Assessment of Transport Risk of Cadmium and Lead on the Basis of Immobilisation Capability of Soil

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Abstract: The objective of this paper is the ambition to elaborate a system of evaluating the potential transport risk of inorganic risk elements, cadmium and lead, and of creating maps of the soil potential for the immobilisation of these risk elements. The categorisation of the potential immobilisation of cadmium and lead was realised on the basis of two layers, the layer of metal concentration (Cd or Pb) and the layer of potential soil sorption. The level of metal concentration was evaluated according to the Slovak Soil Law. The potential soil sorption (PSS) of cadmium and lead is defined by qualitative parameters (soil reaction – pH value, optical parameter of humus quality – Q_6^4) and quantitative factors (Corg, H – depth of humus horizon) and was evaluated according to the Eq.: [PSS] = F(pH) + F(Q_6^4) + F(Corg) × F(H). On the basis of this rating, maps of categorisation of cadmium and lead potential immobilisation were created. These maps of the soil immobilisation potential show the distribution into five categories of Cd and Pb potential immobilisation.

Keywords: inorganic contaminants; cadmium; lead; contamination; immobilisation; soil properties

Many metals and metalloids are toxic in the terrestrial environment, even at very low concentrations (μmole per kg soil). The toxicity of heavy metals varies from one element to another, decreasing in the order of: Hg > Cd > Ni > Pb > Cr (Hansen *et al.* 2001). Some of the heavy metals and metalloids are essential in small concentrations for plants and heterotrophic organisms in soil, e.g. Cr, Cu, Ni, V, and Zn. These elements must therefore be available in the soil at certain concentrations. Pb, Hg, and Cd are non-essential and belong to the most toxic among the heavy metals. Cadmium and lead are highly toxic to plants, animals, and humans. Within the soil profiles, Cd tends to be present at higher concentrations in the topsoil, which is partly a reflection of the input from atmospheric deposition, fertilisers, and cycling through the plants. Cd activity is strongly affected by pH in acid soils. Cd is most mobile in acidic soils within the range of pH 4.5 to 5.5, whereas in alkaline soils Cd is rather immobile. Cd reveals a tendency to be removed from solution in the form of hydroxides or to precipitate on the clay surface with increasing pH (Yong *et al.* 1992; Naidu *et al.* 1996). The organic matter and sesquioxides may largely control Cd solubility, and in alkaline soil, the precipitation of Cd compounds likely accounts for Cd equilibrium. Pb is reported as the least mobile element among the other heavy metals. This statement is supported by the relatively low Pb concentration in natural soil solution. The Pb species can considerably differ from one soil type to another. Pb is associated mainly with clay minerals, Mn, Fe, Al hydroxides, and organic matter (Donisa *et al.* 2003).

The soil reaction, the content and quality of soil organic matter, the content and quality of clay fraction, and iron and manganese oxides belong to the main factors which influence the mobility of the potential risk elements in soil (Zeien &

Brummer 1989; Blume & Brummer 1991; Makovníková 2001; Barančíková & Makovníková 2003; Borůvka & Drábek 2004).

The understanding of the potential risk elements behaviour in the soil system is one of the most important tasks in the evaluation of their immobilisation and transport. Soil contaminants immobilisation means the soil potential to bind the substances and to reduce their leaching into the groundwater and entrance into the food chain.

Slovak Soil Law (2004) classifies total amount of the particular group of inorganic contaminants: Hg, Cd, Pb, Ni, Cr, As, Cu, Zn, Co. In the paper presented, an attempt is made to work up a system of estimating the potential transport risk of Cd and Pb on the basis of the capability of the soil compartment to immobilise these risk elements, and to create the maps of the soil potential to immobilise cadmium and lead.

