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Original Paper

Evaluation of the agricultural soils pollution along the Orava River using pollution indices

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Agricultural soil pollution by potentially toxic elements (PTEs) is a major concern nowadays. We selected 11 soil profiles of Fluvisols used as arable land along the River Orava and two study sites located outside the alluvium (1 soil profile of Cambisol used as a permanent grassland, 1 soil profile of Technosol classified as an environmental burden). We determined basic soil properties, total PTEs content and the mobile fraction using inductive coupled plasma mass spectroscopy. The level of pollution of selected PTEs was assessed by single contamination factor (Cf) and pollution load index (PLI). The total PTEs content indicated their increased concentrations at many study sites. But the mobile form content of PTEs did not exceed the Slovak threshold limits in agricultural soils. Nevertheless, the pollution indices also reached higher values in agricultural soils. According to the Cf, Technosol was very highly polluted by Pb (12.89), Sb (11.94), Cd (11.82), Zn (9.19); considerably polluted by As (5.75), Cu (5.70), Mo (4.86); moderately polluted by Cr (2.47), Co (1.92), Ni (1.48). For Fluvisols, a moderate level of pollution was confirmed, with the exception of Cr (3.24) which confirmed a considerable level of pollution. The average Cf for Fluvisols ranged from 1.02 to 9.00 for Cr, from 0.87 to 1.87 for As, from 0.76 to 2.37 for Pb, from 0.61 to 3.48 for Cd. In Cambisol we recorded a low level of contamination for Zn (0.87), Cu (0.99), and Pb (0.94), and a moderate level of contamination for the other PTEs. The PLI reached in Technosol 6.02, in Fluvisols 1.46 (range from 1.08 to 2.09) and in Cambisol the lowest value (1.15).

Keywords: arable land, soil properties, potentially toxic elements, contamination factor, pollution load index

1 Introduction

Soil pollution by potentially toxic elements (PTEs) is a major concern in agricultural area. Large agricultural area is exposed to external factors in the form of intensive industrial activity, which is the originator of hazardous substances. Some PTEs in soil are essential for crop growth, however, when their accumulation exceeds a certain standard, they are enriched in a food chain, threatening the health of animals, plants, and humans (Feszterová et al., 2021; Huang et al., 2020; Burges et al., 2015; Li et al., 2014). PTEs are nondegradable and biologically toxic, and they can migrate and transform in soil. They also have the ability to enter other environmental media and organisms and may ultimately affect the human body, and thus causing serious health problems (Ke et al., 2017; Hou and Li, 2017; Nanos and Martín, 2012; Huang et al., 2020). The predisposition of this fact is usually the accumulation of PTEs in the soils, which tends to enter plants, and thus contribute to the increased content of hazardous substances in cultivated crops. In this case, the threat is the process of biomagnification, in which the consumer himself becomes endangered as a result of consuming contaminated agricultural crops. The most important in the context of this process is the content of mobile forms of PTEs. Therefore, an assessment of soil contamination by PTEs is necessary and can be carried out in many ways. Nowadays, the most efficient are the contamination factor (Cf) and the pollution load index (PLI). Therefore, the objective of this study is to investigate the concentration of PTEs in agricultural soil resulting

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from the metallurgical industry (due to atmospheric deposition) along the Orava River, and to evaluate the pollution using the total and mobile PTEs forms analysis including Cf and PLI.

2 Material and methods

2.1 The research area

The study area is located along the Orava River. The bedrock consists primarily of sandstones, claystones, conglomerates, and shales, creating a flysh bed. The area belongs to the moderately cool temperate climate region. Most of the study area is covered by intensively used agricultural land.

In general, we selected 13 sampling sites, of which 11 were used as arable land, and classified as Fluvisols (FL) according to the World reference base for soil resources (IUSS Working group WRB, 2015). The sampling points were situated on the river alluvium. Outside the river alluvium, we selected 1 study site used as permanent grassland, representing the soil type Cambisol (CM) located on the slope, and 1 study site referred to as environmental burden, representing the soil type Technosol (TC) (Figure 1).

