Incubation of air-pollution-control residues from secondary Pb smelter in deciduous and coniferous organic soil horizons: Leachability of lead, cadmium and zinc

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ABSTRACT

The leachability of air-pollution-control (APC) residues from a secondary lead smelter in organic soil horizons (F and H) from a deciduous and a coniferous forest during incubation periods of 0, 3 and 6 months were compared in this work. While the concentration of Pb, Zn and Cd associated with the exchangeable/acid extractable fraction in the horizon F from the coniferous forest was higher compared to the deciduous, significantly lower concentrations in the humified horizon H was found. It is suggested that lower pH and a higher share of fulvic acids fraction (FAs) of solid phase soil organic matter (SOM) in the humified soil horizon H from the coniferous compared to the deciduous forest is responsible for a higher metal association with solid phase SOM and therefore a lower metal leaching in a soil system. From this point of view, the humified soil horizon H from the deciduous forest represents a soil system more vulnerable to Pb, Zn and Cd leaching from APC residues.

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1. Introduction

The forest canopy serves as an efficient filter of atmospheric emissions of heavy metals from anthropogenic sources. Forest growths and the density of the tree canopy thus change the magnitude of the metal pollution and also affect the speciation of complexed metal forms bound to the soils in afforested areas [1,2]. The litter-fall and humus rich soil horizons are not the final metal reservoir; instead a significant portion is further filtered down to the deeper mineral soil horizons [3,4]. The presence of soil organic matter (SOM) can, however, lower the solubility and mobility of some metals, e.g., Cu, Pb and Zn [5]. Generally, the solid phase soil organic matter is responsible for metal retention due to processes of sorption while dissolved organic matter (DOC) causes their releasing by dissolution and/or desorption [6]. The DOC plays an important role in metal mobility and bioavailability [4,7–9].

Different tree species produce litter or needles with different chemical compositions, and thus the degradation of such distinct biological materials in soils results in different properties and reactivity of DOC [7]. In addition to this species-dependent control over DOC, the trees may also affect the metal mobility indirectly through their effect on pH in the topsoil. Generally, coniferous trees produce higher amounts of DOC than deciduous ones [7]. Furthermore, the coniferous trees tend to produce higher amounts of low-molecular-weight organic acids (LMWOAs), which are components of DOC, responsible for metal leaching from solid materials [10].

On the other hand, humic and fulvic acids (HAs, FAs) that are the major soil fraction controlling the acid–base properties, strongly influence the mobilization and transport of toxic metals in soils due to their complexation abilities [11]. HAs and FAs differ in structure and chemical behavior. Specifically, HAs are soluble in an alkaline environment and precipitate in acidic solutions, while FAs are soluble in both alkali and acidic solutions [12]. HAs are characterized by a smaller concentration of carboxylic- and phenolic-type functional groups of a higher heterogeneity and embody larger affinities for proton binding [11,13], however, FAs carry more functional groups and under given pH exhibit a higher protonation/deprotonation range than HAs [14]. Despite their obviously different structure,

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chemical properties and protonation behavior, HAs and FAs exhibit a very similar metal binding ability [15]. The metal mobility in soils is controlled by the stability of dissolved organo-metal complexes and their interactions with other soil components, mainly Al, Fe oxyhydroxides, illite, silica, etc. [12,15,16], rather than the complexation properties of the HAs and FAs.

The sorption/desorption of organo-metal complexes depends on many factors, including the concentration of DOC and its chemical composition [11,12,14,17], pH of the soils [12,14,18], the stability of organo-metal complexes and as a function of time and temperature [12,19–21]. The positive ionic-strength dependency of HAs adsorption was suggested by Weng et al. [22,23].

Air-pollution-control (APC) residues from industrial processes are classified as environmentally hazardous materials due to their specific physico-chemical properties, i.e., high concentrations of metals and metalloids present in soluble forms [24]. Although the emissions of such materials are low due to efficient filtration technologies, small amounts of the residues are still emitted and settle into adjacent soil systems [25].

The mineralogy of APC residues from secondary lead smelters has been studied [26] and the leaching behavior using several standardized protocols [24,27], in the presence of LMWOAs [28] or during pH-dependent procedure [25] has been elaborated.

In this study, the APC residues originating from a secondary lead smelter rich in Pb, Cd and Zn (i.e., the same material used by Ettler and other co-workers [24–28]) were incubated in partially (F) and completely humified (H) soil horizons from the coniferous and the deciduous forests to assess the vulnerability of organic soil horizons to smelter-impacted contamination.

2. Materials and methods

2.1. Soil sampling and sample preparation

Two soil samples, partially (F) and completely (H) decomposed organic humified horizons developed under conifers with predominant Norway spruce (*Picea abies* L.) and deciduous trees with beech (*Fagus sylvatica* L.) dominating were taken in this study. The sampling sites both localized in South Bohemia (Czech Republic) were chosen due to the absence of major industrial activities and thus our study site represents an unpolluted area. The coordinates for sampling points of the coniferous and the deciduous forests are: N48°57.926′; E14°14.564′ and 48°59.737′; E14°10.919′, respectively. All soil samples were air-dried to constant weight. The samples were homogenised but not sieved in order to maintain the original soil characteristics.