MATERIALS AND METHODS

The categorisation of the potential transport risk of Cd and Pb was realised only for two layers of agricultural soils the layer of the risk potential for Cd/Pb concentration, and the layer of the potential soil sorption. A similar approach had been used also in our previous more general work (Makovníková *et al.* 2007) for the categorisation of the potential transport risk of all risk elements according Slovak Soil Law. In the present work, we used the same idea, however, with only two specific elements out of the most risky ones – cadmium and lead. It is assumed that the evaluation of the potential transport risk of only the two most hazardous elements can give us a more precise and real view on this environmental problem. The available data sources for the categorisation and mapping are represented by primary (spatial information on the soil bodies – Digital database of soil profiles of Geochemical atlas of Slovakia (Čurlík & Šefčík 1999) and Digital Soil Map of Slovakia (Kobza 1999)) and secondary (data of relevant soil properties) geo-referenced data (Digital database of Soil monitoring of Slovakia (CMSP)). Relevant soil properties data were used from the last sampling of the Soil monitoring (2002). The data from Geochemical atlas of Slovakia soils and those from Digital soil map of Slovakia were used to generate the layer of contamination. The data from CMSP were utilised to generate the layer of potential soil sorption. The territorial unit is soil types/subtypes of PM 400 Database Slovakia. ArcGIS® was applied for the work with the input geo-referenced digital data and implementation of the final digital data layer. This layer represents the categorisation of the potential transport risk of the potential risk elements on the basis of the capability of the soil compartment to immobilise inorganic contaminants.

RESULTS AND DISCUSSION

The potential of soil to immobilise and transport Cd and Pb is dependent on the total amount of these potential risk elements in the soil, and the potential of soil sorbents which are sensitive to Cd and Pb sorption. Generally, a higher amount of the potential risk elements in the soil takes the potential binding positions and consequently decreases the overall potential of the soil for risk elements sorption. However, present soil databases do not incorporate the data on the mobile fractions of cadmium and lead, for that reason only the data on the total content of risk elements could be used.

Layer of risk potential of Cd/Pb concentration: Soil concentration has been estimated as a surface contamination. The data of cadmium and lead concentration were obtained from the relational soil profile database of GchA. The level of Cd/Pb concentration was evaluated according to Slovak Soil Law (Table 1), in which the limit values of the potential risk elements depend on the clay fraction (content of size fraction < 0.01 mm) (Makovníková *et al.* 2007). To determine the appropriate categories of cadmium and lead concentration for

Table 1. Limit values of Cd and Pb in agricultural soils in mg/kg according to the Slovak Soil Law

Content of soil particles < 0.01 mm	Cd	Pb
Lower than 20%	0.4	25
20–45%	0.7	70
Higher than 45%	1.0	115

Table 2. Score for evaluation of cadmium and lead

Criteria		Category	Evaluation
Content of element	lower than 80% of limit	A	0
	equal 80% lower than 120%	B	1
	equal 120% lower than 200%	C	2
	equal or higher 200%	D	3

Table 3. Score values for polygons

Criteria		Category	Evaluation
Arithmetic average of score	< 0.45	A	1
	0.46–1 localities number of B or C < 20%	B	2
	1–2 localities number of D < 20%	C	3
	> 2 localities number of D > 21%	E	4

agricultural soils, the content of Cd and Pb was transformed into a point rating (according Table 2). The construction of this layer is estimated as arithmetic average of the score concentration of separate samples for soil types polygons (separate for arable soils and pasture) presented on map PM 400 in the particular polygons. The point ranking of categories is shown in Table 3.

The layer of the potential soil sorption was created by the rating method described in our previous work (Makovníková *et al.* 2007). The point evaluation of the potential soil sorption (PSS) for soil polygons was calculated according to the score function: [PSS] = F(pH) + F(Q^4_6) + F(Cox) × F(H).

Because of considerable differences between organic carbon content values in arable soils and pasture, the score evaluation was determined separately for different cultivations (Tables 4 and 5).

