Different forms of heavy metals, their concentrations and correlation in various soils of Lithuania

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To find the most suitable method for determining the concentration of heavy metals and the correlation of their different forms in Lithuania's soils, special trials were carried out in 1998–2000. We investigated soils differing in genesis, texture and reaction. The samples were collected in Skėmiai, Kriūkai and Rumokai fertilization trials conducted by the Agrochemical Research Centre. Soil samples from the field crop rotation at the Vokė branch of the Lithuanian Institute of Agriculture were used as well.

General forms of heavy metals in soil samples were determined in HNO_3-HF-$HClO_4$, soluble 2 M HNO_3 and mobile forms in ammonium acetate buffer solution (AAB) pH 4.8. The following heavy metals (microelements) absorbed by plants were determined: Cu, Fe – 1 M HCl in solution, Mn – 0.05 M H_2SO_4 and Zn in ammonium acetate buffer solution, pH 4.8.

To determine the correlation between different forms of heavy metals, 269 soil samples were selected. Summarizing the results of the trials obtained in 2 M HNO_3 extraction it was determined that the concentrations of heavy metals greatly depended on soil texture. All the above-mentioned groups contained average concentrations of heavy metals and standard deviations. Separate methods had coefficients of correlation. It was noted that a reliable correlation was usually found in the forms of mobile and soluble Pb (0.39–0.50), Cu (0.31–0.55) and Zn (0.23–0.62). In sandy and sandy loam soils the medium correlation of Cd and Ni was determined.

The analysis of (microelements of) mobile Cu, Mn, Zn and Fe in soil of different texture and their soluble 2 M HNO_3 concentrations revealed their close correlation: copper– 0.47–0.81, manganese – 0.67–0.83, zinc – 0.23–0.62, iron – 0.38–0.71.

Key words: soil, soil texture, heavy metals

INTRODUCTION

Different forms of heavy metals may be investigated in soils: general, soluble in acid solutions, mobile and soluble in water. Many international organizations and scientists prepared, tested and presented methods of their analysis (Baker, Amacher, 1982; ИЭМ, 1983; ЦИНАО, 1983; UN/ECE, 1993; ISO/DIS 11047:1993). Moreover, new instrumental methods and all-round systems of analysis are constantly prepared. The main problem concerns the fulfilment of requirements and the choice of the adequate method.

The most common and widely used solutions for identification of mobile forms of heavy metals are: acetate buffer solution pH 4.8, 1 M HCl, 1 M HNO_3 (ИЭМ, 1983); 2M HNO_3 (UN/ECE, 1993); 0.1 M HCl, 0.05 M HCl in 0.0125 M H_2SO_4. The DTPA method: 0.005 M DTPA (diethylenetriaminepentaacetic acid) +0.01 M $CaCl_2$ +0.1 M TEA (triethanolamine) pH 7.3 (Baker, Amacher, 1982). The amount of heavy metals strongly depends on the solution used for extraction. The use of stronger solutions helps to determine the forms soluble in acid (1 M HCl, 1 M HNO_3, 2 M HNO_3). It includes not only the forms absorbed by plants but also heavy metals from the nearest reserve, *e.g.* 1 M HCl extracts much more of heavy metals than acetate buffer solution. It is also influenced by the type of soil and its pollution (Зырин и др., 1985).

METHODS

In order to find the most suitable method determining the concentration of heavy metals and the correlation of their different forms in soils, special trials were carried out in 1998–2000. We investigated soils differing in genesis, texture and reaction. The samples were collected in Skėmiai, Kriūkai and Rumokai fertilization trials conducted by the Agrochemical Research Centre. Soil samples from the field crop rotation at the Vokė branch of the Lithuanian Institute of Agriculture were used as well.

The crop rotation fertilization trial in Skėmiai (28 years) was carried out on a sandy light loam Endocalcari-Endohypogleyic Cambisols (RDg 4-k2). Different forms of heavy metals were determined in the samples of two replications of 15 trials: 1. Untreated. 2. $N_0P_{90}K_{90}$. 3. $N_0P_{180}K_{180}$. 4. $N_{90}P_0K_{90}$. 5. $N_{90}P_{90}K_0$. 6. $N_{90}P_{90}K_{90}$. 7. $N_{90}P_{90}K_{180}$. 8. $N_{90}P_{180}K_{90}$. 9. $N_{180}P_0K_{90}$. 10. $N_{180}P_0K_{180}$. 11. $N_{180}P_{90}K_0$. 12. $N_{180}P_{90}K_{180}$. 13. $N_{180}P_{180}K_0$. 14. $N_{180}P_{180}K_{90}$. 15. $N_{180}P_{180}K_{180}$.

