

Risk Elements in Soils of Burdened Areas of Eastern Slovakia

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Abstract

Areal or pointed extension of soil contamination by risk elements was determined in samples from 47 localities of agricultural soils in "pollution-loaded" regions of eastern Slovakia during 2006 and 2008. These regions were primarily the areas of middle Spiš and northern Gemer, where soils were under long-term contamination by solid polluting elements containing risk elements. A source of contamination was metallurgical plants located in the broken terrain with unfavorable dispersion conditions. Risk elements Cd, Pb, Cu, Zn, Ni, Cr, and As were determined in the lixivium of *Aqua regia* and their accessible (mobile) forms in the lixivium of $1 \text{ mol} \cdot \text{dm}^{-3} \text{ NH}_4\text{HNO}_3$. To consider the solubility of the risk elements the lixivium of $0.05 \text{ mol} \cdot \text{dm}^{-3}$ EDTA (mobile and mobilizable forms) and the lixivium of $2 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ (potentially releasable contents) was used. Ascertained contents of the risk elements in the lixivium of *Aqua regia* correspond with the results regarding risk elements that were obtained by reduction in the mixture of inorganic acids before 1990. Then values of the solid polluting elements containing risk elements were the highest. The results confirm the large areal character of soil contamination by Hg and As in the emission areals of metallurgical plants where the natural endogeneous geochemical abnormalities now exist. Extremely high values of Pb, Zn, and Cd in close proximity to the former shaft-furnace (without any possibility of dispersion) are the result of solid polluting elements from Pb, Sn, alloys and ZnSO_4 production facilities. A considerably larger area of contaminated soils by Cu is connected to refined flame furnace copper production and converters and its dispersion into the wider areas. Some isolated locations with Cd, Cu, Ni, Hg, and As excesses are connected to geological-petrographical conditions where polymetallic mineralizing of old environmental loads is characteristic. In the samples with high contents of risk elements in *Aqua regia*, there were also over limit values for accessible plant risk elements. In the sum of mobile and mobilizable forms with relatively the highest content of Cd (36.57%) and the lowest Cr (0.36%) were determined in the following decreasing order $\text{Cd} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Cr}$. The relevant prevalence of risk elements in residual fractions is apparently connected to their emission origin from thermic processes as predominantly insoluble risk element oxides.

Keywords: burdened areas, soil contamination, risk elements

Introduction

Soil as a component of the environment is contaminated with industrial, energy and transport emissions, but also with risk elements of agrochemical residues, a wide range of waste material, etc. Eastern Slovakia also sees occurrences of various ore formation processes with regional diffusive contaminations of natural (geochemical) characteristics. Elements contained in ores have been mined there for a long period, thermally generated, modified and processed, and dispersed in the alluvial areas as clastogenic as well as dissoluble forms [1]. In the Rudňany-Gelnica burdened area it was mainly emissions from a mining and modification complex of iron-ore mines in Rudňany (mining and production of mercury, barite) and Kovohuty in Krompachy (long-term production of copper, manganese, lead, zinc). In the southern parts of the Jelšava-Lubenic area magnesite enterprises process natural magnesite by thermal decomposition in rotary and pit furnaces and produce solid Mg emissions that are highly alkaline and contain caustic magnesium oxide (areas of alkaline rains). In the northern part, in Nižná Slaná, it was long-term mining of iron ore and production of furnace pellets of siderite from local deposits of our most important iron-ore deposits. In the Košice-Prešov area, the main place of solid polluting material with a high risk element is the production of raw iron with metallurgical production (U.S. Steel Košice) as well as the energy systems and old residue of the high dust-producing magnesite industry in Ťahanovce. In the southern part of the Zemplín area includes the Vojany thermal power station, a major source of fly ash in Slovakia. The northern part of this area the environment is impacted especially by the heat stations of chemical and wood processing industries in Strážske, Vranov nad Topľou, and Humenné.

Enterprises in Krompachy, Rudňany, Nižná Slaná, Jelšava, and Lubeník are situated on uneven terrain or depression bases, and a cause of bad conditions for the dispersion of risk elements. U.S. Steel Košice and Vojany thermal power station, as considerably larger pollution sources, have relatively good dispersion conditions in their wide surroundings [2]. The location of burdened areas of east Slovakia are shown in Fig. 1.

