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Heavy metal sorption capacity and mobility in the *Retisol* profile in relation to the contamination

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Abstract

The aim of the research was to evaluate heavy metal contamination, heavy metal sorption capacity and their mobility in the monoliths of the relatively natural and technogenically affected by vehicle emissions *Retisol* profile.
Two objects of the *Eutric Albic Stagnic Bathygleyic Glossic Retisol* were investigated: 1st – relatively natural (350 m from motorway) and 2nd – technogenically affected 20 m from motorway). Total heavy metal amounts in each horizon of the soil profile were determined by flame atomic absorption spectrometry method in the digestate of the HF + HNO_3 + HCl, and mobile heavy metal amounts – in the extract of 1 M CH_3COONH_4 (pH 4.8). In the relatively natural soil, elevated Pb amounts were observed at the topsoil to 10 cm, and Cu – at the depth to 60 cm while Zn contamination was not observed. While heavy metal contamination of the technogenically affected *Retisol* was observed throughout the soil profile to one meter. Percentage of the mobile Pb from total amount in the natural and technogenically affected soil was 11.1–19.6% and 16.7–19.3%, Cu – 13.0–16.7% and 16.1–19.5%, Zn – 18.3–22.5% and 16.4–21.0%, respectively.
Special stands of the model columns (1 m height, 0.15 m diameter) were designed and filled up with undisturbed soil monoliths. Heavy metal sorption capacity and mobility both in the soil profile and each horizon were investigated when saturating them with mixture of Pb, Zn and Cu solutions. Heavy metal sorption capacity in the horizons of the *Retisol* profile varied in the range of 504.40–819.60 mg kg^{-1} for Pb, 498.27–905.63 mg kg^{-1} for Cu and 505.07–983.43 mg kg^{-1} for Zn as well as enrichment factor – 27.4–70.8, 36.0–59.5 and 17.5–53.2, respectively. Percentage of the mobile Pb, Cu and Zn in the saturated natural and technogenically affected soil was 40.6–48.2, 40.4–45.7 and 40.7–48.9 %, respectively.
Consequently, despite the great heavy metal sorption capacity, their mobility and potential bioavailability increase markedly in the contaminated *Retisol*, therefore it is important in the legislations of the food safety and agricultural land protection to strengthen measures of the environmental protection at roadsides, such as sanitary zones of at least 20 m.

Key words: agricultural land, enrichment factor, heavy metal mobility, model columns, sorption capacity, vehicle emissions, *Retisols.*

Introduction

Heavy metal pollution is a serious potential danger for the agricultural lands and environment, therefore great attention of scientists is given to its investigation in Lithuania (Antanaitis, Antanaitis, 2004; Brannval, Spakauskas, 2007; Gregorauskienė, 2012), European Union (CORDIS, 2012; Werkenthin et al., 2014) and worldwide (Knechtenhofer et al., 2003; Xia et al., 2011).

Heavy metal bioavailability and environmental impact depend on complicated soil-heavy metal interactions due to soil polydispersity and heterogeneity. A complex of various heavy metal adsorption-desorption processes are running in the soil depending on its properties, heavy metal origin and competitive sorption (Sabienė, 2004; Anagu, 2011; Chotpantarat et al., 2011 a; b; Pokrovsky et al., 2012), land use (Citeau et al., 2002; Xia et al., 2011), fertilization, tillage effects, and soil contamination (Antanaitis, Antanaitis, 2004; Brannval, Spakauskas, 2007; Chrastný et al., 2012) as well as heavy metal distribution in the soil profile due to water flow paths (Knechtenhofer et al., 2003; Wehrer, Totsche, 2003; Kirkham, 2014). Data of the statistical analysis by artificial neural networks using 13 soil properties (clay, silt and sand content, pH, electrical conductivity, organic carbon, iron, manganese and aluminium oxides (FeO_x, MnO_x and AlO_x), cation exchange capacity, water soluble iron, manganese and aluminium) showed that the most important factor for the heavy metal sorption is soil pH, following organic carbon (only in topsoil samples), clay content, especially for thallium and molybdenum. Influence of the cation exchange capacity varied greatly depending on the soil composition and other factors. Also manganese oxides (MnO_x) had great influence on chromium sorption (Buszewski, Kowalkowski, 2006).

Important findings were published suggesting that soil-heavy metal interactions vary greatly in the soil horizons due to different morphological features resulting from pedogenetic processes (Citeau et al., 2002; Cornu et al., 2007; Anagu, 2011; Montagne et al., 2013). Therefore recent investigations of the heavy metal distribution and transport in the soil profile and in the model columns have become of great importance (Wehrer, Totsche, 2003; Markiewicz-Patkowska et al., 2005; Buszewski, Kowalkowski, 2006; Lewis, Sjöstrom, 2010; Chotpantarat et al., 2011 a; b). However, most of the column experiments were performed in the disturbed soil samples while knowledge about the heavy metal sorption in the undisturbed monoliths of soil profile is very poor.

The aim of the current research was to evaluate the *Retisol* contamination by heavy metals (Pb, Cu and Zn) and its influence on the heavy metal sorption capacity and mobility in the soil monoliths depending on the distance to the pollution source (motorway). *Retisol* was chosen because it is one of the most abundant and characteristic types of the soil. It covers 1,446,668.66 km^2 worldwide and about 20.4% of Lithuania's area.

Materials and methods

Experimental site was chosen at the Kryžkalnis crossroad (55°27′39.28″ N, 22°41′05.67″ E) where main lines of the traffic from East to West of Lithuania (highway A1, Minsk–Vilnius–Kaunas–Kryžkalnis–Klaipėda), from North to South of Eastern Europe (highway E77, Ryga–Šiauliai–Kryžkalnis–Sovetsk–Kaliningrad) cross (Fig. 1 A).

