

The role of Mn and Fe oxides in risk elements retention in soils under different forest types

PAVEL ROTTER^{1,2,*}, JAN KUTA¹, RADIM VÁCHA³, MILAN SÁŇKA¹

¹Research Centre for Toxic Compounds in the Environment, Masaryk University, Brno, Czech Republic

²Department of Forest Ecology, Faculty of Forestry and Wood Technology, Mendel University in Brno, Brno, Czech Republic

³Research Institute for Soil and Water Conservation, Prague, Czech Republic

*Corresponding author: rotter@recetox.muni.cz

ABSTRACT

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Retention of four selected risk elements (SRE) – arsen (As), cadmium (Cd), lead (Pb), zinc (Zn) – by manganese (Mn) and iron (Fe) oxides in different forest soils was investigated. The abundance of oxides and the association between oxides and SRE were observed in 91 soil samples of different forests divided into 5 categories covering the variability of forests in the Czech Republic. The sequential extraction procedure was used for dissolution of Mn and Fe oxide fractions (MnOF and FeOF) separately and together with the associated elements. It was found that Mn associated with MnOF is significantly higher in deciduous forests. These differences were ascribed mainly to the higher pH and lower DOC (dissolved organic carbon) in deciduous forests. The association of SRE with MnOF declines in the order Cd » Pb » Zn » As and the association with FeOF in the order As ≈ Pb » Cd » Zn. Despite their relatively lesser occurrence, MnOFs were found to be very significant for retention of Cd. FeOF is strongly associated with As and Pb. The category of forest has been identified to influence the amount of SRE retained by oxides especially in two cases: (1) the category of forests on Fluvisols differs from the other categories; (2) the retention of Cd by MnOF or FeOF is larger in deciduous forests compared with coniferous forests.

Keywords: heavy metals; immobilization; forest ecosystem; mobility; toxic element

Hydrated manganese (Mn) and iron (Fe) oxides represent one of the most important reactive constituents of forest soil and together with soil organic matter (SOM), pH and to lesser extent also with clay minerals, cation exchange capacity (CEC) and oxyhydroxy complexes of aluminium (Al) they co-determine the fate of risk elements (RE) in forest soils (Borůvka and Drábek 2004, Vega et al. 2006). The specific adsorption, solid phase diffusion and co-precipitation represent the three important mechanisms responsible for the immobilization

of RE by oxides (Young 2013). However, some significant distinctions between both the oxides lead to different selectivity for retention of metals. An example is the different isoelectrical point of both oxides, which lies between pH 7 and 8.5 for most Fe oxides and below pH 4.6 for most Mn oxides (Young 2013). Therefore, in acidic forest soils, Fe oxides adsorb selectively elements as chromium (Cr), arsen (As), phosphorus (P) and selenium (Se), which occur in anionic form (Neaman et al. 2008). The selective relation between oxides and some

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of the RE is assumed to be very strong, as e.g. in the case of Fe oxides and As, where the extraction step for dissolution of amorphous Fe oxides has been suggested for As risk assessment, too (Vácha et al. 2008).

Both oxides can be dissolved during the decrease of soil redox potential (pE), caused most often by wetting of the soil profile, which influences the availability of associated RE (Shaheen et al. 2014). On the other hand, the released metal can be co-precipitated together with Mn and Fe oxides during the re-establishment of aerobic conditions (by drying of the soil profile) (Contin et al. 2007). In dry soil conditions, the Mn and Fe oxides evolve to more stabilize crystalline forms that contribute to the immobilization of RE (Tack et al. 2006). The issue of the importance of Mn and Fe as amendments for immobilization of RE in the soil profile has been discussed in many papers (Komárek et al. 2013).