Soil pH_{KCl} varied from 6.6 to 7.8, mobile P_2O_5 from 67 to 350 mg kg^{-1}, K_2O from 93 to 237 mg kg^{-1}, humus from 2.0 to 2.2%.

The Kriūkai trial (Šakiai district) was established in 1990 on medium loam Epicalcari-Endohypogleyic Cambisols (RDg 5-k1). Samples were taken from three replications of 10 treatments: 1. Untreated. 2. $N_0P_{90}K_{90}$. 3. $N_{90}P_0K_{90}$. 4. $N_{90}P_{90}K_0$. 5. $N_{90}P_{90}K_{90}$. 6. $N_{90}P_{180}K_{90}$. 7. $N_{90}P_{90}K_{180}$. 8. $N_{180}P_{180}K_{90}$. 9. $N_{180}P_{90}K_{180}$. 10. $N_{180}P_{180}K_{180}$.

Soil pH_{KCl} varied from 6.9 to 7.8, mobile P_2O_5 from 123 to 183 mg kg^{-1}, K_2O from 112 to 151 mg kg^{-1}, humus from 2.2 to 2.3%.

Different forms of heavy metals were also determined during the trials in Vilkaviškis district. The trials were carried out at the Rumokai Station of Lithuanian Institute of Agriculture on a limnoglacial silty Calc(ar)I-Epihypogleyic Luvisols (Idg8-k) sandy light loam soil. Its pH $_{KCl}$ was 7.0–7.6, mobile P_2O_5 110–118 mg kg^{-1}, K_2O 138–170 mg kg^{-1}, humus 2.0–2.2%. On a Sandy loam Eutri-Haplic Arenosols (SDp-b) at the Vokė Branch of the Lithuanian Institute of Agriculture the pH_{KCl} was 6.0–6.4, mobile P_2O_5 220–250 mg kg^{-1}, K_2O 220–250 mg kg^{-1}, humus 1.6–2.2%.

Samples of all fertilization trials were taken from the layers of 0–20, 20–40, 40–60 ir 60–90 cm. General forms of heavy metals in soil samples were determined in HNO_3–HF–$HClO_4$, soluble 2 M HNO_3 and mobile forms in ammonium acetate buffer solution (AAB), pH 4.8. The following heavy metals (microelements) absorbed by plants were determined: Cu, Fe – 1 M HCl in solution, Mn – 0.05 M H_2SO_4 and Zn in ammonium acetate buffer solution pH 4.8.

In order to determine heavy metals in extracts such devices as AAS-30 an atomic absorption spectrometer (since 1990) or Analyst-800 (since 1999) with HCl lamps are usually used. To comprehend a corresponding method in laboratory is not enough. First of all the control of precision should be done and then the correctness of the results should be proved. In laboratory the quality is ensured by applying certificed fundamental materials (CFM) – CRM 141R and CRM PL-1 twice per year. Since the price of CFM is rather high, routine tests are carried out by using a well analyzed, homogeneous and stable material (secondary fundamental material) and empty sample analysis. Secondary fundamental materials (SFM 1, SFM-2) are made to the requirements of fundamental material preparation (ГОСТ-1989). Annually, since 1996 the Centre of Agrochemical Investigation takes part in the interlaboratory comparable trials (ICT – organization, conduct and estimation of trials of the same or similar trial objects in two or more laboratories and under already fixed conditions), the results are "satisfactory". ITC covered various projects: ECOSLIT – Lithuania, 1996; AMOS 1997/1998, the executive organization – BAM, Germany, PHARE Service ILS–1 1996/1997 and PHARE Service ILS–2 1997 Vrije University (VU), Holland; PHARE Service–2 (1 and 2 stage) 1998/1999- RIZA, the Netherlands.

RESULTS AND DISCUSSION

To determine the correlation between different forms of heavy metals, 269 soil samples were selected. By generalizing the results of the trials obtained in 2 M HNO_3 extraction it was determined that the concentrations of heavy metals greatly depended on the soil texture (Table 1). Thus, in order to evaluate the concentration data determined by different methods, soils were grouped according to their texture and reaction. Soil texture include the following groups: sand, sandy loam, light loam, medium loam and clay. And according to pH there are such groups as 5.0; 5.1–6.0; 6.1–6.5 and >6.5. All these groups contained an average concentration of heavy metals and standard deviations. Separate methods were used to determine the coefficients of correlation.

