

Methodological aspects of the assessment of roadside *Luvisol* contamination with heavy metals

Algirdas Juozas Motuzas¹,

Virginijus Trimirka¹,

Rimantas Vaisvalavičius¹,

Virginijus Butkus²,

Igoris Prosyčevas³,

Nomeda Sabienė¹,

Danguolė Zakaruskaitė¹,

Zigmas Vaišvila¹

¹ *Lithuanian University of Agriculture, Studentų 11, LT-53361 Akademija, Kaunas distr., Lithuania*
E-mail: algirdas.motuzas@lzuu.lt

² *Kaltinėnai Research Station of the Lithuanian Institute of Agriculture, Varnių 19, LT-75451 Kaltinėnai, Šilalė distr., Lithuania*
E-mail: kaltbs@kaltbs.lzi.lt

³ *Kaunas University of Technology, Savanorių 271, LT-50131 Kaunas, Lithuania*
E-mail: igorpros@mail.ru

In the period 2003–2007, contamination of limnoglacial clay and moraine loam *Luvisols* with heavy metals (HM) (Cr, Pb, Ni, Cu, Zn) in the highway Kaunas–Vilnius impact zone was analysed for the purpose to deepen knowledge of the effect of parent material on HM accumulation under the impact of technogenic pollution. The AAS and XRF methods were used to establish HM concentrations in different extracts: a HF + HCl + HNO₃ mixture was used for total HM concentrations and 2M HNO₃ acid for environmentally dangerous concentrations. Concentrations of mobile HM ions were determined in the extracts of 1N CH₃COONH₄ (pH 4.8) and 0.01 M CaCl₂ solutions. The obtained results showed contamination of the test *Luvisols* with Cr, Cu and Zn to be not dangerous and with Ni and Pb of medium hazardousness ($1 < K_0 < 3$). In the Ap horizon of limnoglacial clay *Luvisol*, total Cr and Pb concentrations by 1.9 times, and those of Ni up to 2.4 times exceeded those in moraine loam *Luvisol* Ap horizon. Cu and Zn concentrations in the *Luvisols* had slight differences. In limnoglacial clay *Luvisol* profile the biggest amounts of Cr and Cu were determined in B_{ckg}, of Zn in the B_t and of Pb and Ni in the Ap and A_{El} horizons. In the moraine loam *Luvisol* profile, the biggest accumulations of Cr, Pb and Ni were found in the Ap horizon, while Cu and Zn were evenly distributed in the entire soil profile. Comparative analysis showed the concentrations of mobile Cr ions in samples of limnoglacial clay *Luvisol* Ap horizon to be up to 1.4 times bigger than those in moraine loam *Luvisol*, of Pb up to 1.7, of Cu up to 2, and those of Ni and Zn showed no difference.

The established very strong Cr ($r = 0.98^{**}$), Pb ($r = 0.944^{**}$), Zn ($r = 0.997$), Cu ($r = 0.98^{**}$) and strong reverse Ni ($r = -0.881^{**}$) linear correlations among total HM concentrations determined by XRF and AAS methods imply that to establish total concentrations of some HM in *Luvisols*, the XRF method can be alternative to the traditional AAS method as it is more rapid and fairly scientific.

Key words: *Luvisols*, heavy metals, technogenic contamination, extraction methods

INTRODUCTION

In Lithuania, pollutants from motor transport make even 58% of all emissions to the atmosphere. They deposit lead, nickel, chromium, zinc, copper, manganese and other heavy metals on roads and in nearby territories (Baltrėnas ir kt., 2003; Brannvall, 2006; Gregorauskienė, 2006; Grigalavičienė, Rutkoviėnė, 2006; Jankaitė, 2007; Juknevičius et al., 2007; Saloman, 1998). Therefore, knowledge of soil pollution with heavy metals is very important for managing the ecological situation near highways. This enables to elaborate soil use and remediation methods.

The following legally good standard criteria are followed in soil and environment estimation: background HM concentrations characteristic of the geological environment of a

particular territory, and the highest permissible concentrations (HPC) which depend on soil and parent material texture (Dirvožemio..., 1997). In Lithuania, the hygiene standard HN 60 : 2004 (MN60–2004) is a valid document of this kind in effect. However, it does not indicate the extract to be used for the determination of total concentrations of chemical elements.

Meanwhile, evaluation of soil contamination strongly depends on the extract and extraction methods chosen. Extracts and methods to determine the content of heavy metals in soil vary not only with different countries but even with separate laboratories in Lithuania (Houba et al., 1997; Sabienė, 2004). For instance, at the laboratory of the Agrochemical Analysis Centre of Lithuanian Institute of Agriculture, total HM concentration is determined in the 2M HNO₃ acid extract according to the

integrated monitoring methodology accepted in the Baltic states (Šakalys et al., 2004), while at the Institute of Physical Electronics of Kaunas University of Technology extracts of concentrated HCl + HNO₃ and HCl + HF mixtures are used for this purpose (Methods..., 1996). According to the USEPA (USA) methodology, soil sample (even hardly degradable silicates) is completely dissolved in a mixture of concentrated HF + HCl + HNO₃ acids. Then the total concentration of the element is determined by methods of atomic absorption spectrophotometry (AAS), inductively actuated plasma atomic emission spectroscopy (ICP-AES), X-Ray fluorescent spectroscopy (XRFS) or by other methods (UN ECE..., 1998). In Europe, the standardized *aqua regia* (HCl + HNO₃ + H₂O₂) solvent has been used to determine total HM concentration. However, in the case of applying this method, some HM remain in soil minerals.

