European Journal of Forest Research (2023) 142:247–257
https://doi.org/10.1007/s10342-022-01519-8

ORIGINAL PAPER

The influence of Norway spruce and European beech on the vertical distribution of Cd, Cu, Pb and Zn in temperate forest soils

David Juřička[1] · **Martin Valtera**[2] · **Radek Novotný**[3] · **Renata Komendová**[4] · **Jakub Černý**[3] · **Václav Pecina**[4]

Received: 1 October 2022 / Revised: 5 November 2022 / Accepted: 24 November 2022 / Published online: 10 December 2022

Abstract

The objective of this study was to assess the influence of European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) H. Karst.) on the vertical distribution of Cd, Cu, Pb and Zn in forest soil. Soil samples were taken from six beech- and six spruce-dominated mature (80–100-year-old) forest stands. In total, 420 composite soil samples were collected from the organic horizons, and at depths of 0–2, 2–10, 10–20 and 20–30 cm in the mineral soil, of 84 plots in a hexagonal sampling design. A direct influence of forest type was confirmed for Zn, which showed increased soil accumulation under beech. In spruce stand soils, Zn is likely to have leached more due to lower pH levels. While a minor influence of tree species on the vertical distribution of Cd, Cu and Pb was also confirmed, particularly as regards accumulation in the F + H layer of spruce stands, the results suggest a more dominant effect of other site-specific conditions at the scale studied, such as topography and atmospheric deposition, despite homogenous forest stand conditions. Furthermore, the C:N ratio had a significant impact on both Cd and Cu content, regardless of forest type, highlighting the importance of specific site conditions for driving decomposition of organic matter, a primary factor affecting Cd and Cu mobility in soil.

Keywords *Picea abies*, *Fagus sylvatica* · C:N · Metal mobility · Forest-type effect

Introduction

Along with other ecological and socio-economic functions, forests and their soils play a significant role in global biogeochemical cycles. However, industrially emitted waste products, such as sulphur (S) compounds, metals and other potentially toxic chemical substances, can have wide-ranging negative impacts on forest vitality and ecosystem services (Helmisaari et al. 1995; Frey et al. 2006; Kandziora-Ciupa et al. 2016; Novotný et al. 2017; Vacek et al. 2021; Pecina et al. 2022). Regarding the environmental persistence of metals, a long-term perspective is crucial to determine their critical loads (Helmisaari et al. 1995), risks and behaviour in forest soils.

While forest floor contamination with metals will strongly reflect local sources and influences (Sucharová et al. 2011), differing environmental conditions can have a strong influence on their dynamics in mineral soils (Sucharová et al. 2011, 2012), with parent rock, soil processes and forest composition amongst the most important factors (Ranger and Nys 1994; Augusto et al. 1998, 2002; Andersen et al. 2004; Svendsen et al. 2007; Mihaljevič et al. 2010; Augusto et al. 2015; Bai et al. 2022). The vertical distribution of metals in forest soil will depend both on the particular metal and a range of soil properties (Hernandez et al. 2003), with pH as a key parameter affecting metal mobility in soil (Römkens and Salomons 1998; Kelly et al. 2003; Taiz and Zeiger 2010). Likewise, the soil texture (Tang et al. 2021) and the quantity and quality of soil organic matter (OM) will also have an important effect (Andersen et al. 2002, 2004; Svendsen et al.

Communicated by AGUSTIN MERINO.

✉ Václav Pecina
xcpecina@fch.vut.cz

[1] Department of Geology and Soil Science, Faculty of Forestry and Wood Technology, Mendel University in Brno, Zemědělská 3, 61300 Brno, Czech Republic

[2] Department of Forest Botany, Dendrology and Geobiocoenology, Faculty of Forestry and Wood Technology, Mendel University in Brno, Zemědělská 3, 61300 Brno, Czech Republic

[3] Forestry and Game Management Research Institute, Strnady 136, 25202 Jíloviště, Czech Republic

[4] Institute of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 61200 Brno, Czech Republic

2007; Liénard and Colinet 2016; Wieczorek et al. 2018). However, factors such as the carbon-to-nitrogen ratio (C:N) are rarely evaluated in relation to metal mobility in forest soils, despite being one of the most important OM quality indicators. Metal-specific interactions with OM components affect their behaviour in soil, with lead (Pb) and copper (Cu), for example, having a greater affinity to fractions with a high molecular mass, causing them to accumulate predominantly in humus-rich topsoil. Owing to its strong bonding to OM, therefore, Pb mobility is reduced (Probst et al. 2003; Ruan et al. 2008). In comparison, zinc (Zn) and cadmium (Cd) migrate together with soluble organic fractions of medium molecular weight, allowing them to penetrate more easily into the deeper soil layers (Hernandez et al. 2003; Li et al. 2009). In general, conventional metals can be arranged depending on their mobility in forest soils as follows: Zn > Cd > Cu > Pb (Borůvka et al. 2015).

