautrumo riba**

Table 2. **Experimental design and impact type tested in West Lithuanian Albeluvisols** 2 lentelë. **Tyrimø schema ir tirtas poveikis Vakarø Lietuvos balkðvaþemiams**

Soil type		Soil texture   Plot size $m^2$	Impact type $(+)$						
			Mineral fertilising	Organic fertilising	Soil liming				
<b>V1.</b> Slacked lime (single application of 6.6 t ha <sup>-1</sup> CaCO <sub>3</sub> in 1948)									
Dystric Albeluvisol (ABd)	Silty loam	75			$\pm$				
<b>V2.</b> Liming & manuring (manure every 7 years 120 t ha <sup>-1</sup> since 1959 applied twice in rotation 60 t ha <sup>-1</sup> )									
Dystric Albeluvisol (ABd)	Silty loam	38	$^{+}$ $\pm$						
V3. Periodical liming (every 7 years since 1949)									
Dystric Albeluvisol (ABd)	Silty loam	60			$\pm$				
V4. Liming (every 7 years from 1976 liming to target pH level) with annual high rates of NPK fertilisation									
Dystric Albeluvisol (ABd)	Silty loam	112	$\mathrm{+}$						

each treatment. The western zone is the region of the most intensive soil leaching and the weakest decomposition of organic substances. The annual precipitation here reaches 700–800 mm, *versus* 500–600 in East Lithuania. In each trial, samples were taken from the control and anthropogenic (most intensively fertilized or limed depending on a trial scheme) treatments of each replication. The field trial location, soil group and study treatments are shown in Tables 2–4. The size of treatment plots in separate trials varied from  $30 \text{ m}^2$  to 112 m<sup>2</sup>. The field trials were established and carried out in accordance with the standard field trial methods (Tonkûnas, 1957; Little & Hills, 1978).

Soil samples were collected in triplicate using a stainless steel sampling tube. Soil samples were composited and brought to the laboratory. For laboratory studies, all samples were air-dried. Soil samples for geochemical composition analysis were sieved through a 1-mm sieve. The analyte  $(< 1$  mm) part was powdered. Applying the atomic absorption spectrophotometry (AAS) method, 17 elements were established (Ag, Al, B, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sn, V, Zn). For their identification a broad scope of spectral lines is used, and their detection limits is low enough to state their natural background level (Table 1). Another method of analysis, which allows to expand the list of the identification elements studied, is radiofluorescence analysis

(RFA), which was used to determine Sr levels. The Sr detection limit is 2 mg  $kg^{-1}$ .

The sample, like in the AAS method, should not be dissolved but is directly analysed with X-rays upon fine grinding (Lis et al., 1999). The soil was analysed at the Institute of Geology & Geography laboratory. Soil texture type was classified according to International Soil Science Society (ISSS) classification.

Data of laboratory analysis were systematized and statistically processed using the statistical method of disperse analysis (ANOVA). The statistical reliability of data was assessed by the absolute limit of least essential difference (P < 0.05) (Little & Hills, 1978).

Soil pollution was assessed according to the national hygiene norms with regard to the maximum permissible concentration (PC) (Lithuanian hygiene norm HN 60:2004; Kadûnas et al. 1996).

As the background value of a chemical substance, its content in non-fertilized soil was analyzed. Anthropogenic impact was assessed according to the ratio of element concentrations: CB (control background) / AI (under agrogenic impact).