Single- or multi-stage chemical extraction methods involving the use of one or several different solvents are applied to determine the concentration of mobile heavy metals which have an important environmental impact due to their migration in soil (Motuzas et al., 2003; Quevauviller, 1998; Sabienė, 2004). Inorganic salt solutions are normally used (Ramos et al., 1994). There is a number of opinions about the best solvent for evaluating soil contamination with mobile HM ions. Some scientists give preference to 1 M HCl solvent, others to ammonium acetate buffering solution pH 4.8, and still others to NH₄-EDTA (Maizet et al., 2000; Sabienė, 2004). Participants of the EU financed project suggest application of 0.01 M CaCl₂ salt for this soil analysis according to the presented methodics (Houba et al., 1997). Therefore, results of investigations are difficult to compare, and sometimes the real state of soil contamination with heavy metals is unclear.

Considering the metodological problems of a complicated evaluation of the impact of heavy metals on environment and soil, this work aims to determine their total and mobile ions' concentrations in *Luvisols* of different parent material, situated near highways, by applying different solvents and measurement methods.

OBJECTS

In the period 2003–2007, contamination of *Luvisols* with heavy metals was analysed in two zones in the country: limnoglacial clay soil of the Baltic highland soil zone situated near the Vilnius–Kaunas highway at Rumšiškės, Kaišiadoriai distr. (abbreviation R1) and IDg8-k; *Calcari-Epihypogleyic Luvisol*, LV *g-p-w-cc* of the Middle Lithuanian soil zone near the Kaunas–Klaipėda highway at Giraitė, Kaunas distr. (abbreviation G2).

Limnoglacial clay *Luvisol* is of a very poor skeletal structure; dust fraction (41.3%) dominates in its upper horizons and clay fraction (57.3%) in deeper ones. The soil is alkaline (pH 7.1–7.4), its arable layer is medium humus rich (2.48%; organic carbon 1.4%), containing low amount of nitrogen (0.21%), medium amount of phosphorus (146.3 mg kg⁻¹) and a low amount of potassium (57.6 mg kg⁻¹); the parent material has a medium carbonate content of soil calcareousness (14.4%).

Moraine loam *Luvisol* has a medium skeletal structure, soil fraction, particles 2.0–0.02 mm dominate in its Ap and AEl horizons (51.5–59.1%) and in the deepest BCKg horizon (45.1%).

Dust (0.02–0.002 mm) fraction dominates in the B₁tg horizon (44.5%). The soil is alkaline (pH 7.4–7.7), its arable layer has a low humus content (2.22%; organic carbon 1.29%), a low nitrogen content (0.19%), a low phosphorus content (76.2 mg kg⁻¹) and a low potassium content (91.2 mg kg⁻¹); the parent material has a medium carbonate content of soil calcareousness (12.6%).

METHODS

Soil observations were carried out in specially chosen observation sites (10 × 10 m) according to the monitoring requirements integrated by the Baltic states (Maizet et al., 2000). Combined samples for soil analyses were taken at a 20-m distance from the source of pollution (highway) in five layers of a soil pit profile down to 1 m of depth and with soil auger within the boundaries of the investigation site and down to the same depth. The investigation sites were overgrown with perennial grasses. The soil samples were dried to air-dry mass, homogenized and kept in plastic containers. Results of chemical analyses were recalculated for the mass of absolutely dry soil dried at a temperature of 105 °C.

Total concentrations of heavy metals (Cr, Pb, Ni, Cu, Zn) in soil were determined in extracts of HF + HCl + HNO₃ mixture and 2M HNO₃ by the method of atomic absorption spectrometry (AAS) with a Perkin-Elmer M403 atomic absorptive spectrometer (Maizet et al., 2000; Šakalys et al., 2004) and by the method of X-ray fluorescent spectra (XRFS) analysis in the extract of HF + HCl + HNO₃ mixture with a VRA-2.0 X-ray fluorescent crystal diffractive spectrometer (Bertin, 1978). Operating conditions of this device have the following characteristics: X-ray lamp Rh K_α, voltage 35 kV, current strength 26 mA, measuring time 100 s, filter diameter 20 mm. All measurements were done in three repetitions, device error being 0.5%. Samples in the “thin” layer were calibrated as radiators, which had only one element or a full complex of heavy metals – Cr, Pb, Ni, Cu and Zn – with a similar concentration of each test element.

The concentration of mobile ions of heavy metals (Cr, Pb, Ni, Cu, Zn) in soil was analysed by the atomic absorption spectrometry (AAS) method in 1N CH₃COONH₄ (pH 4.8) and 0.01 M CaCl₂ solutions with a Perkin-Elmer M403 atomic absorptive spectrometer (Manual..., 1993; Methodology..., 1997; Methods..., 1986; Sabienė et al., 2004).

Data on soil pollution with heavy metals were objected to the ANOVA statistical results management package. The phenomena interdependence degrees were established, linear regression equations, correlation coefficients (r) and determination indices (D) were presented.