2.2. Basic soil characteristics

Soil pH was measured using a 1:5 (v/v) ratio of soil and deionized water or 1 M KCl solution [29] using an inoLab Level 1 pH-meter. The concentrations of total organic carbon (TOC) and total S (S_{tot}) were determined by catalytic oxidation (1350 °C) using a combination of ELTRA Metalyt CS 500 and Metalyt CS 530 elemental analyzers. In order to determine the cation exchange capacity (CEC), the soil was saturated with Ba^{2+} cations using 0.1 M $BaCl_2$. Barium was subsequently released using $MgSO_4$ [30]. The acid oxalate extraction (0.2 M ammonium oxalate/oxalic acid at pH 3) for the determination of amorphous and poorly crystalline Fe-, Mn- and Al-oxides/hydroxides was performed according to McCarty et al. [31] on heavy particle size fractions separated from the organic soil horizons F and H. The foregoing separation process excluded organic mass completely because the acid oxalate extraction is not designed for such organic soil horizons. The separation of organic mass from heavy particle size fraction was done in a

liquid of 1,1,2,2-tetrabromethane and dioxane mixed to a final density of 1.99 g cm^{-3}. Mg, Fe, Mn and Al were determined by means of a flame atomic absorption spectrophotometer (FAAS, Varian SpectrAA 200HT). Humus quality was determined according to Chen et al. [32] as a ratio of optical densities or absorbances of dilute, aqueous humic and fulvic acid solutions in NaOH at 465 and 665 nm. One gram of each soil sample was weighed into a 250 mL polyethylene flask and extracted with 50 mL of 0.5 M NaOH for 2 h. The solutions were then centrifuged and the UV absorption spectra in the individual supernatants (465 and 665 nm) were recorded using UV-Vis spectrophotometer (Hewlett Packard 8453, USA). Water soluble and hot water extractable carbon concentration (WSC and HWC) were determined according to Ghani et al. [33] and the TOC in appropriate extracts was determined using the Skalar TOC Analyzer Formacs HT as WSC concentration.

In order to obtain the chemical fractionation forms of the studied metals (Pb, Zn, Cd) in incubated soils, the modified BCR sequential extraction procedure (SEP) by Quevauviller [34] was used. The SEP for each sample was carried out in duplicate. The background Pb, Zn and Cd concentrations were obtained on the basis of *aqua regia* extraction because the same procedure is used in SEP protocol as a pseudo-total concentration. The determination of Pb, Zn and Cd in total decomposed, *aqua regia* extracted and SEP samples was performed using an inductively coupled plasma mass spectrometer (ICP-MS, X-Series, Thermo Scientific, Germany) under standard analytical conditions.

2.3. Incubation experiments

In order to study the leachability of metals from APC residues in organic soil horizons, an incubation experiment was performed for a period of 0, 3 and 6 months. Twenty g of well homogenised soil samples was placed into acid-cleaned 100-mL polyethylene bottles and the amount of 100 mg of APC was added and homogenised on an end-over-shaker for 6 h. The absolute dose (based on bulk Pb concentration in the APC used in this study) of Pb added to soil samples was 20 mg (1 g Pb per 1 kg of soil sample). This concentration is relatively high but reflects the real situation of heavily polluted forest soils near secondary lead smelters [35]. Deionised water (Milli-Q; 60% WHC) was added to the mixtures of APC and soils; the 60% WHC was used to better simulate real moisture conditions commonly observed in soil systems. The effect of concomitant salts in APC residues was evaluated by the same incubation procedure with the Pb mixture containing a synthetically prepared anglesite ($PbSO_4$) mixed with $PbCl_2$ (analytical grade, Lachema, Czech Republic) in the ratio of 6:1 (by weight), respectively to obtain approximately the same ratio of these compounds as in APC sample. The chemical and mineralogical composition of APC used in this study is published by Ettler et al. [28]. Anglesite (prepared from lead acetate by precipitation with sulphuric acid and re-crystallised under 80 °C for three days) structure was confirmed by XRD (PANalytical X'Pert Pro diffractometer equipped with a diffracted beam monochromator and an X'Celerator multichannel detector). The soils were incubated with the synthetic mixture to obtain the same Pb concentration of 1 g Pb kg^{-1} as in the case of APC.

The polyethylene bottles were covered with caps and stored in the dark at a constant temperature of 20 °C. The bottles were periodically (twice a week) opened and aerated; the WHC level was checked by weight. The mixture of soil and contaminating material at an aliquot of 1 g of dry mass were taken in duplicates (after 0, 3, 6 months) and the sequential extraction was performed with the wet sample for 3 and 6 months of incubation and dry sample for the control (0 months).