Besides the identified air pollution sources, secondary pollution sources are present in eastern Slovakia such as old environmental burdens following mining, dumping grounds, and settling pits [3]. Today's most significant source of PM_{10} pollutants (solid polluting material up to 10 μm) are small pollution sources of wood combustion (the reason is the price increase of natural gas).

The un-degradable mineral substances of alkaline and metallic contaminants have culminated in soils for a long time, and may cause their contamination or even deterioration.

For the objective evaluation of agricultural soils with risk elements in Slovakia, there is a necessary focus on the results of the complex environmental and geological program, within which the Geochemical Atlas of the Slovak Republic as a part of the international geological program "International Correlation Geological Program No. 259" (approved by ENUSCO in 1988) was accepted, as priority. The results or source information enables researchers to submit an integrated image of the areal distribution of overall contents of risk elements in A (humus) and C (soil-formation): geogenically and antropogenically-based higher concentrations including remote transmission and an image of the determination of background values for individual soil types [4]. Monitoring of the attributes of main soil types is carried out by the Soil Science and Conservation Research Institute in Bratislava. A subsystem of the monitoring is the "Areal Research of Soil Contamination," which is carried out by the Central and Testing Institute in Agriculture in Bratislava for selected areas. This monitoring has been carried out since 1992 in regular 5-year cycles in the lixivium of HNO_3 with $c=2 \text{ mol}\cdot\text{dm}^{-3}$. Through this potential, mobilizable content of risk elements has been observed. According to soil monitoring results [5] about 15,000 hectares of contaminated soils have been determined – in which at least one risk element exceeds a limit value of legislation. The results of the examination of contaminated soils in the individual cycles were oriented on detailed monitoring of those areas in which soil contamination had been discovered before. Vertical transmission of risk elements in soil profiles has been proved and a number of areas exceeding the limits in the lixivium of HNO_3 with $c=2 \text{ mol}\cdot\text{dm}^{-3}$ has decreased.



Fig. 1. Location of burdened areas of eastern Slovakia.

In research in areas of eastern Slovakia the effort was to bring a more complex view on the state of soil hygiene with the inclusion of economic analyses, legislative and juridical aspects in evaluating damage of soils, and crops caused by industrial emissions. Special attention was paid to the possibilities of decreasing risk element penetration into plants from soils. The results have been published in monographs and in other works [6-8, 21, 22].

This article is the result of the agricultural soils research in the areas of their potential deterioration. Source data were obtained for the project "Identification of Changes of Environmental Components in Problem Areas of Eastern Slovakia" funded by the Slovak Research and Development Agency in 2006-08.

Materials and Methods

In the identified areas of eastern Slovakia research methods quantified cadastral areas and parcels with relatively the most disturbed production and ecological qualities according to the results of soil contamination research submitted by the Central and Testing Institute in Agriculture in Bratislava and previous long-term results of research on soil contamination. The parcels were characterized by soil and ecological parameters, parameters of soil deterioration, and resistance against chemical degradation [9, 22]. The sites of soil sampling on forty seven parcels in 2006-08 were selected in places of prevailing emission extension from the sources of solid polluting material and known natural geochemical anomalies. The positions of the sampling sites of the A horizon (0.00 m-0.20 m) samples were recorded by GPS to be identifiable in the future and were designated by the coordinates and photo documentation according to the individual emission areas: (Krompachy 11 samples, Nižná Slaná 16 samples, Jelšava 4 samples, Košice 8 samples, Strážske 4 samples, and Vojany 4 samples).

Examining the soil contamination according to Act No. 200/2004 was in compliance with EU norms (working out the situational plan, plan of sampling, protocol of sampling, executing analyses, analyses of risks). The content of risk elements was determined after a method with NH_4NO_3 was used. For the evaluation of soil contamination with regard to the elements penetration into the food chain and biological cycle, the contents of mobile, mobilized, and potentially mobilized contents in extracting solvents of different aggressiveness were determined.