The level of the test soil pollution with HM (Cr, Pb, Ni, Cu, Zn) was evaluated by comparing the obtained results with the highest permissible (HPC) and background concentrations indicated in the Lithuanian Hygiene Standard document HN 60 : 2004.

RESULTS AND DISCUSSION

Total and environmentally hazardous concentrations of heavy metals. The obtained results show a reliable difference among the total concentrations of HM (Cr, Pb, Ni, Cu, Zn)

Table 1. Total concentrations of heavy metals determined with different extracts (a – HF + HCl + HNO₃; b – 2M HNO₃), in *Luvisols* of different parent material

Horizon and depth of sampling, cm		HM concentration, mg kg ⁻¹									
		Cr		Pb		Ni		Cu		Zn	
		a	b	a	b	a	b	a	b	a	b
Limnoglacial clay <i>Luvisol</i> (R1)											
Ap	0–10	53.4	20.2	107.2	22.4	94.6	19.2	10.7	7.64	22.2	14.1
Ap	10–20	86.3	30.3	100.7	25.1	103.9	20.3	13.0	9.1	22.3	14.6
AEI	20–30	83.6	20.4	98.2	20.2	105.0	20.3	12.4	9.84	28.7	15.0
Bt	40–50	94.0	23.7	95.3	22.0	86.3	27.6	22.0	14.0	45.0	15.0
BCKg	90–100	101.3	24.9	80.8	14.3	96.7	23.7	25.0	7.84	37.7	9.99
Moraine loam <i>Luvisol</i> (G2)											
Ap	0–10	32.1	18.5	57.1	16.1	94.6	27.1	13.1	8.92	17.9	13.8
Ap	10–20	44.8	19.2	96.6	18.8	42.5	19.0	14.5	5.98	19.2	11.1
AEI	20–30	28.2	19.6	90.5	13.6	33.6	18.8	10.9	3.84	21.9	10.4
B ₁ tkg	40–50	28.0	26.6	119.1	14.2	23.3	23.4	17.2	16.0	21.4	12.3
BCKg	90–100	32.4	21.0	49.3	13.2	30.5	22.7	12.2	6.9	21.7	12.6
LSD ₀₅ AB		3,18	0.26	2.56	0.18	2.90	0.55	0.41	0.37	0.78	0.24

determined with the same extract in the *Luvisols* of different parent material (Table 1). In limnoglacial clay *Luvisol* (R1), the total concentrations of chromium, plumbum and partially nickel are reliably higher, irrespective of the extract applied, in comparison with adequate concentrations in moraine loam *Luvisol* (G2); in the former case in the arable Ap horizon the concentration reached 86.1, 107.2 and 103.9 mg kg⁻¹ and in the second case 44.8, 96.6 and 94.6 mg kg⁻¹, respectively. In this horizon of different parent material *Luvisols*, differences between total concentrations of copper and zinc are significantly lower. Obviously, this again confirms the reason for the regularity by a dissimilar size distribution of soil particles in the rocks (Kadūnas ir kt., 1999): sand fractions (particles >0.005 mm) prevail in moraine loams, while dust (particles 0.05–0.002 mm) and clay (<0.002 mm) fractions prevail in limnoglacial clays. The better sorption characteristics of limnoglacial clays are undoubtedly determined by differences in mineral composition as they contain more minerals belonging to the group of expanding crystal lattice smectites which have a bigger cation exchange capacity (Rauret, 1998).

Total HM concentration in soil pollution data evaluation does not reveal the influence of parent material characteristics only because the amount of motor emissions plays an important role in the zone of intensive technogenic pollution.

Analysis of HM total concentrations in *Luvisol* profiles reveals the following regularities: pollutants mostly accumulate in the top humus-rich Ap horizon, but their distribution is influenced by the process of lessivage when, due to deposited polluted clay particles, they accumulate in illuvial Bt and deeper BC horizons.

Environmentally dangerous HM concentrations determined in 2 M HNO₃ extract do not exceed the HPC in any of the test samples (Table 1). Comparison of the obtained data with the background concentrations of the test HM showed that the content of Cr and Zn did not exceed them, while the content of Pb, Ni and Cu exceeded it up to 1.5 times.

The obtained results on heavy metals taken from the soil by means of various extracts have a different numerical expression: in all cases the amounts of HM obtained with the help of HF + HCl + HNO₃ extract are 2–3 times bigger than those in

the case of 2 M HNO₃ extract application. This means that most HM are contained by insoluble or hardly soluble silica minerals which can be dissolved by fluorine acid (HF) only. Such understanding brings to the statement that most HM are of lithogenic origin and the technogenic impact is not strong. Summarized data on HM distribution in profiles of the test *Luvisols* indicates that motor transport has the most important influence in soil contamination with Pb and Ni.

Table 2 presents results of linear regression dependency analysis of total HM concentrations in the test *Luvisols*, determined in the HF + HCl + HNO₃ extract and environmentally hazardous concentrations determined in 2 M HNO₃ extract.