Owing to their greater overall leaf area (Fang et al. 2019; Andronikov et al. 2021) and their evergreen nature, conifers intercept more atmospheric gaseous and dust pollution per year than deciduous broadleaves (de Schrijver et al. 2007). Several studies have addressed this issue by comparing Norway spruce (*Picea abies* (L.) H. Karst.) and European beech (*Fagus sylvatica* L.), these being two of the most important tree species in Europe (Bosela et al. 2021; Vacek et al. 2021). The substances captured more efficiently in spruce stands are then flushed into the soil by precipitation (Vannier et al. 1993; Augusto et al. 2002), resulting in increased throughfall deposition of contaminants (e.g. S and N compounds) compared with beech stands (Rothe et al. 2002; Berger et al. 2008; Andronikov et al. 2021). In addition to deposition-related contaminant levels, tree species can also influence other soil properties and processes, with leaching of N and S compounds generally being higher in spruce stands and pH and OM decomposition being lower (Rothe et al. 2002; Andersen et al. 2004; Berger and Berger 2012). While the vertical distribution of C has been shown to differ between beech and spruce forests (Ransedokken et al. 2019), the influence of beech and spruce forests on the content and vertical distribution of metals in forest soil in general has still not been sufficiently described. In most related studies, the conclusions are insufficiently supported statistically, they draw conclusions based on few samples or sites and they either fail to describe sufficiently or homogenise forest stand conditions.

The intention of this study, therefore, is to address these weaknesses by providing a reliable methodology for assessing the influence of spruce and beech on the vertical distribution of Cd, Cu, Pb and Zn in forest soils. Comparing these species, we hypothesise that (1) metal accumulation will be higher in the OM-rich organic F + H horizons and topsoil of beech stands despite the lower deposition potential and (2) metal enrichment will be increased in deeper soil layers of spruce stands due to spruce-related acidification and increased metal mobility. The study is part of a research project focused on the influence of beech and spruce on metals in forest soils. The aim of the project is to understand the effect of the species on the accumulation and redistribution of metals in forest environment regarding their toxicity-related long-term threat to humans and forest biota. This study complements the already published studies on content of Cd, Cu, Pb and Zn in surface horizons of forest soils (Novotný et al. 2021), pollution of forest soils and edible mushrooms with these metals (Pecina et al. 2022) and vertical distribution of Hg in forest soils and it´s transfer to edible mushrooms (Pecina et al. 2021).

Material and methods

Study area

This study was carried out in the Jeseníky Mountains in the Czech Republic (Fig. 1), a region marginally affected by long-term atmospheric deposition of metals from heavy industry (Novák et al. 2003; Zapletal et al. 2007; ČHMÚ 2022a, 2022b). The region has an average annual precipitation of 810 mm and a mean annual temperature of 7.8 °C (1989–2019; CHMI 2021a). The study sites themselves (see below) were located at altitudes of 587–990 m. They had mainly northern exposure (Novotný et al. 2021), similar climate conditions defined by the conditions of the region and comparable levels of atmospheric deposition (available data for $Cd = 0.3–0.6\ ng/m^3$ and $Pb = 5.1–5.5\ ng/m^3$; CHMI 2021b) without extreme deviations. Furthermore, based on a preliminary field survey, all study sites had a similar geology with the parent rock consisting of acidic metamorphic rocks (phyllites and gneiss). Forest stands in the area are dominated by spruce and beech. They were mostly established as man-made even-aged monocultures and due to long-term intensive commercial cultivation, spruce stands occur across the entire altitudinal gradient of the study.

Sampling design

Six beech- and six spruce-dominated (representation > 80%), even-aged (80–100-years-old) stands of > 1 ha were selected for soil sampling. Soil samples were collected at seven plots distributed over a hexagonal design (Fig. 1D) in each stand. For each plot, we obtained composite soil samples comprising individual samples from three soil pits spaced 4–8 m from each other, each soil pit being situated under the projection of different tree. In each case, samples were taken from the F + H organic layer and from different depths in the mineral layers (i.e. 0–2, 2–10, 10–20, and 20–30 cm) and