The determination of the potential risk elements sorption by the soil constituents is mostly accomplished through the selective sequential extraction of the potential risk elements from the soil samples. The Cd/Pb percentages in various fractions depend on the soil type, pH, ionic strength, complexation by organic ligands, and competition with other cations. The distribution of Cd fractions in Slovakian soils is different from the distribution of Pb fractions (Figures 1 and 2) (Makovníková 2001). As to Cd, a considerable fraction of the total content is represented by potential mobile pools, while high proportions of Pb are bound in soil organic matter and occluded on poorly and well crystalline Fe-oxides. Therefore, different ratings were used for Cd and Pb applying two qualitative parameters, pH value and quality

Table 4. Score values of soil-properties-influenced potential soil sorption of Cd (pH/$CaCl_2$, C_{org} content, quality of organic matter and depth of humus horizon)

	Arable land category			Grassland		
		$pH/CaCl_2$	score	category	$pH/CaCl_2$	score
$pH/CaCl_2$	1	< 5.5	4	1	< 4.50	4
	2	5.51–6.00	3.2	2	4.51–5.00	3.2
	3	6.01–6.50	2.4	3	5.01–5.50	2.4
	4	6.51–7.00	1.6	4	5.51–6.00	1.6
	5	> 7.0	0.4	5	> 6.00	0.4
		C_{ox}	score	category	C_{ox}	score
C_{org} content in %	1	< 1.0	1.00	1	< 2	1.00
	2	1.0–1.5	0.80	2	2–3	0.80
	3	1.5–2.0	0.60	3	3–4	0.60
	4	2.0–2.5	0.40	4	4–5	0.40
	5	> 2. ,5	0.10	5	> 5	0.10
		Q^4_6	score	category	depth	score
Quality of organic matter* – Q^4_6	1	> 6.01	1.00	Depth of humus horizon* (cm): 1	> 20 cm	2
	2	5.51–6.00	0.80	2	21–30 cm	1
	3	5.01–5.50	0.60	3	< 30 cm	0.5
	4	4.51–5.00	0.40			
	5	< 4.5	0.10			

*joint categories for arable soils and pasture

Table 5. Score values of soil-properties-influenced potential soil sorption of Pb (pH/$CaCl_2$, C_{org} content, quality of organic matter and depth of humus horizon)

	Arable land category	pH/$CaCl_2$	score	Grassland	category	pH/$CaCl_2$	score
pH/$CaCl_2$	1	< 4.0	2		2	4.01–4.50	1.6
	2	4.01–4.50	1.6		3	4.51–5.50	1.2
	3	4.51–5.50	1.2		4	5.51–6.00	0.8
	4	5.51–6.00	0.8		5	> 6.0	0.2
	5	> 6.0	0.2		5	> 6.00	0.4
		C_{ox}	score		category	C_{ox}	score
C_{org} content in %	1	< 1.0	1.00		1	< 2	1.00
	2	1.0–1.5	0.80		2	2–3	0.80
	3	1.5–2.0	0.60		3	3–4	0.60
	4	2.0–2.5	0.40		4	4–5	0.40
	5	> 2. ,5	0.10		5	> 5	0.10
		Q_6^4	score		category	depth	score
Quality of organic matter* – Q_6^4	1	> 6.01	2	Depth of humus horizon* (cm)	1	> 20 cm	2
	2	5.51–6.00	1.6		2	21–30 cm	1
	3	5.01–5.50	1.2		3	< 30 cm	0.5
	4	4.51–5.00	0.8				
	5	< 4.5	0.2				

*joint categories for arable soils and pasture

of organic matter. Cd-fractionation and Pb -fractionation by Zeien and Brummer in various soil types of Slovakia are shown in Figure 1.

The overall rating is determined as the sum of the risk potential of Cd/Pb concentration in soil (risk concentration score values for soil polygon) and potential soil sorption (PSS value for soil polygon) (Table 6). The high Cd/Pb soil concentration was evaluated by the high point value and presents a high risk. On the other hand, a high soil sorption potential results in a low point value and decreases the potential transport risk of hazardous elements in the soil.

The final map of the soil immobilisation potential for the potential risk elements (Cd and Pb) was created by fusion of two layers, the layer of the risk potential of metal concentration, and the layer of the potential sorption by soil. Figure 2 shows the distribution of five categories of the potential immobilisation of cadmium, Figure 3 shows the distribution of five categories of the potential immobilisation of lead.