Table 2. Dependency equations of total HM concentrations determined in HF + HCl + HNO₃ (x) and 2M HNO₃ (y) extracts

HM	Linear regression equations	r	Determination index (D) %
Cr	y = 9.53 + 0.23x	0.969**	93.9
Pb	y = 8.35 + 0.14x	0.761**	58.0
Ni	y = 17.67 + 0.05x	0.331	11.0
Cu	y = 10.34 – 0.189x	–0.228	5.2
Zn	y = 6.76 + 0.33x	0.500*	25.0

* Reliability level 95%.

** Reliability level 99%.

Statistical parameters of linear regression equations show a different dependency of various HM concentrations in the tested extracts. At a 99% reliability level, data on total and environmentally dangerous concentrations of Cr have a very strong dependency (r = 0.969, D = 93.9%), and on Pb a strong dependency (r = 0.761, D = 58.0%). At a 95% reliability level, data on total and environmentally hazardous concentrations of Zn in *Luvisols* have a medium-strong dependency (r = 0.5, D = 25.0%), and of Ni a weak dependency (r = 0.331, D = 11.0%). In the test soil extracts, no linear dependency has been established between the total and environmentally hazardous concentrations of Cu. Considering different dependencies of total and environmentally hazardous HM concentrations in the test *Luvisols*, which is very likely determined by a different chemical nature of HM,

the HF + HCl + HNO₃ extract is recommended for determination of total concentrations. Moreover, at present, the application of this extract (or alkaline extracts) is recommended at the international level (ISO... 1995, 2001, 2002).

The coefficients for the ecological evaluation of the test soils (K_0) calculated by the ratio of total HM concentrations in HF + HCl + HNO₃ extract and HPC (Table 1) show the contamination with Cr, Cu and Zn to be not hazardous ($K_0 < 1$). Contamination with Ni in the entire limnoglacial clay *Luvisol* (R1) profile and moraine loam *Luvisol* (G2) Ap horizon, and with Pb only in the limnoglacial clay *Luvisol* (R1) Ap horizon is medium hazardous ($1 < K_0 < 3$).

The coefficients of HM concentrations K_x , calculated from the ratio of total HM concentrations in the HF + HCl + HNO₃ extract, and the background concentrations (Table 1) show that in the Ap horizons of the test soils, the background concentration of Pb is exceeded up to 7 times, that of Ni up to 5.8 times, of Cu up to 1.3 times, and of Cr up to 2 times only in the Ap horizon of soil R1. In the Ap horizons of the test soils, Zn concentrations did not exceed the background concentrations.

Concentrations of mobile HM ions. Literature sources indicate that data on HM total concentrations in soil do not provide a complete picture of the real situation and the influence these pollutants make on the environment, therefore, soil investigations should supply data on the concentrations of mobile HM ions (Lietuvos..., 2001; Rauret, 1998).

AAS method has been used to detect the concentrations of mobile ions of heavy metals (Cr, Pb, Ni, Cu, Zn) in 1 N CH₃COONH₄ (pH 4.8) and 0.01 M CaCl₂ extracts. These concentrations, determined in the same solvent, appear to be different in *Luvisols* of various parent materials, although their numerical expression is quite similar (Table 3). Samples from the limnoglacial clay *Luvisol* (R1) Ap horizon, in comparison with those from moraine loam *Luvisol* (G2), have concentrations of mobile Cr ions bigger up to 1.4 times, of Pb – up to 1.7 times, of Cu up to 2 times and similar concentrations of mobile Ni and Zn ions. In the R1 *Luvisol* profile, mobile Cr and Pb ions are concentrated mostly in Ap and AEl horizons, mobile

Cu ions in Bt horizon, while those of Ni and Zn are evenly distributed in the entire *Luvisol* profile. In the G2 *Luvisol* profile, the concentrations of mobile Cr and Zn ions are highest in Ap horizon, of mobile Pb ions in Bt horizon, and mobile Ni ions are evenly distributed in the profile.

In various soil extracts, concentrations of mobile HM ions are different: in most cases their number in 1 N CH₃COONH₄ (pH 4.8) extract up to 2.3 times exceeds that in 0.01 M CaCl₂ extract. Such difference is due to a more acid medium of the former solvent. Acid acetate extracts more HM ions than neutral salt does, as not only exchange but in carbonates also fixed HM are combined. Besides, when HM are extracted with acetate solution, soluble complex solutions that hinder re-adsorption of HM ions and formation of insoluble compounds are formed (Sabienė, 2004).

Table 4 presents results of linear regression analysis of a dependency between the concentrations of HM mobile ions in the test *Luvisols*, obtained in a 0.01 M CaCl₂ extract, and those obtained in a 1 N CH₃COONH₄ (pH 4.8) extract.

According to statistical parameters of linear regression equations, this dependency varies with different HM. A medium-strong dependency has been determined only for Cu ($r = 0.672$, $D = 45.1\%$) and Pb ($r = 0.53$, $D = 28.1\%$). Meanwhile, no dependency has been established between the concentrations of other HM mobile ions and different extracts.