Despite the proven significance of Mn and Fe oxides for RE retention and immobilization, still little is known about the variation of this significance among forests with different compositions of tree species. Therefore, this study aims at examining the importance of Fe and Mn oxides for retention of SRE (selected risk elements) – As, Cd, Pb, Zn – in different forest soils. An analysis was performed of soil samples collected from 91 sampling sites from the Czech Republic divided into 5 categories, which vary in elevation and tree species composition (coniferous, deciduous, mixed). The chosen forest categories (FC) were forests on Fluvisols (flu), coniferous forests (conif), deciduous forests (decid), mixed forests (mixed)

and mountain forests (mount) (Table 1). The study addressed mainly the following questions: (1) what is the range of Mn or Fe stored in responsible oxide fraction (OF) and denoted as Mn_{ox} or Fe_{ox} ; (2) what is the relative amount (related to pseudototal content) of Mn and Fe denoted as Mn_{rel} or Fe_{rel} , respectively, associated with corresponding oxide fraction in dependence on FC; and (3) what are the relative contents (related to the pseudototal) of SRE associated with MnOF and FeOF, denoted as M_{rel} , and how they vary together with FC.

MATERIAL AND METHODS

Sampling sites and soil sampling design. In total, 91 sampling sites were designed in order to capture the variability of forest ecosystems across the Czech Republic (Table 1). A minimum distance from cities of 500 m and a minimum distance from the forest edge of 200 m were chosen as additional criteria for the location of sampling sites. GIS techniques were used to perform a random selection of sampling sites in each category.

All samples were taken according to unified methods. At each site a probe was dug at least 50 cm deep, then, four smaller side pits were dug at a distance of 6 m from the central one, directed towards the cardinal directions. Samples from the A horizon were taken in a constant thickness of 2 cm after the removal of the L + F + H horizons from each spot. This layer is marked as hor2 in the text below. Then, samples from the layer under the A horizon in a thickness of 8 cm

Table 1. Categorization of forests and numbers of sampling sites according to category and horizon

Category	Specification	Num. samples		Prevailing tree composition	Range of altitude (m a.s.l.)	pH _{KCl}		SOC	
		hor2	hor3			± SD hor2	± SD hor3	± SD hor2	± SD hor3
Flu	forests on Fluvisols	10	10	oak, ash, maple	150–366	5.3 ± 0.94	5 ± 0.98	6 ± 1.9	3.1 ± 0.9
Conif	coniferous forests	23	22	spruce, pine	245–939	2.9 ± 0.42	3.2 ± 0.30	11.2 ± 8	2.4 ± 1.3
Decid	deciduous forests	25	25	beech, oak	193–860	3.7 ± 0.49	3.5 ± 0.26	7.6 ± 3.9	3 ± 1.8
Mixed	mixed forests	23	23	spruce, beech, oak	270–885	3.5 ± 0.73	3.4 ± 0.38	9.8 ± 5.1	3.1 ± 1.6
Mount	mountain forests	10	10	spruce	821–1243	3 ± 0.22	3.4 ± 0.33	11.3 ± 5.4	4.1 ± 2

Basic characteristics of each category: pH_{KCl} and soil organic carbon (SOC, %) are stated as arithmetic means with standard errors (SD)

were taken in a similar fashion and are denoted as hor3 below. Mixed samples were prepared for each horizon separately. Fresh soil samples were air-dried, gently crushed with a mortar and pestle and passed through a 2 mm sieve. The dried and homogenized samples were handed over for chemical soil analysis.

Chemical soil analysis. The soil exchangeable pH (pH_{KCl}) was measured in soil samples following ISO 10390 (2005) standards. The soil organic carbon (SOC) was analysed according to the accredited method SOP 4/02, which is a modification of the ISO 14235 (1998) standard. The determination procedure is based on the oxidation of organic carbon by $\text{Cr}^{(\text{VI})}$ under the abundance of sulphuric acid and elevated temperature. Remaining $\text{Cr}^{(\text{VI})}$ is then determined by the iodometric method. The pseudototal contents of selected risk elements were determined from *aqua regia* extractions following the procedure ISO 11466 (1995).