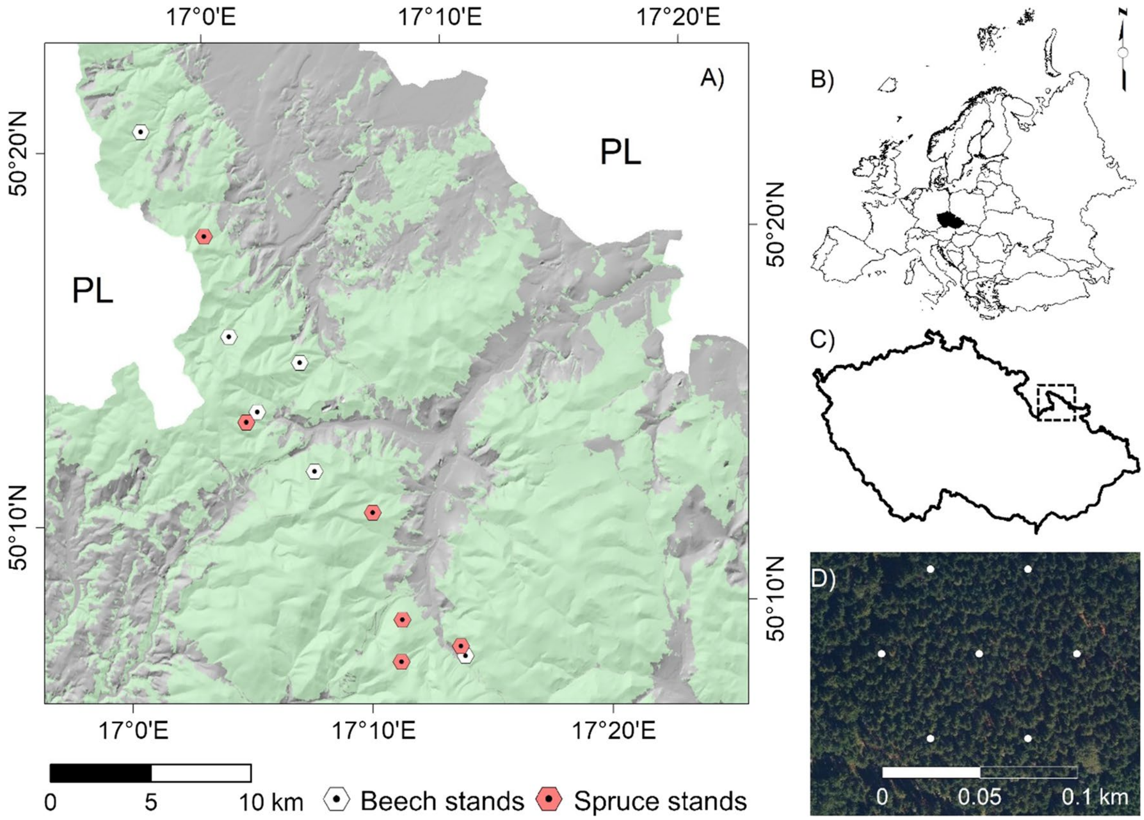

Fig. 1 **A** Study area in the Jeseníky Mountains, northern Czech Republic, with sampling sites indicated on the background layer derived from regional forest development plans (forest areas in green), based on a digital shading model of the Czech Republic; PL = Poland; **B** location of the Czech Republic within Europe; **C** location of the study area in the Czech Republic; **D** example of sampling design within a forest stand

then placed into labelled polyethylene bags. Overall, a total of 420 composite soil samples were collected from 84 plots.

To prevent any influence from the surrounding stands, the samples were collected at a minimum distance of 25 m from the edge of the stand being investigated. Likewise, to prevent any distortion of the results through local contamination, sites situated near potential sources of pollution (e.g. roads, mines, built-up areas) and sites visibly affected by surface erosion were eliminated from sampling during a preliminary field survey.

Sample preparation and laboratory analysis

All samples were dried at room temperature and then processed into a fine fraction (< 2 mm; ČSN ISO 11464), with organic soil samples being further ground to dust in a ball mill for metal content analyses. Subsequently, each sample was analysed for soil properties characterising quantity (C, N and S) and quality (pH and C:N) of OM (Cools et al. 2014).

A suspension of both mineral and organic soil in water (1:5 ratio) was used to measure pH, while total C and N content was determined using a VarioMAX CNS elementary analyser (Elementar Analysensysteme GmbH, Germany), following standard method ČSN ISO 10694. In mineral soil samples, the texture of the main grain fractions was determined according to USDA standards by dry sieving and pipette analysis (Burt 2004).

For metal contents (Cd, Cu, Pb and Zn) analysis, the pre-prepared soil samples were digested in aqua regia (HNO_3 and HCl at a ratio of 1:3) in an ETHOS EASY microwave digestion device (Milestone, Italy). After digestion, the samples were quantitatively transferred using Milli-Q water (Merck, Germany) to a volume of 25 ml. The concentration of elements in the digested sample was measured using a ContrAA 800D atomic absorption spectrophotometer (Analytik Jena, Germany) with a continuous source of radiation (Xe lamp), a high-resolution monochromator and an optical system based on a high-resolution Echelle monochromator and a sensitive charge coupled device (CCD) detector. Content of Cd, Cu and Pb was determined using the electrothermal atomiser (ET-AAS) method, while Zn content was determined using the dual flame system (FAAS) method. All measurements were controlled using blanks, triplicate measurements and matrix reference materials, i.e. METRANAL

31 (light sandy soil), METRANAL 33 (clay loam soil) and METRANAL 34 (loamy soil) (Analytika, Czech Republic). The detection limits for Cd, Cu, Pb and Zn were 0.003, 0.012, 0.033 and 0.007 mg/kg, respectively.