Establishment of HM total concentration by XRF method. A search for comprehensive information about the natural environmental situation and its contamination with HM asks for the methods that increase the determination sensitivity and accuracy of chemical elements, especially under conditions of technogenic pollution (Motuzas et al., 2000). In such a case, X-ray fluorescent spectra (XRF) analysis enables a rapid and accurate determination of the element composition of separate soil components in soil units of different genetics. A comparison of the limiting concentrations of chemical elements and their average amounts in soils all over the world shows the sensitivity of this method in slightly contaminated soils to be insufficient (Jones, 1991). However, abroad, employing special equipment,

Table 3. Concentrations of mobile HM ions in *Luvisols* of various parent material, determined in different soil extracts (a – 1N CH₃COONH₄ (pH 4.8); b – 0.01 M CaCl₂)

Horizon and depth of sampling, cm		HM concentration, mg kg ⁻¹									
		Cr		Pb		Ni		Cu		Zn	
		a	b	a	b	a	b	a	b	a	b
Limnoglacial clay <i>Luvisol</i> (R1)											
Ap	0–10	24.0	11.4	19.2	12.5	18.4	15.3	10.2	7.60	11.9	11.5
Ap	10–20	22.7	15.1	23.2	7.16	17.5	17.4	9.4	6.1	12.0	13.3
AEl	20–30	20.5	18.9	23.7	10.2	18.7	14.5	9.0	4.84	12.0	8.82
Bt	40–50	15.5	14.5	20.2	12.2	21.9	20.6	11.5	6.08	11.3	8.6
BCkg	90–100	21.7	12.9	13.1	9.34	18.3	13.4	10.9	7.08	13.7	9.86
Moraine loam <i>Luvisol</i> (G2)											
Ap	0–10	17.7	11.9	7.08	5.88	17.9	10.2	8.5	2.92	17.2	7.92
Ap	10–20	20.4	8.64	11.4	5.58	17.4	17.1	4.54	3.8	18.6	6.54
AEl	20–30	17.4	9.66	10.3	3.2	16.6	8.9	6.32	2.52	16.0	3.46
B ₁ tg	40–50	12.1	6.5	10.4	7.96	17.2	15.3	12.9	5.44	12.0	5.4
BCkg	90–100	20.7	6.82	11.2	4.1	17.6	13.6	9.06	2.46	12.2	9.78
LSD ₀₅ AB		0,48	1.03	0.81	0.34	0.55	0.26	0.41	0.17	0.54	0.37

Table 4. Dependency equations of HM mobile ion concentrations determined in different extracts 0.01 M CaCl₂ (y) and 1N CH₃COONH₄ (x)

HM	Linear regression equation	r	Determination Index (D) %
Cr	$y = 6.46 + 0.25x$	0.27	7.3
Pb	$y = 4.28 + 0.23x$	0.53*	28.1
Ni	$y = 31.92 - 0.95x$	-0.141	2.0
Cu	$y = 0.39 + 0.58x$	0.672**	45.1
Zn	$y = 8.05 + 0.31x$	0.078	0.6

* Reliability level 95%.

** Reliability level 99%.

X-ray fluorescent spectra (XRF) analysis is widely applied in soil chemical analyses (Caridad Cancela et al., 2002; USEPA..., 1996). No data has been found about the direct application of this method in Lithuania.

Errors of HM concentrations determined by the method of X-ray fluorescent spectra (XRF) analysis are presented in Table 5.

Table 5. Errors of determination of HM concentration in soil by the XRF method

Chemical element									
Cr		Pb		Ni		Cu		Zn	
a	b	a	b	a	b	a	b	a	b
4.75	4.89	0.07	5.35	3.42	4.82	1.58	3.48	0.57	2.04

a – error of single element concentration (%); b – error of element concentration in a group with others (%).