The experimental site is located at the plain of Samogitian upland with hilly ravine terrain relief in Western Lithuania, where sandy loam and sandy clay loam *Retisols* are predominant (Fig. 1 B). The average yearly precipitation amounts to 600–650 mm leading to soil leaching mode. The predominant soil type is automorphic *Retisol* with weak gleyic features while in the lowest areas of the region the *Gleysols* and *Hystosols* occur. Soil cover is of high to medium diversity but contrasting.

Description of the soil profile (Fig. 1 C): type – *Eutric Albic Stagnic Bathygleyic Glossic Retisol* according to the international WRB system (2014). Horizons: Ap (0–37 cm) – surface plough horizon, dark yellowish brown colour (10YR 4/2), medium granular structure, friable sandy clay loam; AElj (37–44 cm) – transitional surface plough – subsurface eluviated (leached) stagnic horizon, greyish brown colour (2.5Y 5/2), medium granular structure, very friable sandy clay loam; ElBtj (44–74 cm) – transitional eluviated stagnic subsoil horizon with some illuviation of clay, greyish brown colour (2.5Y 5/2) coarse subangular blocky, friable structure sandy clay loam; Btj (74–88 cm) – stagnic subsoil horizon with some illuviation of clay, light olive brown colour (2.5Y 5/3), nutty subangular blocky structure, firm sandy clay loam; Bj (88–104 cm) – stagnic weakly expressed subsoil horizon, light olive brown colour (2.5Y 5/3), subangular blocky structure, firm sandy clay loam; BC (g) (104–121 cm) – gleyic transitional subsoil-parent material horizon, light olive grey (5Y 5/2), subangular blocky prismatic structure, firm sandy clay loam.

A B C

Figure 1. Position of the experimental site (red dot) related to the traffic mainlines (A): arrows show directions of the traffic mainlines: motorways E77 and A1; the experimental area (B) and profile (C) of the investigated *Eutric Albic Stagnic Bathygleyic Glossic Retisol*

Two experimental plots (objects) were chosen at the site: 1st object – relatively natural (background pollution), 350 m from the motorway; 2nd object – technogenically affected (vehicle emissions), 20 m from the motorway. The composite soil samples were sampled from each genetic horizon of the soil profile in three replicates with a soil auger (ISO 10381-1:2002. Soil quality. Sampling. Part 1: Guidance on the design of sampling programmes; ISO 10381-2:2002. Soil quality. Sampling. Part 2: Guidance on sampling techniques; ISO 10381-3:2001. Soil quality. Sampling. Part 3: Guidance on safety; ISO 10381-4:2003. Soil quality. Sampling. Part 4: Guidance on the procedure for investigation of natural, near-natural and cultivated sites; ISO 10381-5:2005. Soil quality. Sampling. Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination). For the laboratory analysis soil samples were air-dried, sieved through 2 mm mesh sieve, homogenised and stored according to the standard ISO 11464:2006 (Soil quality. Pretreatment of samples for physico-chemical analysis). Soil texture was determined by sieving and sedimentation method (ISO 11277:2009. Soil quality. Determination of particle size distribution in mineral soil material. Method by sieving and sedimentation). Soil texture class was determined by FAO/UNESCO (2006) methodology according to the particle size distribution (WRB, 2014). Soil pH was determined with 780 pH-meter 2.780.0010 Methrohm with electrode 6.0258.600 in 1 M KCl suspension (mass to volume ratio 1:2.5) (ISO 10390:2005). Amount of carbonates ($CaCO_3$) was determined by calcimeter test, organic carbon (OC) – with elemental analyzer by dry combustion at 850°C. Total nitrogen (N) was determined by the modified Kjeldahl method (ISO 11261:1995. Soil. Determination of total. Modified Kjeldahl method), available P_2O_5 and K_2O – by Egner-Riehm-Domingo (A-L) method (ГОСТ 26208-91). Sum of sorbed bases was determined by complexometric titration (Houba et al., 1995). Data of the soil texture and agrochemical properties are presented in Tables 1 and 2.

Table 1. Texture of the *Eutric Albic Stagnic Bathygleyic Glossic Retisol* investigated

Soil horizon depth cm	Soil texture fractions %				
	>2 mm	0.05–2.00 mm	0.02–0.05 mm	0.002–0.05 mm	<0.002 mm
Ap 0–10	6.2	58.2	11.3	26.6	15.2
Ap 20–25	1.6	60.3	10.2	24.5	15.2
AElj 39–43	1.4	61.8	8.8	19.8	18.4
ElBtj 56–61	2.8	53.2	8.9	22.1	24.7
Btj 78–83	1.9	53.1	11.0	24.2	22.7
Bj 95–100	0.5	48.8	14.1	28.9	22.3

Table 2. Agrochemical properties of the *Eutric Albic Stagnic Bathygleyic Glossic Retisol* investigated

Soil horizon depth cm	pH (KCl)	$CaCO_3$ %	OC %	Total N %	Sum of sorbed bases mequiv kg^{-1}	P_2O_5 mg kg^{-1}	K_2O mg kg^{-1}
Ap 0–10	6.00	0.00	1.27	0.16	98.7	80	101
Ap 20–25	5.40	0.00	0.69	0.10	78.4	20	57
AElj 39–43	5.80	0.00	0.13	0.04	75.7	26	72
ElBtj 56–61	5.70	0.00	0.14	0.04	144.8	88	105
Btj 78–83	5.40	0.00	0.08	0.02	131.8	169	116
Bj 95–100	5.70	0.00	0.07	0.02	135.8	204	113