Table 1
Basic soil physico-chemical characteristics.

	Horizon (depth/cm)	pH_{H_2O}	pH_{KCl}	TOC %	CEC (cmol kg^{-1})	WSC (mg C g^{-1})	HWC (mg C g^{-1})	HA/FA	Background metal level (mg kg^{-1})			Oxalate extractions (mg kg^{-1})		
									Pb	Zn	Cd	Mn	Fe	Al
Coniferous	F (1–3)	4.2	4.1	47.5	134	7.78	19.1	0.157	28.5	66.0	0.37	3.81	7.39	0.83
	H (3–7)	3.6	3.0	31.3	123	3.78	13.3		45.1	47.0	0.32	3.79	49.9	23.7
Deciduous	F (1–5)	5.3	5.1	38.9	114	10.2	15.8	0.324	27.6	102	0.72	7.90	2.83	6.30
	H (5–9)	4.1	3.9	11.1	82.5	2.39	6.20		47.2	50.0	0.34	22.4	721	48.4

2.4. QA/QC procedure

Results obtained from the SEP were controlled by the comparison of the sum of all fractions compared to total metal concentration for each soil sample. The relative standard error expressed as a difference between the sum of all fractions and independently performed total concentrations (HCl/HF/HNO$_3$) did not exceed 10% in both directions. The *aqua regia* extraction and total digestion procedure were evaluated using the certified reference material Light Sandy Soil 7002 (Analytica, Prague, Czech Republic). The relative standard error of Pb, Zn and Cd concentrations found compared to certified was less than 5%.

2.5. Statistical analyses

Data obtained from total digestion and the SEP were subjected to statistical analysis of variance (ANOVA) with a consequent Tukey test. The results were evaluated on the basis of homogenous groups at a given significance level ($p < 0.05$). Each SEP fraction was tested separately. The tested factors were: (i) incubation period (0, 3 and 6 month), (ii) soil type (the coniferous × the deciduous forests), (iii) soil horizon (partially F and completely H soil horizons) and in the case of Pb the type of contamination (synthetic mixture × APC residues). The relative data (in percentages) were transformed before the statistical treatment using arcsin transformation.

3. Results and discussion

3.1. Physico-chemical properties selected soil samples

Selected physico-chemical properties of organic soil horizons are summarized in Table 1. Both soils developed under the coniferous and the deciduous forests were acidic with a lower pH found in the organic horizon H (Table 1). During the process of decomposition the production of organic acids increases. The higher production of the organic matter (Table 1) and the lower pH under the coniferous (Norway spruce) compared to the deciduous forest (beech) are in an agreement with earlier findings by Strobel et al. [7] and Andersen et al. [9]. Although the organic soil horizons had a very high CEC, some differences between the two forest soils were found. In partially and completely decomposed organic soil horizons (F and H) from the coniferous forest, the CEC had similar value (134 and 123 cmol kg^{-1}, respectively), while in the deciduous forest soil, the CEC values were significantly lower (from 114 to 82.5 cmol kg^{-1} for horizons F and H, respectively, Table 1). The different chemical composition and degradability of litter and needles lead to a different composition of humic substances, where the ratio HAs/FAs was higher in soil developing under the deciduous compared to the coniferous trees (0.32–0.16, respectively, Table 1).

The WSC and HWC values are summarized in Table 1. In general, both soils had a high WSC and HWC level which corresponds to the fact that native forests maintain high carbon inputs relative to decomposition [33]. A higher amount of WSC and HWC was found in the deciduous forest soil despite the lower TOC

concentration (Table 1). This finding is consistent with the conclusion by Frouz et al. [36] that deciduous forests support the storage of the organically complexed C in soils more than coniferous. The WSC (pool of highly labile organic C) is a fraction of HWC. The WSC concentration in the coniferous forest soil horizon accounted for about 41 and 28% (in F and H soil horizons, respectively) and 64 and 38% for F and H in the deciduous soil horizon, respectively. These values are much higher compared to the results by Ghani et al. [33] where WSC ranged between 3 and 6% of HWC, although it is not clear whether the authors discussed forest soils as well. In any case, the ratio of highly labile organic matter (defined by Ghani et al. [33] as the WSC) to HWC was higher in the upper organic soil horizon and the deciduous trees produced a higher amount of this fraction than the conifers (Table 1). The soils had very low Fe, Mn and Al oxalate extractable concentrations (Table 1). The humified soil horizons H from the coniferous forest had a higher Fe oxalate extractable content compared to the same soil horizon from the deciduous forest (49.9 mg kg^{-1} and 721 mg kg^{-1} from the coniferous and the deciduous forests, respectively, Table 1). A relatively higher Mn oxalate extractable concentration was found in the humified soil horizon H from the deciduous forest (22.4 mg kg^{-1}, Table 1). Generally, the concentration of Fe, Mn and Al oxyhydroxides in the organic soil horizons is limited and solid SOM is the predominant phase responsible for metal adsorption.