Modified sequential extraction procedure. The modified sequential extraction procedure proposed for temperate forest soils (Krasnodebska-Ostrega et al. 2001) was followed in the study in order to dissolve Mn and Fe oxides and associated elements selectively. The first step (exchangeable fraction): the soil sample (0.5 g) was placed in a centrifuge tube and 10 mL of 1 mol/L NH_4NO_3 (Merck, 1 mol/L solution for DIN 19730) was added. The sample was shaken in a horizontal position for 1 h at 200 rpm, then centrifuged for 10 min at 6000 rpm. Finally, the supernatant was removed, filtered through a 0.45 μm membrane syringe filter and acidified by addition of 100 μL of concentrated HNO_3 (Merck). Second step (carbonate fraction): 10 mL of 0.1 mol/L CH_3COOH (freshly prepared from glacial acetic acid, Merck) solution was added to the residue of soil from the first step, with the following actions being analogous to the first step. Third step (MnOF): 10 mL of 0.05 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ (freshly prepared from the hydroxylamine hydrochloride, Lach-ner, p.a.) solution was added to the residue of soil from the second step and the pH was adjusted by dropping 5 μL of HNO_3 . Next, the sample was shaken in a horizontal position for 30 min at 200 rpm, with the following actions being analogous to the previous steps. Fourth step (FeOF): 10 mL of 0.1 mol/L ascorbic acid (freshly prepared from ascorbic acid, Lach-ner, p.a.) in a 0.2 mol/L oxalate buffer (freshly prepared from ammonium oxalate and oxalic acid, Sigma-Aldrich, p.a.) was added

to the residue of soil from the third step, with the following actions being analogous to the previous steps. At least three blanks were co-prepared for each set of samples in each step of sequential extraction.

Determination of risk elements by ICP-MS. An Agilent 7700x ICP –MS instrument (Agilent Technologies, Tokyo, Japan) was used for determination of As, Cd, Pb and Zn contents in solutions after extractions. All analyses were performed in helium (He) collision mode using an Octopole Reaction System for reduction of polyatomic interferences originating from the sample matrix. A 200 $\mu\text{g/L}$ solution of internal standards (Ge, In, Bi; Astasol, Analytika s.r.o, Prague, Czech Republic) was used for correction of matrix effects and drift. Method validation parameters were verified by repeated analysis of samples spiked with a known amount of analytes.

Statistics. Analysis of variance (ANOVA) with the Tukey's *HSD* (honest significant difference) for post-hoc analyses and paired *t*-tests were performed for statistical analysis of the obtained data. Mn_{ox} , Mn_{rel} , Fe_{ox} , Fe_{rel} and all M_{rel} had to be log-transformed to comply with the assumption of normality and thus the results are presented in figures with a log-transformed *x* axis to maintain consistency with the performed ANOVAs.

Statistical significance was accepted at $\alpha = 0.05$ for all performed analyses. Statistical analyses were performed in *R* (version 3.2.2), an open source language and environment for statistical computing and graphics (<http://lib.stat.cmu.edu/R/CRAN/>) (Ihaka and Gentleman 1996) and by using the package ggplot2 (Wickham 2009).

RESULTS AND DISCUSSION

In the results and discussion section relative contents M_{rel} are often mentioned, which are defined as the ratio of metal content in a given oxide fraction (MnOF or FeOF) to its pseudototal content.

Differences in oxides' absolute or relative contents. The FC was revealed to be a significant factor for differences in the content of Mn_{ox} , Mn_{rel} and Fe_{rel} and the horizon for Fe_{ox} . The forests with a prevalence of conifers (categories conif and mount) have significantly less Mn_{ox} than forests with a prevalence of deciduous trees or mixed forests. The comparison of Mn_{rel} brought similar results

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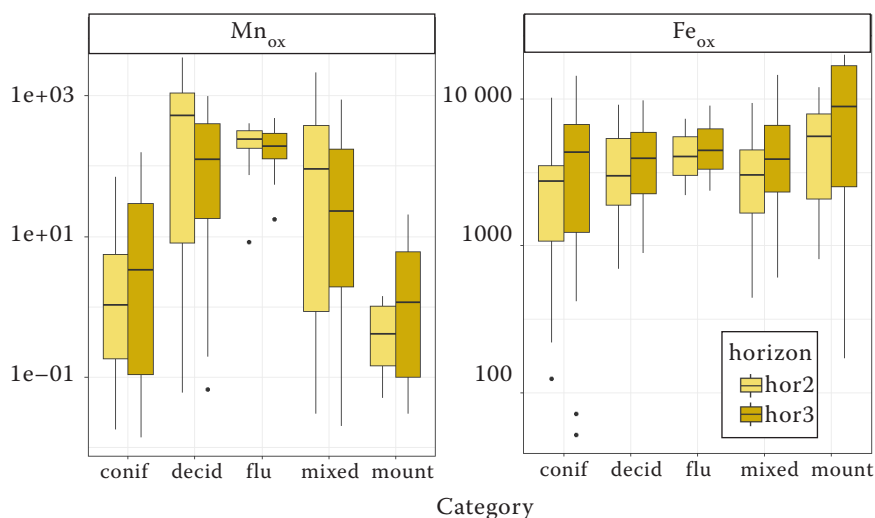