Heavy metals were determined using atomic absorption spectrometer M403 (Perkin-Elmer, USA). For total heavy metal amounts soil samples were digested in the mixture HF + HNO_3 + HCl while mobile heavy metal amounts were determined in the 1 M CH_3COONH_4 (pH 4.8) extraction (Methods of soil analysis, 1996; ISO 14869-1:2001. Soil quality. Dissolution for the determination of total element content. Part 1: Dissolution with hydrofluoric and perchloric acids). Two stands of the four model columns (height 1 m, diameter 0.15 m) each were designed and filled with the *Retisol* profile monoliths: 1st object – relatively natural soil, 2nd object – technogenically affected soil (Fig. 2).


A B C

Figure 2. Filling (A) and final stand (B, C) of the model columns of the soil monoliths

Ion selective electrodes ("Kritur", the Czech Republic, and "Econics", Russia) were installed into each horizon of the soil profile of the first column for the investigation of the heavy metal sorption dynamics (Fig. 2 B). Ion metric data of the heavy metal concentrations were controlled in the time periods of 24 hours in the sequence of the increasing concentration from 0.01 to 1.0 g L^{-1} until the full heavy metal sorption capacity of the soil was reached.

The static heavy metal sorption was investigated in other 2 columns (2 replicates). The fourth column was left as control, and was leached with appropriate amount of deionised water (Fig. 2 C). Soil monoliths were saturated with solution of the lead (Pb), copper (Cu) and zinc (Zn) acetates. Concentration of each metal in the solution was equal to 1 g L^{-1}. Velocity of the solution leaching was 1 L per 12 hours. Leachate was sampled each 12 hours for the heavy metal determination. The provision was accepted that soil monoliths were saturated with heavy metal when Pb, Cu and Zn concentrations in leachate became equal to 1 g L^{-1} each. After that model columns were mounted out and amounts of adsorbed total and mobile heavy metals were determined throughout the soil profile and in each horizon. Adsorbed heavy metal amounts C/C_0 were calculated according to the equation:

$$C/C_0 = \frac{C_0 - (C_{leachate} - C_{control})}{C_0} \qquad (1),$$

where C_0 – heavy metal concentration in the initial solution, 1 mg L^{-1}; $C_{leachate}$ – heavy metal concentration in the leachate, mg L^{-1}; $C_{control}$ – heavy metal concentration in the leachate of the control column.

Heavy metal sorption capacity was evaluated by enrichment factor (Ef) according to the equation:

$$Ef = \frac{C/C_0 - C_{initial}}{C_{initial}} \qquad (2),$$

where C/C_0 – adsorbed heavy metal amount in the saturated soil, mg kg^{-1}; $C_{initial}$ – heavy metal amount in the natural soil before saturation, mg kg^{-1}.

Results and discussion

Total heavy metal amounts in the natural and saturated Retisol monoliths. In the relatively natural soil (1st object) Cu amounts (15.4–23.3 mg kg^{-1}) exceeded background concentrations in the depth to 61 cm, Pb (18 mg kg^{-1}) – at the topsoil to 10 cm while Zn did not exceed them according to the Lithuanian legislative document HN 60:2004. Technogenic soil contamination (2nd object) was observed throughout soil profile. Heavy metal amounts (Pb – 18.6–29.0, Cu – 12.8–22.7, Zn – 29.6–47.2 mg kg^{-1}) exceeded the background concentrations and were 1.5–2 times higher compared to relatively natural soil of the 1st object (Table 3).

Maximum permissible concentrations were not exceeded. Comparing the data to urban and roadside soils worldwide (10–240 mg kg^{-1} Pb, 15–212 mg kg^{-1} Cu and 4–308 mg kg^{-1} Zn) according to the data of Xia et al. (2011) and Werkenthin et al. (2014) heavy metal amounts in the topsoil of the *Retisol* investigated were low. Our findings confirm the Brannvall and Spakauskas (2007) model showing that the highest heavy metal contamination is at the distance of 20 m from roadside. But at the distance of 350 m from roadside we still found elevated Pb and Cu concentrations in upper horizons of the soil profile. It could be due to more distant air transfer of finer particles, long-range transboundary transport of pollutants from Western Europe, also due to greater affinity of Pb and Cu to soil constituents and possibility to accumulate in the topsoil (Podlesakova et al., 2001; Brannvall, Spakauskas, 2007).

Table 3. Total heavy metal amounts in the *Eutric Albic Stagnic Bathygleyic Glossic Retisol* investigated

No.	Investigated soil	Soil horizon depth cm	Average amount mg kg^{-1} ± SD		
			Pb	Cu	Zn
1.	1st object – relatively natural (background pollution, 350 m from motorway)	Ap 0–10	**18.0 ± 0.10**	**23.30 ± 0.20**	19.10 ± 0.10
		Ap 20–25	14.20 ± 0.50	**18.20 ± 0.18**	18.50 ± 0.15
		AElj 39–43	9.70 ± 0.25	**15.70 ± 0.10**	15.20 ± 0.12
		ElBtj 56–61	9.00 ± 0.20	**15.40 ± 0.09**	12.90 ± 0.20
		Btj 78–83	9.20 ± 0.12	10.80 ± 0.14	9.50 ± 0.08
		Bj 95–100	8.70 ± 0.10	10.20 ± 0.17	10.50 ± 0.18
2.	2nd object – technogenically affected (20 m from motorway)	Ap 0–10	**29.00 ± 0.38**	**22.70 ± 0.08**	**47.20 ± 0.03**
		Ap 20–25	**24.30 ± 0.71**	**19.30 ± 0.05**	**44.50 ± 0.02**
		AElj 39–43	**23.10 ± 0.84**	**17.70 ± 0.10**	**41.30 ± 0.05**
		ElBtj 56–61	**20.40 ± 0.63**	**17.10 ± 0.07**	**37.30 ± 0.05**
		Btj 78–83	**19.30 ± 0.40**	**16.10 ± 0.04**	**35.80 ± 0.07**
		Bj 95–100	**18.60 ± 0.52**	**12.80 ± 0.09**	**29.60 ± 0.04**
Background concentration (HN 60:2004)			15	8.1–11	26–36
Maximum permissible concentrations (HN 60:2004)			100	100	300