#### **RESULTS**

#### *West Lithuania – Samaliðkës trials*

The West Lithuanian zone of soils comprises the Pajûris Lowland and the Þemaièiai Highland. Here,

Table 3. **Changes of topsoil geochemical composition in West Lithuanian Albeluvisols**

3 lentelë. **Armens geocheminës sudëties pokyèiai Vakarø Lietuvos balkðvaþemiuose**

Ele-	PC	V1		$\rm V2$		$_{\rm V3}$		V4	
ments				Percentage of					
		CB	PC	CB	PC	CB	PC	CB	<sub>PC</sub>
Ag	$\boldsymbol{2}$	98	5	113	5	100	5	119	6
B	50	96	68	108	68	100	66	104	67
Ba	600	83	67	106	81	98	56	99	77
Co	30	114	25	100	21	82	21	93	20
Cr	100	102	52	99	49	95	52	147	49
Cu	100	76	8	92	11	95	9	97	11
Mn	1500	92	72	130	72	90	55	85	58
Mo	5	93	15	116	15	84	13	113	18
Ni	75	103	26	114	26	92	23	100	23
Pb	100	99	17	99	14	85	15	103	18
Sn	10	102	27	97	26	95	27	108	27
Sr		120		177		123		214	
$\mathbf V$	150	80	33	102	38	94	37	102	36
Zn	300	67	11	117	16	79	11	85	14

Note. Statistically significant  $(R_{05})$  differences are bolded.

**Site VI**  $\Omega$  $20$ 40 60 80 100 120 **Elements** Al Ca Fe Mg **% □** % of CB **Site V2**  $\Omega$ 50 100 150 200 250 300 **Elements** Al Ca Fe Mg **% ∞ 6 6 % ∞ 6 ∞ 6 ∞ 6 ∞ 6 ∞ 6 ∞ 6 ∞ 6 ∞ 6 ∞ Site V3**  $\overline{0}$ 50 100 150 200 250 300 350 **Elements** Al Ca Fe Mg  **%** ■% of CB **Site V4**  $\Omega$ 50 100 150 200 250 300 **Elements** Al Ca Fe Mg  **%** % of CB



the pedogenic rocks comprise mostly light and medium sandly loam. Climatic conditions in the zone favour the processes of soil leaching and podzolization (Juodis, 2001). In the current study, the zone is represented by four field trials, all in Samaliðkës location of Klaipëda Region (West Þemaièiai plateau). The trial soils are typical of the zone and are Albeluvisols (Table 2).

The investigation in the Samaliðkës field trials allowed to assess a combined agrogenic impact on the arable layer of soil, exerted by liming of various intensity combined with mineral and organic fertilization (Table 3 and Fig. 2).

The geochemical composition of regulary fertilised arable soil at site V1, which 55 years ago had been limed with an aggressive compound (slack lime), reliably differed from that of non-limed soil. In the anthropogenic treatment, statistically reliably lower was the total content of four elements: Mg – 78%, Ba – 83%, Cu – 76% and Zn – 67% of their background level. The total stock of elements exceeding the background level in an increasing order form the following sequence: Cr &  $Sn > Ni > Co$ > Sr. Their content reached 102% to 120% of background values. Assessing the content of elements with regard to PC, it should be noted that none of

> the elements studied exceeded the PC, the highest levels being shown by Ba, B and Mn (67–72% of PC).

In the regularly fertilised arable soil layer at site V2, which had been periodically (every 7 years) limed and abundantly fertilised with organic (120 t ha– 1 ) fertilizers for a period of 45 years, the content of Ca, Fe, as well as of B, Ni, Sr and Zn was reliably higher. Due to a regular long-term liming the content of Ca increased even 2.79 times. Sr content was 1.77 times higher compared to the background level in a nonmanured and non-limed soil. Alongside the abovementioned elements, in the following increasing sequel, also  $V > Fe > Ba > Al$ > B > Ag > Ni > Mo > Zn > Mn exceeded the background level (from 102% to 130%). None of the elements studied by their total values exceeded

100 120  $140$ 

 **%**

**Site V8**

■% of CB





**Fig. 3.** Changes of topsoil macroelement composition in East Lithuanian Luvisols **3 pav.** Makroelementø pokyèiai Rytø Lietuvos iðplautþemiø armenyse

the PC, the highest levels being shown by B, Mn and Ba (68–81% of PC).