2.2 Sampling and analysis of soil samples

Soil samples were collected in October 2019 at a depth of 0–10 cm. We determined the basic chemical (pH/H_2O, pH/KCl, soil organic carbon – SOC, total nitrogen content – Nt, humic and fulvic acids ratio – CHA/CFA) and physical (soil texture) soil properties. To determine soil reaction, potentiometric measurement was used. We determined the Nt (mg kg^{-1}) according to Jodlbauer, and the SOC (mg kg^{-1}) according to Turin in the Nikitin modification (Fiala et al., 1999). The soil texture was determined by the gravimetric leaching method.

The total content and mobile form of selected PTEs from the group of heavy metals (Cr, Ni, Co, Cu, Zn, Mo, Cd, Pb) and metalloids (As, Sb) was determined using inductive coupled plasma mass spectroscopy (ICP-MS). The measured concentrations of PTEs in the soil were compared with the limit values according to national (MARD SR, 2013) and foreign standards (MEF, 2007; CCME, 1999).

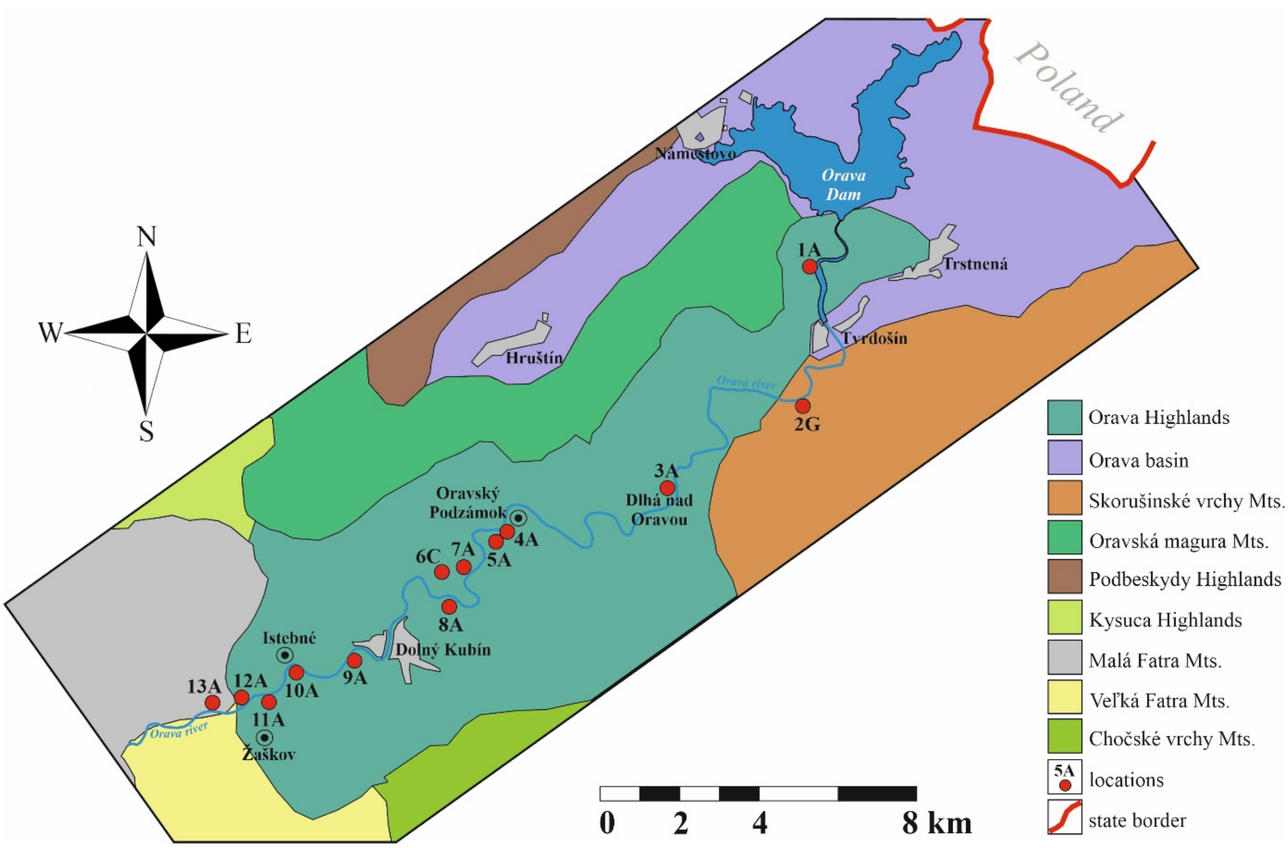

Figure 1 Map of the 13 study sites at the Orava River alluvium

The degree of soil pollution was evaluated by the contamination factor (Cf) according to Varol (2011) and the pollution load index (PLI) according to Tomlinson et al. (1980) using formulas (1) and (2):