SD – standard deviation; bold – exceeded background concentrations

Heavy metal concentrations in the saturated monoliths of the model columns showed high heavy metal sorption capacity of the *Retisol* investigated (Table 4).

Pb sorption capacity varied in the range 504.4–819.6 mg kg^{-1}, Cu – 498.3–905.6 mg kg^{-1} and Zn – 505.1–983.4 mg kg^{-1}. Literature data show that heavy metal sorption capacity varies greatly depending on the lithogenic factors, soil texture, competitive sorption, pH, and other factors. In the roadside soil Cu sorption capacity varied in the range 600–4500, Zn – 1024–1083 mg kg^{-1}. Pb sorption capacity ranged from 579 mg kg^{-1} at the multi-elemental to 615 mg kg^{-1} at the single batch sorption

Table 4. Total heavy metal concentrations (numerator) and their enrichment factors (denominator) in the saturated *Eutric Albic Stagnic Bathygleyic Glossic Retisol*

No.	Investigated soil	Soil horizon depth cm	Average heavy metal concentration mg kg^{-1} ± SD Enrichment factor (Ef)		
			Pb	Cu	Zn
1.	1st object – relatively natural (background pollution, 350 m from highway)	Ap 0–10	819.60 ± 22.90 45.5	854.77 ± 42.65 36.7	983.43 ± 4.53 51.5
		Ap 20–25	782.10 ± 35.33 55.1	727.33 ± 69.63 40.0	851.73 ± 14.98 46.0
		AElj 39–43	686.97 ± 37.35 70.8	685.63 ± 29.28 43.7	663.90 ± 57.81 43.7
		ElBtj 56–61	610.57 ± 53.56 67.8	635.73 ± 37.48 41.3	662.53 ± 33.95 51.4
		Btj 78–83	504.40 ± 64.70 54.8	498.27 ± 48.84 46.1	505.07 ± 24.14 53.2
		Bj 95–100	507.43 ± 62.82 58.3	506.07 ± 10.23 49.6	525.67 ± 13.98 50.1
2.	2nd object – technogenically affected (20 m from highway)	Ap 0–10	800.40 ± 20.62 27.6	905.63 ± 26.41 39.9	871.77 ± 4.07 18.5
		Ap 20–25	733.47 ± 7.3 30.2	816.63 ± 2.82 36.0	785.57 ± 15.81 17.7
		AElj 39–43	632.27 ± 20.03 27.4	767.33 ± 14.40 43.4	722.63 ± 10.90 17.5
		ElBtj 56–61	631.77 ± 14.21 31.0	759.07 ± 8.43 44.4	663.80 ± 22.50 17.8
		Btj 78–83	683.37 ± 26.09 35.4	792.10 ± 27.84 41.0	754.23 ± 7.10 25.5
		Bj 95–100	695.53 ± 2.04 37.4	761.73 ± 12.35 59.5	705.17 ± 35.17 23.8

SD – standard deviation

experiment in the urban soils enriched with organic residuals (pH 2) while Cu – from 280 to 1059 mg kg^{-1}, respectively. Zn sorption there was not observed at pH 2. When pH was increased to 7, sorption capacity of zinc increased to 718 mg kg^{-1} at the multi-elemental, and to 817 mg kg^{-1} at the single batch sorption experiment (Markiewicz-Patkovska et al., 2005). The mineral phase (excluding organic matter) of deeply weathered tropical soils in the batch adsorption experiments from multi-elemental solution depending on pH (4.5–7.4) adsorbed 99.4–993.6 mg kg^{-1} Pb, 98.6–961.0 mg kg^{-1} Cu and 20.8–655.2 mg kg^{-1} Zn, respectively (Fontes, Gomes, 2003). In batch multi-elemental sorption experiments Pb sorption capacity varied in the range of 1058–3229.2 mg kg^{-1}, Cu – 755.2–1958.4 mg kg^{-1} and Zn –366–760.5 mg kg^{-1} in the soils from New Valley, Egypt (Usman, 2008). So, heavy metal sorption capacity of the investigated *Retisol* monoliths was in the range of the soil sorption capacity worldwide. Generally, organic matter retains more heavy metals in the topsoil layer Ap while clay particles adsorb more heavy metals in the deeper layer Bt (Podlesakova et al., 2001; Anagu, 2011; Chrastný et al., 2012). Also water movement in the heterogenic soil profile due to different soil properties has great influence on the heavy metal distribution (Wehrer, Totsche, 2003).