Concentrations of heavy metals in 2 M HNO_3 extract are not high and none of the investigated metals exceeds the maximum limit of concentration (MLC). However, in soils of different location their concentration was not the same: on average Cr constituted 5.0–15.1, Cd – 0.48–0.51, Pb – 8.7–13.2, Ni – 4.3–12.6, Cu – 2.9–7.2, Zn – 17.7–34.3, Mn – 180.8–263.7 and Fe – 4419–7632 mg kg^{-1} of soil (Table 1). Lower contents of heavy metals were found in the samples of sand and sandy loam soils, while their levels was higher in loam and clay soil samples. Mobile in comparison to soluble forms (2 M HNO_3) of all the heavy metals studied (in ammonium acetate buffer solution, pH 4.8) were not great in number: Cr – 0.43–0.57, Cd – 0.15–0.18, Pb – 1.38–1.48, Ni – 0.59–0.78, Cu – 0.23–0.51; Zn – 1.47–2.03, Mn – 12.6–21.0 and Fe 23.8–86.6 mg kg^{-1}.

Table 1. **Content of heavy metals of various forms in the soils of different texture, mg kg⁻¹**

1997–1999

HM	HM form	Sand	Sandy loam	Light loam	Medium loam-clay
		$\bar{x}$ ± s			
Cr	SF*	4.96 ± 1.53	6.87 ± 2.14	9.53 ± 2.72	15.14 ± 3.01
	MF	0.43 ± 0.13	0.46 ± 0.4	0.51 ± 0.16	0.57 ± 0.15
Cd	SF	0.48 ± 0.45	0.5 ± 0.25	0.51 ± 0.24	0.49 ± 0.19
	MF	0.17 ±0.04	0.16 ± 0.05	0.15 ± 0.06	0.18 ± 0.03
Pb	SF	8.,7 ± 2.26	9.46 ± 1.94	10.11 ± 1.86	13.25 ± 2.51
	MF	1.48 ± 0.48	1.38 ± 0.43	1.46 ± 0.32	1.41 ± 0.25
Ni	SF	4.25 ± 1.48	6.37 ± 2.13	8.55 ± 2.39	12.61 ± 2.44
	MF	0.59 ± 0.28	0.72 ± 0.49	0.78 ± 0.43	0.7 ± 0.18
	SF	2.95 ± 1.22	3.7 ± 1.4	5 ± 1.7	7.18 ± 1.48
Cu	MF	0.23 ± 0.11	0.24 ± 0.08	0.29 ± 0.12	0.51 ± 0.51
	TM	1.75 ± 1.16	1.7 ± 0.55	2.19 ± 0.73	2.99 ± 0.86
Zn	SF	17.75 ± 7.7	21.24 ± 5.54	24.93 ± 7.5	34.28 ± 6.69
	MF	2.03 ± 0.93	1.94 ± 2.17	1.76 ± 0.74	1.47 ± 0.34
	SF	180.8 ± 99.2	191.9 ± 75.3	207.1 ± 79.7	267.3 ± 81.7
Mn	MF	12.6 ± 6.5	13.7 ± 7.7	17.5 ± 10.2	21 ± 8.9
	TM	56.6 ± 23.2	65.6 ± 20.3	70 ± 24.6	75.2 ± 22.3
	SF	4419 ± 2022	5777 ± 1786	7632 ± 2314	1799
Fe	MF	23.8 ± 7.9	24.7 ± 8.6	26.2 ± 13.5	86.6 ± 23.3
	TM	1487 ± 1844	1290 ± 352	1799 ± 575	2476 ± 721
	n	84	88	70	27

* SF – soluble forms (2M HNO_3); MF – mobile forms (AAB pH 4.8); TM – trace elements (Cu, Fe – 1 M HCl, Mn – 0.05 M H_2SO_4.

The levels of mobile Cr, Cd, Pb, Ni directly little depended on soil texture, and the content of Cu in loam and clay soils was 2.2, Mn – 1.7, Fe –3.6 times higher than in sand soils. The concentrations of mobile forms in comparison to those soluble in acid were as follows: Cr –3.8–8.8; Cd – 29.4–35.4; Pb – 10.7–17.0; Ni – 5.6–13.7; Cu – 5.8–7.8; Zn – 4.3–9.1; Mn – 7.0–8.5; Fe – 22.3–33.7%. The majority of heavy metals in light, medium loam and clay are much more mobile than those in sandy and sandy loam soils. On the average plant-absorbed Cu constituted 1.75–2.99 mg kg^{-1}, Mg – 56.6–75.2, Zn – 1.47–2.03 and Fe 1290–2476 mg kg^{-1}.