The background Pb, Zn and Cd concentrations are presented in Table 1. The soils are relatively poor from metal contamination and in the case of Pb, the highest natural background concentration (47.2 mg Pb kg^{-1} in horizon H from the deciduous forest) does not exceed more than 5% from spiked concentration (1000 mg Pb kg^{-1}).

3.2. Pb fractionation forms

The results of Pb fractionation during the incubation experiment are presented as Fig. 1. Despite the acidic conditions of the soils, a lower solubility of Pb in the first step of the SEP was achieved which is consistent with findings by Pueyo et al. [37] even though the authors studied soils contaminated with Pb sulphides. On the other hand, a statistically significant increase of Pb exchangeable fraction during the incubation was observed in both F and H soil horizons of the coniferous and the deciduous forests (Fig. 1). In the deciduous forest soil, the steep increase of Pb in the exchangeable/acid extractable fraction in the humified H (compared to the F soil horizon) (Fig. 1) is probably due to the relevant decrease of CEC with soil depth (Table 1). As found by Sterckeman et al. [4], the CEC can be one of the important soil properties controlling metal retention in soils. It is apparent from Fig. 1 that a higher solubility was achieved in the synthetic mixture compared to APC residues. The stability of APC residues seems to be supported with the other minerals and salts accompanying them which are presumably responsible for the mineralogical transformation into more stable forms, e.g., anglesite or PbSO$_3$ [25]. These phases are probably insoluble or with very limited solubility even in the last step of the BCR SEP (*aqua regia* extraction).

In addition, a significantly higher Pb concentration associated with the oxidizable fraction was detected in the partially
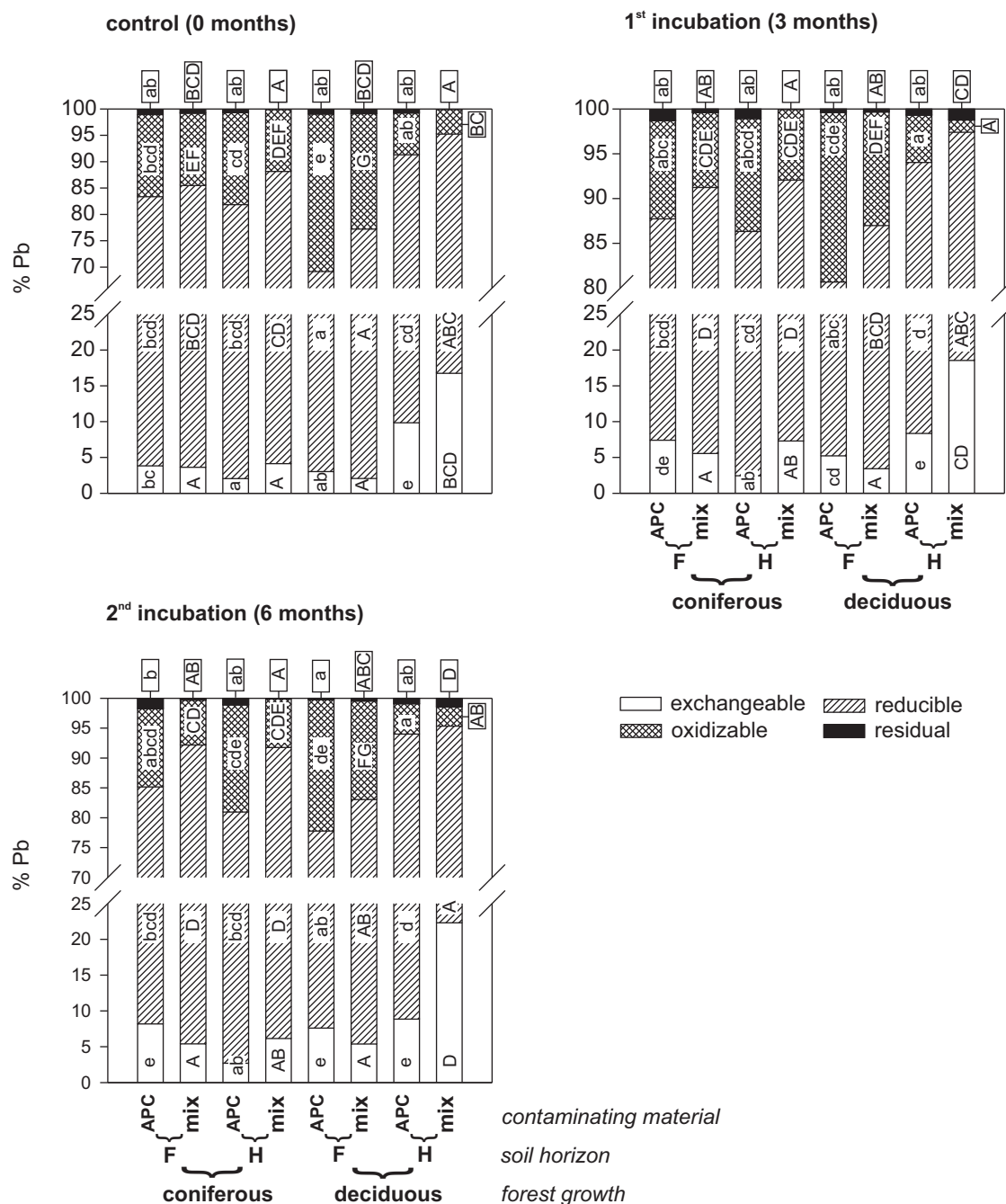
Fig. 1. Fractionation forms of lead originated from the incubation of air-pollution-control residues (APC) and synthetic mixture in the organic soil horizons from the coniferous and the deciduous forest stands. The statistical comparison (Tukey test) were performed for each fraction separately.

decomposed organic horizon F from the deciduous forest, while in the deeper horizon H, Pb concentration reached its minimum in this fraction (Fig. 1). One possible reason for this behavior can be related to the sorption ability of SOM under lower pH. The degradation of tree needles led to higher acidification of the soils compared to the litter degradation which can be seen in Table 1 ($pH_{KCl} = 4.09$ compared to 5.13 for the upper organic soil horizon from the coniferous and the deciduous forest, respectively). As was found by Borůvka and Drábek [38] in a fractionation study of metals bound to solid SOM, more than 82% of Pb bound to organic matter was associated with FAs compared to HAs fraction. According to the factor analyses the decreasing pH increased the Pb sorption on both fractions. This effect was also mentioned by Impellitery et al. [6]. They found that Pb is strongly associated with solid SOM under low pH but a

significant increase in extractable Pb occurred at the pH level over 5 [6]. The humified horizon H from the coniferous tree forest contained a higher portion of FAs compared to HAs and had a lower pH compared to the horizon H from the deciduous forest and therefore higher sorption of Pb onto solid SOM was found in our study (Fig. 1).

3.3. Zn fractionation forms

The fractionation forms of Zn in the control and after 3 and 6 months of the incubation period are presented in Fig. 2. The Zn fractionation pattern was different compared to Pb (Fig. 1.) since Zn was mainly present in the first two SEP fractions (Fig. 2).

In general, the main changes during the incubation periods of 3 and 6 months occurred between the exchangeable and
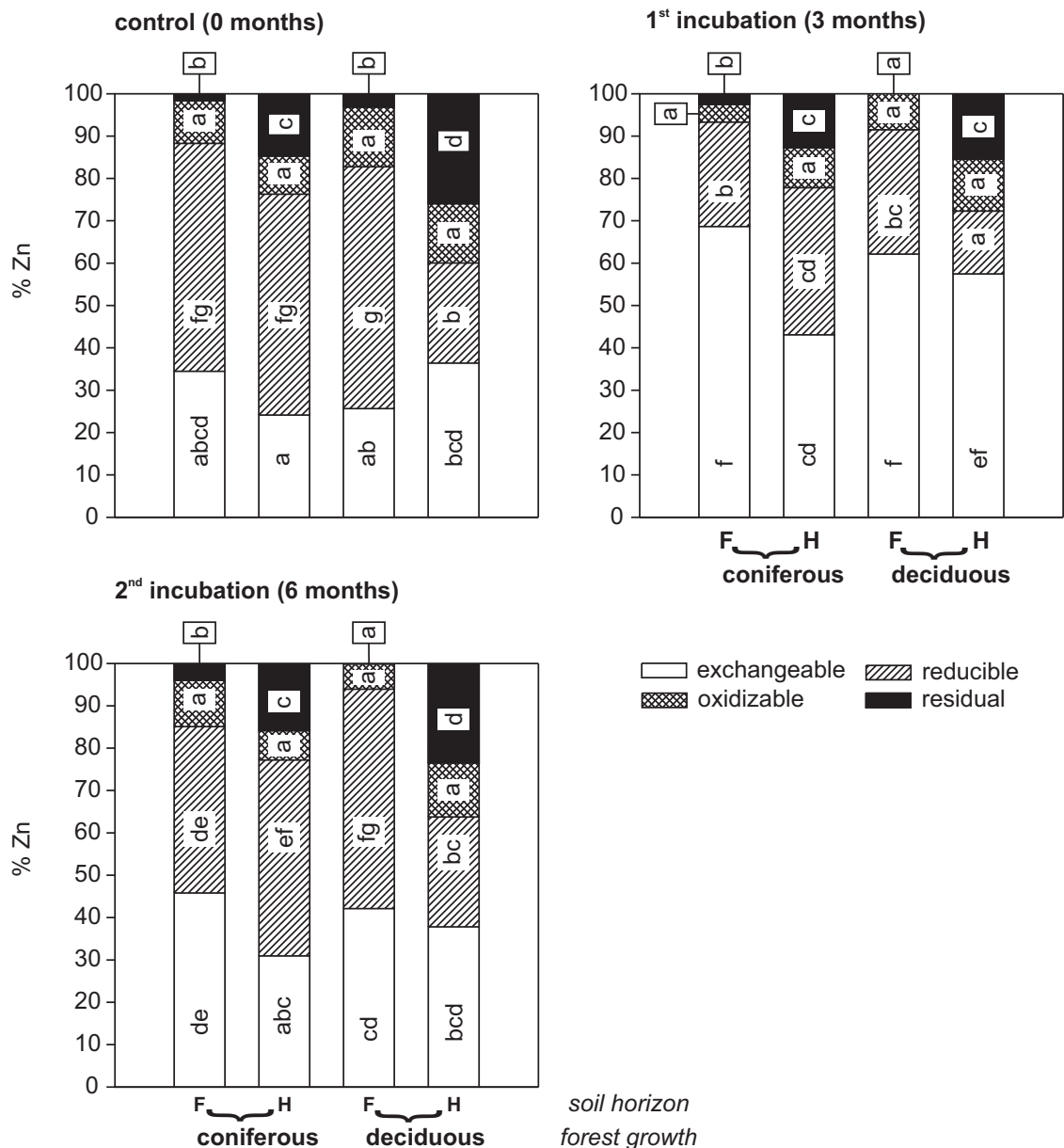
Fig. 2. Fractionation forms of zinc originated from incubation of air-pollution-control residues (APC) in the organic soil horizons from the coniferous and the deciduous forest stands. The statistical comparison (Tukey test) were performed for each fraction separately.