In the model columns of the relatively natural (1st object) *Retisol* monoliths total heavy metal concentrations decreased evenly throughout the soil profile, while trend of the heavy metal accumulation in the Btj horizon of the technogenically affected soil (2nd object) was observed. Enrichment factors (Ef) varied from 17.5 for Zn to 70.8 for Pb (Table 4). It is believed that heavy metal distribution in soil horizons depends on the pedogenetic processes (Podlesakova et al., 2001). Typical *Retisols* are characterised by the formation of glosic tongues that involve dispersion and eluviation of clay minerals due to Fe (III) reduction resulting in mobilization of the clay particles (Cornu et al., 2007). Deeper *Retisols* have argic clay illuvial subsoil horizon where Fe hydroxides and clay particles accumulate. Therefore the majority of elements and heavy metals should be leached from the elluvial and accumulate in the illuvial horizons. Eluviation of silt particles (0.002–0.05 mm) from upper Ap and AELj horizons (from 26.6% to 19.8%), and illuviation into the ElBtj, Btj and Bj horizons (22.1–28.9%) of the *Retisol* investigated was observed. Eluviation of the clay particles (<0.02 mm) was less evident. The clay fraction was lower in Ap horizon (15.2%), then increased in AElj and ElBtj (18.4–24.7%) and, finally, decreased in Btj and Bj horizons (22.7–22.3%) (Table 1). Enrichment factor (Ef) revealed Pb eluviation-illuviation phenomenon more clearly: it increased from 45.5 to 70.8 in the upper Ap and AElj horizons while decreased from 67.8 to 58.3 in the deeper ElBtj and Bj horizons. Cu and Zn accumulation in the subsoil horizons was less evident: Cu enrichment factor increased in the range 36.7–43.7 in the upper Ap and AElj horizons while from 41.3 to 46.1 in the deeper ElBtj and Bj horizons. Enrichment factor (Ef) of the Zn decreased from 51.5 to 43.7 in the upper Ap and AElj horizons while fluctuated from 51.4 to 53.2 and 50.1 in the deeper ElBtj, Btj and Bj horizons (1st object) (Table 4). Enrichment factors (Ef) of Pb and Zn were lower and increased within the soil profile from 27.6 to 37.4 and from 18.5 to 25.5, respectively in the model columns of the technogenically affected *Retisol* monoliths (Table 4, 2nd object). These findings confirm statements that mobility of heavy metals of the technogenic origin is increased (Chrastný et al., 2012). Cu sorption was more even and enrichment factor increased in the range 36.7–49.6 showing greater Cu affinity to the soil solids (Podlesakova et al., 2001; Sabienė, 2004; Anagu, 2011).

Mobile heavy metal amounts in the natural and saturated Retisol monoliths. Amounts of the mobile heavy metals determined in the 1 M CH_3COONH_4 (pH 4.8) extract in the natural *Retisol* investigated and their percentages from the total heavy metal amounts are presented in Table 5.

Table 5. Mobile heavy metal amounts (numerator) and their percentage from the total heavy metal amounts (denominator) in the *Eutric Albic Stagnic Bathygleyic Glossic Retisol* investigated

No.	Investigated soil	Soil horizon depth cm	Average heavy metal amount mg kg^{-1} ± SD Percentage from the total heavy metal amount %		
			Pb	Cu	Zn
1.	1st object – relatively natural (background pollution, 350 m from highway)	Ap 0–10	2.00 ± 0.05 11.1	3.50 ± 0.10 15.0	3.50 ± 0.17 18.3
		Ap 20–25	1.90 ± 0.08 13.4	2.40 ± 0.17 13.2	3.50 ± 0.10 18.9
		AElj 39–43	1.90 ± 0.04 19.6	2.10 ± 0.04 13.4	3.20 ± 0.15 21.1
		ElBtj 56–61	1.40 ± 0.07 15.6	2.00 ± 0.12 13.0	2.90 ± 0.10 22.5
		Btj 78–83	1.60 ± 0.05 17.4	1.80 ± 0.15 16.7	1.80 ± 0.10 18.9
		Bj 95–100	1.10 ± 0.10 12.6	1.40 ± 0.10 13.7	1.20 ± 0.21 11.4
2.	2nd object – technogenically affected (20 m from highway)	Ap 0–10	5.40 ± 0.35 18.6	4.40 ± 0.33 19.4	9.90 ± 0.41 21.0
		Ap 20–25	4.70 ± 0.30 19.3	3.70 ± 0.35 19.2	8.70 ± 0.55 19.6
		AElj 39–43	4.40 ± 0.33 19.0	3.40 ± 0.28 19.2	7.90 ± 0.56 19.1
		ElBtj 56–61	3.90 ± 0.30 19.1	3.00 ± 0.29 17.5	6.70 ± 0.58 18.0
		Btj 78–83	3.40 ± 0.28 17.6	2.60 ± 0.21 16.1	6.10 ± 0.40 16.4
		Bj 95–100	3.10 ± 0.29 16.7	2.50 ± 0.22 19.5	5.60 ± 0.44 18.9

SD – standard deviation

Amounts of the mobile heavy metals in the relatively natural soil (1st object) were as low as 1.10–2.00 mg kg^{-1} Pb, and amounted 11.1–19.6% of the total Pb amount; 1.40–3.50 mg kg^{-1} Cu, and amounted 13.2–16.7% of the total Cu amount; 1.20–3.50 mg kg^{-1} Zn and amounted 18.3–22.5% of the total Zn amount (Table 5). Mobility of the heavy metals in the *Retisol* investigated increased in the order Pb < Cu < Zn. In the technogenically affeted soil (2nd object) mobile heavy metal amounts were higher: Pb – in average 2.5, Cu – approximately 1.5 and Zn 5 times. These data confirm increased heavy metal mobility in the technogenically contaminated soil (Podlesakova et al., 2001; Chrastný et al., 2012). But changes of their percentage from total heavy metal amounts were negligible and amounted for Pb, Cu and Zn to 16.7–19.3, 16.1–19.5 and 16.4–21.0 %, respectively (Table 5).

In the saturated *Retisol* monoliths mobile heavy metal concentrations in the upper Ap (0–10 cm) horizon were in average: Pb – 332.60 (1st object) – 356.47 (2nd object) mg kg^{-1}, Cu – 345.03 (1st object) – 399.50 (2nd object) mg kg^{-1} and Zn – 400.37 (1st object) – 375.97 (2nd object) mg kg^{-1} (Table 6).

It is obvious that there were more mobile heavy metals except Zn in the technogenically affected soil. Mobile heavy metal amounts decreased within soil depth in the saturated relatively natural soil (1st object) and were the least in the Btj horizon, in average: Pb – 222.73 mg kg^{-1}, Cu –212.87 mg kg^{-1} and Zn – 221.67 mg kg^{-1} while slightly increased in the Bj horizon. The sequence of the mobile heavy metal concentrations decrease (by times) was as follows: Zn (1.91) > Cu (1.63) > Pb (1.58). In the saturated technogenically affected

Table 6. Mobile heavy metal concentrations (numerator) and their percentage from the total adsorbed heavy metals content (denominator) in the saturated *Eutric Albic Stagnic Bathygleyic Glossic Retisol*

No.	Investigated soil	Soil horizon depth cm	Average heavy metal concentration mg kg^{-1} ± SD (n = 5) Percentage from the total heavy metal amount %		
			Pb	Cu	Zn
1.	1st object – relatively natural (background pollution, 350 m from highway)	Ap 0–10	332.60 ± 7.95 40.6	345.03 ± 17.54 40.4	400.37 ± 3.69 40.7
		Ap 20–25	320.23 ± 15.22 40.9	295.27 ± 28.01 40.6	346.9 ± 6.78 40.7
		AElj 39–43	282.67 ± 15.08 41.1	282.27 ± 12.81 41.2	271.27 ± 24.22 40.9
		ElBtj 56–61	252.20 ± 21.62 41.3	264.53 ± 14.91 41.6	272.70 ± 12.89 41.2
		Btj 78–83	210.07 ± 26.07 41.6	210.60 ± 18.71 42.3	209.10 ± 9.2 41.4
		Bj 95–100	222.73 ± 28.13 43.9	212.87 ± 2.12 42.1	221.67 ± 6.02 42.2
2.	2nd object – technogenically affected (20 m from highway)	Ap 0–10	356.47 ± 6.99 44.5	399.50 ± 12.73 44.1	375.97 ± 1.11 43.1
		Ap 20–25	340.07 ± 4.22 46.4	361.13 ± 2.86 44.2	348.87 ± 1.90 44.4
		AElj 39–43	292.77 ± 10.43 46.3	341.47 ± 4.24 44.5	331.80 ± 3.04 45.9
		ElBtj 56–61	304.60 ± 10.65 48.2	344.13 ± 4.12 45.3	324.73 ± 14.55 48.9
		Btj 78–83	311.43 ± 10.29 45.6	361.77 ± 12.15 45.7	333.07 ± 7.87 44.2
		Bj 95–100	307.60 ± 1.32 44.2	340.93 ± 7.43 44.8	314.57 ± 15.47 44.6

SD – standard deviation

soil (2nd object) decrease of the mobile heavy metal concentrations within the depth of soil profile was less and almost equal, respectively Pb (1.22) > Zn (1.20) > Cu (1.17). Percentage of the mobile heavy metals from the total adsorbed heavy metal content was in the range of 40.4 to 43.9 in the relatively natural soil (1st object) while 43.1–48.9 in the technogenically affected soil (2nd object) (Table 6).

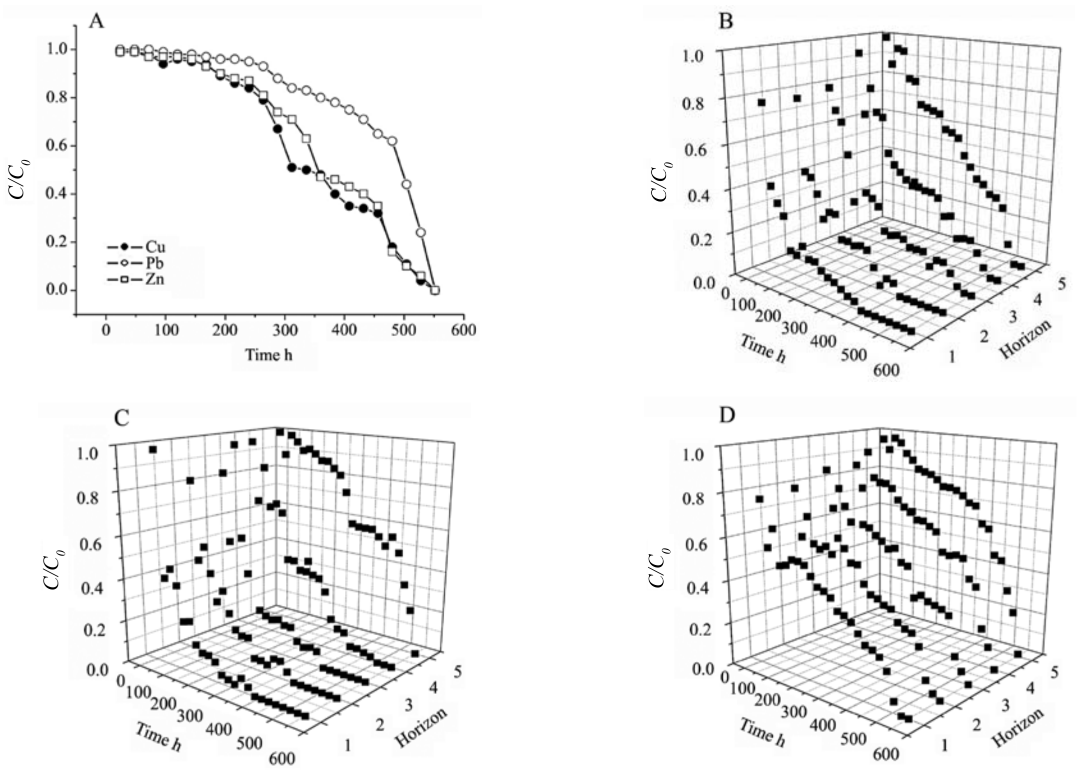
Similar percentages of the mobile heavy metals from total adsorbed heavy metals content in all horizons of the *Retisol* investigated lead to suggestion that heavy metal adsorption-desorption equilibrium is governed by the ion exchange process, also their competitive effects rather than other stronger sorption processes, such as chemical sorption (Podlesakova et al., 2001; Markiewicz-Patkowska et al., 2005; Chotpantarat et al., 2011 a).

Dynamics of the heavy metals sorption in the Retisol monolith. Saturation of the *Retisol* monolith by heavy metals took 600 hours. Pb sorption was quickest while Zn and Cu was slower and almost equal (Fig. 3 A).

Cu and Pb were more quickly adsorbed by Ap (0–10 cm), Ap (20–25 cm) and AElj (39–43 cm) horizons (1–3) timing to 400 hours while slower by ElBtj (56–61 cm) horizon (4) following the Btj (78–83 cm) horizon (5) timing to 600 hours (Fig. 3 B, C). Zn sorption was slower in all horizons while in Btj (78–83 cm) horizon (5) it began only after 50 hours from the beginning of the heavy metal solution filtration (Fig. 3 D).

Heavy metal sorption in the soil monoliths was much slower compared to batch experiments where as much as 80% of heavy metals were adsorbed by soil within the first 5 minutes (Markiewicz-Patkowska et al., 2005). Heavy metal sorption retardation in the soil monolith could be due to peculiarities of the solution filtration through the soil profile (Knechtenhofer et al., 2003). It is known that water infiltration time is about 2 hours in sandy soils while 200 years in clay soils (Kirkham, 2014). Therefore solution filtration as well as heavy metal sorption in the deeper, richer in clay horizons ElBtj and Btj was greatly restricted.

Findings of the heavy metal sorption experiment in the model columns of the soil monolith show that heavy metal sorption behaviour is comparable with the data of the batch experiments, but vary more and heavy metal sorption capacity is less (Fontes, Gomes, 2003; Sabienė, 2004; Markiewicz-Patkowska et al., 2005; Usman, 2008; Pokrovsky et al., 2012). Moreover, in column experiments different behaviour of the heavy metal sorption in different soil horizons is evident. Therefore data of the heavy metal adsorption-desorption processes in model columns of soil monoliths are more related to



Horizons: 1 – Ap (0–10 cm), 2 – Ap (20–25 cm), 3 – AElj (39–43 cm), 4 – ElBtj (56–61 cm), 5 – Btj (78–83 cm)

Figure 3. Dynamics of the heavy metal sorption (C/C_0) throughout the *Retisol* monolith profile (A) and horizons of the model columns: Cu (B), Pb (C) and Zn (D)

the natural conditions than those of the batch experiments. Therefore combining data of column leaching and batch experiments could give a deeper understanding about the heavy metal sorption processes in the soils of different pedogenetic types.

Conclusions

1. Technogenic contamination by vehicle emissions (20 m from motorway) was observed throughout the *Retisol* profile: Pb (18.6–29.0 mg kg^{-1}), Cu (12.8–22.7 mg kg^{-1}) and Zn (29.6–47.2 mg kg^{-1}). In the relatively natural soil (350 m from highway), elevated Cu concentrations (15.4–23.3 mg kg^{-1}) were observed at the depth to 61 cm, Pb (18 mg kg^{-1}) – at the topsoil to 10 cm while technogenic Zn contamination was not observed.

2. In the technogenically affected soil (20 m from motorway) percentage of the mobile Pb amounted to 16.7–19.3%, Cu – 16.1–19.5% and Zn – 16.4–21.0% from the total heavy metal amounts while in the relatively natural soil (350 m from highway) – 11.1–19.6, 13.2–16.7 and 18.3–22.5 %, respectively.

3. Heavy metal sorption capacity in the *Retisol* for Pb varied in the range 504.4–819.6 mg kg^{-1}, Cu – 498.3–905.6 mg kg^{-1} and Zn – 505.1–983.4 mg kg^{-1} as well as enrichment factor (Ef) – from 17.5 for Zn to 70.8 for Pb showing great ability of the *Retisol* ecological function as sink for pollutants.

4. Mobile heavy metal concentrations (Pb – 210.07–332.60, Cu – 212.87–345.03 and Zn – 221.67–400.37 mg kg^{-1}) decreased throughout the profile of saturated relatively natural *Retisol*, but their percentages from total adsorbed heavy metal content varied negligibly, from 40.4% to 42.3%.

5. Mobile heavy metal concentrations (Pb – 292.77–356.47, Cu – 340.93–399.50 and Zn – 314.57–375.97 mg kg^{-1}) distributed more evenly in the profile of the saturated technogenically affected *Retisol* and varied in the range 43.1–48.2% showing the higher heavy metals mobility in it.

6. Full heavy metal sorption in the model columns of the *Retisol* monolith was timing from 400 to 600 hours in the sequence Pb > Cu~Zn and was slower in the deeper ElBtj and Btj horizons. This means that the heavy metal sorption capacity of the *Retisols* is limited.

7. Conclusions presented above lead to the suggestion that agricultural land at the motorway can be dangerous for the safe food production due to increased heavy metal amounts and their mobility as well as plant availability. Therefore appropriate protection measures of the agricultural lands, such as roadside sanitary zones of at least 20 m, have to be provided in the environmental legislation.

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Sunkiųjų metalų sorbcijos talpa ir jų judrumas balkšvažemio profilyje priklausomai nuo jo užterštumo

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Santrauka

Tyrimo tikslas – įvertinti pakelės balkšvažemio profilio užterštumą sunkiaisiais metalais, jų judrumą, sorbcijos talpą ir pernašą modelinėse dirvožemio profilio monolitų kolonose. Tyrimui parinkti du pasotinto stagniškojo balkšvažemio (*Eutric Albic Stagnic Bathygleyic Glossic Retisol*) objektai Kryžkalnyje: I – sąlygiškai natūralus (350 m nuo kelio), II – technogeniškai paveiktas (20 m nuo kelio). Kiekviename dirvožemio profilio horizonte sunkiųjų metalų bendrosios koncentracijos nustatytos liepsnos atominės absorbcijos spektrometrijos metodu, mėginius mineralizavus koncentruotų rūgščių HF + HNO_3 + HCl mišiniu, o judriųjų sunkiųjų metalų jonų koncentracijos – juos ekstrahavus 1 M CH_3COONH_4 (pH 4,8) tirpalu.

Sąlygiškai natūraliame dirvožemyje (I objektas) didesni nei foniniai (HN 60:2004) kiekiai švino (Pb) nustatyti dirvožemio viršutiniame (10 cm), vario (Cu) – 60 cm sluoksnyje, cinkas (Z)n foninių kiekių neviršijo. Technogeniškai paveikto balkšvažemio (II objektas) didesni nei foniniai sunkiųjų metalų kiekiai nustatyti visame profilyje. Judrieji Pb jonai sudarė 11,1–19,6 % (I objektas) ir 16,7–19,3 % (II objektas), Cu – 13,0–16,7 % (I objektas) ir 16,1–19,5 % (II objektas), Zn – 18,3–22,5 % (I objektas) ir 16,4–21,0 % (II objektas) bendrojo šių sunkiųjų metalų kiekio.

Sunkiųjų metalų sorbcijos eksperimentui buvo sumontuoti specialūs stovai, sudaryti iš keturių modelinių 1 m aukščio ir 0,15 m skersmens kolonų, pripildytų dirvožemio monolitų. Į pirmąją kiekvieno stovo koloną buvo įmontuoti jonams selektyvūs elektrodai sunkiųjų metalų dinamikai dirvožemio profilyje tirti. Kitos dvi kolonos buvo skirtos tirti dirvožemio sunkiųjų metalų sorbcijos talpą, jį pasotinant Pb, Zn ir Cu acetatų tirpalu, kuriame kiekvieno metalo koncentracija sudarė po 1 g L^{-1}. Tirpalo pylimo greitis – 1 l per 12 val. Ketvirtojoje (kontrolinėje) kolonoje ant dirvožemio monolito buvo pilamas toks pat kiekis distiliuoto vandens tokiu pačiu režimu. Buvo priimta sąlyga, kad dirvožemio monolitai pasotinti sunkiaisiais metalais, kai filtrate jų koncentracijos tapo lygios pirminio tirpalo koncentracijoms (1 g L^{-1}). Tada kolonos buvo išardytos, o dirvožemio mėginiuose nustatytos bendrosios sunkiųjų metalų ir jų judriųjų jonų koncentracijos. Adsorbuoti sunkiųjų metalų kiekiai apskaičiuoti pagal 1 lygtį, o sorbcijos talpa įvertinta apskaičiavus papildymo koeficientą (Ef) (angl. *enrichment factor)* pagal 2 lygtį.

Dirvožemio profilio horizontuose adsorbuotos bendrosios Pb koncentracijos kito 504,40–819,60 mg kg^{-1}, Cu – 498,27–905,63 mg kg^{-1}, Zn – 505,07–983,43 mg kg^{-1}. Pb papildymo koeficientas (Ef) sudarė 27,4–70,8, Cu – 36,0–59,5, Zn – 17,5–53,2. Judrieji Pb jonai pasotintame sunkiaisiais metalais dirvožemyje sudarė 40,6–48,2 %, Cu – 40,4–45,7 %, Zn – 40,7–48,9 % bendro adsorbuotų sunkiųjų metalų kiekio.

Tyrimo rezultatai leidžia daryti išvadą, kad, nepaisant didelės dirvožemio sunkiųjų metalų sorbcinės gebos, jų judrumas ir potencialus patekimas į augalus bei kitus gyvuosius organizmus pasiekiamumas užterštame balkšvažemyje žymiai padidėja, todėl maisto saugos ir žemės ūkio paskirties dirvožemių naudojimo reikalavimuose svarbu sugriežtinti pakelių dirvožemių aplinkosauginius reikalavimus, t. y. sanitarines zonas įvesti nors 20 m atstumu nuo kelio.

Reikšminiai žodžiai: modelinės kolonos, papildymo koeficientas, sorbcijos talpa, sunkiųjų metalų judrumas, transporto emisijos, žemės ūkio paskirties žemė, balkšvažemiai.

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