**Elements** Al Ca Fe Mg

 **%**

In the arable soil layer at site V4, which had been intensively fertilized with mineral fertilizers and limed, the Ca and Sr levels were statistically reliably higher as compared to non-fertilized and non-limed soil. Under these conditions of intensive agrogenic impact, the content of Ca was 2.48 times and of Sr 2.14 times higher. The background level was exceeded, in the following increasing sequel, also by  $V >$  $Pb > B > Al > Sn > Mo > Ag > Mg > Cr$  (from zone is most remote from the sea, and the climate is continental here. In the East Lithuanian sandy soil region (one of the three zone regions) the pedogenic rocks are fluvioglacial sands. In the region common sandy soils prevail; the agronomic value of soils is very low (Juodis, 2001). The zone is represented by three field trials in Dainava Plain, Vokë trial plots (sites V7–V9), in Vilnius District. The trial soils were Luvisols (Table 4). Studies at the Voke sites allowed to asses a combined agrogenic impact on the arable soil layer of substances used for li-

Table 4. **Experimental design and impact type tested in East Lithuanian Luvisols** 4 lentelë. **Tyrimø schema ir tirtas poveikis Rytø Lietuvos iðplautþemiams**

Soil type		Soil texture   Plot size $m^2$	Impact type $(+)$						
			Mineral fertilising	Organic fertilising	Soil liming				
V7. Calcareous sapropel (200 t ha <sup>-1</sup> single application in 1984) with annual NPK fertilisation									
Haplic Luvisol (LVh)	Silty loam	40		$\pm$					
V8. Dust limestone (single application of 7.18 t ha <sup>-1</sup> CaCO <sub>3</sub> in 1972) with annual NPK fertilisation									
Haplic Luvisol (LVh)	Silty loam	30	$\mathrm{+}$		$\pm$				
<b>V9.</b> Liming (periodical, 24.64 t ha <sup>-1</sup> CaCO <sub>3</sub> applied since 1973) with annual NPK fertilisation									
Haplic Luvisol (LVh)	Silty loam	30							

102% to 147%). None of the elements studied exceeded the PC, and the highest levels were shown by Mn, B and Ba, which reached 58–77% of PC.

In the regularly fertilised arable soil layer at site V3 which had been periodically limed, the level of Ca was even 3.28 times higher. This element introduced with lime and fertilizers has accumulated in the soil. The levels of Al (74%), Fe (80%) and Co (82%) were reliably lower. The background level was exceeded only by Mg and Sr (101% and 123%, respectively). None of the elements studied exceeded the PC; the highest levels were shown by Ba and B, which reahed 56– 66% of PC.

#### *East Lithuania – Vokë trials*

The East Lithuanian soil

Table 5. **Changes in topsoil geochemical composition in East Lithuanian Luvisols**

<b>Elements</b>	PC	V7		V <sub>8</sub>		V9	
				Percentage of			
		CB	PC	CB	PC	CB	PC
Ag	$\boldsymbol{2}$	100	4	103	4	85	4
$\, {\bf B}$	50	99	57	101	54	58	31
Ba	600	95	52	99	64	88	73
Co	30	110	19	95	13	121	17
Cr	100	96	39	104	41	95	40
Cu	100	94	8	122	10	119	9
Mn	1500	114	46	112	45	106	41
Mo	$\overline{5}$	110	13	85	8	109	13
Ni	75	102	17	102	17	87	16
Pb	100	113	15	97	14	102	14
Sn	10	89	25	99	22	120	24
Sr		179		115		179	
V	150	106	26	101	28	98	26
Zn	300	94	3	97	8	100	6

5 lentelë. **Armens geocheminës sudëties pokyèiai Rytø Lietuvos iðplautþemiuose**

Note. Statistically significant  $(R_{05})$  differences are bolded.

ming of various intensity, as well as of mineral and organic mineralization (Table 5 and Fig. 3)