The concentration of mobile as well as soluble forms is somewhat lower in soils of more acidic reaction (pH up to 6.0) than in soils with neutral reaction. Part of heavy metals is considered to migrate from the upper horizons into the deeper ones. Migration conditions are better in sand and sandy loam soils than in loam and clay soils.

Mineral NPK fertilizers slightly changed the concentrations and correlation of heavy metals in the Skėmiai crop rotation fertilization trial on a leached RDg 5-k1 sandy light loam soil and in Kriūkai trial on a sod-gleyic medium loam soil. The concentration of different heavy metal forms among the replications of treatments varied like in separate treatments. The concentrations of heavy metals reflect mostly variations of soil rather than its change caused by long-term application of mineral fertilizers.

A comparison of the amount of general and soluble 2 M HNO_3 forms of Cr, Cd, Pb, Ni, Cu, Zn, Mn and Fe and their distribution in soil layers differing in genesis and texture showed that their concentrations were lower in a moraine sandy light loam (RDg 4-k2) in the Skėmiai trial and in a sandy loam (SDp-b) of the Vokė trial. Higher amounts of heavy metals were found in a sod podzolic light loam soil in the Rumokai trial and the highest in a limnoglacial silty soil (VG_1^J $p_1/p_1/m$) in the Kriūkai trial (Figure).

The upper 0–20 cm layers contained general Cr 18–73; Cd – 0.2–0.7; Pb – 15–26; Ni – 14–41; Cu – 12–25; Zn – 22–52 and Mn – 251–325 mg kg^{-1}. The 2 M HNO_3 solution gave the following extractions of general forms: Cr from 27 to 54, Cd from 58 to 100, Pb from 42 to 77, Cu from 23 to 95 and Zn, Mn from 80 to 100%. Significantly lower levels of Cr and Ni in 2 M HNO_3 solution in comparison to the level of general forms are found in a heavier