• contamination factor:

$$Cf = \frac{Cn}{Cb} \qquad (1)$$

where:
Cn – potentially toxic element content in the soil of the contaminated area; *Cb* – content of the potentially toxic element in the background soil

• pollution load index:

$$PLI = \sqrt[n]{Cf1 \times Cf2 \times Cf3 ... Cfn} \qquad (2)$$

The scale of the degree of soil pollution based on the pollution indices presents Table 1.

3 Results and discussion

Table 2 presents the basic soil properties of Technosol, Fluvisols (as a mean value) and Cambisol. The soil reaction reached medium alkaline values in Technosol, neutral to weakly alkaline values in Fluvisols, and weakly acidic in Cambisol. The pH of the soil significantly affects the availability of soil nutrients and the form of PTEs (Li et al., 2018). The SOC content decreased in order TC > CM > FL with values 26,030 mg kg^{-1} >19,280 mg kg^{-1} >18,640 mg kg^{-1}. The highest value of Nt was measured in Cambisol (2,210 mg kg^{-1}), followed by Fluvisols (2,010 mg kg^{-1}) and Technosol (1,140 mg kg^{-1}). The values of the CHA/CFA were below 1 in all soil types. According to Kobza (2013), this criterion defines organic content as of lower quality.

The total PTEs content of the study areas together with the Slovak, Finish and Canadian limit values are presented in Table 3. The highest total content of PTEs was measured in Technosol (6C) in the case of Zn (612.3 mg kg^{-1}), Pb (249.4 mg kg^{-1}), As (39.1 mg kg^{-1}), Sb (12.3 mg kg^{-1}), Cd (3.9 mg kg^{-1}) and in Fluvisol (11A) in the case of Cr (513.0 mg kg^{-1}), Ni (48.8 mg kg^{-1}), and Mo (7.2 mg kg^{-1}). In Technosol, we recorded a high content of all observed PTEs except Ni, Cu, and Mo. In Cambisol, we observed slight chromium and arsenic pollution. In Fluvisols, we recorded As and Cr as the most important contaminants exceeding limit values in the most alluvial localities, for As in all study sites, and for Cr in 6 of 11 study sites. Within the agricultural soils, no limit values exceedance was recorded for Co, Cu, and Pb. We consider as the main source of agricultural soil pollution air emissions from Orava ferro-alloy plants in Istebné and Široká with active industrial activity since 1952.

The toxicity of PTEs is related not only to the total content in the soil, but also to the distribution of its fractions. From the point of potential food chain contamination, the most important are mobile and thus bioavailable

Table 1 The scale of the degree of soil pollution using the contamination factor and the pollution load index

Cf		*PLI*	
Scale	level of contamination	Scale	level of contamination
Cf <1	low	*PLI* <1	uncontaminated
1≤ *Cf* <3	moderate	*PLI* >1	contaminated
3≤ *Cf* <6	considerable		
Cf >6	very high		

Table 2 Basic chemical and physical soil properties at a depth of 0 – 10 cm

Soil type	Chemical soil properties					Physical soil properties				
	pH/H_2O	pH/KCl	SOC	Nt	CHA/CFA	content of particle size classes				
						clay (0.002 mm)	medium and fine silt (0.002–0.01 mm)	coarse silt (0.01–0.05 mm)	fine sand (0.05–0.10 mm)	coarse sand (0.10–2.00 mm)
			(mg.kg^{-1})			%				
TC	7.90	7.95	26,030	1,140	0.70	6.06	11.80	16.59	7.30	58.25
FL*	7.40	6.88	18,640	2,010	0.60	10.33	16.72	19.19	14.20	39.56
CM	6.53	5.81	19,280	2,210	0.33	9.93	16.15	19.74	15.42	38.76

* the mean value of Fluvisols

Table 3 Total PTEs content in soil (depth 0–10 cm) with basic statistical characteristics compared to different threshold values (mg kg^{-1})