Figure 1. The amount of manganese (Mn) associated with Mn oxides fraction (Mn_{ox}, mg/kg) and the amount of iron (Fe) associated with Fe oxides fraction (Fe_{ox}, mg/kg) divided according to forest categories and horizons. The Y-axis was log-transformed to be visually compatible with the results of performed ANOVAs

among the categories. The mixed category stands between conifers and broadleaved. The reason for this might lie in the lower pH and higher DOC (dissolved organic carbon) that occur under conifers (David and Driscoll 1984). These conditions can lead to dissolution or reductive dissolution of oxides (Shaheen et al. 2014), especially in the case of Mn oxides, which are generally more prone to dissolution (Young 2013). The role of DOC in oxides dissolution seems to be more complex. Low pH has been found to enhance the complexation of organic matter with oxides (Allard et al. 2017), which can be accompanied by electron transfer leading to the reduction of oxides by DOC (Chorover and Amistadi 2001). Moreover DOC can create complexes with released metals (Laveuf and Cornu 2009), which can further boost the process of oxides dissolution. Thus, the variations in soil conditions related to different

trees and litter nature could be responsible for the observed differences in Mn_{ox} and Mn speciation but insufficient to cause significant variation in Fe_{ox} (Table 1, Figures 1 and 2).

However, the FC has been found to significantly influence also Fe_{rel}, and moreover in the opposite way, compared with Mn_{rel} (Figure 2). The Fe_{rel} was detected to be significantly higher in coniferous forests compared with deciduous ones (in hor2 and hor3) and with mixed forests (in hor2). It was assumed that the observed pattern in Fe_{rel} might be caused by factors related to podzolization occurring under conifers. The lower pH and higher DOC hinder the accumulation of the labile form of Fe (e.g. amorphous Fe oxides), which contributes to the relatively higher content of FeOF.

The Fe_{ox} was significantly higher in hor3 than in hor2. Although the distribution of Fe_{ox} was not investigated along the whole soil profile, the

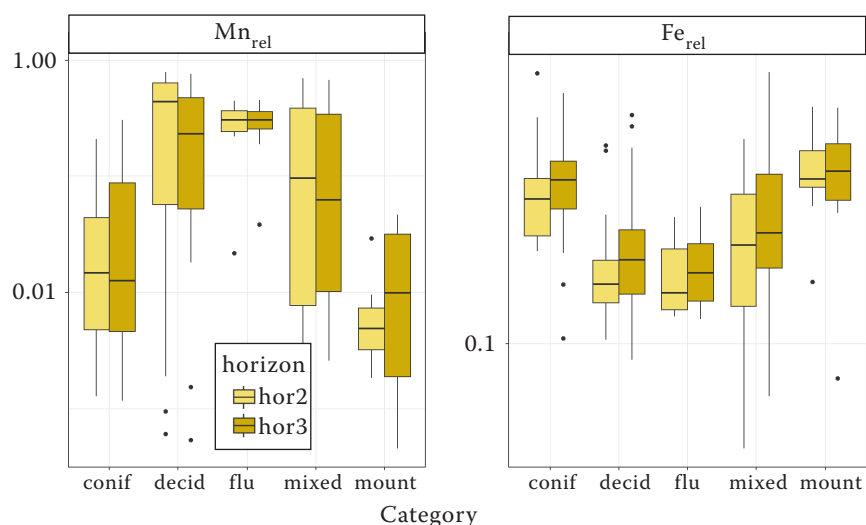


Figure 2. Relative amount of manganese (Mn) associated with Mn oxides fraction (Mn_{rel}) and relative amount of iron (Fe) associated with Fe oxides fraction (Fe_{rel}) divided according to forest categories and horizons. The Y-axis was log-transformed to be visually compatible with the results of performed ANOVAs

observed increase of Fe_{ox} from the A horizon to various B horizons agrees with other research focusing on iron and iron oxide distribution in soil (Stonehouse and Arnaud 1971).