The geochemical composition of a regularly fertilized arable soil (site V7), which 19 years ago had been fertilized with large amounts of calcareous sapropel, showed no reliable difference as compared to non-fertilized soil. Only Sr content was increased, though rather significantly (by 179%). The background level was exceeded also by Al, Mg, Co, Mn, Mo, Ni, Pb and V (from 102% to 115%). The sum total of elements that exceeded the background level made the following increasing sequel:  $Ni > V > Co$  $> Mo > Mg > Pb > Mn > Al$ . None of the elements by their total content in the soil exceeded the PC; Ba and B, which showed the highest content, reached 52–57% of the PC.

A single liming of soil 21 years ago and ever since applied fertilization (site V8) did not induce significant changes in Luvisol. Only the content of Cu was reliably higher (by 22% compared to nonfertilized and non-limed soil). The background level was exceeded, in increasing order, also by B & V  $>$  $Ni > Ag > Cr > Mg > Al > Mn > Sr > Cu > Ca$ (from 101% to 124%). None of the elements studied exceeded the PC; B and Ba showed the highest content, but reached only 54–64% of the PC.

The third Vokë trial (site V9) revealed more significant changes induced in the geochemical composition of Luvisol by liming and fertilization that had lasted over 20 years. Due to the agrogenic impact, the content of Ca (147%), Co (121%) and Sr (179%) exceeded the level of the background treatment, as

did also Cu, Mn, Mo, Pb and Sn (from 102% to 120%). The elements that exceeded the background levels comprised the following sequel (in increasing order): Pb > Mn > Mo > Cu > Sn > Co > Ca > Sr. None of the elements exceeded the PC requirements; Ba, which showed the highest total level, reached 73% of the PC.

#### **DISCUSSION**

Summarizing the results of the investigation, we found that all soils had been affected by agrogenic agricultural activities. Direct introduction of more or less significant amounts of various elements influences also their distribution into groups. However, the degree of the agrogenic impact differed depending on both the peculiarities of a zone and the effect of the means applied.

In Albeluvisols of the Western zone, under various fertilization and liming conditions, the total levels of all elements except Cu were enhanced, whereas in Luvisols of the Eastern zone in all fertilization and liming conditions the levels of Fe, Ba and Zn remained unchanged.

In the Western zone, among the 18 elements studied, the anthropogenic agrogenic impact was reflected in reliable differences of 11 elements. Five of them (Al, Mg, Ba, Co and Cu) showed decreased total levels. Fe and Zn levels varied depending on fertilization and liming peculiarities. The levels of Sr were higher in periodically limed and fertilized arable soil (site V2) and showed a direct dependence on fertilization intensity (site V4). This element in the arable soil layer becomes immobilized at higher Ca levels and lowered soil acidity (at pH increased). When the soil regains its natural acidity, Sr levels show no reliable changes (site V1).

In the Eastern zone, among the 18 elements studied, four (Ca, Co, Cu, Sr) showed a reliable increase in their content under the agrogenic impact. The intensively limed arable soil regularly fertilized with mineral fertilizers was affected most significantly. Worth noting here is an enhanced level of Sr in conditions of agrogenic impact. This element gets into soil as a constituent part of fertilizers (dolomite, potassium, nitrogen of phosphate substances), or its content undergoes changes caused by the altered Sr uptake in polluted soils (Bohlke & Horan, 2000). Increased stores of Cu resulted from impurities in compound fertilizers (Brække, 1999). Earlier research on similar soils (Rimšelis et al. 1997) showed that liming and fertilization had a noticeable effect on the content of mobile forms of heavy metals in such soils, Cu and Zn in particular.