Statistical analysis

Linear mixed models were constructed using the 'lme4' package (Bates et al. 2015) in the R software package v.4.0.5 (R Core Team 2021). To enable direct comparison of model regression coefficients, soil data were centred and standardised to unit variance prior to analysis. Model assumptions were assessed by visual inspection of model residuals. The validity of the fixed effect terms was assessed based on the likelihood ratio (LR) test. The F-value statistics for fixed effects were used to select among competing models. All statistical differences were considered significant at $p < 0.05$. To assess the separate effect of tree species on metal contents, tree-species identity was introduced as the factor variable of fixed effects, and sample plot ID was used as the factor variable of random effects for each separate model of different soil layers. Random effect covered site-specific differences enabling the interaction of many factors, such as topography or atmospheric deposition. In contrast, for comparing metal contents between different soil layers, sample plot ID was introduced as a factor variable of random effects and the soil layer identity was used as the factor variable of fixed effects. The multiple comparisons between soil layers were further assessed with Tukey's post-hoc test using the *glht* function in the R 'multcomp' package (Hothorn et al. 2008). To identify reliable predictors of metal contents across the study sites in specific soil layers, the site ID was used as the factor variable of random effects and the independent soil variables such as C, N, and S contents, the C:N ratio, pH, or the proportions of sand, silt, and clay in mineral soil were used as fixed effects in separate competing models. Finally, whenever the interaction between tree-species identity and the explanatory soil variable was significant based on the likelihood test, the interaction term was included into fixed effects of the final model.

Results

Vertical distribution of metals in the soil profile

A significant difference in overall metal content between beech and spruce stands was only confirmed for Zn, with levels being significantly higher in all soil layers in beech stands (Fig. 2). Significant differences in vertical distribution of metals between forest types were observed for Cd and Cu, with no significant differences with increasing profile depth in beech stands but significant accumulation in the F + H horizons compared to mineral soil in spruce stands. Cu showed a significant vertical decline down to 10 cm in spruce stands, after which levels did not change significantly. The vertical distribution of Pb between beech and spruce stands only differed in local maximum levels, with highest values being found in the F + H layer in spruce stands and in the 0–2 cm layer in beech stands. Subsequently, Pb content then decreased gradually to a depth of 20 cm in both forest types. Conversely, lowest Zn content was found in the upper soil profile layers and increased with depth (Fig. 2).

Effect of soil properties on soil profile metal distribution

The vertical distribution of metals was influenced by the various properties found in the individual soil layers (Table 1), especially those linked with the quantity (C, N, S) and quality (pH, C:N) of OM. Quantity of OM had a significant effect on Cd (positive) and Zn (negative) content in the F + H layer, and on Pb (positive) in mineral soil (Table 1), while OM quality affected the content of all metals in the F + H layer, Cu at depths of 0–2 cm (negative effect of C:N) and 20–30 cm (positive effect of pH) in mineral soil, and Zn content throughout the profile (Fig. 2). The physical properties of mineral soil (sand, silt and clay content) were of limited significance for Pb and Zn content, with no effect on Cd or Cu.

The best regression models of metal contents in Table 2 revealed that the marginal R^2 (attributed to the selected soil properties) were often relatively low compared to the conditional R^2 (including random effects). This indicated that the distribution of metals was strongly site-specific (high contribution of random R^2, Table 2). In the F + H layer for Pb and Zn contents and in the 20–30-cm depth for Cu contents, the fixed effects also included the interaction with tree species, as the regression model with explanatory soil variable was significant either for spruce or beech (Table 2). Overall, random effects explained 15.3–26.8%, 36.9–46.8%, 13.3–35% and 44.3–63.6% of the variation in Cd, Cu, Pb and Zn contents, respectively, across all assessed layers. For Cu and Zn, the influence of random effects was greater than that of fixed effects (soil variables) across the soil profile. For Pb, however, the relative importance of random effects decreased continuously with soil depth.