Retention of SRE by MnOF and FeOF. The significance of oxide, FC and horizon as factors was assessed in the framework of the two-factored mixed design ANOVA separately for MnOF and FeOF or separately for hor2 and hor3. The results have confirmed that M_{rel} differ significantly among FC as factor with the exception of As_{rel} . The OF and horizon have been determined to be significant factors for variance in the case of all M_{rel} . The post-hoc comparisons between oxides or among categories were performed by paired *t*-tests or by the Tukey's *HSD*. It follows from the results that FeOF always retained more M_{rel} compared with MnOF oxides in both horizons with the exception of Cd_{rel} (Figures 3 and 4). This was true especially for As and Pb, where significant differences were revealed in the order of magnitude in stored M_{rel} in favour of the Fe oxides for both horizons and all categories.

It was found that As_{rel} (its arithmetic means) associated with FeOF ranges from 0.29 ± 0.14 to 0.36 ± 0.11 in hor2 and from 0.36 ± 0.15 to 0.47 ± 0.15 in hor3. In the case of As, the findings have confirmed the results of previous studies

(Krasnodebska-Ostrega et al. 2001, Vácha et al. 2008), highlighting the importance of Fe oxides for retention and immobilization of As. The reason for this lies in the ability of As to co-precipitate together with Fe oxides and create a number of relatively insoluble $Fe^{(II/III)}$ -As minerals, enhancing As immobilization in soils (Komárek et al. 2013).

The results show that MnOF is important for retention of Cd and the relatively small amount of Mn oxides (Figure 1) binding from 0.15 ± 0.06 to 0.42 ± 0.12 of Cd_{rel} in hor2 and from 0.12 ± 0.05 to 0.41 ± 0.15 of Cd_{rel} in hor3. The association of Cd_{rel} with MnOF was significantly larger compared with FeOF for all categories in hor2 and for decid, flu and mixed in hor3. These results are in accordance with the conclusions of adsorption and desorption studies dealing with Mn and Fe oxides' affinity to Cd (Tack et al. 2006, Shaheen et al. 2013) and also with a study comparing directly the storing capacity of Mn and Fe oxides to Cd (Arenas-Lago et al. 2014). The significant difference in Cd_{rel} between MnOF and FeOF in flu could point to the contamination that accompanied flood events and subsequent absorption of Cd onto Mn oxides in the process of co-precipitation. This assumption is based on the higher extractability of Cd as the indicator of anthropogenic loads in