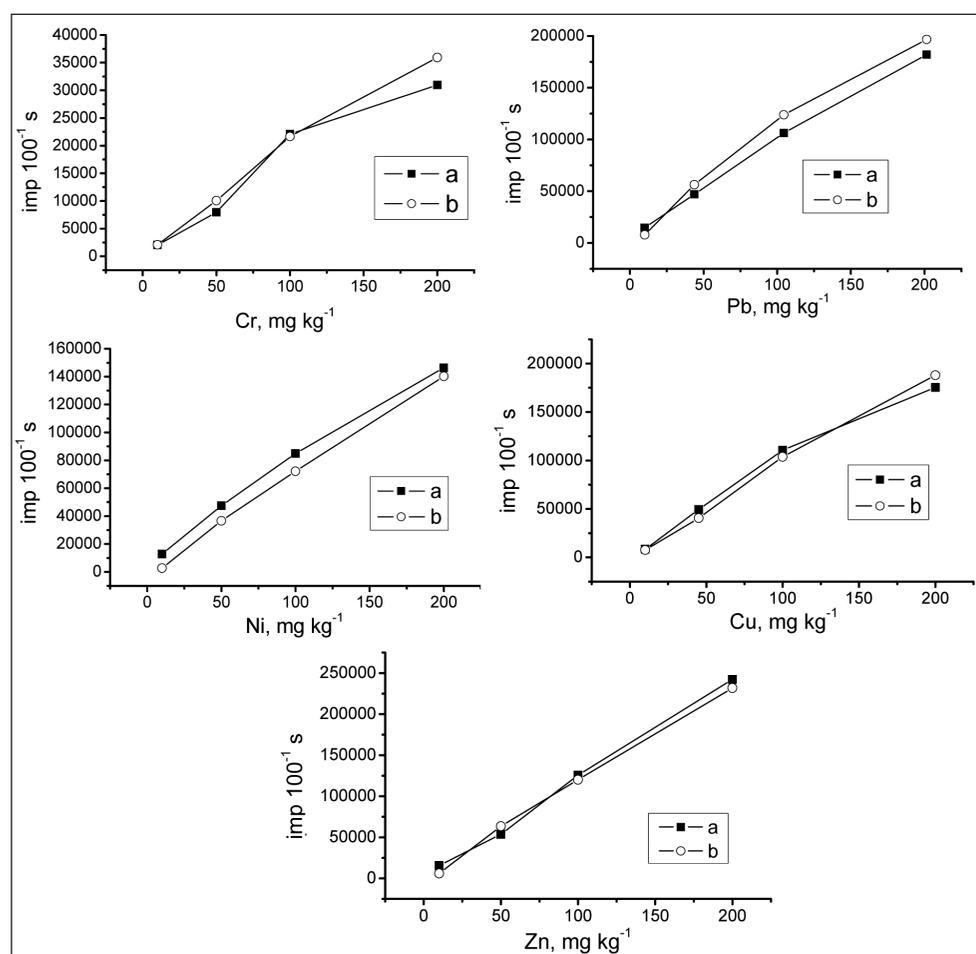


Figure. Calibration curves of total HM concentrations (reliability level 95%): a – with one HM in the solution; b – in group with other HM

In both cases (single element and in group with others), the biggest error has been determined for Cr (4.75% and 4.89%) and the least one for Zn (0.57% and 2.04%). This implies that one element calibration curve can be used for determination of low HM concentrations in soil, and element concentration in group with other calibration curves can be used for determination of large concentrations (Figure).

The total pollution of moraine *Luvisol* with HM, determined by the XRF method in the HCl + HF + HNO₃ extract, is compared with data of AAS analysis in the same extract.

According to statistical parameters of linear regression equations, this dependency varies with different HM (Table 6). At the reliability level of 99%, in the entire soil the total concentration data of Cr ($r = 0.998$, $D = 99.5\%$), Pb ($r = 0.944$, $D = 89.1\%$) and Zn ($r = 0.997$, $D = 99.5\%$) are distinguished for a very strong dependency and of Cu ($r = 0.852$, $D = 72.6\%$) for a strong dependency. A strong reverse dependency is characteristic of the total concentration data on Ni ($r = -0.881$, $D = 77.6\%$).

Table 6. Dependency equations of total HM concentrations in *Luvisol*, determined by AAS (y) and XRFs (x) methods

HM	Linear regression equations	r	Determination index (D) %
Cr	$y = -12.38 + 1.178x$	0.998**	99.5
Pb	$y = 16.91 + 0.48x$	0.944**	89.1
Ni	$y = 115.56 - 1.26x$	-0.881**	77.6
Cu	$y = 19.02 + 0.91x$	0.852**	72.6
Zn	$y = -1.72 + 1.01x$	0.997**	99.5

** Reliability level 99%.

According to the data of this investigation, different methods of analysis used for the determination of total HM concentrations in *Luvisols* are not equivalent only for single chemical elements (Ni). This implies that the XRFs method can be an alternative to the traditional AAS method in determining the total concentrations of some HM in *Luvisols* as it requires less time for the preparation of samples for analysis, which makes it more rapid and fairly accurate.

CONCLUSIONS

1. Pollution of the test *Luvisols* with Cr, Cu and Zn is not dangerous ($K_0 < 1$). The medium hazardousness level ($1 < K_0 < 3$) has been determined for the pollution with Ni in the entire profile of limnoglacial clay *Luvisol* (R1) and in the Ap horizon of moraine loam *Luvisol* (G2), and with Pb – only in the Ap horizon of limnoglacial clay *Luvisol* (R1).

2. In the Ap horizon of limnoglacial clay *Luvisol* (R1), the total concentrations of Cr and Pb are up to 1.9 times and of Ni 2.4 times higher than those in the same horizon of moraine loam *Luvisol* (G2). Differences between Cu and Zn concentrations in the Ap horizon of the test *Luvisols* of different parent material are significantly lower.

3. In the profile of limnoglacial clay *Luvisol*, the highest total concentrations of Cr and Cu were found in BCkg, of Zn in the Bt, and of Pb and Ni in the Ap or the AEl horizons. In the profile of moraine loam *Luvisol*, bigger accumulations of total Cr, Pb and Ni were determined in the Ap horizon, and the content of Cu and Zn was evenly distributed in the entire soil profile.

4. The Ap horizon of limnoglacial clay *Luvisol* (R1) in comparison with that of moraine loam *Luvisol* (G2) has concentrations of mobile Cr ions bigger by up to 1.4 times, of Pb up to 1.7 times, of Cu up to 2 times, and similar concentrations of mobile Ni and Zn ions.

5. In limnoglacial clay *Luvisol* (R1) profile, mobile Cr and Pb ions are mostly concentrated in the Ap and AEl horizons, mobile Cu ions prevail in the Bt horizon, while those of Ni and Zn are evenly distributed in the entire *Luvisol* profile. In moraine loam G2 profile, the biggest concentrations of mobile Cr and Zn ions are found in the Ap horizon, of mobile Pb ions in the Bt horizon, and mobile Ni ions are evenly distributed.