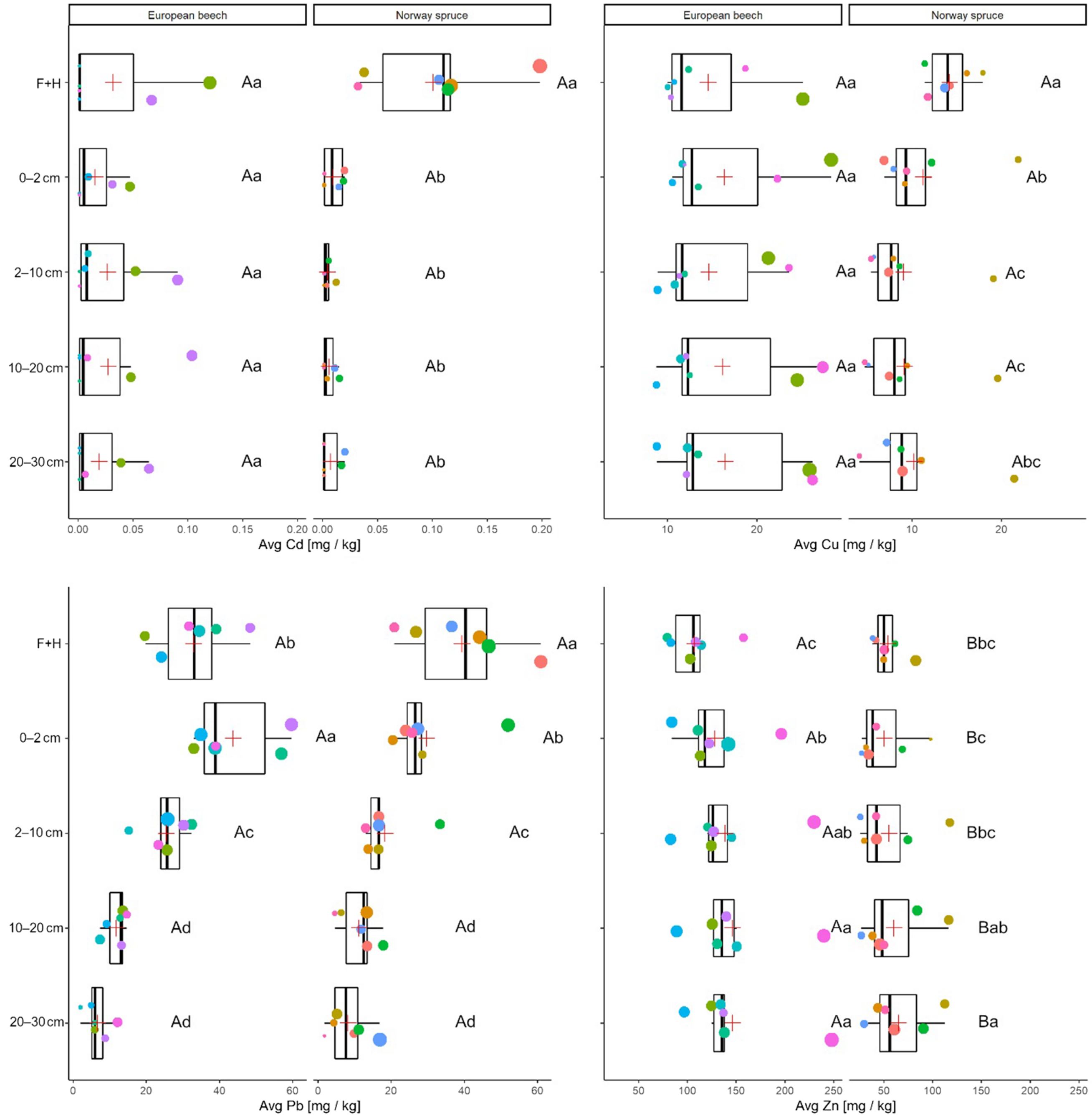

Fig. 2 Vertical distribution of metals in the soil profile. Different uppercase letters indicate significant differences between forest types, while different lowercase letters indicate significant differences between sampling depths within a forest type; boxes represent quartiles, red crosses represent arithmetic means, points represent mean values at a site (differentiated by colour), with point size proportional to the in-site standard deviation ($n = 7$)

Discussion

Metal content depending on soil properties

Cadmium

Both the quantity and quality of OM (Table 1) were shown to affect Cd content in the F + H layer, with the positive correlation of OM quantity and Cd content related to the high affinity of Cd to OM (Andersen et al. 2002; Holm et al. 2003; Kabała and Singh 2006; Luo et al. 2019). However, we could find no published work linking Cd and C:N in forest

Table 1 Regression coefficients of fixed effects in mixed models of metal content and soil properties at different soil depths

Variable	Soil layer	OM content			OM quality		Soil texture		
	(depth in cm)	C	N	S	C:N	pH	Sand	Silt	Clay
Cd	F + H	0.449	0.389	0.417	0.357	– 0.332	*NA*	*NA*	*NA*
	0–2	–	–	–	–	–	–	–	–
	2–10	–	–	–	–	–	–	–	–
	10–20	–	–	–	–	–	–	–	–
	20–30	–	–	–	–	–	–	–	–
Cu	F + H	–	–	–	– 0.331	–	*NA*	*NA*	*NA*
	0–2	–	–	–	– 0.275	–	–	–	–
	2–10	–	0.282	0.270	–	–	–	–	–
	10–20	–	–	0.239	–	–	–	–	–
	20–30	–	–	–	–	0.504	–	–	–
Pb	F + H	–	–	0.515	–	– 0.392	*NA*	*NA*	*NA*
	0–2	0.500	0.539	0.361	–	–	–	–	–
	2–10	0.633	0.672	0.456	–	–	– 0.357	0.359	–
	10–20	0.719	0.743	0.491	–	– 0.335	– 0.388	0.360	–
	20–30	0.493	0.514	0.374	–	– 0.272	–	–	–
Zn	F + H	– 0.402	– 0.187	– 0.184	– 0.453	0.407	*NA*	*NA*	*NA*
	0–2	–	–	–	– 0.341	0.218	–	–	–
	2–10	–	0.143	0.106	– 0.267	0.135	– 0.120	0.138	–
	10–20	–	–	–	– 0.324	0.172	–	–	–
	20–30	–	–	–	– 0.258	0.134	–	–	–