reducible fractions, while the oxidizable remained proportionally constant. The concentration of Zn associated with exchangeable/acid extractable fraction had an increasing trend after both incubation periods compared to the control in both the horizons F and H from the coniferous and the deciduous forests (Fig. 2); however, the slight increase of this fraction in horizon H of the deciduous forest was not statistically significant (Fig. 2). The observed steep increase after 3 months of the incubation period (for more than 30% in F horizon, the coniferous forest, Fig. 2) was due to reducible and partly residual (horizon F and H, the deciduous forest, Fig. 2) fractions. The Zn mobilization in the upper organic soil horizons were higher compared to both horizons H (Fig. 2). The soil samples from the coniferous forest, both partially and completely decomposed organic soil horizons, had a comparable CEC while the pH values decreased from the upper to the deeper horizon (from the value of 4.1 to 2.9, respectively, Table 1).

Zinc can form negatively charged complexes with LMWOAs (e.g., Zn-citrate⁻ etc.) which can be adsorbed on the positively charged

surfaces of organic matter under acidic soil pH [25]. It is suggested that higher amounts of simple organic ligands are generally present in the completely decomposed organic soil horizon which is more acidic.

After 6 months of incubation, redistribution of Zn fractionation forms took place (Fig. 2). For example, the whole mobilization of Zn from the control to the end of incubation increased by 12% for F horizon of soil from the coniferous and by more than 16% from the deciduous forest.