In the case of one element map (cadmium or lead), differences can be seen between the soil immobilisation potential for all contaminants (Makovníková *et al.* 2007) and for only one risk element. Table 7 shows the distribution of five categories of the potential immobilisation of cadmium and lead on agricultural land of Slovakia.

A very high potential for cadmium immobilisation is found with 22.5% of Slovak agricultural soils, a high potential with 27.5%, medium potential with 33.9%, a low potential with 15.6%, and a very low potential for cadmium immobilisation with only 0.6%. The categories with very high and high immobilisation potentials for Cd and, in consequence, with a low risk of transport, cover 50% of all agricultural soils of Slovakia, more than in the case of all risk elements . Most of the arable soils located in the Danube lowland, Slovensky kras, and East-Slovak lowland, with a high productive potential, belong to the categories with very high or high potentials for immobilisation, therefore with a low risk of heavy metal transport. The soil reaction of these soils on carbonate rocks, loesses, and calcareous fluvial sediments reaches pH value above 6 (Čurlík & Šefčík 1999). Soils in the

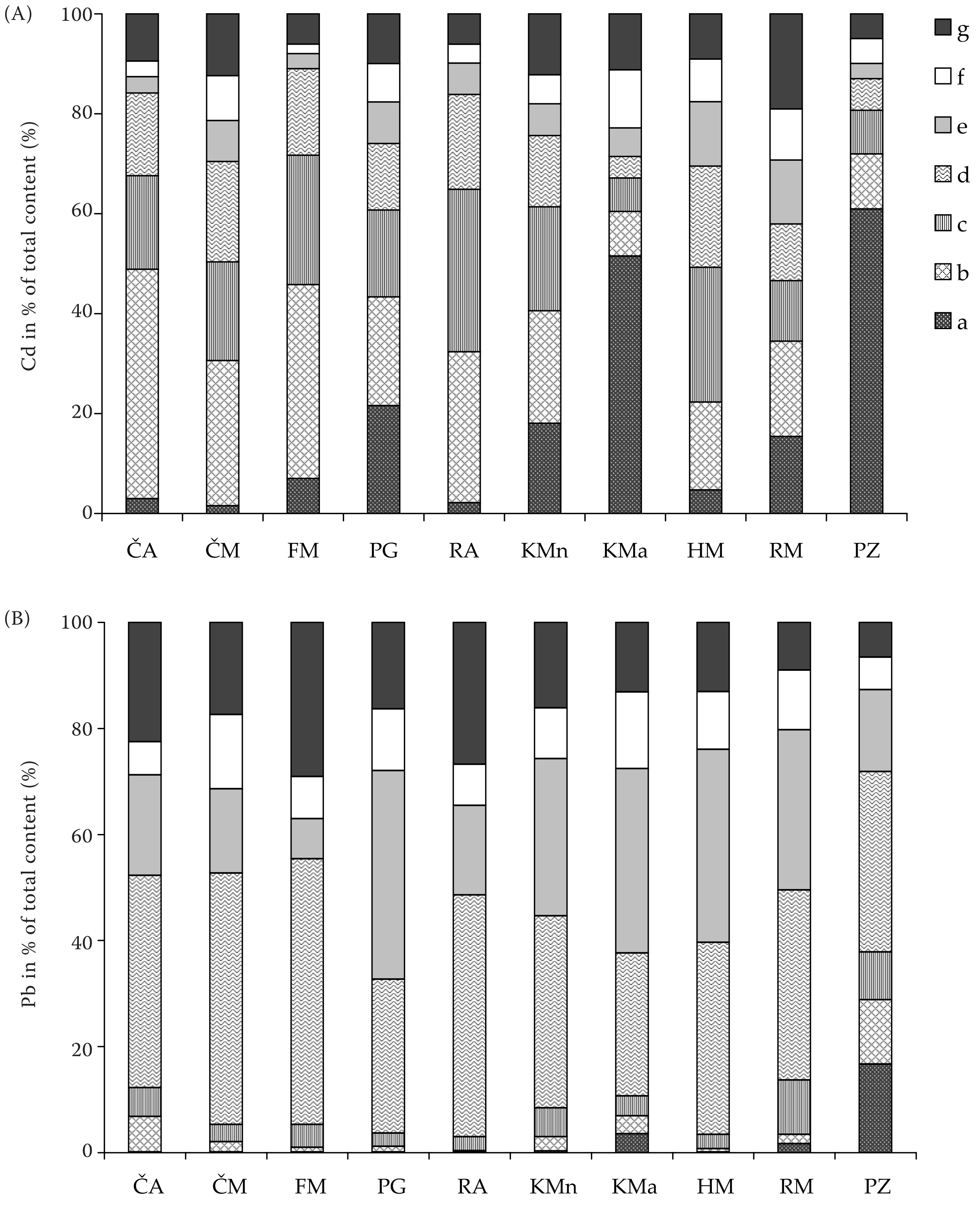

Figure 1. Efractionation by Zeien and Brummer (A) Cd and (B) Pb

a–g – fractions of Cd/Pb by Zeien and Brummer, a – 1. fraction (mobile), b – 2. fraction (easily mobile), c – 3. fraction (occluded on Mn oxides), d – 4. fraction (organic bond), e – 5. fraction (amorphous Fe-oxides bond), f – 6. fraction (crystalline Fe-oxides bond, g – 7. fraction (residual bond)

Soil types: ČA – Mollic Fluvisols, ČM – Chernozems, FM – Fluvizem-Eutric Fluvisols, FM – Fluvizem-Eutric Fluvisols, RA – Rendzina-Rendzic Leptosols, RA – Rendzina-Rendzic Leptosols KM[a]-Kambizem var. kyslá- Dystric Cambisols, HM – Hnedozem-Haplic Luvisols, RM – Regozem-Eutric Regosols, PZ – Podzol-Haplic Podzols

Table 6. Criteria for categorising

Score values for polygons	Soil categories of potential immobilisation
< 3.0	very high
3.1–4.0	high