Sample number	Heavy metals								Metalloids	
	Cr	Ni	Co	Cu	Zn	Mo	Cd	Pb	As	Sb
Technosol										
6C	141.0	32.5	16.7	112.8	612.3	4.5	3.9	249.4	39.1	12.3
Cambisol										
2G	86.0	27.9	10.8	19.7	57.9	2.1	0.3	18.1	7.7	1.3
Fluvisols										
1A – RS	57.0	22.0	8.7	19.8	66.6	0.9	0.3	19.4	6.8	1.0
3A	234.0	27.4	8.2	19.1	58.8	2.1	0.2	16.4	5.9	1.1
4A	72.0	33.2	9.2	27.0	72.1	1.2	0.4	20.6	9.5	1.0
5A	58.0	24.8	7.7	18.8	69.8	0.8	0.3	18.0	9.4	1.0
7A	97.0	34.9	10.9	71.1	157.0	2.1	1.2	45.8	12.7	2.1
8A	60.0	25.4	6.8	24.2	87.5	1.0	0.3	26.5	7.8	1.5
9A	102.0	26.1	8.8	29.1	84.5	2.5	0.3	24.2	10.4	1.5
10A	246.0	29.6	9.4	25.4	98.9	4.1	0.3	21.9	8.7	1.2
11A	513.0	48.8	13.1	31.0	93.1	7.2	0.3	21.6	10.4	1.7
12A	325.0	23.3	8.1	17.6	63.6	3.8	0.3	14.7	7.3	1.1
13A	142.0	29.2	7.9	25.9	72.1	2.4	0.4	18.4	7.3	1.2
$\bar{x}$	173.3	29.5	9.0	28.1	84.0	2.6	0.4	22.5	8.7	1.3
min	57.0	22.0	6.8	17.6	58.8	0.8	0.2	14.7	5.9	1.0
max	513.0	48.8	13.1	71.1	157.0	7.2	1.2	45.8	12.7	2.1
Limit values (according to different threshold values)										
1a	100	40	15	30	100	–	0.4	25	10	–
1b	150	50	15	60	150	–	0.7	70	25	–
2	100	50	20	100	200	–	1	60	5	2
3	200–300	100–150	100–250	150–200	250–400	–	10–20	200–750	50–100	10–50
4	64	45	40	63	250	5	1.4	70	12	20
5	87	89	300	91	410	40	22	600	12	40

A – locality on the alluvium, C – locality on contaminated area, G – locality on permanent grassland, RS – reference site, $\bar{x}$ – arithmetic mean, min – the lowest measured value, max – the highest measured value, 1 – national limit values according to the Decree of the MARD SR no. 59/2013 Coll. for loamy-sand soils (1a) and for sandy-loam and loamy soils (1b), 2 – threshold values of PTEs according to the MEF (2007), 3 – range of limit values based on environmental and health risks according to the MEF (2007), emphasizing the need for remediation, 4 – agricultural soil quality limit values for the protection of environment and human health according to the CCME (1999), 5 – industrial soil quality limit values for the protection of environment and human health according to the CCME (1999)

Table 4 Mobile forms of PTEs in soil (depth 0–10 cm) in comparison with limit values of hazardous substances as amended by the Decree of MARD SR no. 59/2013 Coll. (mg kg^{-1})

Sample number	Heavy metals								Metalloids	
	Cr	Ni	Co	Cu	Zn	Mo	Cd	Pb	As	Sb
Technosol										
6C	<0.01	<0.03	<0.01	0.065	<0.02	<0.02	<0.01	<0.03	0.05	0.02
Cambisol										
2G	<0.01	<0.03	<0.01	0.034	<0.02	<0.02	<0.01	<0.03	<0.01	<0.01
Fluvisols										
1A	<0.01	<0.03	<0.01	0.049	<0.02	<0.02	0.01	<0.03	<0.01	<0.01
3A	<0.01	<0.03	<0.01	0.115	<0.02	0.05	<0.01	<0.03	0.01	<0.01
4A	<0.01	<0.03	<0.01	0.161	<0.02	<0.02	<0.01	<0.03	0.01	<0.01
5A	<0.01	<0.03	<0.01	0.084	<0.02	<0.02	<0.01	<0.03	0.01	<0.01
7A	<0.01	<0.03	<0.01	0.143	<0.02	<0.02	<0.01	<0.03	0.02	<0.01
8A	<0.01	<0.03	<0.01	0.087	<0.02	<0.02	<0.01	<0.03	<0.01	0.02
9A	<0.01	<0.03	<0.01	0.056	<0.02	<0.02	<0.01	<0.03	<0.01	<0.01
10A	<0.01	0.03	<0.01	0.155	<0.02	0.17	<0.01	<0.03	0.03	<0.01
11A	<0.01	<0.03	<0.01	0.137	<0.02	0.07	<0.01	<0.03	<0.01	<0.01
12A	<0.01	0.17	<0.01	0.151	<0.02	0.06	<0.01	<0.03	0.03	<0.01
13A	<0.01	<0.03	<0.01	0.099	<0.02	0.03	<0.01	<0.03	0.02	<0.01
Limit values (according to Decree of MARD SR no. 59/2013 Coll.)										
1	–	1.5		1.0	2.0		0.1	0.1	0.4	–

A – locality on the alluvium, C – locality on contaminated area, G – locality on permanent grassland

fractions. The measured values of mobile PTEs fractions were bellow the Slovak threshold limits and often also bellow the detection limit (Table 4).

Nevertheless, we calculated pollution indices using the total PTEs content values as is the standard procedure applied particularly in environmental analyses (Figs 2–5). In this way, we confirmed the highest level of contamination expressed by Cf in Technosol, where the level of contamination in most PTEs reached medium to very high pollution. The moderate level of contamination (1≤ Cf <3) was confirmed for Ni, Co and Cr with Cf values of 1.48, 1.92 and 2.47. We confirmed the considerable level of pollution with Cf values ≥3 and <6 for 3 PTEs, Mo (4.86), Cu (5.70) and As (5.75). Very high levels of pollution with Cf values >6 were confirmed for Zn (9.19), Cd (11.82), Sb (11.94) and Pb (12.89). In Fluvisols, a moderate level of contamination was confirmed for most of the monitored

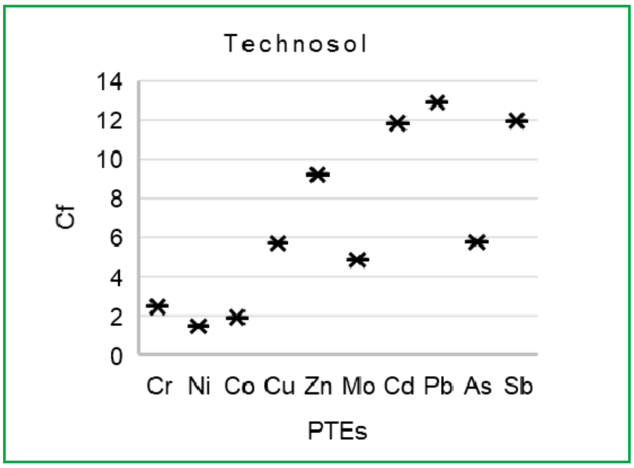

Figure 2 Contamination factor in Technosol

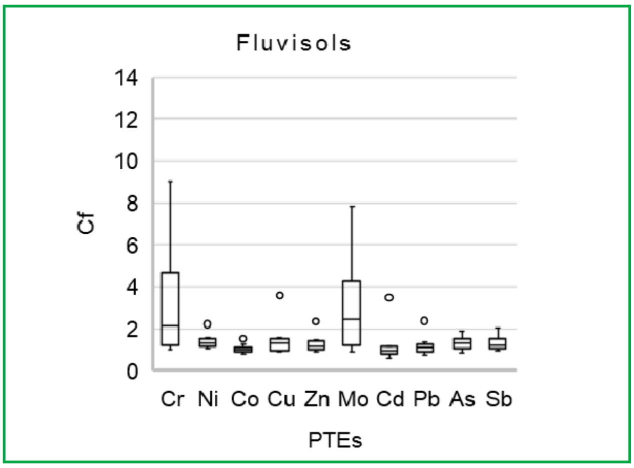

Figure 3 Contamination factor in Fluvisols

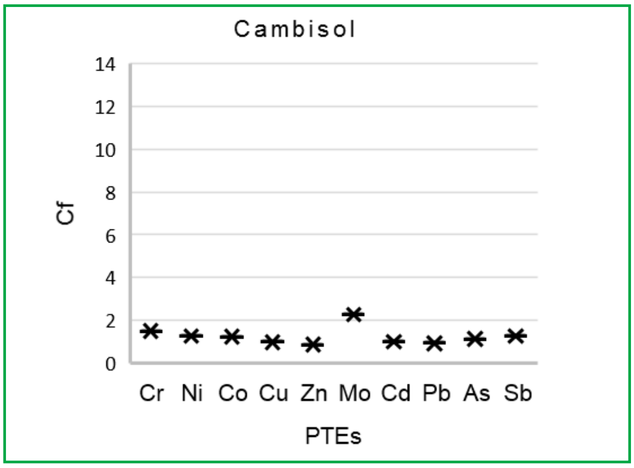

Figure 4 Contamination factor in Cambisol

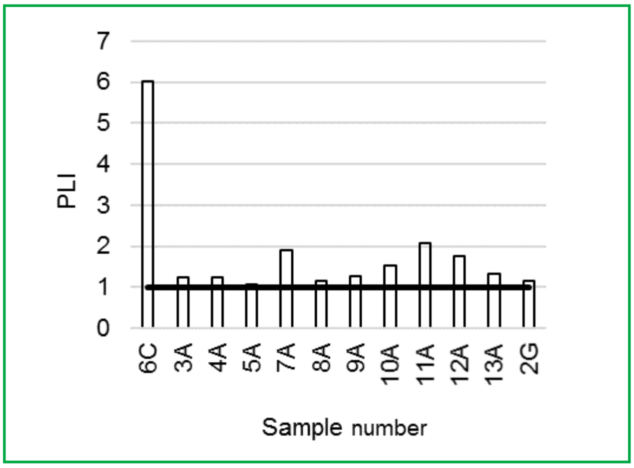

Figure 5 Pollution load index at study sites

PTEs. An exception was Cr for which a considerable level of contamination was confirmed with a Cf value of 3.24. In Cambisol, we recorded low to medium pollution for Zn (0.87), Cu (0.99), and Pb (0.94). The moderate level of contamination was confirmed for the others monitored PTEs (Figs 2–4). Hashmi et al. (2013) also studied contamination of alluvial sites and confirmed a very high level of pollution for Cd (15.01) and Zn (9.87), a considerable level of pollution for Pb (4.67), and moderate level for Cu (2.89) and Cr (2.37). Based on many studies (Balali-Mood et al., 2021; Feszterová et al., 2021; Ahmad et al., 2021) it is well known, that lead, cadmium, and arsenic are among the elements that most threaten not only the environment, but also human health.