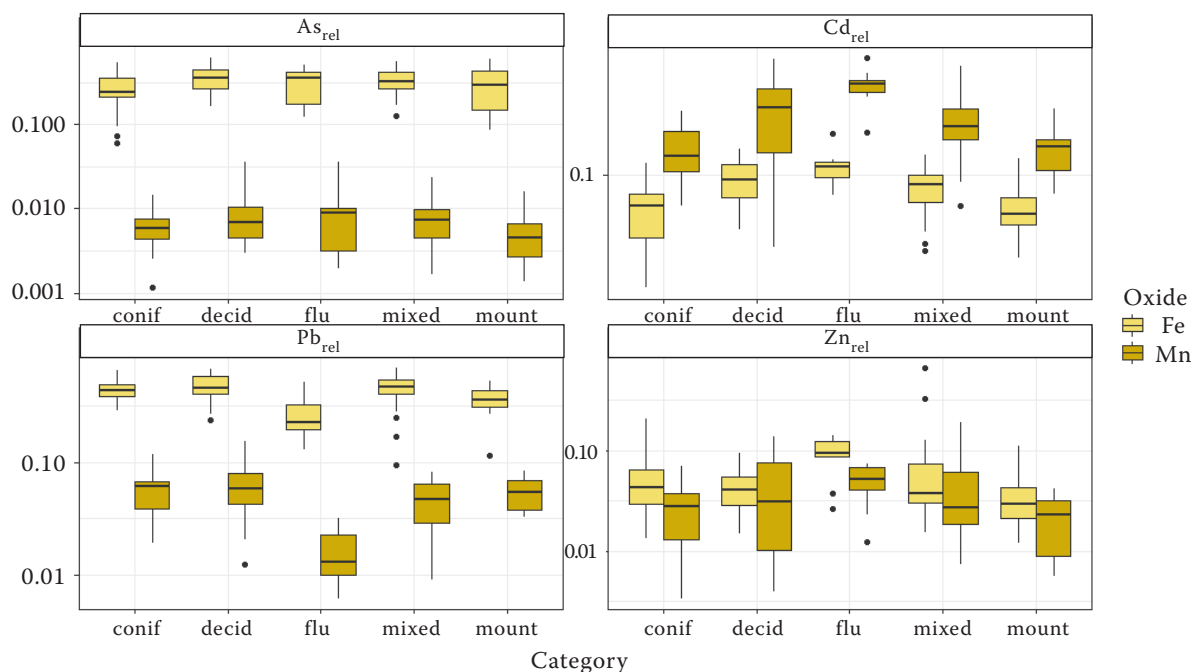


Figure 3. Relative amount (related to pseudototal content) of arsenic (As), cadmium (Cd), lead (Pb) and zinc (Zn) (As_{rel} , Cd_{rel} , Pb_{rel} and Zn_{rel}) associated with manganese (Mn) oxides fraction (beige box) or associated with iron (Fe) oxides fraction (brown box) divided according to forest categories in horizon 2 (hor2). The Y-axis was log-transformed to be visually compatible with the results of performed ANOVAs

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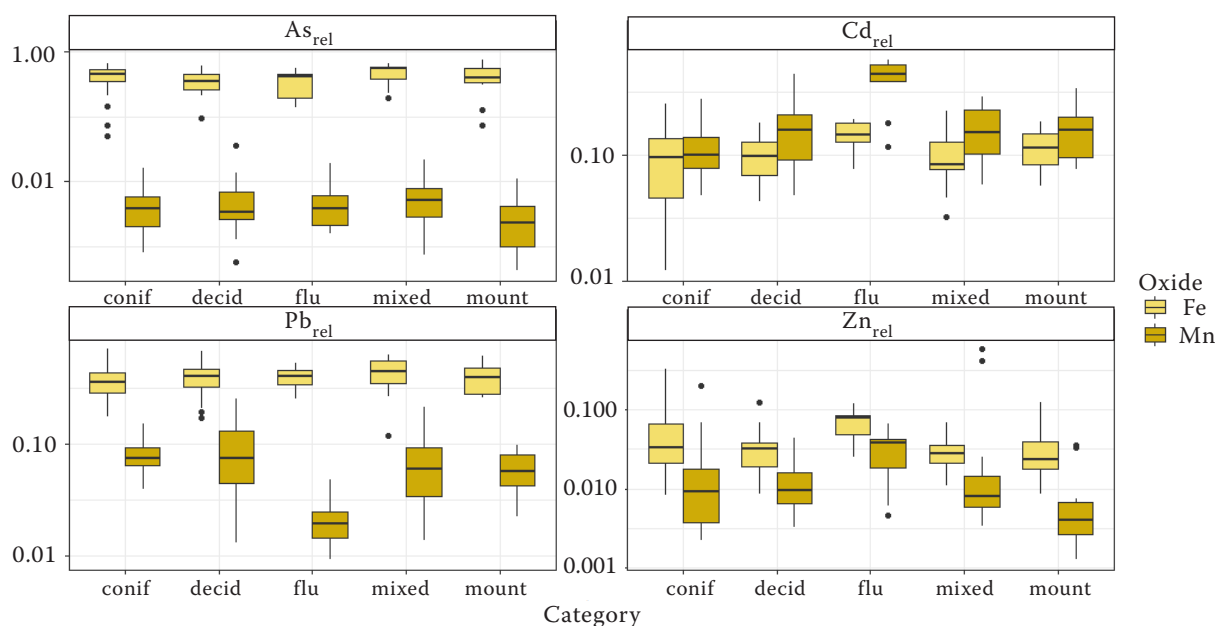


Figure 4. Relative amount (related to pseudototal content) of arsenic (As), cadmium (Cd), lead (Pb) and zinc (Zn) (As_{rel} , Cd_{rel} , Pb_{rel} and Zn_{rel}) associated with manganese (Mn) oxides fraction (beige box) or associated with iron (Fe) oxides fraction (brown box) divided according to forest categories in horizon 3 (hor3). The Y-axis was log-transformed to be visually compatible with the results of performed ANOVAs

fluvisols (Vácha et al. 2013) and on the problem of anthropogenic contamination of fluvisols by Cd in general (Zerling et al. 2006).

In the literature, Pb is reported to adsorb onto Mn oxides more efficiently than Fe oxides, especially due to the large specific surface areas and low isoelectrical point of Mn oxides (Feng et al. 2007). In spite of this fact, the results show that FeOF is by an order of magnitude more important sink for Pb in forest soils. The FeOF retains from 0.28 ± 0.14 to 0.48 ± 0.13 of Pb_{rel} in hor2 and from 0.37 ± 0.12 to 0.44 ± 0.14 in hor3, probably due to the substantially larger abundance of Fe oxides in soils as emphasized by Komárek et al. (2013). Moreover, as Mn oxides are important for retention of Cd and Pb, rain simulation studies performed with contaminated soil have shown important redistribution of both metals, where significant leaching of Pb from the easily reducible fraction was observed in contrast with Cd (Ash et al. 2015). Our results have confirmed the outcomes of some other studies emphasizing the importance of Fe oxides for Pb retention in soils (Krasnodebska-Ostrega et al. 2001, Arenas-Lago et al. 2014).

The Zn_{rel} is distributed uniformly among MnOF and FeOF in the case of the decid, mixed and mount categories of hor2, which is accordance with Arenas-Lago et al. (2014). However, FeOF stored significantly more Zn_{rel} for conif and flu in hor2.

Zn and Pb are assumed to adsorb preferentially to Fe oxides compared with some other metals like Cd or Co (Shaheen et al. 2013). Our results could support this finding, as the significantly higher Zn_{rel} was associated with FeOF compared with MnOF for all categories in hor3. The reason for this might lie in competition among ions for adsorption or incorporation into oxide structures in combination with differences in the abundances of both oxides, or in the mostly geogenic origin of Zn in hor3.

The relative contents of SRE among categories. Two general patterns have been identified with regard to the influence of the chosen forest categories on M_{rel} : (1) the category flu always differs from the other categories in the M_{rel} linked to the given oxide; (2) the Cd_{rel} bonded to MnOF or FeOF is significantly larger in deciduous forests compared with coniferous ones in hor2, and it is largest for the flu category (Figures 3 and 4).

The forest category does not influence As_{rel} distribution among forest soils, which applies for both horizons. Cd_{rel} associated with MnOF simply follows the differences in Mn_{ox} among categories for hor2, but not in hor3. More surprisingly, this applies also for Cd_{rel} bound to FeOF in hor2 (Figures 1–3). It is assumed that low pH and large DOC play the crucial role for the smaller association of Cd_{rel}

with MnOF and FeOF under conifers. The low pH maintains substantial free ion activity and together with high DOC it impedes metal sorption on iron oxides (Degryse et al. 2009). These effects are the most obvious in the case of Cd_{rel} probably due its high mobility and strong association with relatively mobilizable MnOF. The Pb_{rel} and Zn_{rel} differ among the categories only in the case of the category flu. The significantly larger Cd_{rel} and Zn_{rel} associated with MnOF or FeOF in flu could suggest a different origin of Cd together with Zn in fluvisols compared with other categories. The higher Cd and Zn in Fluvisols and their relatively easier extractability point to anthropogenic inputs (Vaněk et al. 2005, Vácha et al. 2013). As Cd_{rel} and Zn_{rel} were found to be elevated in Fluvisols, the Pb_{rel} was smaller in this category, which could be explained as the consequence of leaching of Pb from oxides, which was observed by Ash et al. (2015).

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