The proportions of Zn associated with the residual fraction increased during the incubation period in both soil horizons of the coniferous forest soils (Fig. 2). At the control, the residual Zn content accounted for 1.65 and 14.7% and after the 6 months incubation period increased to 3.97 and 15.9% for the coniferous F and H soil horizons, respectively. However, with the only exception of the F horizon from the deciduous forest soil, such changes were statistically insignificant. The same effect of immobilization of Zn and Pb through redistribution towards the residual fraction was
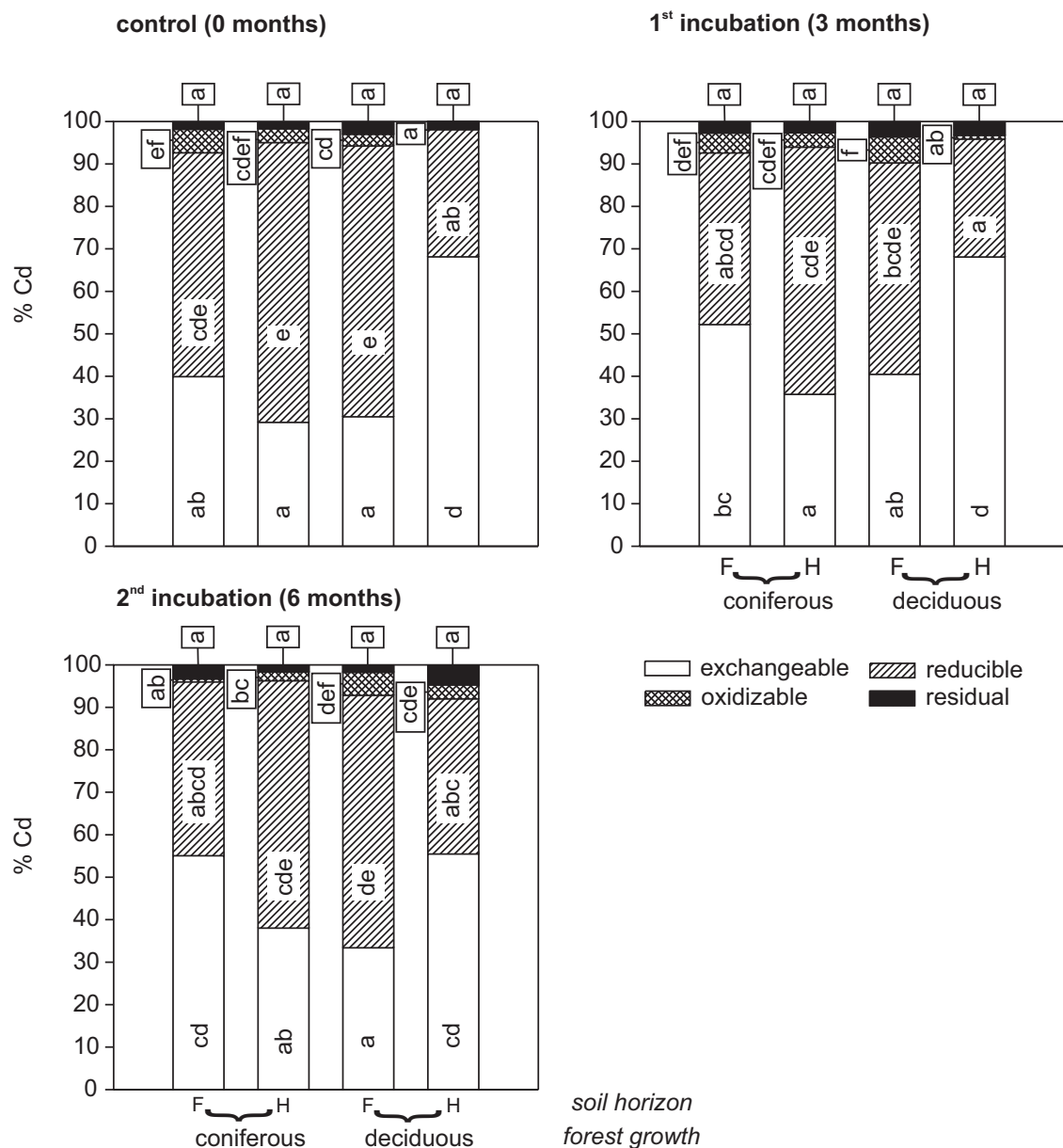
Fig. 3. Fractionation forms of cadmium originated from incubation of air-pollution-control residues (APC) in the organic soil horizons from the coniferous and the deciduous forest stands. The statistical comparison (Tukey test) were performed for each fraction separately.

found by Clemente and Bernal [39] for contaminated soils treated with HAs. They attributed this effect to the HAs–metal interaction leading to precipitation or flocculation. On the other hand, a substantial decrease of the residual Zn during the 6 month incubation period in the decidous soil horizons (from 3.17 to 0.28% for F and from 26 to 23.5% for H soil horzion, Fig. 2) was found. Moreover, the decrease of the residual Zn concentration was accompanied by a massive increase of Zn associated with the exchangeable/acid extractable fraction in the F horizon (Fig. 2).

3.4. Cd fractionation forms

The dominant Cd fractionation forms are exchangeable and reducible (Fig. 3). Compared to Zn, the oxidizable fraction was of minor importance and accounts for a maximum of about 6% in horizon F from the deciduous forest after 3 months of incubation (Fig. 3). Contrary to our results, Pueyo et al. [37] found a higher amount of Cd (almost 20%) associated with the oxidizable fraction (according

to the BCR SEP) in acidic soils contaminated with materials from an opencast mine (mainly pyrite sludge and acidic waste water). The oxidizable fraction in soil is due to the incomplete pyrite oxidation and not to really be associated with organic matter [37]. On the other hand, when the soils are contaminated with acidic water containing soluble Cd forms, the distribution of the fractionation forms are very comparable to our results [37]. Despite the highly soluble Cd content in APC residues [25,28] the affinity of Cd to SOM was not proven.

The exchangeable fraction of Cd exhibited a different behavior in the chosen soil type. In the control, the highest Cd concentration associated with the exchangeable fraction (almost 70%) was found in the H soil horizon (Fig. 3) from the deciduous forest. However, in the same soil from the coniferous forest, the exchangeable Cd concentration reached the minimum (Fig. 3). This trend remained the same throughout the incubation period (Fig. 3). The humified soil horizon from the deciduous forest had the lowest CEC found (82.5 cmol kg^{-1}) (Table 1). While the highest mobilization after the

incubation process was found in horizon F from the coniferous forest (from the initial 40 in the control to 55% at the end of incubation, Fig. 3) and in horizon H from the deciduous forest decreased from 68 to 55%, the Cd concentration in this fraction remained still much higher compared to the humified horizon H from the coniferous forest (about 38% at the end of incubation) (Fig. 3).

Although exchangeable Cd in horizon F from the deciduous forest was the lowest, which according to the studies by Sterckeman et al. [4] or Pueyo et al. [37] can be related to the soil pH (Table 1), the mobilization of Cd in horizon H exhibited its maximum. Moreover, the higher Cd stabilization in the deeper soil horizon was achieved in the soils from the coniferous tree forest. This behavior can be explained by the role of HAs and FAs and is further discussed.

3.5. The role of humic and fulvic acids on metal mobilization

Solid SOM as the predominant sorbent in organic soils (Table 1) plays the key role for metal retention in soils. According to an earlier study [38] concerning the distribution of Pb, Zn and Cd between HAs and FAs in soils heavily contaminated from smelting process, higher Pb, Zn and Cd concentrations were detected in FAs fraction of solid SOM. With respect to our study a several fold higher share of FAs over HAs fraction was detected in the humified soil horizon from the coniferous forest, therefore a higher metal retention here is expected.

In the case of Pb the main differences between humified soil horizons from the coniferous and the deciduous forests took place in exchangeable and oxidizable fractions (Fig. 1). While Pb concentration associated with the exchangeable/acid extractable fraction in the horizon H from the coniferous forest was the lowest in the control and remained very low after 6 months of incubation time, the same fraction of Pb in the deciduous horizon H was very high and in the case of the synthetic mixture reached even the highest value (Fig. 1). The Pb concentration associated with the oxidizable fraction presented exactly the opposite trend (Fig. 1).

In addition to metal bearing phases, the APC residues contain a higher amount of salts (up to 48% of NaCl and Na_2SO_4, [25]). The ionic strength of soil solution was in the case of APC incubation much higher compared to the synthetic mixture and was thus responsible for larger Pb adsorption to solid SOM.

A significantly lower Zn concentration associated with the exchangeable/acid extractable fraction was found in the humified horizon H from the coniferous forest. The main changes in Zn distribution were due to exchangeable/acid extractable, reducible and residual fractions (Fig. 2) while the oxidizable fraction became constant in all soil horizons for the whole incubation period. A noticeably higher concentration of Zn in residual fraction was detected in the humified horizon from the deciduous forest (Fig. 2). This fraction in this soil horizon is responsible for the lower non-residual (sum of fractions A–C) Zn share compared to the same soil horizon from the coniferous forest (Fig. 2).

The Cd concentration associated with the exchangeable/acid extractable fraction was lower in the coniferous humified soil horizon H compared to the deciduous one (Fig. 3). As suggested from an earlier study by Borůvka and Drábek [38], the Cd adsorption onto solid SOM is more influenced by the fulvic acid fraction. Moreover, the changes in exchangeable/acid extractable fraction in both humified soil horizons after the incubation period was mainly due to reducible fraction and also a significant increase of Cd associated with the oxidizable fraction in the horizon H from the deciduous forest took place (Fig. 3). The reducible soil phases (mainly Fe, Mn oxyhydroxides) are not presented in organic soil horizons (Table 1). Therefore, the Cd (and also other metals) associated with the reducible fraction cannot be really bound to oxides but is probably weakly or strongly adsorbed onto solid SOM. From this point

of view it can be concluded that Cd was weakly bound in the deciduous compared to the coniferous humified soil horizon.

4. Conclusions

In organic soil horizons the leaching Pb, Zn and Cd from APC residues was shown which should indicate that at least a partial alteration of Pb bearing mineral phases took place. From the changes in solid speciation between dry and wet samples (control against the two incubation periods) it is shown that the reaction of APC residues was relatively slower compared the aqueous environment where based on previous studies the reaction proceeded quasi instantaneously. In organic soils the predominant sorbent of metals is the solid phase of SOM. The consequent mobilization/retention of metals from APC residues is a complex process depending not only on soil properties such as pH, TOC, CEC but also on HAs to FAs ratio when humified soil horizons are taken into consideration.

According to the SEP, the lowest mobilization of Pb bearing phases took place in the humified H horizon from the coniferous forest. On the other hand, the highest Pb concentration was found in the humified horizon H from the deciduous forest when the synthetic mixture was incubated. This was caused by the stabilization effect of the concomitant phases accompanying APC residues compared to the synthetic mixture.

The higher mobilization effect of Zn and Cd (expressed as the increase of metal associated with the exchangeable/acid extractable fraction) took place in the upper soil horizon F from the coniferous forest, however, the significantly lower concentrations were detected in the humified horizon H from the coniferous compared to the deciduous forest. In other words, although Zn and Cd were more mobile in the coniferous litter, consequently higher immobilization in the coniferous humus soil horizon took place. We therefore suggested that a lower pH of soils and a higher amount of FAs fraction of solid phase SOM is responsible for higher metal retention in organic soils. From this point of view, the soil system more vulnerable to mobilization of metals leached from APC residues is that of the deciduous forest because of its lower level of FAs and generally higher pH.

Regardless the SEP is operationally defined, it presents an efficient tool for comparison of metal binding strength in a real soil system provided that the interpretation is done with respect to the given soil type.

Acknowledgements

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