Individual contamination factor values were used for the calculation of the pollution load index (Figure 5). For each soil type, we recorded the PLI index with values >1, which generally allows the localities to be considered as contaminated. The lowest value of the PLI index (1.15) was recorded in Cambisol (2G). We recorded a slightly higher average value (1.46) in Fluvisols. The value of the PLI index in Technosol (6.02) was the highest. The high accumulation of heavy metals in industrial lands is also confirmed by a study of Ghorbani et al. (2015) and Rinklebe et al. (2019).

4 Conclusions

Chromium and arsenic were identified as the elements that contribute the most to contamination in the investigated area, in which at least one limit value was exceeded the most often. The total contents of PTEs confirmed the highest concentration of hazardous substances in the case of Technosol (6C), developed directly on the industrial waste from the production of ferro-alloys. The exceedance of the limit values for the total PTE content was observed at several Fluvisol study sites. The exceedance of the limit values for mobile forms of monitored PTEs was not recorded in Fluvisols used as agricultural land.

In Technosol, according to the Cf, a very high level of contamination dominates (Zn, Cd, Pb, Sb), followed by a considerable (Cu, Mo, As) and moderate (Cr, Ni, Co) level of pollution. In Fluvisols, a moderate level of contamination was confirmed for most of the monitored PTEs. An exception was Cr, which confirmed a considerable level of contamination. In Cambisol, we recorded from low to medium pollution.

The PLI index in all localities reaches values >1, which indicates from important to very significant level of pollution. The lowest value of the PLI index was recorded in Cambisol.

Despite the high values of the pollution indices calculated from the total contents, the mobile forms of PTEs did not exceed the Slovak threshold limits. On the basis of the findings, we can concluded that PTEs do not currently pose a risk to plant production. But the cumulative effect of total PTEs content can pose a risk in the future.

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