6. The established very strong dependency for Cr, Pb, Zn, Cu and a strong reverse dependence for Ni linear relation between total HM concentrations determined by the X-ray fluorescence

and AAS methods, show that the XRFs method can be an alternative to the traditional AAS method in determining the total concentrations of selected HMs in *Luvisols*; it is more rapid and fairly accurate.

Received 16 June 2008

Accepted 11 July 2008

References

- Baltrėnas P., Kliaugienė E., Jankaitė A. Dirvožemio užterštumas sunkiaisiais metalais prie Via Baltica automagistralės ir Klaipėdos žiedo // Journal of Environmental Engineering and Landscape Management. 2003. Vol. XI. Suppl. 1. P. 3–10.
- Brannvall E. Sunkiųjų metalų ir naftos produktų kelio aplinkoje tyrimai ir mažinimas naudojant gamtinius sorbentus. Summary of doctoral dissertation. Vilnius, 2006. 24 p.
- Caridad Cancela R., Abreu C. A., Paz-Gonzalez A. Total trace element contents in natural soils by two methods // 17th World Congress of Soil Science. Bangkok, Thailand, 2002. Vol. 1. Symposium N 08. P. 243–251.
- Dirvožemio užterštumo cheminėmis medžiagomis higieninis vertinimas. Metodiniai nurodymai. Vilnius, 1997. 11 p.
- Bertin E. P. Introduction to X-ray spectrometric analysis. New York and London: Plenum Press, 1978. 88 p.
- Gregorauskienė V. Mapping of geochemical contamination in urban areas of Lithuania // Journal of Environmental Engineering and Landscape Management. 2006. Vol. XIV. N 1. P. 52–57.
- Grigalavičienė I., Rutkoviėnė V. Sunkiųjų metalų koncentracijos miško dirvožemiuose bei samanose šalia greitkelio Vilnius–Kaunas // Miškininkystė. 2006. Nr. 2(60). P. 12–19.
- HN 60-2004. Pavojingų cheminių medžiagų didžiausios leidžiamos koncentracijos dirvožemyje // Valstybės žinios. 2004. P. 41–1357.
- Houba V., Novozamsky I., Temiminhof E. Soil analysis procedures: extraction with 0.01 M CaCl₂ (Soil and Plant Analysis, Part 5A). Wageningen, 1997. 95 p.
- ISO 11466 : 1995. Soil quality – Extraction of trace elements soluble in aqua regia.
- ISO 14869-1 : 2001 Soil quality – Dissolution for the determination of total element content – Part 1 : Dissolution with hydrofluoric and perchloric acids.
- ISO 14869-2:2002 Soil quality – Dissolution for the determination of total element content – Part 2 : Dissolution by alkaline fusion.
- Jankaitė A. Research on heavy metals in roadside and evaluation of their influence on the environment. Summary of doctoral dissertation. Vilnius: Technika, 2007. 24 p.
- Jones A. A. X-ray Fluorescence analysis. In: Smith K. A. (Hrsg). Soil Analysis, 2. New York: Marcel Dekker, 1991. 287 p.
- Juknevičius S., Matyžiūtė-Jodkonienė D., Sabienė N. Contamination of soil and grass by heavy metals along the main roads in Lithuania // Ekologija. 2007. Vol. 53. No. 3. P. 70–74.

16. Kadūnas V., Budavičius R., Gregorauskiene V. ir kt. Lietuvos geocheminis atlasas. Vilnius: Geologijos institutas, 1999. 90 p.
17. Lietuvos dirvožemiai (sud. M. Eidukevičienė, V. Vasiliauskiene). Vilnius: Lietuvos mokslas, 2001. Kn. 32. 1244 p.
18. Maizet L., Esnaola M. V., Millan E. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis // *Environmental Pollution*. 2000. Vol. 110. P. 3–9.
19. Manual for Integrated Monitoring. Programme phase 1993–1996. Helsinki, 1993. 114 p.
20. Methodology for determination of heavy metal standards for soil. Phase I: Definition study. Research report. Delft Hydraulics. 1997. 185 p.
21. Methods of Soil and Plant Analysis. MTTV-Jokionen, Finland, 1986. P. 1–45.
22. Methods of soil analysis. Part 3 – Chemical Methods, SSSA Book Series: 5 (eds. D. L. Sparks et al.). USA, 1996.
23. Motuzas A., Prosyčevs I., Vaisvalavičius R. et al. Application of atomic absorption spectrophotometry for determining heavy metals amount in soil using different extractive solutions // *Environmental Research, Engineering and Management*. 2000. N 3(13). P. 67–73.
24. Motuzas A., Vaisvalavičius R., Prosyčevs I. ir kt. Sunkiųjų metalų kiekio dirvožemyje ir jo molio frakcijoje tyrimas rentgeno fluorescencinės spektrinės analizės metodu // *Vagos. LŽŪU mokslo darbai. Akademija*. 2003. Nr. 59(12). P. 63–68.
25. Quevauviller Ph. Operationally defined extraction procedures for soil and sediment analysis // *Trends in Analytical Chemistry*. 1998. Vol. 17. P. 289–298, 632–642.
26. Ramos L., Hernandez L. M., Gonzalez M. J. Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Doñana National Park // *Journal of Environmental Quality*. 1994. Vol. 23. P. 50–57.
27. Rauret G. Extraction procedure for the determination of heavy metals in contaminated soil and sediment // *Talanta*. 1998. Vol. 46. P. 449–455.
28. Sabienė N. Sunkiųjų metalų poveikio aplinkai priklausomybė nuo dirvožemio kokybės veiksnių. Daktaro disertacija. Akademija, 2004.
29. Sabienė N., Brazauskienė D., Rimmer D. Determination of heavy metal mobile forms using different extraction methods // *Ekologija*. 2004. Nr. 1. P. 36–41.
30. Saloman E. Extraction of soil potassium with 0.01 M calcium chloride composed of official Swedish methods // *Communications of Soil Science and Plant Analysis*. 1998. Vol. 29. Iss. 19–20. P. 2841–2854.
31. Šakalytė J., Kviatkus K., Valiulis D. Variation tendencies of heavy metal concentrations in the air and precipitation // *Environmental and Chemical Physics*. 2004. Vol. 26. N 2. P. 61–67.
32. UN ECE ICP on IM. Manual for Integrated Monitoring. 1998.
33. USEPA. Microwave-assisted acid digestion of siliceous and organically based matrices // *Test Methods for Evaluating Solid Waste (SW-846), Method 3052*, U. S. EPA, Washington, D. C., USA, 1996.
34. Савичев А. Т., Сорокин С. Е. Рентгенофлуоресцентный анализ содержания микроэлементов и тяжелых металлов в почвах // *Агрехимия*. 2000. № 12. С. 71–74.

Algirdas Juozas Motuzas, Virginijus Trimirka,
Rimantas Vaisvalavičius, Virginijus Butkus,
Igoris Prosyčevs, Nomeda Sabienė,
Danguolė Zakarauskaitė, Zigmas Vaišvila

PAKELĖS IŠPLAUTŽEMIŲ (*LUVISOLS*) UŽTARŠOS SUNKIAISIAIS METALAIS VERTINIMO METODOLOGINIAI ASPEKTAI

Santrauka

Siekiant pagausinti dirvodarinės uolienos poveikio sunkiųjų metalų (SM) kaupimuisi dirvožemyje technogeninės taršos sąlygomis žinias, 2003–2007 m. buvo atlikti limnoglacialinio molio ir moreninio priemolio išplautžemių (*Luvisols*) užtaršos SM (Cr, Pb, Ni, Cu, Zn) tyrimai auto-transporto magistralės Kaunas–Vilnius poveikio zonoje. SM koncentracijos buvo nustatytos AAS ir XRF metodais skirtinguose ekstraktuose: suminėms SM koncentracijoms buvo naudojamas HF + HCl + HNO₃ mišinys, o aplinkai pavojingoms koncentracijoms – 2 M HNO₃ rūgštis. Judriųjų SM jonų koncentracijos buvo nustatytos 1N CH₃COONH₄ (pH 4,8) ir 0,01 M CaCl₂ tirpalų ekstraktuose. Gauti rezultatai parodė, kad tirtų išplautžemių užtarša Cr, Cu ir Zn nepavojinga, o Ni ir Pb yra vidutinio pavojingumo ($1 < K_0 < 3$). Limnoglacialinio molio išplautžemio Ap horizonte bendrosios Cr ir Pb koncentracijos buvo iki 1,9 karto, o Ni – iki 2,4 karto didesnės, negu moreninio priemolio išplautžemio Ap horizonte. Cu ir Zn koncentracijų skirtumai tirtuose išplautžemiuose buvo nedideli. Limnoglacialinio molio išplautžemio profilyje daugiausia Cr ir Cu nustatyta BCkg, Zn – Bt, o Pb ir Ni – Ap ir AEL horizontuose. Moreninio priemolio išplautžemio profilyje daugiau Cr, Pb ir Ni kaupėsi Ap horizonte, o Cu ir Zn visame dirvožemio profilyje buvo pasiskirstę tolygiai. Judriųjų Cr jonų koncentracijos limnoglacialinio molio išplautžemio Ap horizonto mėginiuose, palyginti su moreninio priemolio išplautžemiu, buvo didesnės iki 1,4 karto, Pb – iki 1,7, Cu – iki 2, o Ni ir Zn – nesiskyrė.

Aptiktas labai stiprus Cr ($r = 0,98^{**}$), Pb ($r = 0,944^{**}$), Zn ($r = 0,997$), Cu ($r = 0,98^{**}$) ir stiprus atvirkštinis Ni ($r = -0,881^{**}$) tiesinės priklausomybės ryšys tarp SM bendrųjų koncentracijų, nustatytų Rentgeno fluorescenciniu metodu (XRF) ir AAS metodu, leidžia teigti, kad XRF metodas gali būti alternatyvus tradiciniam AAS metodui kai kurių SM bendrosioms koncentracijoms išplautžemiuose (*Luvisols*) nustatyti, nes yra spartesnis ir pakankamai tikslus.

Raktažodžiai: išplautžemis, sunkieji metalai, technogeninė dirvožemio tarša, sunkiųjų metalų (SM) ekstrahavimo metodai