"–" means no valid model with a significant effect, *NA* not applicable

soils, despite a thorough examination of the literature. In our study, the positive correlation between C:N and Cd indicated increasing accumulation of Cd as OM quality decreased, most likely in relation to potential fixation of soil N and deceleration of decomposition (Cools et al. 2014). In such cases, differing levels of metal biosorption are caused by variations in the composition of extracellular polymeric substances (EPS; Yuncu et al. 2006), which in turn is significantly affected by the C:N ratio (Durmaz and Sanin 2001). Furthermore, Yuncu et al. (2006) noted that the affinity of Cd to carboxylic groups in EPS increased as C:N increased, resulting in an increase in Cd biosorption.

The solubility of Cd, and its ability to migrate to lower soil layers, increases as pH decreases (McBride 1989), which is generally expressed as a positive correlation between Cd and pH. The unusual negative correlation between pH and Cd found in the F + H layer in this study (Table 1) may be related to its origin from acidic atmospheric depositions (see "Lead" section).

Copper

Cu content was affected by factors related to the quality and quantity of OM (Table 1). Strong absorption of Cu by OM has been confirmed by several studies (e.g. Bruemmer et al. 1986; Kabata-Pendias and Mukherjee 2007). In the present study, Cu content in OM-rich layers (F + H and 0–2 cm) was explained and negatively correlated with the C:N ratio (Table 1, Fig. S1). Wang et al. (2019) showed that the negative correlation of Cu with C:N in forest soils was caused by immobilisation of Cu as the level of OM decomposition increased, while Yuncu et al. (2006) explained the increase in Cu biosorption as C:N declined as being due to the affinity of Cu to amine groups in EPS. This was also confirmed by Andersen et al. (2004), who stated that spruce stands, which have a significantly higher C:N ratio, and consequently a lower degree of OM decomposition (Cools et al. 2014), have a significantly greater ability to increase Cu solubility than beech stands.

The content of Cu at depths > 2 cm in mineral soil was also explained, though to a lesser degree, by the quantity of OM ($R^2 = 6–7\%$ for S) and pH ($R^2 = 9\%$, Table 2). However, based on the low Cu content and low coefficient of determination for covariates, we consider the impact of these factors on Cu content in mineral soils as negligible.

Lead

Content of Pb in the F + H layer was best explained by the content of S and the pH value (Table 1). The significance of S and pH in the F + H layer contrasts with previous studies showing a determining relationship between Pb and OM (Egli et al. 1999; Kushwaha et al. 2018). Owing to the naturally low content of Pb and Cd in most mineral

Table 2 The best models for metal content as a response variable, with selected independent soil variables (covariates) as fixed effects

Variable	Soil layer	Fixed effects						R^{2} [b]	
	(depth in cm)	Variable[a]	Coefficient Estimate	Std.Error	p-value	F-value	p-value	Marginal	Conditional
Cd	F + H	C	0.449	0.095	9.62e–06 ***	22.24	8.81e–06***	0.21	0.37
	0–2	–	–	–	–	–	–	–	–
	2–10	–	–	–	–	–	–	–	–
	10–20	–	–	–	–	–	–	–	–
	20–30	–	–	–	–	–	–	–	–
Cu	F + H	C:N	− 0.331	0.126	0.0106*	6.90	0.0113*	0.10	0.43
	0–2	C:N	− 0.275	0.125	0.032*	4.82	0.0405*	0.08	0.46
	2–10	S	0.270	0.094	0.00548**	8.14	0.0050**	0.07	0.55
	10–20	S	0.239	0.107	0.0284*	4.98	0.0276*	0.06	0.51
	20–30	pH (spruce)	0.504	0.173	0.00467**	4.34	0.0151*	0.09	0.46
		pH (beech)	–	–	n.s				
Pb	F + H	S (spruce)	0.515	0.124	8.27e–05***	8.82	0.0003***	0.11	0.56
		S (beech)	–	–	n.s				
	0–2	C	0.500	0.079	1.57e–08 ***	39.6	1.04e–08 ***	0.27	0.61
	2–10	C	0.633	0.086	1.20e–10***	54.4	8.80e–11 ***	0.39	0.59
	10–20	C	0.719	0.096	9.01e–11***	56.3	8.75e–11 ***	0.44	0.58
	20–30	N	0.514	0.113	3.52e–05***	20.8	1.50e–05 ***	0.25	0.38
Zn	F + H	C (spruce)	–	–	n.s	19.30	9.40e–08***	0.09	0.86
		C (beech)	− 0.402	0.067	1.99e–07***				
	0–2	C:N	− 0.341	0.074	1.36e–05***	21.4	2.37e–05***	0.17	0.81
	2–10	C:N	− 0.267	0.062	4.91e–05***	18.5	5.21e–05***	0.10	0.87
	10–20	C:N	− 0.324	0.069	9.93e–06***	22.2	1.20e–05***	0.15	0.85
	20–30	C:N	− 0.258	0.075	0.0010***	11.8	0.0012**	0.09	0.84