Methods for determination (Supplement No. 2 to Act No. 220/2004) [10] were as follows:

- Extraction of risk elements by *Aqua regia* – STN ISO 11466
- Extraction of risk elements by NH_4NO_3 s c = 1 mol·dm⁻³ (for the determination of the content of risk elements accessible for plants – DIN 19730:06.95)
- Extraction with 0.05 mol·dm⁻³ EDTA (10 g sample added to 10 ml redestilated water and shaking cold for 1 hour); determination by means of AAS method – mobile and mobilizable forms of risk elements

- Extraction by means of HNO_3 with c = 2 mol·dm⁻³ (10 g sample added to 100 ml redestilated water, shaking cold for 6 hours), the analytical end point was AAS – potentially mobilizable content of risk elements
- Cd, Cr, Cu, Pb, Ni, and Zn were determined by AAS method (ISO 11047), As (STN N 373), and Hg – overall content (STN 465735).

For evaluating the determination of the risk elements in soils, the limits of the risk elements in the lixivium of *Aqua regia* for clay soils and clay-sandy soils and limits in the extraction solvent of NH_4NO_3 s c = 1 mol·dm⁻³ according to Supplement No. 2 to Act No. 220/2004 were applied.

Comparing the contents of the risk elements in the burdened areas of eastern Slovakia with those for the Slovak Republic the following statistical values – average, modus, median, standard deviation) were applied. For the graphic expression of element accessibility in percentages, mobile forms – A, mobile and mobilizable forms – B, potentially mobilizable contents – C, and residual fractions – D from the content in *Aqua regia* lixivium column graphs were used.

Results and Discussion

Tables 1 and 2 show the results of determining risk element contents in agricultural soils after the dissociation in *Aqua regia* and ammonium nitrate lixiviums are displayed. The contents after the dissociation in *Aqua regia* lixivium are in compliance with the results of the evaluation of overall risk element contents according to the Decision of the Ministry of Agriculture of the Slovak Republic No. 531/1994 after the dissociation by a mixture of the following inorganic acids: $\text{HF} + \text{HNO}_3 + \text{HClO}_4$, realized within the areal research of soil contamination. The determined contents of the risk elements in agricultural soils are as provided by permitted deviations valid for the determination methods prior to 1990. It is also caused by a decrease of several production processes in the areas but also by a reconstruction of separating systems, optimization of combustion regimes, installations of ecological systems, and other factors [8]. According to the data of the Ministry of the Environment the emissions of individual risk elements have been decreasing since 1990. The most apparent was the decrease of the emissions from the thermal processes in metallurgical industry. In 1990 it was 675.55 t, in 2006 it was only 287.77 t. In comparison with 1990 in 2006 the emissions of risk elements decreased to 8.20%, Hg to 13.00%, Cd to 75.98%, Pb to 31.18%, Zn to 48.31%, and Ni to 37.89%.

Risk elements from a group of heavy metals and metalloids as components of input ore raw material and fossil fuels undergo thermal dissociation and oxide reduction processes during combustion. They concentrate in fractions smaller than 10 μm , most often in the forms of oxides and chlorides, especially chalkophilous elements (As, Cd, Pb, and Zn) and lipophilous elements (Mg, Ca, K, and Na). Most of the emitted solid fractions have a diameter from 0.1 μm to 10 μm . Hg and Se are partially accessible in the forms of steam, Cu and Zn are in the steams in a carbonyl form, Pb and Cd in the forms of dissolving steams.

Table 1. Contents of heavy metals in $\text{mg}\cdot\text{kg}^{-1}$ in soils of areas in eastern Slovakia determined after dissociation by *Aqua regia*.