4.1–5.0	medium
5.1–6.9	low
> 6.9	very low
	Soil categories of potential transport
< 3.0	very low
3.1–4.0	low
4.1–5.0	medium
5.1–6.9	high
> 6.9	very high

Table 7. Soil categories of potential immobilisation of Cd and Pb (in % of Slovak agricultural soils)

Soil categories of potential immobilisation	Cadmium	Lead
Very high	22.5	22.8
High	27.5	9.1
Medium	33.9	31.4
Low	15.6	35.5
Very low	0.6	1.2

West-Carpathian region, some non-calcareous Fluvial soils located in alluvial areas (along the rivers Slaná, Ipeľ, Hornád), and in isolated cases of the Záhorie lowland and Kysuce region, reveal very low or low abilities for Cd immobilisation.

A very high potential for the immobilisation of lead is found with 22.8% of Slovak agricultural soils, a high potential with 9.1%, medium potential with 31.4%, a low potential with 35.5%, and a very low potential with 1.2%. The categories with very high and high immobilisation potentials for Pb and, in consequence, with a low risk of transport, cover 32% of all agricultural soils of Slovakia, less than in the case of cadmium as well as in the case of all risk elements (Makovníková *et al.* 2007). A relatively high percentage of the agricultural soils (predominant grasslands) belongs to the category with a low potential for lead immobilisation in comparison with cadmium as well as with all risk elements as a total. Generally, a high risk of lead transport is inherent in soils with a low content and quality of organic matter, a low pH value, and a high level of lead concentration. Most of the arable soils with a high productive potential belong to the categories with very high or high potentials for immobilisation, therefore with a low risk of heavy metal transport. Soils in the West-Carpathian region, some Fluvial soils located in alluvial areas (along the rivers Hron, Ipeľ, Hornád), in isolated cases in the Kysuce region and in areas where smelters and ore processing facilities are located like the Banská Štiavnica region, Banská Bystrica region, and Spiš region, possess very low or low abilities for Pb immobilisation.