[a] In a few cases, interaction with forest type was used in relation to fixed effects, i.e. whenever model performance was significantly improved based on the LR test. [b] The proportions of variance explained by fixed effects (marginal R^2) and by the whole model (conditional R^2) are provided for each soil layer

soils (Kabata-Pendias and Mukherjee 2007), which was also confirmed in this study, one can assume an almost exclusively anthropogenic origin via S-rich acidic atmospheric deposition (ČHMÚ 2022a, 2022b). This is also supported by i) their close relationship in the F + H layer (Fig. S2), and ii) the positive correlation of Pb and Cd to S in the F + H layer (Table 1) which, for Pb, prevailed throughout the profile. This relationship was not observed for Cd in mineral soils, probably because of a high number of samples below the detection limit. Thus, the significant negative relationship between Pb and pH in the F + H layer may directly indicate a more decisive effect of acidic deposition load than OM-related biogeochemical processes. In contrast, a more balanced influence of these factors may be expected for Cd. In mineral soil, the significant impact of OM quantity ($R^2 = 27-44\%$ for C, $R^2 = 25\%$ for N; Table 2) predominated, in compliance with previous studies that have shown heavy absorption of Pb by OM (Bruemmer et al. 1986; Kushwaha et al. 2018).

Zinc

Content of Zn in the F + H layer was best explained by both the quality and quantity of OM, and almost exclusively by the C:N ratio and pH value in mineral soil (Table 1). The negative correlation between Zn and C, N, S and C:N in the F + H layer, and the negative correlation between Zn and the key explanatory variable C:N in mineral soil (Table 2), despite the high affinity of metals to OM, indicates that Zn content is not primarily affected by its affinity to OM but by pH, with which Zn correlates positively (Table 2, Fig. S2). While unusual, the more significant effect of OM quantity and C:N to the detriment of pH (Hernandez et al. 2003) in mineral soil is probably an expression of the well-known negative correlation between pH and C:N (Cools et al. 2014), also evident from PCA (Fig. S2). Yuncu et al. (2006) also noted that Zn biosorption displayed no increasing or decreasing trend with C:N.

Based on the predominantly low pH observed in this study (Fig. S1), and the known dominant effect of pH on Zn mobility in the soil (Hernandez et al. 2003), we suggest that pH is the crucial factor influencing Zn distribution. In an acidic environment, which in this study was represented especially by the upper soil horizons, these being the main recipients of atmospheric deposition (Andronikov et al. 2021), Zn is converted into an exchangeable form that is highly soluble and can migrate to lower layers in the soil profile more quickly (Billett et al. 1991; Hernandez et al. 2003; McLaren et al. 2004; Chrastný et al. 2012), where its migration is slowed by increasing pH, causing its gradual accumulation (Figs. 2 and S1). This is also confirmed by Hernandez et al. (2003), who reported an increase in Zn content with increasing depth. Other contributors to this phenomenon may include i) accelerated transport of highly mobile Zn from the strongly acidic topsoil through washout by heavy rain (Svendsen et al. 2007), ii) effective competition between Pb and Cu with Zn, which has lower affinity to OM, leading to its displacement and mobilisation (Svendsen et al. 2007), and iii) lowered emission inputs over recent years. In the case of variant iii, there would be no accumulation of Zn in the upper OM-rich horizons, as recorded by Svendsen et al. (2007) at a site very close to acute source of pollution. However, Pecina et al. (2022) found high Zn and Cd contents in mushrooms in our study area and linked this with precipitation-related atmospheric deposition and the high mobility and bioavailability of these metals. Consequently, we suggest that the low atmospheric deposition of highly mobile Cd in our study area (0.2–0.3 ng.m^{-3}/5 years; 2016–2020; ČHMÚ 2022b) is probably almost completely absorbed by mushrooms or plants, while the higher deposition of Zn (Andronikov et al. 2021) probably allows for both its absorption (Pecina et al. 2022) and mobility into the deeper soil layers (Fig. 2).

The influence of beech and spruce on vertical distribution of metals in the soil profile

Despite it being generally accepted that metal contents tend to be higher in coniferous stands (Andersen et al. 2004), we were only able to confirm a significant impact of forest composition on content of Zn with higher values in beech stands (Fig. 2). Therefore, hypothesis 1 was confirmed only for this metal. The impact of C content of beech stands in the F + H layer (Table 2) was unlikely to be the primary factor determining Zn distribution in the soil, rather it was an expression of the negative correlation with pH value, which was also evident from PCA (Fig. S2). The lower Zn content recorded in spruce stands (as opposed to beech stands), despite higher Zn throughfall in conifers (Andronikov et al. 2021), was most likely caused by i) higher Zn solubility and mobility resulting from a lower soil pH (Sect. 4.1, Fig. S1), and ii) absorption of mobilised Zn by living organisms.