Area	Number of samples	Cd	Pb	Cu	Zn	Ni	Cr	As	Hg (total)
Kropachy	11	2.21	191.77	268.19	398.94	37.16	44.38	101.85	8.05
Nižná Slan	16	0.65	62.70	52.43	94.71	36.46	47.23	132.37	2.54
Jelšava	4	0.50	23.65	24.25	56.15	30.85	47.35	16.05	0.26
Košice	8	0.65	39.14	40.70	75.63	30.48	42.88	17.54	0.34
Strážske	4	0.45	20.85	18.15	50.25	35.15	34.90	5.58	0.19
Vojany	4	0.63	27.40	26.75	67.65	46.45	50.55	3.64	0.08
Statistic									
Minimum		0.36	15.40	14.60	39.20	11.8	29.8	0.00	0.00
Maximum		12.26	1238.00	546.00	1344.40	75.00	121.20	1147.00	30.10
Median		0.66	33.20	33.20	77.80	32.00	41.00	24.80	0.57
Standard deviation (n-1)		1.73	179.83	135.02	238.16	15.34	15.05	179.99	5.84

Table 2. Contents of heavy metals in $\text{mg}\cdot\text{kg}^{-1}$ in soils in eastern Slovakia determined after dissociation by $1\text{ mol}\cdot\text{l}^{-1}$ ammonium nitrate lixivium.

Area	Number of samples	Cd	Pb	Cu	Zn	Ni	Cr	As
Kropachy	11	0.13	0.70	4.87	5.38	0.22	0.08	0.13
Nižná Slaná	16	0.04	0.17	0.48	0.12	0.15	0.06	0.11
Jelšava	4	0.03	0.04	0.09	0.06	0.11	0.07	-
Košice	8	0.04	0.08	0.28	0.08	0.15	0.05	-
Strážske	4	0.03	0.05	0.09	0.15	0.18	0.04	-
Vojany	4	0.06	0.06	0.19	0.18	0.39	0.08	-
Statistic								
Minimum		0.02	0.02	0.05	0.02	0.06	0.02	0.01
Maximum		0.78	5.07	10.16	17.87	0.78	0.19	0.22
Median		0.04	0.07	0.24	0.10	0.15	0.06	0.05
Standard deviation (n-1)		0.11	0.74	2.67	3.42	0.12	0.03	0.09

The fractions are part of remote cross-border transport. Atmospheric deposition of risk elements is the most significant source of the soil contamination by undegradable risk elements at the present time [11, 12].

The results of the soil studies from 2006-08 showed a large-surface dimension of soil contamination by mercury. This is evident especially in middle Spiš and northern areas of Gemer – in the emission areas of Rudňany, Kropachy, and Nižná Slaná, where there are also natural endogenic geochemical anomalies of siderite lode systems (the surroundings of Rudňany, Gelnica, Kropachy, Slovinky, and Markušovce). One of the sources of Hg is also evaporation from mining in the Rudňany-Poráč area, from stacks, settling pits, etc.

The contamination of soil by arsenic is related to the metallurgy industry in Kropachy, Nižná Slaná, and Rudňany, as well as with the natural resources in the ore zones of the Spišsko-Gemerské Rudohorie Mountains and the transport of As by Hornád and Slaná catchment areas. Arsenic is concentrated in sub-micronic fractions of solid polluting substances, where the efficiency of dissociation devices is relatively low. These most subtle fractions of arsenic are adsorbed in the form of As_2O_3 , As_2O_5 , or as $\text{Ca}_3(\text{AsO}_4)_2$.

Extremely high contents of lead and zinc in the soils of the proximate surroundings of the enterprise in Kropachy are the result of the solid pollutants emitted from the 20-40 m high chimneys in the pit furnaces, which contained about

Table 3. Intervals of concentrations of risk elements determined in *Aqua regia* lixivium ($\text{mg}\cdot\text{kg}^{-1}$ and %) in burdened areas, eastern Slovakia.

Element	Measurement unit	Range of concentrations			
		A	B	C	D
Cd	$\text{mg}\cdot\text{kg}^{-1}$	0.30	0.31-0.69	0.70-1.40	1.41
	%	0.00	54.35	34.78	10.87
Pb	$\text{mg}\cdot\text{kg}^{-1}$	23.00	23.10-69.99	70.0-140.0	140.10
	%	17.39	60.87	10.87	10.87
Cu	$\text{mg}\cdot\text{kg}^{-1}$	16.00	16.10-59.99	60.0-120.0	120.10
	%	8.70	54.34	17.39	19.57
Zn	$\text{mg}\cdot\text{kg}^{-1}$	64.00	64.10-149.99	150.0-300.0	300.10
	%	32.60	45.66	8.70	13.04
Ni	$\text{mg}\cdot\text{kg}^{-1}$	23.00	23.10-49.99	50.0-100	100.10
	%	19.57	63.04	17.39	0.00
Cr	$\text{mg}\cdot\text{kg}^{-1}$	35.00	35.10-69.99	70.0-140.0	140.10
	%	13.04	82.61	4.35	0.00
As	$\text{mg}\cdot\text{kg}^{-1}$	6.90	6.91-24.99	25.0-50.0	50.10
	%	13.04	43.48	15.22	26.09
Hg	$\text{mg}\cdot\text{kg}^{-1}$	0.09	0.09-0.49	0.50-1.00	1.10
	%	21.74	26.09	13.04	39.13

A – concentrations below background values for cambisols [1]

B – concentrations above background values to limit for sandy-clay, clay soils in SR (Supplement 220/2004 Z.Z [10])

C – concentrations within limit value-double limit excess

D – concentrations above double limit

60% Zn and 18% Pb (the production of zinc vitriol, electrolysis of Mn, Pb-Sn alloys). And it is considerably higher is the area of soils contaminated with copper. This is connected with the emissions from copper concentrate processing in the flame furnaces and converters with a content of 30% Cu, which are (at the height of the chimney 200 m) dispersed into a relatively large surrounding area. Isolated locations contaminated with Cd, Cu, Ni, Hg, and As are in a causative relationship with the geological and petrographic conditions characterized by the polymetallic ore formation processes and metallurgical and modification processing of these ores in the past (e.g. around Nižná Slaná mining and processing of iron ore have more than a 70-year tradition). Exceeded contents of Cd are the result of a phosphoric fertilizer application (especially phosphorites from Morocco and Tunis).

In addition to the high values of the risk element contents, after the dissociation by *Aqua regia* (Table 1), the limit values of the risk elements accessible for plants (Cu, Pb, Zn, and Cd) in the lixivium with NH_4NO_3 s c = 1 $\text{mol}\cdot\text{dm}^{-3}$ were exceeded (Table 2). In comparison with the identified elements of As in the samples of extremely high contents after the dissociation by *Aqua regia* was under the critical value 0.4 $\text{mg}\cdot\text{kg}^{-1}$ in the lixivium of NH_4NO_3 s c = 1 $\text{mol}\cdot\text{dm}^{-3}$ (Supplement No. 2 to Act No. 220/2004).

In Table 3 the intervals of the risk elements determined by *Aqua regia* lixivium are submitted in $\text{mg}\cdot\text{kg}^{-1}$ and % as follows:

- A background median values for cambisols as prevailing soils in the burdened areas of eastern Slovakia
- B concentrations above the background values to the limits for prevailing sandy-clay and clay soils
- C concentrations within the range of the limit value – double excess of the limit
- D concentrations above the double limits

The background (median) values of the risk elements are shown according to the Geochemical Atlas of the Slovak Republic for cambisols (prevailing soil types of the examined soil samples). The values are determined in the lixiviums in a mixture of inorganic acids, with the exception of Hg, which was determined directly from the sample.

In comparison with Clark levels (background worldwide values), the contents in the cambisols of Slovakia are considerably higher for Cd and As (Clark level of cadmium is 0.1 $\text{mg}\cdot\text{kg}^{-1}$, As 1.5 $\text{mg}\cdot\text{kg}^{-1}$). In the soils of the Slovak Republic as well as in those of the Czech Republic [13] and other industrial countries, this is the result of long-term combustion of fossil fuels. As for Ni, Hg, Pb, Cr, and Zn, the background values in the Slovak cambisols are basically at the Clark levels except for Cu, the content of which is lower

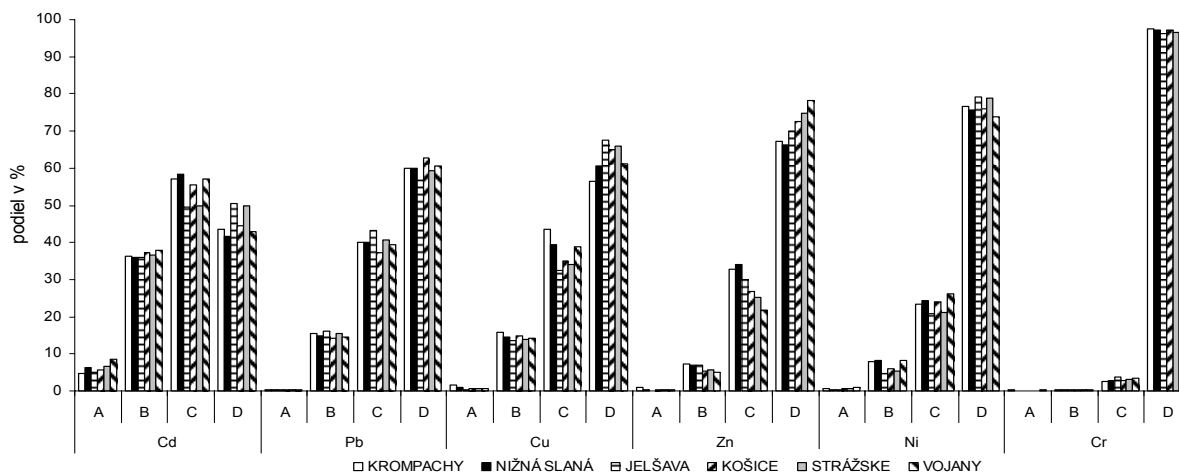
with the exception of considerable geochemical anomalies in middle Spiš and the northern parts of Gemer [14, 21].

Below the background values of the cambisols, as evident from Table 3, in the case of Zn, 32.6% of the analyzed samples; in the case of Hg 21.74%; Ni, 19.57%; Pb, 17.39%; As, 13.04%; Cr, 13.04%; and Cu, 8.7%. As for Cd analysis, all the results are above the background values. In the interval of the limit value concentrations – double excess of the limits, a descending order of the risk elements is as follows: Cd > Cu > Ni > As > Hg > Pb > Zn > Cr. The concentrations exceeding the double are in this order: Hg > As > Cu > Zn > Cd > Pb. The areal distribution of the exceeding content limit of the risk elements, except for a few isolated samples, is present in the area of middle Spiš and northern Gemer around the metallurgical and natural geochemical anomalies in the middle and eastern parts of the Slovenské Rudohorie Mountains. In comparison of the risk elements in the agricultural soils of the areas in the northwestern part of the Czech Republic [15], the characteristic for intensive mining of coal processed by power stations, numerous metallurgical enterprises, local heat stations, and other sources of risk elements, the situation in middle Spiš and northern Gemer is unfavourable from the point of view of soil hygiene. The soils of these areas are within Slovakia, but also in Europe, among the most contaminated with Hg, As, Cu, Zn, and Pb.

The current conditions in these areas should require regulatory intervention to protect agricultural soils [16, 22]. When the values of risk elements contents are exceeded, there is the obligation to decrease the dissolubility of dangerous elements by petrification to transform them into an indissoluble compound (by calcification of acid soils, increasing humus content, applying certified organomineral sorbents, etc.). After exceeding a double hygiene limit it is necessary to take into account the exclusion of a contaminated surface for growing crops for foods or fodders and to find substitute methods for the exploitation of contaminated soils (e.g. production of technical crops, crops for production of biofuels, etc.).

A significant problem are the gardens in the intravillains of the villages that have not been the subject to some research or monitoring. The result of the analyses of the samples collected from the gardens in northern Gemer (seven samples) showed that the influence of risk elements is generally higher than in the other examined areas.

For the evaluation of the accessibility of Cd, Pb, Cu, Zn, and Cr according to their dissolubility in extraction, solvents of various levels of average percentage contents of: mobile forms – A, mobile and mobilized forms – B, potentially releasable forms – C, and residual fractions – D from the content of the risk elements in *Aqua regia* lixivium (Fig. 2). In mobile forms we determined from 5.97% Cd to



Statistic	Cd				Pb				Cu			
	A	B	C	D	A	B	C	D	A	B	C	D
Minimum	3.44	30.90	43.40	29.90	0.07	11.25	35.60	52.20	0.28	12.84	29.00	54.10
Maximum	11.11	40.25	70.10	58.85	0.41	17.65	45.10	64.40	2.30	18.40	45.90	71.00
Median	5.97	36.57	55.50	44.50	0.22	14.90	40.01	59.99	0.74	14.33	38.40	61.60
Standard deviation (n-1)	1.68	2.30	6.62	6.87	0.07	1.52	2.63	2.87	0.53	1.29	4.51	4.51
Statistic	Zn				Ni				Cr			
	A	B	C	D	A	B	C	D	A	B	C	D
Minimum	0.03	4.26	20.64	44.20	0.08	4.01	16.60	68.35	0.01	0.14	0.98	94.28
Maximum	1.45	9.20	55.80	79.36	1.43	11.92	31.65	83.40	0.40	0.71	5.72	99.02
Median	0.14	6.45	30.06	69.99	0.49	7.21	23.71	76.30	0.14	0.36	2.90	97.06
Standard deviation (n-1)	0.45	1.30	6.74	6.74	0.28	1.98	4.12	4.11	0.07	0.13	1.08	1.07

Fig. 2. Percentage contents of mobile (A), mobile and mobilizable (B), potentially releasable (C), and residual forms (D) of risk elements.

0.14% Zn and Cr in the following descending order: Cd > Cu > Ni > Pb > Zn > Cr. They are dissoluble interchangeable cations of risk elements and easily dissoluble compounds of organic chelates, accessible for plants, determined in a salt lixivium. They introduce danger for the hydrosphere and in individual types of water their highest concentrations are legislatively stated.

For the evaluation of soil concentrations with reference to the risk element penetration into the biological cycle with ISO recommendation, the determination of the risk elements in EDTA lixivium as a compound with complex-formation attributes is verified. The determined contents, with their mobile forms, represent immobilizable forms in which the risk elements occur tied to amorphous manganese, iron and aluminium oxides that are occluded on the surface of the colloid material of clay minerals tied to less dissoluble chemical compounds made accessible by microorganisms, root excretion, increasing of soil acidity by acid immersions and physiologically acid fertilizers, reductive soil processes, etc. [17, 18, 22].

From the statistics to Fig. 2, in the sum of mobile and mobilizable forms, it was determined relatively the highest Cd content 36.57% and the lowest Cr content 0.36% in the following descending order: Cd > Pb Cu > Ni > Zn > Cr, with small differences of Pb and Cu and dissolubility of Ni and Zn.

The determination of potentially dissoluble forms in the lixivium with 2 mol·dm⁻³ HNO₃ is utilized in the areal research of soil contamination. The determined limits represented reference (background) values of risk elements in soils until 2004. In comparison with the lixivium of neutral salt and EDTA it is a more aggressive solvent, in which 55.50% Cd, 40.01% Pb, 38.40% Cu, 30.06% Zn, 23.71% Ni, and 2.90% Cr from the contents determined in *Aqua regia* lixivium.

It is evident from the results of the high contents of the risk elements in *Aqua regia* lixivium in mg·kg⁻¹, the percentage distribution of the risk elements in the extraction solvents of different aggressiveness is not basically changed. Also, high contents of mobile and mobilizable forms as well as potentially mobilizable forms were determined.

Besides their physical and chemical attributes, the dissolubility of risk elements in soil depends on dynamic soil qualities (soil reaction, content and quality of humus, content of clay particles), which causes the comparative heterogeneity of the attained results. Prevailing risk elements, especially Cr, Ni, Zn, Cu, and Pb in residual fractions can be connected with their immission origin from the thermal processes in the burdened areas, mainly in the form of dissoluble oxides and silicates. In clay minerals risk elements can be located to build in a crystal grid to increase their contents in residual fractions.

According to more publicized information, the bioaccessibility of heavy metals is the result of interactions among various forms of risk elements, soil attributes, and mechanisms of plant reception [19, 20]. For the quantification of different dissolubilities of transfer, coefficients should be recommended. In emission conditions their

determination based on the content of risk elements in soil and plants is deformed by a foliar absorption of atmospheric deposits.

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