Analysis with regard to the PC showed that in the Western zone the levels of the elements studied, even those whose levels were highest, did not exceed the PC (Mn 58–72%, B 66–68% and Ba 56–

81%). Even Ag and Cu levels were as low as 5– 11%. Most often their total stores as compared to the background treatment were lower in limed soils fertilized with mineral fertilizers and higher in soils fertilized with organic fertilizers. The reasons can be both introduction of these elements with organic fertilizers and the effect of fertilizers enhancing the accumulation of these elements in soil. Neither in the Eastern zone the content of the study elements, even of those that showed the highest levels (B 54–57% and Ba 52–73%), ever exceeded the PC. Even Ag, Zn and Cu levels were as low as 3–10%. The reported medium for Ba in agricultural soil on a Lithuanian scale is from 307 (sandy soils) to 422 mg/kg (loamy soils), for B – 23.9 and 32.2, respectively (Kadûnas et al., 1999). Boron is an essential micronutrient for plants, but the range between deficient and toxic B concentration is smaller than for any other nutrient element (Goldberg, 1997). There is little documentation addressing Ba in contaminated environments. Ba is known to be rather immobile in soils (Mineral elements, 1978; Kabata-Pendias & Pendias, 1992; Pichtel et al. 2000).

Numeriuos investigations on the Middle Lithuania soils concluded that the content of heavy metals determined in the arable land with diferent soil texture even under long-term intensive fertilizing did not exeed the standart background levels (Lubytë & Adomaitis, 1996; Adomaitis et al., 2003).

Our studies showed that the anthropogenic impact on soil with respect to geochemical composition is more pronounced in naturally acid field trial soils of the Western zone, which undergo periodical liming. These soils also by their granulometric structure were somewhat heavier compared to the Eastern zone soils, therefore they are regarded as less resistant to pollution.

#### **CONCLUSIONS**

1. As compared to the background levels of the elements studied, the anthropogenic agrogenic impact in the Western zone of Lithuania was revealed in the statistically reliable deviations of 11 elements (Al, Ca, Fe, Mg, B, Ba, Co, Cu, Ni, Sr, Zn), while in the Eastern zone only four elements (Ca, Co, Cu, Sr) showed such deviations.

2. Regarding the anthropogenic impact, significant changes (>2 *versus* the background levels) in the Western zone were shown only by Ca (2.48–3.28 times) and Sr (2.14 times) and in the Eastern zone only by Ca (2.83 times).

3. The total levels of the elements tested never exceeded the maximum permissible level, thus the soils were assessed as non-polluted. Somewhat higher values were revealed for Ba (up to 73% in the East and 81% in the West Lithuanian soils). However, these levels showed no dependence on the agrogenic impact.

4. It should be emphasized that a long-term agrogenic impact does not yet result in the changes of soil chemical composition (18 elements tested) able to disturb the health of man by a long-term or even life-long exposure to the mentioned elements via plants, water or air and has no direct or indirect effect on hereditability and future generations.

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#### **References**

- Abdel-Haleem A. S., Sroor A., El-Bahi S. M., Zohny E. 2001. Heavy metals and rare earth elements in phosphate fertilizer components using instrumental neutron activation analysis. *Applied Radiation and Isotopes. 55.* 569–573.
- Agbenin J. O., Felix-Henningsen P. 2001. The status and dynamics of some trace elements in a savannah soil under long-term cultivation. *The Science of the Total Environment. 277.* 57–68.
- Adomaitis T., Maþvila J., Eitminavièius L. 2003. A comparative study of heavy metals in the soils of cities and arable lands. *Ekologija. 3.* 12–17.
- Baltakis V. 1993. Foniniai mikroelementø pasiskirstymai ir jø tarpusavio ryðiai Lietuvos dirvoþemiuose. *Geologija. 15.* 32–42.
- Bohlke J. K., Horan M. 2000. Strontium isotope geochemistry of groundwaters and streams affected by agriculture, Locust Grove, MD. *Applied Geochemistry. 15.* 599–609.
- Brække F. H. 1999. Drainage, liming and fertilization of organic soils. II. Distribution of macro elements and heavy-metal accumulation. *Scandinavian Journal of Forest Research. 14.* 64–77.
- Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. *Official Journal* L'1986 No. 181–6.
- Dach J., Starmans D. 2005. Heavy metals balance in Polish and Dutch agronomy: Actual state and previsions for the future. *Agriculture, Ecosystems & Environment. 107*(*4***)**. 309–316.
- Goldberg S. 1997. Reactions of boron with soils. *Plant and Soil*. *193*(*2*). 35–48.
- Hesterberg D. 1998. Biogeochemical cycles and processes leading to changes in mobility of chemicals in soils. *Agriculture, Ecosystems & Environment. 67.* 121–133.
- Jones K. C., Symon C. J., Johnston A. E. 1987. Retrospective analysis of an archived soil collection I. *Met. Sci. Total Environ. 61.* 131–144.
- *Juodis J. 2001. Soil regions.* Lithuanian soils*. Eds M. Eidukeviciene & V. Vasiliauskiene. Collective monograph. Lithuaniae academia scientiarum. 669–708.*
- Kabata-Pendias A., Pendias H. 1992. Trace Elements in Soils and Plants, 2nd ed. CRC Press, Boca Raton, FL. 365 p.
- Kadûnas V., Katinas V., Radzevièius A., Zikuntë R., Taraðkevièius R., Gregorauskienë V. 1996. Geochemical mapping of the zones of increased technological load in Lithuania. Marsina, K. & Vrana K. (eds.). *Environmental Geochemical Baseline Mapping in Europe*. 76–79.
- Kadûnas V. Gamtinës geocheminës anomalijos Lietuvos dirvoþemiuose. 1998. *Geologija. 26.* 27–37.
- Kadûnas V., Budavièius R., Gregorauskienë V., Katinas V., Kliaugienë E., Radzevièius A., Taraðkevièius R. 1999. Geochemical Atlas of Lithuania. Geological Survey of Lithuania – Geological Institute. Vilnius. 96 p.
- Lavado R. S., Porcelli C. A., Alvarez R. 1999. Concentration and distribution of extractable elements in a soil as affected by tillage systems and fertilization. *The Science of the Total Environment. 232.* 185–191.
- Lis J., Pasieczna A., Taraðkevièius R. 1999. Total and partial extraction of selected elements in soil of the Polish–Lithuanian borderland. *Journal of Geochemical Exploration. 66*(*1–2*)*.* 211–217.
- Lithuanian hygiene norm HN 60:2004. Ministry of Health Care of the Republic of Lithuania|Order|V-114|03/08/ 2004. *Valstybës þinios.* Nr. 41–1357.
- Little T. M., Hills F. J. 1978. Agricultural Experimentation: Design and Analysis. John Wiley & Sons, New York. 350 p.
- Lubytë J., Adomaitis T. 1996. The influence of anthropogenic activities on soil and plant contamination*. Agricultural sciences. 2.* 68–76.
- Maþvila J. 1998. Soil acidity and liming of Lithuanian Soils. *Agrochemical Properties of Lithuanian Soils and Their Changes.* Ed. J. Maþvila. *Kaunas. 23–30.*
- Maþvila J., Adomaitis T. 2001. Heavy metals in Lithuanian's soil regions. *Heavy Metals in Lithuanian Soils and Plants*. Ed. J. Maþvila. Kaunas. 112–142.
- Maþvila J., Adomaitis T., Eitmanavièius L. 2001. Heavy metal dependence upon various soil properties. *Heavy metals in Lithuanian soils and plants*. Ed. J. Maþvila. Kaunas. 92–111.
- Mineral Elements in Finnish Crops and Cultivated Soils. 1978. *Acta agriculturae Scandinavica*. Supplementum *20.* Stockholm. 113 p.
- Mortvedt J. J. 1987. Cadmium levels in foils and plants from some long-term soil fertility experiments in the United State of America. *Journal of Environmental Quality. 16.* 137–142.
- Mortvedt J. J., Beaton J. D. 1996. Heavy metal and radionuclide contaminants in phosphate Fertilizers. *Phosphorus in the Global Environment*. SCOPE 54. Wiley & Sons, Chichester. 93–107.
- Murray K. S., Rogers D. T., Kaufman M. M. 2004. Heavy metals in an urban watershed in Southeastern Michigan. *Journal of Environmental Quality. 33.* 163–172.
- Pauliukevièius G. 1986. Cheminiø elementø kiekiai landðafte. Vilnius. 128 p.
- Pichtel J., Kuroiwa K., Sawyer H. T. 2000. Distribution of Pb, Cd and Ba in soils and plants of two contaminated sites. *Environmental Pollution. 110.* 171–178.
- Rimšelis J., Greimas G., Ignotas V. 1997. The amount and activity of heavy metals in soddy podzolic sandy loam soil at different cultivation levels. *Agricultural Sciences. 4.* 3–8.
- Rutherford P. M., Dudas M. J., Arocena J. M. 1996. Heterogeneous distribution of radionuclides, barium and strontium in phosphogypsum by-product. *The Science of The Total Environment. 180.* 201–209.
- Seredina V. P., Kulizhskii S. P. & Afanas'eva N. N. 2003. Agrogenic transformation of Chernozems in the Koibal Steppe (Khakassiya). *Eurasian Soil Science. 36.* 209– 217.
- Švedas A. 1997. Prospects for the use of the Lithuanian climate potential. *Prospects for Rational Use of the Lithuanian Climate and Soil Potential*. Dotnuva-Akademija. 19–25.
- Todorova E. I., Dombalov I. P. 1995. Production of phosphoric acid with a low content of impurities. *Fert Res. 41*. 125–128.
- Tonkûnas J. 1957. Lauko bandymø metodas. Vilnius: Valst. polit. ir moksl. leidykla. 252 p.
- Vareikienë O. 1998. The influence of agriculture on the background values of microelements in Lithuanian soils. *Geologija. 26.* 61–67.
- Ñàåò Þ. Å. 1990. Ãåîõèìèÿ îêðóæàþùåé ñðåäû. Ìîñêâà. 335 ñ.
- Ñàïðûêèí Ô. ß. 1984. Ãåîõèìèÿ ïî÷â è îõðàíà ïðèðîäû. Ëåíèíãðàä. 231 ñ.