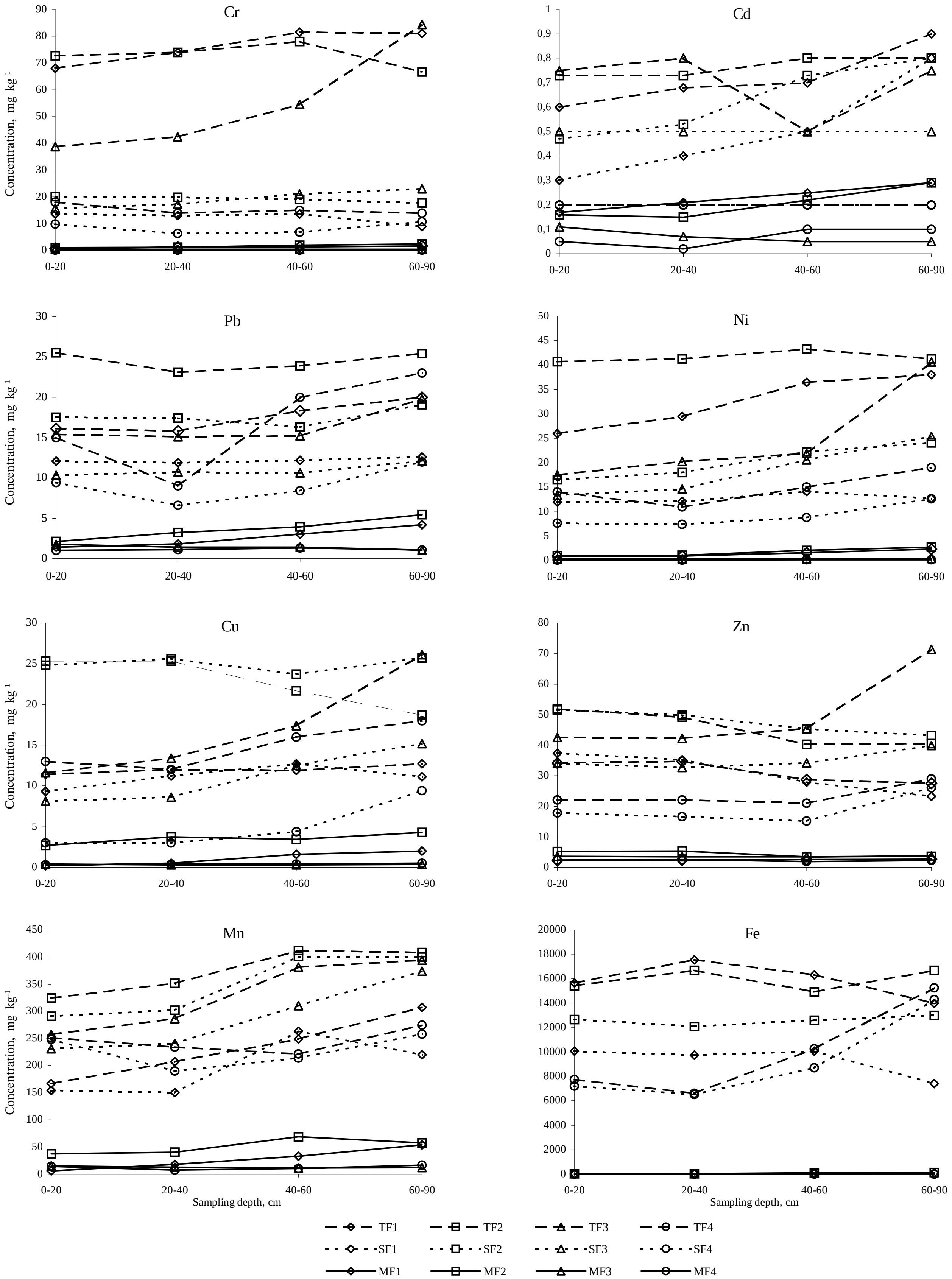

Figure 1. Amount of different forms of heavy metals in the soils mg kg$^{-1.}$ TF – total forms (HNO_3-HF-$HClO_4$); SF – soluble forms (2M HNO_3); MF – mobile forms (AAB pH 4,8)

1. Radviliškis r., Skėmiai, 1998 (Sandy light loam Endocalcari-Endohypogleyic Cambisols). 2. Šakiai r., Kriūkai, 1998 (medium loam Epicalcari-Endohypogleyic Luvisols). 3. Vilkaviškis r., Rumokai, 1998 (sandy light loam Calc(ar)i-Epihypogleyic Luvisols). 4. Trakai r., Vokė, 2000 (sandy loam Eutri-Haplic Arenosols).

soil texture. The levels of other metals (except Cu in the Vokė trial where it constituted 23%) was less diverse. There are reasons to believe that intensive farming may cause biological Cu accumulation.

Concentrations of mobile heavy metal (Cr, Cd, Pb, Ni, Cu, Zn, Mn) forms in ammonium acetate buffer solution, pH 4.8, were from 2.7 to 50.7 times lower than in 2 M HNO_3 and from 4 to 107,8 times lower than their general amount. The amount of Fe was lower from 662 to 912 and from 526 to 847 times, respectively. Fe is less mobile, more mobile are Cr, Ni, mobile are Pb, Cu, Zn, Mn and the most mobile is Cd. Besides other metals, part of not soluble Cd units dissolve in ammonium acetate buffer solution and contribute to technogenic pollution.

In deeper (20–40 cm and 40–60 cm) layers of the majority of soils the number of general and mobile Ni, Cu, Mn and mobile Cd, Pb ir Fe were slightly higher, showing migration of these elements. The levels of other heavy metals in all soil layers were similar.

Analysis of mobile (absorbed by plants) and soluble 2 M HNO_3 levels of heavy metals in soil of different texture and pH showed that the difference of correlation depended on soil texture (Table 2). The number of samples is presented in Table 1. The largest numbers of reliable coefficients of correlation among the forms of heavy metals determined by different methods were in soils with pH 5.1–6.0 and 6.1–6.5.

Unreliable coefficients of correlation were obtained by generalizing a smaller number of soil samples. The coefficients of correlation were more reliable in sandy and sandy loam soils, less reliable in loam, and little reliable in clay soils.

The correlation was usually reliable in the forms of mobile and soluble Pb (0.39–0.50), Cu (0.31–0.55) and Zn (0.23–0.62). In sandy and sandy loam soils a medium correlation of Cd and Ni was determined.

Table 2. **Correlation between various forms of heavy metals determined by solvents in soils with different texture**