This work shows some differences between the evaluation of the potential immobilisation of all

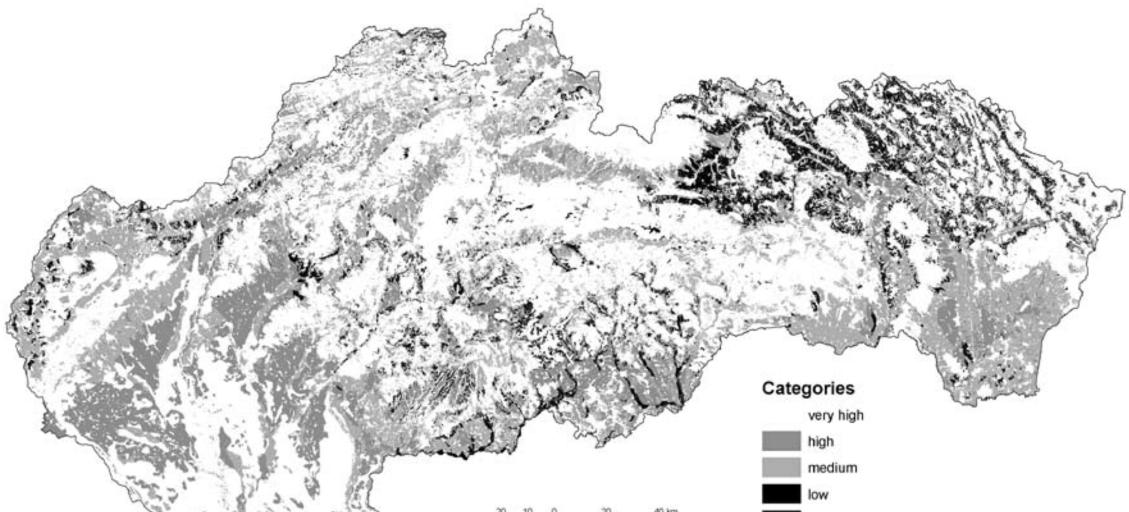

Figure 2. Soil immobilisation potential for cadmium

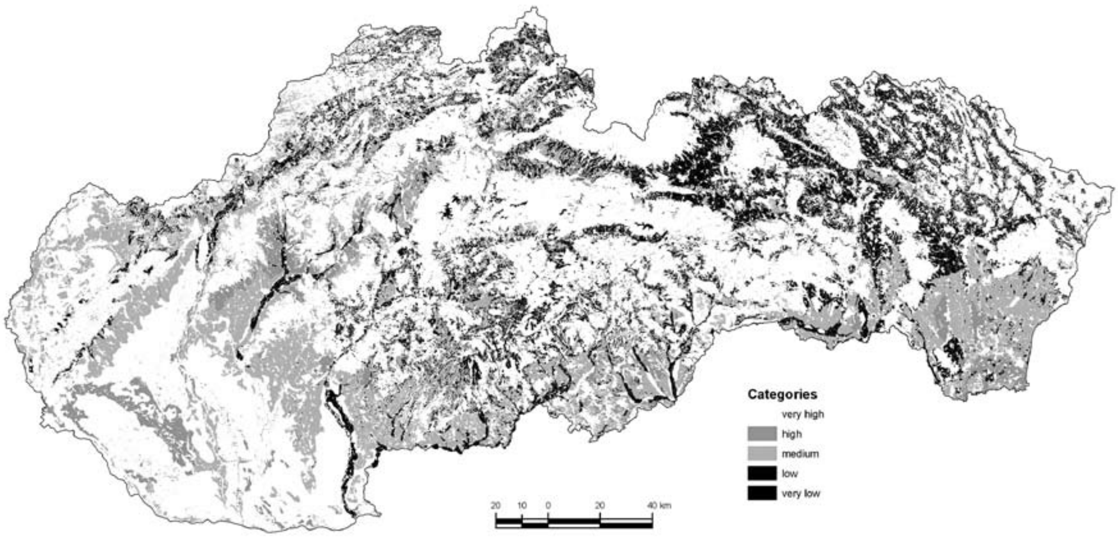

Figure 3. Soil immobilisation potential for lead

elements and one element (Cd/Pb) categorisation. We assume that this approach (one element approach) to the potential element mobility evaluation is more precise and can provide a more realistic view on the fate of the risk elements in soil compartments.

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