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#### **ILGALAIKIS AGROGENINIS POVEIKIS DIRBAMØ RYTØ IR VAKARØ LIETUVOS DIRVOÞEMIØ GEOCHEMINEI SUDËÈIAI**

#### Santrauka

Tyrimø metu geochemiðkai ávertintas antropogeninis poveikis dirbamø dirvoþemiø armeniui, pasireiðkiantis tiesiogiai patekusiø elementø ar jø iðprovokuotø kitø elementø persiskirstymu. Ilgalaikiø lauko bandymø parinktuose variantuose, panaudojant atominës absorbcijos analizës ir rentgeno fluorescencinës analizës metodus, nustatyta, kad visi tirti dirvoþemiai buvo paveikti agrogeninës þemës ûkio veiklos. Suminës kai kuriø elementø koncentracijos padidëjo dël agrogeninio poveikio, taèiau vienos jø nebuvo statistiðkai patikimos, kitos nustatytos tik vienuose bandymuose. Vakarø Lietuvos balkðvaþemiuose tarp 18 tirtø elementø antropogeninis agrogeninis poveikis patikimais skirtumais pasireiðkë 11 elementø (Al, Ca, Fe, Mg, B, Ba, Co, Cu, Ni, Sr, Zn), tuo tarpu Rytø Lietuvos iðplautþemiuose – tik keturiø elementø patikimais skirtumais (Ca, Co, Cu, Sr). Pagal antropogeniná poveiká reikðmingi pokyèiai (>2) Vakarø zonoje pasireiðkë tik Ca ir Sr atþvilgiu, o Rytø – tik Ca atþvilgiu.

Nustatyti suminiai elementø kiekiai në vienu atveju nevirðijo DLK, todël dirvoþemiai ávertinti kaip neuþterðti.

**Ñàóëþñ Ìàðöèíêîíèñ, Áðîíèñëàâàñ Êàðìàçà, Ýóãåíèÿ Áàêøåíå, Ëþäìèëà Òðèïîëüñêàÿ, Äîíàòàñ Êîí÷þñ, Äàíóòå Îæåðàéòåíå, Ðåãèíà Ðåïøåíå**

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#### Ð å ç þ ì å

Äàíà ãåîõèìè÷åñêàÿ îöåíêà àíòðîïîãåííîãî âîçäåéñòâèÿ íà ïàõîòíûé ñëîé îáðàáàòûâàåìûõ çåìåëü, îêàçûâàåìîãî êàê íåïîñðåäñòâåííî âíåñåííûìè õèìè÷åñêèìè ýëåìåíòàìè, òàê è âëèÿíèåì ïîñëåäíèõ íà ïîäâèæíîñòü äðóãèõ ýëáì áí òî â. Â î òî áðàí í ûõ âàðèàí òàõ äëèòàëüí ûõ ïîëåâûõ îïûòîâ ñ ïîìîùüþ ìåòîäîâ àòîìíîé àáñîðáöèè è ðåíòãåíîâñêîé ôëóîðåñöåíöèè áûëî

óñòàíîâëåíî, ÷òî âî âñåõ èññëåäîâàííûõ ïî÷âàõ âûÿâëåíû ãåîõèìè÷åñêèå èçìåíåíèÿ, ïðîèñøåäøèå âñëåäñòâèå àíòðîïîãåííîãî âîçäåéñòâèÿ. Ïîâûñèëàñü îáùàÿ êîíöåíòðàöèÿ íåêîòîðûõ ýëåìåíòîâ, îäíàêî íå âî âñåõ îïûòàõ èçìåíåíèÿ áûëè ñòàòèñòè÷åñêè äîñòîâåðíû, â íåêîòîðûõ ñëó÷àÿõ èçìåíåíèÿ íîñèëè ðàçíîíàïðàâëåííûé õàðàêòåð. Ðàññìîòðåíû 18 õèìè÷åñêèõ ýëåìåíòîâ â äåðíîâî-ïîäçîëèñòûõ ïî÷âàõ Çàïàäíîé Ëèòâû. Çàïàäíîé Ëèòâa àíòðîïîãåííîå (àãðîãåííîå) âîçäåéñòâèå ïðîÿâèëîñü äîñòîâåðíûì èçìåíåíèåì êîíöåíòðàöèè 11 ýëåìåíòîâ (Al, Ca, Fe, Mg, B, Ba, Co, Cu, Ni, Sr, Zn), â òî âðåìÿ êàê â Âîñòî÷íîé Ëèòâå – òîëüêî 4-åõ ýëåìåíòîâ (Ca, Co, Cu, Sr). Ïðè ýòîì ñóùåñòâåííûå èçìåíåíèÿ (óâåëè÷åíèå áîëåå ÷åì â 2 ðàçà) â çàïàäíîé çîíå óñòàíîâëåíû ëèøü ó Ca è Sr, â âî ñòî ÷í î é çî í à - òî ëüêî ó Ca. Óñòàí î âëàí í û à î áùèå êî ëè÷àñòâà âñaõ èññëaäî âàí í ûõ ýëàì aí òî â âî âñåõ ñëó÷àÿõ íå ïðåâûøàëè äîïóñòèìûõ íîðì (ÏÄÊ), ïîýòîìó ïî÷âû Çàïàäíîé è Âîñòî÷íîé Ëèòâû ìîæíî îöåíèòü êàê íåçàãðÿçíåííûå òÿæåëûìè ìåòàëëàìè.