1997–1999

pH	SF (x) with MF(y)								SF(x) with TM(y)			SF(x) with TM(y)	
	Cr	Cd	Pb	Ni	Cu	Zn	Mn	Fe	Cu	Mn	Fe	Cu	Mn
							Sand						
4.3–5.0	0.19	–	0.04	0.19	–0.06	0.36	–0.17	–	0.41	0.75*	0.66	0.81*	0.04
5.1–6.0	0.18	0.00	0.35	0.46*	0.40*	0.18	0.33	–	0.67*	0.85*	0.31	0.94*	0.67*
6.1–6.5	0.18	–0.53	0.27	0.66*	0.58*	0.77*	–0.03	0.06	0.27	0.74*	0.83*	0.35	0.62*
>6.5	0.44	0.42	0.67*	0.32	0.26	0.74*	0.48	–0.60	0.71	0.84*	0.54	1.00*	0.85
4.3–7.5	0.21	–0.44*	0.39*	0.53*	0.52*	0.62*	0.17	–0.08	0.47*	0.83*	0.38*	0.55*	0.59*
							Sandy loam						
4.2–5.0	0.35	0.00	0.10	0.54	0.29	–0.09	–0.12	0.38	0.56	0.86*	0.80*	1.00*	0.20
5.1–6.0	0.41*	0.09	0.42*	0.19	0.61*	0.07	0.03	–0.57	0.77*	0.77*	0.70*	0.89*	0.31
6.1–6.5	0.07	–0.44	–0.01	0.35	0.39	0.17	0.08	–0.30	0.82*	0.75*	0.82*	0.99*	0.28
>6.5	0.17	–0.39	0.50	0.18	–0.06	0.32	–0.37	0.07	0.95*	0.96*	0.28	0.52	0.74
4.2–7.2	0.26*	0.53*	0.52*	0.40*	0.31*	0.23*	0.39*	–0.16	0.73*	0.80*	0.71*	0.87*	0.23
							Light loam						
4.5–5.0	0.29	–	0.23	0.44	0.78	0.43	0.95*	–	–	0.75	0.91*	–	0.77
5.1–6.0	0.33	–	0.72*	0.08	0.66*	0.27	0.46*	–	0.86*	0.87*	0.41	1.00*	0.48*
6.1–6.5	0.31	0.00	0.03	0.08	0.84*	0.20	0.19	–0.56	–	0.56*	0.81*	–	0.55*
>6.5	–0.07	–0.48	0.19	–0.05	0.10	0.61*	0.11	–0.15	–	0.72*	0.83*	–	0.34
4.5–7.4	0.15	–0.32	0.40*	0.16	0.55*	0.45*	0.28*	–0.36	0.81*	0.71*	0.68*	1.00*	0.55*
							Medium loam-clay						
4.0–5.0	0.21	–	0.75	–0.83	0.55	–0.13	0.63	–	–	–	–	–	–
5.1–6.0	0.04	–	0.15	–0.50	–0.35	0.42	0.13	–	0.52	0.74*	0.31	–0.29	0.31
6.1–6.5	0.08	–	0.79*	0.03	0.58	0.32	0.43	–	0.67	0.69	0.26	0.97*	0.18
>6.5	0.74	–	0.22	0.03	0.98*	–0.11	0.54	–	0.97*	0.49	–0.69	0.99*	–0.02
4.0–6.8	0.23	0.00	0.50*	–0.26	–0.15	0.22	0.25	0.94	0.59*	0.67*	0.29	–0.13	0.19

* Correlation significant at 95% probability.
SF – soluble forms (2 M HNO_3), MF – mobile forms (AAB pH 4.8); TM – trace elements (Cu, Fe – 1 M HCl, Mn – 0.05 M H_2SO_4).

Table 3. **Correlation between various forms of heavy metals determined by solvents in the soil**

HM	Regression equation			Correlation coefficient R
	x^2	x	a	
Šakiai r., Kriūkai, 1999 (medium loamy soil)				
AAB(y) with HNO_3- HF-$HClO_4$(x)				
Cr	0.0004	–0.065	3.63	0.40*
Pb	0.006	–0.271	5.04	0.45*
Ni	0.0015	–0.129	3.75	0.40*
Cu	–0.02	1.163	–12.69	0.40*
Zn	0.011	–1.131	31.61	0.49*
Mn	–0.0006	0.410	–30.44	0.47*
Fe	$-3 \cdot 10^{-8}$	0.002	–8.74	0.45*
Pb	0.012	–0.256	3.00	0.58*
Cu	–0.011	0.666	–6.84	0.43*
Zn	0.006	–0.733	25.58	0.62*
Fe	$6 \cdot 10^{-7}$	–0.017	138.0	0.42*
2MHNO_3(y) with HNO_3- HF-$HClO_4$(x)				
Cr	–0.006	1.001	–21.48	0.52*
Cd	–0.148	0.816	–0.02	0.55*
Pb	0.012	–0.321	17.90	0.69*
Ni	–0.003	0.413	5.03	0.57*
Cu	–0.012	1.373	–3.14	0.84*
Zn	0.063	–5.69	178.2	0.86*
Mn	0.003	–1.600	441.5	0.78*
Fe	$3 \cdot 10^{-6}$	–0.480	20331	0.40*
Radviliškis r., Skėmiai, 1999 (sandy light loamy soil)				
AAB(y) with 2M HNO_3 (x)				
Cu	0.021	–0.360	1.86	0.40*
Zn	0.012	–0.854	16.83	0.41*
Mn	–0.002	0.668	–36.59	0.43*

*Correlation significant at 95% probability.