The absence of any significant difference between Cd and Cu contents (Fig. 2) was probably affected by the scale of the assessed area, which enabled the interaction of many uncontrolled factors, such as topography, atmospheric deposition or microclimate conditions. In the case of Cd, Cu and Zn, the contribution of site identity was even higher than the effect of explanatory soil variables, as suggested by the difference between fixed and random effects (Table 2), while the role of site-specific differences apparently declined in deeper soil layers for Pb. Varying natural conditions may have had a considerable influence on the process of OM accumulation and decomposition, i.e. the quality and quantity of OM (Coûteaux et al. 1995; Prescott and Grayston 2013), which has a direct impact on metal content in OM-rich horizons (Andersen et al. 2004).

The significant impact of tree species on metal content was also evident in their differing vertical distribution, particularly the contrasting accumulation of Cd, Cu and Pb in the F + H layer in spruce stands (Fig. 2). This differentiating effect of spruce on the accumulation of metals, which has been confirmed by other studies (Andersen et al. 2002, 2004; Svendsen et al. 2007), results especially from its ability to capture atmospheric pollution more effectively on an assimilation apparatus (Rothe et al. 2002). This was also indicated by the significantly higher content of S in the F + H layer in spruce stands (Fig. S1). Zapletal et al. (2007) were able to show that spruce stands enable wash out and foliar leaching of SO_4 from atmospheric deposition of industrial pollutants, the primary source of S and metal deposition in the Jeseníky Mountains (Novák et al. 2003; Zapletal 2012). The exclusively spruce-related significant effect of S as the main explanatory variable of Pb content in the F + H layer (Table 2) confirms the supposition of a dominant anthropogenic origin, as well as the importance of the interaction between spruce and atmospheric deposition. Spruce stands also influence soil metal content through slow decomposition of litter, which then accumulates (Berger and Berger 2012), leading to a significantly higher C content in the F + H layer and reduced variability in the C:N ratio (generally higher than in beech stands; Fig. S1), a factor affecting the biosorption of Cd, Cu and Pb (Yuncu et al. 2006). However, this phenomenon seems to be significant only for the distribution of metals in the soils of spruce stands; it is not decisive for their total content in the studied scale of soil profile compared to beech stands as already partially mentioned and hypothesised (hypothesis 1). Accordingly, the second hypothesis is rejected. If increased metal enrichment in deeper soil layers of spruce stands due to spruce-related acidification and related metal mobility occurs, then at depths greater than 30 cm.

Increased accumulation of Pb in OM-enriched mineral soil horizons (0−2 cm) provided a clear example of the effect of beech stands on the mobility of metals (Fig. 2). This can be explained by either i) decomposition of metal-absorbing OM and its reabsorption as a solid phase, ii) the varying intensity of OM decomposition in OM-enriched horizons, or iii) washout by heavy rain (Svendsen et al. 2007). Similar conclusions were reached by Novotný et al. (2021), who explained the higher content of Pb in OM-enriched mineral soil horizons under beech stands as Pb being released from F + H layers as a result of more rapid OM mineralisation.

Conclusion

In this regional-scale evaluation of metals distribution in soil, we showed that Cd and Cu content in OM-rich horizons is directly linked to the intensity of OM decomposition (represented by C:N), regardless of forest type. Decomposition of OM is mainly driven by heterogenous environmental conditions, which were partly controlled in our models by the random effects. As the level of OM decomposition increased, Cd content decreased and Cu content increased. Content of Pb, on the other hand, was influenced by S, pH and random effects, regardless of forest type, indicating that atmospheric deposition was a primary factor affecting Pb content in soil, rather than OM-related biogeochemical processes. Zn was the only metal whose content was significantly affected by forest type, with Zn mobility being reduced and affinity to OM increased as a result of the higher pH under the beech stands, leading to accumulation of Zn downward in the soil profile. Despite only having unambiguous evidence for Zn, stands dominated by beech or spruce clearly had a differing influence on the distribution of metals in all cases.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10342-022-01519-8.

Acknowledgements This research was financially supported through the Technology Agency of the Czech Republic under Project TJ02000128; the Ministry of Education, Youth and Sports of the Czech Republic under Project FCH-S-22-8001; and the Ministry of Agriculture of the Czech Republic, under Institutional Support MZE-RO0118. The authors are grateful to Dagmar Obšilová and Ivana Kušnierová, Petr Rolinc, †Petr Skočdopole and the 'Arcibiskupské lesy a statky (Archbishop's Forests and Estates) Olomouc s.r.o.' for providing information and enabling research within their lands.

Author contributions D.J.: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft. M.V.: Software, Visualization, Data curation, Writing – review & editing. R.N.: Conceptualization, Funding acquisition, