Water Air Soil Pollut (2015) 226:15
DOI 10.1007/s11270-014-2253-x

Impact of Floods and Their Frequency on Content and Distribution of Risk Elements in Alluvial Soils

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Received: 25 July 2014 / Accepted: 2 December 2014

Abstract The aim of this study was to compare the pollution levels of risk elements in flooded and non-flooded alluvial soils as a function of inundation frequency and river distance, depth of soil horizon, and pollution origin. Totally, 43 soil profiles of flooded and non-flooded soils were sampled in two layers (topsoil and subsoil). The total contents of As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn were measured and grouped according to the assumed geogenic or anthropogenic origin. Flooded soils were classified according to inundation stage/river distance. Concerning the depth gradient, it can be concluded that the content of anthropogenic risk elements decreased with the depth, while geogenic risk elements revealed no trend. The distance from the river had no influence on the distribution of anthropogenic risk elements in soil. On the contrary, geogenic risk elements showed increasing concentrations with increasing distance. These results indicate that frequency of floods has no influence on the risk elements distribution in soil. The process of sedimentation seems to be the main factor influencing the level of pollution, it differs between groups of anthropogenic and geogenic risk elements. The result of this country-wide study shows higher levels of soil contamination in flooded areas even without significant point sources of pollution, than in non-flooded areas in standard agricultural conditions.

Keywords Risk element · Floodplain · Soil contamination · Agricultural soils

1 Introduction

Alluvial soils (fluvisols) (IUSS Working Group WRB 2007) rank among the most fertile soils. Therefore, they have been used for agricultural purposes for centuries. At the same time, they are exposed to strong anthropogenic impacts, including pollution, which may be altering the soil functions and properties. In this way, the quality of agricultural production as well as the whole soil ecosystem can be affected (Jones et al. 2012). This fact has been described in many studies including the part of the EU-funded project "Integrated Modeling of the River-Sediment-Soil-Groundwater System, Advanced tools for the Management of Catchment Areas and River Basins in the Context of Global Change" (AquaTerra) (Barth et al. 2007).

Among contaminants, the risk elements (REs) are important since the REs pollution of the river system may arise somewhere in the whole catchment area. The both sources of pollution, point and diffuse, have to be considered (Du Laing et al. 2007; Fabietti et al. 2009), e.g., atmospheric deposition, industrial activity, inadequate waste and wastewater recycling, agriculture, transport, and natural weathering. According to Jones et al. (2012), the three major pathways responsible for

Electronic supplementary material The online version of this article (doi:10.1007/s11270-014-2253-x) contains supplementary material, which is available to authorized users.

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the introduction of diffuse contaminants into soil are atmospheric deposition, agriculture, and flood events. The causes of diffuse contamination tend to be dominated by excessive nutrient and pesticide applications, risk elements, persistent organic pollutants, and other inorganic contaminants. Pollution by risk elements is probably one of the most serious problems, since such contamination is practically irreversible (Jones et al. 2012).

Although river pollution has diminished in recent years, some old burdens in sediments can still act as a secondary pollutant sources mainly due to remobilization, transport, and redistribution of contaminants associated with sediment particles (Förstner 2004; Heise and Förstner 2007; Hilscherová et al. 2007). One of the pathways for the transport and redistribution of (potentially contaminated) sediment is its deposition in floodplain areas during flood events, which is a natural way of creating fluvisols. The content and distribution of REs in soil depend on geological material as well as on anthropogenic sources. REs are noteworthy as they do not degrade and some are also essential in certain amounts. The behavior of REs in soil is determined mainly by the chemical forms. The properties of REs such as mobility and availability in soil are determined by interactions with the soil matrix, closely connected to the overall conditions (redox status; adsorption/desorption processes; salinity; the presence of organic matter, sulphur, and carbonates; pH value; and plant growth) (Du Laing et al. 2009). Due to the potential toxicity of REs, various threshold values were defined for the protection of considered receptors (microbes, animals, and humans) as well as for the protection of all soil functions. The threshold values, however, can vary according to the environmental variables that are used for their calculation and that affect the bioavailability of REs (Lado et al. 2008).

The content thresholds of REs should be defined on national or regional scale to allow for varying natural conditions (Kibblewhite et al. 2008), as suggested in the relevant European Commission document (Gawlik and Bidoglio 2006), which takes varying conditions into consideration and establishes different threshold levels.

The more frequent and more extensive flood events occurring in the recent years can be probably attributed to the global climate change (Wölz et al. 2008). The growing probability of these events increases the need for the assessment of regularly flooded rivers in order to understand and predict the possible toxicological and ecotoxicological consequences of such events (Wölz et al. 2008).