The correlation between mobile and soluble forms of chromium, manganese and iron was controversial, since sometimes the correlation was only very weak and not always reliable.

Analysis of (microelements of) mobile Cu, Mn, Zn and Fe in soils of different texture and their soluble 2 M HNO_3 concentrations revealed their close correlation: copper 0.47–0.81, manganese 0.67–0.83, zinc 0.23–0.62, iron 0.38–0.71. The equation expressing the correlation of concentrations of general and soluble heavy metals in heavy loam soil of the Kriūkai trial had the coefficient of determination R^2 0.16–0.74, which is usually reliable (Table 3).

A relation between general and soluble forms of copper, zinc and manganese was strong. The relation of other metals was medium.

The reliability was considerably lower between mobile and soluble concentrations and the least between general and mobile ones. The greatest number of relations was determined by analyzing Cu, Mn, and Pb. The correlation of concentration of soluble and mobile heavy metals in the Skėmiai trial is presented in Table 3. This trial in comparison to that conducted in Kriūkai contained less reliable correlations and had lower coefficients of determination.

A correlation of the content of different heavy metal forms obtained by analysis of various methods in soils of different texture is shown in Table 4. The concentrations of heavy metals in one solution together with the presented equations helped to calculate their content in the other ones rather precisely.

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Table 4. **Correlation between various forms of heavy metals determined by solvents in soils with different texture, mg kg^{-1}**

Methods of analysis	HM	n	Regression equation			Correlation coefficient R
			x^2	x	a	
1	*2*	*3*	*4*	*5*	*6*	*7*
Sand						
	Cr	78	0.013	–0.114	0.66	0.38*
AAB (y) with 2 M HNO_3 (x)	Cd	24	–0.313	0.301	0.13	0.46*
	Pb	78	0.020	0.063	0.78	0.46*
	Ni	78	0.015	–0.028	0.40	0.58*
	Cu	78	0.001	0.038	0.11	0.54*
	Zn	78	0.002	–0.119	1.48	0.65*
	Mn	78	–0.0001	0.069	5.93	0.29*
1 M HCl (y) with 2 M HNO_3 (x)	Cu	60	0.188	–0.884	2.44	0.56*
AAB (y) with 2 M HNO_3 (x)	Zn	60	0.002	–0.119	1.48	0.65*
0.05 M H_2SO_4 (y) with 2 M HNO_3(x)	Mn	60	–0.0002	0.283	19.31	0.83*
1 M HCl (y) with 2 M HNO_3 (x)	Fe	58	$3 \cdot 10^{-5}$	–0.113	1077	0.84*
AAB (y) with 1 M HCl (x)	Cu	54	–0.029	0.231	–0.05	0.84*

Table 4 (continued)

1	2	3	4	5	6	7
AAB (y) with 0.05 M H_2SO_4 (x)	Mn	54	–0.0001	0.193	3.27	0.58*
			Sandy loam			
AAB (y) with 2 M HNO_3 (x)	Cr	88	0.010	–0.096	0.62	0.27*
	Cd	33	0.868	–1.490	–0.77	0.54*
	Pb	88	0.022	–0.323	2.42	0.52*
	Ni	88	0.007	–0.005	0.42	0.40*
	Cu	88	–0.009	0.088	0.05	0.38*
	Zn	88	0.005	–0.130	2.31	0.25*
	Mn	88	–0.0001	0.051	9.04	0.39*
	Fe	98	$5 \cdot 10^{-7}$	–0.008	49.40	0.25*
1 M HCl (y) with 2 M HNO_3 (x)	Cu	55	–0.019	0.472	0.34	0.73*
AAB (y) with 2 M HNO_3 (x)	Zn	55	0.005	–0.130	2.31	0.25*
0.05 M H_2SO_4(y)with 2 M HNO_3 (x)	Mn	55	–0.001	0.4131	12.03	0.82*
1 M HCl (y) with 2 M HNO_3 (x)	Fe	38	$4 \cdot 10^{-7}$	0.151	468	0.71*
AAB (y) with 1 M HCl (x)	Cu	55	–10.097	11.634	–0.46	0.90*
			Light loam			
AAB (y) with 2 M HNO_3 (x)	Pb	70	0.013	–0.216	2.22	0.45*
	Cu	70	0.003	–0.0003	0.19	0.56*
	Zn	70	0.002	–0.072	1.97	0.50*
	Mn	70	–0.0002	0.116	2.53	0.32*
1 M HCl (y) with 2 M HNO_3 (x)	Cu	15	–0.050	0.962	–1.26	0.85*
AAB (y) with 2 M HNO_3 (x)	Zn	49	0.002	–0.072	1.97	0.50*
0.05 M H_2SO_4 (y)with 2 M HNO_3 (x)	Mn	49	–0.001	0.541	–0.68	0.77*
1 M HCl (y) with 2 M HNO_3 (x)	Fe	49	$1 \cdot 10^{-5}$	–0.023	1284	0.71*
AAB (y) with 1 M HCl (x)	Cu	50	$3{,}6 \cdot 10^{-5}$	0.142	0.001	1.0*
AAB (y) with 0.05 M H_2SO_4 (x)	Mn	50	–0.0039	0.795	–13.13	0.62*
			Medium loam–clay			
AAB (y) with 2 M HNO_3 (x)	Cd	22	–0.625	1.000	–0.20	0.90*
	Pb	27	–0.002	0.123	0.24	0.51*
	Fe	27	$-1.6 \cdot 10^{-5}$	–0.262	1171	1.0*
1 M HCl (y) with 2 M HNO_3 (x)	Cu	27	–0.125	2.207	–6.25	0.66*
0.05 M H_2SO_4 (y)with 2 M HNO_3 (x)	Mn	23	–0.0003	0.286	13.01	0.67*
1 M HCl (y) with 2 M HNO_3 (x)	Fe	23	$9 \cdot 10^{-5}$	2.070	–3429	0.54*

* Correlation significant at 95% probability.

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ĮVAIRIŲ FORMŲ SUNKIŲJŲ METALŲ KONCENTRACIJOS IR JŲ TARPUSAVIO RYŠIAI SKIRTINGUOSE LIETUVOS DIRVOŽEMIUOSE

S a n t r a u k a

Siekiant rasti tinkamiausią metodą sunkiųjų metalų koncentracijoms bei jų įvairių formų koreliacijos ryšiams Lietuvos dirvožemiuose nustatyti, 1998–2000 m. atlikti tyrimai. Tirti skirtingos genezės, granuliometrinės sudėties, reakcijos Lietuvos dirvožemiai. Mėginiai rinkti ir iš Lietuvos žemdirbystės instituto (LŽI) Agrocheminių tyrimų centro tręšimo bandymų laukų Skėmiuose, Kriūkuose ir Rumokuose. Taip pat naudoti LŽI Vokės filialo dirvožemio mėginiai, paimti iš lauko sėjomainos.

Dirvožemio mėginiuose sunkiųjų metalų bendrosios formos nustatytos HNO_3-HF-$HClO_4$, tirpiosios – 2 M HNO_3 ir judriosios – amonio acetato buferiniame tirpale (AAB), kurio pH 4,8. Augalų pasisavinami sunkieji metalai (mikroelementai) nustatyti: Cu, Fe – 1 M HCl tirpale, Mn – 0,05 M H_2SO_4 ir Zn – amonio acetatiniame buferiniame tirpale, kurio pH 4,8.

Koreliaciniams įvairių sunkiųjų metalų formų ryšiams nustatyti buvo atrinkti 269 dirvožemio mėginiai. Apibendrinus 2M HNO_3 ištraukoje gautus tyrimų rezultatus, nustatyta, kad sunkiųjų metalų koncentracijos labai priklauso nuo dirvožemio granuliometrinės sudėties. Todėl sunkiųjų metalų koncentracijų, nustatytų įvairiais metodais, duomenims įvertinti dirvožemiai sugrupuoti pagal granuliometrinę sudėtį ir reakciją. Visų grupių dirvožemiams nustatytos vidutinės sunkiųjų metalų koncentracijos ir standartiniai nuokrypiai, o tarp atskirų metodų – koreliacijos koeficientai.

Judriųjų ir tirpiųjų formų švino – 0,39–0,50, vario – 0,31–0,55 ir cinko – 0,23–0,62 koreliacijos ryšys dažniausiai yra patikimas. Smėlio ir priesmėlio dirvožemiuose kadmio ir nikelio ryšys nustatytas vidutinio stiprumo.

Išanalizavus skirtingos granuliometrinės sudėties dirvožemiuose augalų pasisavinamus (mikroelementus) Cu, Mn, Zn ir Fe ir tirpiąsias (2 M HNO_3) koncentracijas, paaiškėjo dažniausiai glaudus jų koreliacijos ryšys (*r*): vario – 0,47–0,81, mangano – 0,67–0,83, cinko – 0,23–0,62, geležies – 0,38–0,71.

Raktažodžiai: dirvožemis, dirvožemio struktūra, sunkieji metalai