Many papers have been focused on the areas affected by industry or urban contamination (Baborowski et al. 2007; Kruger et al. 2005; Schwartz et al. 2006; Turner et al. 2008; Vandecasteele et al. 2003; Zerling et al. 2006), whereas few assess less affected areas or rural contamination (Maliszewska-Kordybach et al. 2011; Martin 2000; Schipper et al. 2008). While some of them deal with the impact of average floods (Baborowski et al. 2007; Martin 2000, 2009; Matys Grygar et al. 2013; Schipper et al. 2008; Schwartz et al. 2006), the others describe an impact of rather severe floods (Hilscherová et al. 2007; Kruger et al. 2005; Maliszewska-Kordybach et al. 2011; Turner et al. 2008; Vácha et al. 2003; Zerling et al. 2006). The aim of this study was to describe, evaluate, and compare the levels of contamination in flooded and non-flooded soils in conditions with no strong industrial impact, especially to (a) compare RE contents in flooded and non-flooded soils, (b) identify the anthropogenic and geological impact with respect to the geological substrate, and (c) describe the translocation of REs in the soil profile and the impact of different intensities of flooding on the contamination level.

2 Materials and Methods

2.1 Data Set

In the Czech Republic, fluvisols cover about 6 % of agricultural land. However, their importance in food production is much higher; the 75 % of fluvisol areas is the arable land with good quality and fertility (Skála et al. 2013). A set of data from 12 fluvisols soil profiles of flooded soils in the Zlínsko region (in the south-east of the Czech Republic) was evaluated with a representative number (31 profiles) of non-flooded grassland soil profiles from the program of the basal soil monitoring scheme (BSMS) (Sáňka et al. 1998) covering the whole country (Fig. 1). Those databases enable to compare these two datasets:

(a) Flooded—fluvisols were taken from a specific region (the Zlín area) characterized by a high percentage of alluvial areas and anthropogenic impact. The advantage for the using of soils from this area also lies in the fact that the alluvial deposits are of a uniform geological origin (Carpathian Flysch rocks), which enables

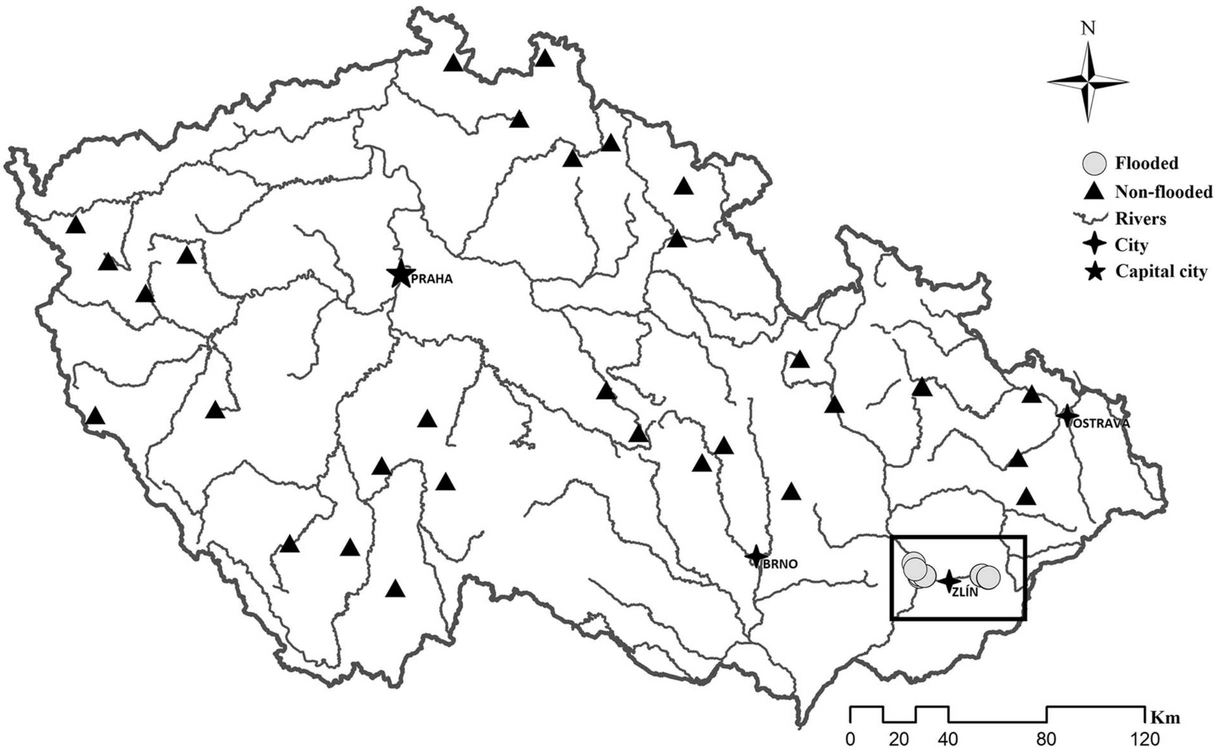

Fig. 1 Distribution of sampled soil profiles in non-flooded grassland in the Czech Republic and location of the Zlín pilot area with sampled flooded soil profiles (*in rectangle*)

geogenic and anthropogenic pollution sources to be distinguished, as the geologically increased levels are without significant differences among all flooded sites in all assessed horizons. Also, data on geochemistry of Carpathian Flysch rocks are available (Beneš 1993). In order to define intensity and frequency of floods as factors which can influence the level of pollution, the localities from this dataset were classified in four categories of fluvisol inundation stage (FIS) (Table 1). Classification of localities in FIS was made according to precisely described parameters: flooding frequency, distance from the river, diagnostic horizons in a soil pit, and level of pedogenesis.

The sites in this region are distributed along the rivers Bratřejovka, Lutonínka, Dřevnice, and Morava. The average river discharge measured at flow measuring stations near our sampling sites ranged from 0.6 to 55.4 $m^3 s^{-1}$. More information about the region can be found in papers assessing other types of pollution as well as the geochemical characteristics and toxicology of sediments (Bábek et al. 2008; Bláha et al. 2010; Hilscherová et al. 2007; Hilscherová et al. 2010; Nehyba et al. 2010). The catchment area of the Dřevnice River encompasses of 434.6 km^2; the Morava River basin area is 7891 km^2.

(b) Non-flooded—grassland soils were taken from the national basal monitoring scheme, which characterizes background conditions for agricultural soil in the Czech Republic.

Table 1 Description of fluvisol inundation stage (FIS)

Fluvisol inundation stage	Description
I	Very close to the river, flooded every year—practically alluvial sediment with no signs of pedogenesis
II	Close to the river, flooded periodically with floods approximately every 5 years, also without signs of pedogenesis
III	Far from the river, flooded only during extreme floods (Q_{50})
IV	Very far from the river, fluvisols but without recent floods, showing signs of pedogenetic development (to Cambisols)

Both datasets represent agricultural land used as grassland and come from sampling undertaken in 2005 (flooded) and 2007 (non-flooded).

2.2 Sampling and Analysis

The methods of soil sampling and analyses were identical for both flooded and non-flooded soils. A soil pit was dug at each locality up to a depth of about 120 cm and the diagnostic horizons were described. The soil samples were taken from two layers: (1) topsoil layer, depth of 0–10 cm; (2) subsoil layer, depth of 20–40 cm. Furthermore, a substrate layer from a depth of 40–100 cm was also sampled (H3) with respect to flooded soil. Five individual samples were taken to create about 1 kg of mixed sample from each horizon in the soil pit. All samples were dried and sieved through a 2-mm sieve. The contents of following risk elements (aqua regia extraction, ISO 11466) were determined in samples: As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, and Zn. Inductively coupled plasma mass spectrometry (ICP-MS) was used for elemental determinations. In addition, basic soil properties were analyzed: pH exchangeable ($CaCl_2$), cation exchange capacity (CEC), organic matter content (TOC), and percentage of clay particles <0.01 mm (Zbíral 1997).

For the purpose of statistical analysis, two groups of REs were specified according to the source of pollution: (a) elements with origins predominantly from geogenic sources (GREs) and (b) elements importantly influenced by anthropogenic activity (AREs). The main representatives of GREs are Co, Cr, Ni, and V, while those for AREs are typically Cd, Pb, and Zn. This general differentiation is supported by many previous studies (Bábek et al. 2008; Borůvka et al. 2005; Desaules 2012; Lado et al. 2008; Němeček et al. 1996, Vácha et al. 2013), although exceptions from this categorization for some elements are possible according to specific sources of pollution in regional studies.

2.3 Statistical Analysis

The *t* test was used for the detection of significant differences in contaminant levels and physical-chemical properties between flooded and non-flooded soils as well as between topsoils and subsoils; for flooded soil, the deepest available horizon (H3) was also evaluated.

To determine the relationships among contaminants, Pearson's correlation analysis was used. For visualization of the relationships among metals and sediment properties, PCA analysis based on the correlation matrix was performed. The variables with non-normal distribution were logarithmically transformed before analysis. PCA analysis was conducted for each dataset and it was based on standardized concentrations of risk elements; the other variables (physical-chemical properties) were visualized in the same ordination space for interpretational purposes. All statistical analyses were performed by the STATISTICA program (version 9.1, StatSoft, Inc.).

3 Results

3.1 Comparison of Measured RE Concentrations with Threshold Values

For the comparison of measured levels of contamination with standardized values, the proposed preventive and indication limits were used (Sáňka et al. 2002; Vácha et al. 2014). The preventive limits were derived based on statistical evaluation of the REs background values measured in Czech agricultural soils. It means that they are not effect-based and also not relevant for geochemically anomalous soils. Exceeding of these limit values do not represent any risk; however, increased anthropogenic pollution is indicated and further increase of REs concentration should not be allowed. On the other hand, the indication limits are derived as effect-based, i.e., a certain level of risk is indicated if they are exceeded.

Basic statistical information (Median, 5 %, 95 %) and threshold values of risk element concentrations are summarized in Table 2. Concerning flooded soils, the limits were exceeded for Ni, Zn, Cd, and Cr, whereas concentrations of As, Co, Cu, Pb, and V were below the limit for all samples; for Mo, there is no defined concentration limit. Concerning Ni, the concentration limit was exceeded in 58 % of the flooded samples; even median value was above the limit. Concerning Zn, Cd, and Cr, the limits were exceeded in 19, 8, and 6 % of samples, respectively. The limits were exceeded the most dramatically for Cr, when two samples exhibited the permitted concentration more than twice. Regarding non-flooded soils, the limits for Co, Cu, Pb, and V were not exceeded at any sampled site. As, Cr, Zn, Cd, and Ni exceeded the limits in 10, 6, 6, 5, and 5 % of samples, respectively.

The limit was the most dramatically exceeded in the case of As for one locality, where both the soil horizon samples contained twice higher concentration of As than the permitted level is. Proposed indication limits were not exceeded in any case.

The preventive limits related to agricultural soils in the Czech Republic are generally stricter than those in Germany or Poland (Table 2). After the comparison of the measured values to German and Polish limits, As, Co, and Cr were above these limit values at 6, 5, and 2 % of both flooded and non-flooded samples, respectively.

3.2 Difference in RE Contents—Topsoil Versus Subsoil

Statistically significant differences in concentrations between topsoil and subsoil were found for lead and cadmium only, where concentrations were generally higher in topsoil for both flooded and non-flooded locations. However, for Cd, the results of statistical tests were not so reliable due to many values below detection limit (74 %). Flooded topsoil had lower median concentrations of Ni and Cr than subsoil and H3, but the differences in concentration were not statistically significant due to high variance.

Concerning physical-chemical properties, only TOC differed between topsoil and subsoil in both flooded and non-flooded soils. Higher values of CEC in topsoil were found at a lower statistical level of significance ($p<0.1$) for non-flooded soil. This result can also be seen in flooded soil, but only at deeper soil levels, i.e., between topsoil and H3.

3.3 Difference in REs Contents—Flooded Versus Non-Flooded Soils

In contrast to the topsoil versus subsoil, statistically significant differences between flooded and non-flooded soils were found for both anthropogenic and geogenic REs at all depths. Median concentrations of REs were higher in flooded soil except for As, Pb, and V. The biggest differences were found for Ni and Cu in topsoil; flooded samples showed twice higher concentrations of these REs. The similar effect was observed for Cr in subsoil.

As for physical-chemical properties, significant differences were observed for TOC and pH for both topsoil and subsoil. Concerning the clay content, the comparison was possible only for topsoil, where the difference between non-flooded and flooded soils was statistically significant. All results of statistical tests are summarized in Table 3.

3.4 Gradients of RE Distribution

Principal component analysis (PCA) based on the dataset of RE concentrations in flooded soils explained a large degree of variability (72 %). Two main gradients from PCA analysis were identified (Fig. 2). One was connected with the distance from a river (FIS) and the second one was connected with the soil depth defined by soil horizons. The results show the different behavior of risk elements according to these gradients. Concentrations of AREs are distributed along the gradient of depth, where the concentrations are decreasing with the depth. Whereas GREs are distributed along the river distance gradient, the concentrations are increasing with the distance; this gradient has no influence on AREs. PCA based on the dataset of non-flooded soil concentrations explained 58 % of the variability. There is a relationship among the concentrations of elements inside the two groups (AREs, GREs), but it is not among concentrations of elements between the two groups (Fig. 3). This is valid for both soil datasets. Concerning the relation between concentrations of REs and soil properties, a relationship was found only between AREs and TOC. The other important soil properties, namely CEC and clay content, were found to be related to GREs, more significantly in flooded soils than in non-flooded soils (Figs. 2 and 3). For quantification of these relationships, the correlation coefficients among risk elements and physical-chemical properties are shown in Tables S1 and S2. According to the PCA results, the distribution patterns for AREs and GREs are very similar in flooded and non-flooded soils; the differences are only in the levels of concentrations (Fig. 4). The basic soil characteristics for individual datasets, such as pH, CEC, clay content, and TOC, are shown in Table 2.

4 Discussion

4.1 Comparison of Measured RE Concentrations with Threshold Values

The proposed preventive limit values (Sáňka et al. 2002) for the protection of agricultural soil were exceeded for Ni, Zn, Cd, As, and Cr. Increased concentrations of Ni

Table 2 Statistical summary: median (5 %, 95 %) in mg kg^{-1} of risk elements concentration and physical-chemical properties for different depth and soil subsets

Parameter	Topsoil and subsoil		Topsoil		Subsoil		H3	Limit value[a]	Action value[b]	Limit value[c]
	Flooded (n=24)	Non-flooded (n=62)	Flooded (n=12)	Non-flooded (n=31)	Flooded (n=12)	Non-flooded (n=31)	Flooded (n=12)			
Cd	0.3 (0.1, *0.8*)	0.1 (0.1, 0.4)	0.3 (0.2, *0.9*)	0.1 (0.1, 0.5)	0.2 (0, *0.8*)	0.1 (0.1, 0.4)	0.1 (0.1, 0.3)	0.5	20	4
As	7.2 (5.9, 10.3)	7.7 (4.3, *27.8*)	7.5 (5.1, 17.9)	8 (4.3, *27.8*)	6.9 (5.9, 10.3)	7.5 (4.3, *31*)	6.2 (4, 8.6)	20	50	20
Zn	91.5 (68, *158*)	82.4 (39.9, *121.5*)	94 (80, *159*)	84.9 (39.9, *123*)	88.5 (66, *137*)	76.1 (39.5, *121.5*)	76 (40, *127*)	120		300
Pb	20 (15.3, 28.7)	22.7 (14.5, 48.6)	23.7 (15.3, 29.7)	25.3 (16.2, 50.2)	17.5 (15.2, 28.7)	18.9 (14.1, 39.2)	13.9 (9.6, 20.3)	60	1200	100
Ni	*56.7* (31, *83.5*)	22.4 (10.8, 45.7)	*54.5* (31, *77.1*)	22.4 (9.6, *50.4*)	*63.3* (30.4, *87.4*)	22.4 (10.9, 45.7)	*62.1* (27.2, *86.6*)	50	1900	100
Cr	56.2 (32.1, *208*)	37.2 (17.7, *93.1*)	51.8 (32.1, *208*)	40.8 (17.7, *100.6*)	61.5 (31.9, *241*)	35.8 (17.2, 72.6)	50.7 (25.4, 72.2)	90		150
Co	14.5 (9.6, 17.8)	11.6 (4.6, 20.9)	13.9 (9.6, 17.8)	11.2 (4.3, 20)	14.6 (9.6, 18.4)	11.9 (4.8, 23)	13 (8.4, 18.1)	30		20
V	44.7 (28, 73.2)	50.3 (21.3, 89.6)	44.4 (26, 75.6)	50.1 (21.5, 89.8)	46.8 (28, 73.2)	50.6 (18.9, 89.6)	39.1 (23.3, 62.7)	130		150
Cu	36.3 (27.2, 47)	17.4 (6.7, 41.3)	36.8 (27.2, 47)	18.2 (7.2, 44.6)	36.1 (23.7, 54.9)	15.9 (5.5, 41.3)	35.4 (19.1, 49.5)	60	1300	
Mo	0.4 (0.4, 0.5)	0.2 (0.2, 1.2)	0.4 (0.4, 0.5)	0.2 (0.2, 1.2)	0.4 (0.3, 0.5)	0.2 (0.2, 1.3)	0.3 (0.2, 0.4)			
CEC (meq/100 g)	12.8 (8.9, 17.4)	11.3 (6.7, 28.0)	13.3 (10.2, 17.4)	13.0 (7.7, 31.8)	12.2 (7.8, 20.1)	9.4 (6.6, 26.4)	9.2 (5.8, 19.6)			
TOC (%)	2.6 (1.2, 5.5)	1.5 (0.8, 3.2)	4.4 (1.7, 7.7)	2.3 (1.2, 3.4)	1.9 (1.1, 2.8)	1.2 (0.8, 2)	1.2 (0.4, 2.4)			
Clay (%)	24.5 (10, 38)	29.5 (15.2, 53.6)	22.5 (10, 43)	28.5 (17.8, 53.6)	24.5 (13, 36)	29.9 (15.2, 50.6)	24 (11, 34)			
pH	6.7 (5.1, 7.2)	5.6 (4.6, 6.4)	6.8 (4.8, 7.2)	5.6 (4.4, 6.2)	6.7 (5.5, 7.2)	5.5 (4.6, 6.5)	6.6 (5.5, 7.4)			

Numbers in italic mean exceeding of the proposed preventive limit value

[a] Sáňka et al. (2002) Preventive values for contents of risk elements in soil. In: Critical values of risk elements and persistent organic pollutants in soils and their uptake by plants. Final report of research project of the Ministry of Environment of the Czech Republic, Praha

[b] Action threshold values for grassland (BBodSchG 1999)

[c] Polish limit values (Dz. U. 02.165.1359 2002) for the upper layers (0–30 cm) of soils in agricultural use

Table 3 Results of statistical differences (*t* test) among different depths and between flooded and non-flooded soil samples

	Flooded vs non-flooded			Flooded			Non-flooded
Parameter	Topsoil and subsoil	Topsoil	Subsoil	Topsoil vs subsoil	Topsoil vs H3	Subsoil vs H3	Topsoil vs subsoil
Cd[a]	**	–	**	–	**	*	**
As	–	–	–	–	**	**	–
Zn	**	**	**	–	**	**	–
Pb	**	*	–	**	**	**	**
Ni	**	**	**	–	–	–	–
Cr	**	*	**	–	–	–	–
Co	–	–	–	–	–	–	–
V	–	–	–	–	–	–	–
Cu	**	**	**	–	–	–	–
Mo[b]	–	–	–	**	**	**	–
CEC	–	–	–	–	*	–	*
TOC	**	**	**	**	**	**	**
Clay	**	**	–	–	–	–	–
pH	**	**	**	–	–	–	–

*0.05=>p<0.1; **p<0.05; "–" without statistical significance

[a] 76 % values below detection limits

[b] 56 % values below detection limits

and Cr in the Zlín area can be connected with Carpathian Flysch sediments (Beneš 1993), except for peak Cr values, which probably indicate an anthropogenic point source described in Bábek et al. (2008), who assessed sediment cores in the same area. Concentrations of Cd, As, and Zn exceeding their limits in both flooded and non-flooded samples were probably mostly of anthropogenic origin. Concerning pollution level in flooded soils, our results are in agreement with other studies evaluating contamination in Zlínsko region. These studies (Bábek et al. 2008; Bednarova et al. 2013; Bláha et al. 2010; Hilscherová et al. 2007; Hilscherová et al. 2010; Nehyba et al. 2010) have found no specific significant sources of pollution. Based on those studies, the area was classified as moderately polluted with contaminants originating from urban, industrial, as well as agricultural sources.

4.2 REs Group Differentiation

Based on the PCA analysis, two groups of REs were impacted by either geogenic or anthropogenic contamination source determined, although there is a slight difference between flooded and non-flooded soils (Figs. 2 and 3). Elements like Cu and Zn can be considered as transitional between the groups of GREs and AREs. A similar correlation pattern for GREs is described by Borůvka et al. (2005), who assigned Cu and Zn to the group of GREs. Although, these REs were also influenced by anthropogenic pollution at some localities. A mixed origin of pollution from natural and anthropogenic sources was also described by Wahsha et al. (2014) for Zn and Lado et al. (2008) for Cu. In our study, there were Mo and As as two other compounds influenced by both anthropogenic and geogenic impacts.

4.3 Flooded Versus Non-Flooded Soils; the Depth Gradient

According to our results, there were found significantly higher concentrations in flooded soils than in non-flooded soils for both AREs and GREs (Table 2, Fig. 4). However, the distribution of contamination in the soil profile differed between these groups of elements. While the contents of AREs were decreasing from topsoil to subsoil, the contents of GREs were not influenced by the depth. In the case of Cr and Ni in topsoil, the concentrations were even lower (Fig. 4). This depth gradient for AREs was also identified by

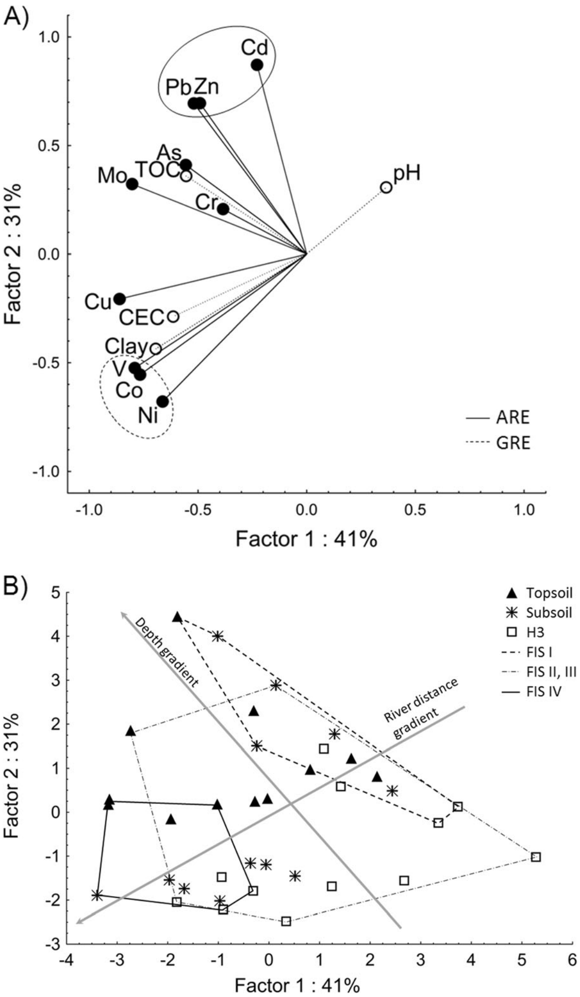

Fig. 2 Principal component analysis (*PCA*) performed on soil contaminants from the flooded area. **a** The ordination diagram shows the relationships among contaminants and physical-chemical properties. Variables displayed by *full circles* were used for creating PCA. Variables displayed by *empty circles* were shown in the same ordination space, but they were not used for creating PCA (supplementary variables). *Ellipses* indicate groups of correlated contaminants. **b** Soil samples distributed along the gradients of depth (soil horizons) and river distance frequency of inundation stage (*FIS*)

PCA analysis (Fig. 2). Statistically, significant differences in concentrations between topsoil and subsoil were found for Pb and Cd only (Table 3); however, other ARE median concentrations were higher in topsoil as well. This is in agreement with other studies, where the concentrations up to proximately 40 cm in depth were comparable (Kruger et al. 2005; Zerling et al. 2006). Some significant changes were found in concentrations between topsoil and the deeper horizon (more than 50 cm in depth), the AREs often reached

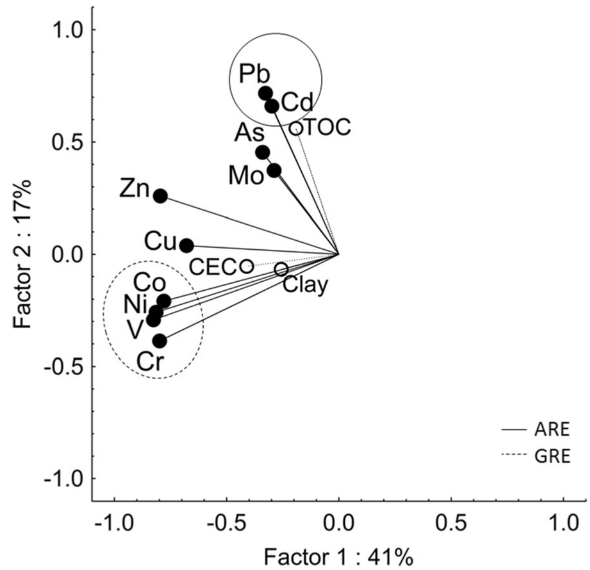

Fig. 3 Principal component analysis (*PCA*) performed on contaminants from non-flooded soil samples from the whole area of the Czech Republic. The ordination diagram shows the relationships among contaminants and physical-chemical properties. Variables displayed by *full circles* were used for creating PCA. Variables displayed by *empty circles* were shown in the same ordination space, but they were not used for creating PCA (supplementary variables). *Ellipses* indicate groups of correlated contaminants

background level values there (Borůvka et al. 2005; Zerling et al. 2006). Similar results were published by Martin (2000), who compared samples from the depth of 5 cm and below 50 cm, and there were found statistically significant differences between these two depths for anthropogenic metals (Cu, Pb, and Zn). Also, Zerling et al. (2006) found different concentrations

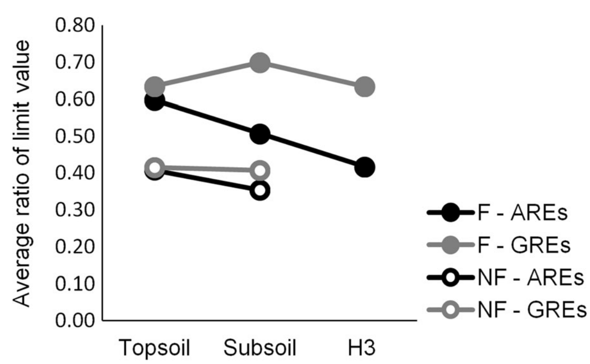

Fig. 4 General trends of ARE (Cd, Cu, Pb, and Zn) and GRE (Co, Cr, Ni, and V) concentrations in soil horizons in both flooded and non-flooded areas. Concentrations of all REs were expressed relatively to the appropriate prevention limit. Then, for the groups of GREs and AREs, the average value of these numbers were expressed individually for each sampled horizon in both flooded and non-flooded sites

among topsoil and deeper horizons for both geogenic and anthropogenic REs; the borderline depth in soils for background concentrations of GREs was around 45 cm, for AREs it was deeper. Contrarily, Maliszewska-Kordybach et al. (2011) assessed a rural area without significant urban or industrial pollution; there was not found any difference between topsoil (0–30 cm) and subsoil (30–60 cm). With respect to highly polluted areas, all of our measured concentrations were below the median concentrations in topsoils from German parts of the River Elbe, summarized in Kruger and Grongroft (2003), with the exception of Ni in flooded soils.

For flooded soils, the observed lower concentrations of Ni and Cr in topsoil compared to subsoil can be a result of a long-term natural (pre-industrial) accumulation of these elements in deeper layers of alluvial sediments originating from the uniform geological substrate of Carpathian Flysch (sedimentary rocks, mostly shales), where the concentrations of GREs are higher than in other substrates (Beneš 1993). The second likely reason of this could be leaching of these elements from topsoil to deeper horizons for long period of time, as it was demonstrated by Borůvka et al. (2005).

4.4 Basic Soil Characteristics and REs Mobility

The mobility and solubility of REs in soil are different according to their origin and environmental conditions. AREs in soil have higher solubility and mobility than risk elements originating from the geological substrate (Alloway 1990; Wahsha et al. 2014; Vácha et al. 2002).

The influence of soil properties on the concentrations, mobility, and availability of REs is more evident in AREs and in non-flooded soils, where CEC, TOC, and pH are higher in topsoil layer as a result of typical pedogenetic processes, especially accumulation of organic matter in topsoil horizons. In flooded soils with varying physical-chemical properties in the soil profile, the original source of pollution (both geogenic and anthropogenic) is the main factor influencing the contents of REs. In the case of Pb, a strong relationship with TOC was found in both flooded and non-flooded soils, which is in correspondence with strong affinity of lead to organic matter. A statistically significant difference of pH was observed between flooded and non-flooded soils. The median value for flooded soils was ranged between 6.6 and 6.8, which is very similar to the findings of Maliszewska-Kordybach et al. (2011). This level suggests only moderate mobility of Zn and Cd, and low mobility of Ni (Kabata-Pendias 2011).

4.5 Influence of Inundation

Results discussed above indicate that the inundation clearly influences the level of soil contamination, which is reflected in the higher concentrations of both AREs and GREs in flooded soils. However, the frequency of floods is probably not the main factor in this process. The more important factor seems to be the process of sedimentation, which is influenced by the intensity of flood (FIS, see Table 1) along the flooded alluvial plains. This phenomenon is connected with the findings that REs are transported more in fine sediment, which is deposited in a greater distance from a river, where the sedimentation prevails over erosion (Lair et al. 2009; Thonon Ivo 2006). For GREs, this process takes very long time (also before anthropogenic activity), which probably influenced the increase in GREs concentration farther from the river (Fig. 2) and in the subsoil of flooded soils as well (Fig. 4). Increasing RE concentrations with increasing distance were described also in Schipper et al. (2008) or Zerling et al. (2006). In the case of AREs, the process can be different since the fluvial deposition took place recently (several decades) during few big flood events across the whole fluvisols area. Moreover, if the accumulation takes place only in the topsoil layer, it can be also influenced by erosion process during average flood events, close to the river. That is why the concentrations of AREs may not exhibit any dependence on the distance from the river or, the concentrations can decrease, as was seen in the study of Martin (2000) for Cu, Pb, and Zn.

It would be useful to confirm these findings in areas with higher levels of pollution, where the described trends should be more evident.

5 Conclusions

The influence of inundation on soil contamination was proven even in moderately polluted area without large pollution sources. The contamination level, however, was not critical in flooded soils: legislative limits were slightly exceeded only in several cases. The reason of higher concentration of REs in flooded soil can be the accumulation of diffuse contamination (geogenic or anthropogenic) from the watershed into alluvial deposits or the contamination of sediments from point sources during floods. This trend was not proven in the case of As, Pb, and V; the median values of these REs were higher in non-flooded soils. The results indicated different behavior of geogenic and anthropogenic risk elements in both flooded and non-flooded soils. The concentrations of AREs generally decreased with the depth in both flooded and non-flooded soils. On the contrary, the concentrations of GREs were either not influenced by the depth or were even higher in subsoil (Cr, Ni).

No dependence of the distance from a river on the contents of AREs in soil was found. In contrast, the concentrations of GREs showed an increasing tendency with increasing distance from a river. This can be the result of long-term sedimentation of fine particles enriched by GREs during weathering and erosion processes in watersheds. On the other hand, the contents of AREs were influenced only recently by sedimentation of particles enriched by AREs mainly from atmospheric deposition and agricultural sources. The results of this complex study show that the main factor influencing the soil pollution by inundation is the process of sedimentation of suspended fine particles in which the intensity of floods plays an important role, while the frequency of floods seems to be not so important factor.

Acknowledgments This work was supported by the project of MV No. VG20102014026 and by the European Social Fund in the Czech Republic (OP Education for Competitiveness), and the state budget of the Czech Republic.

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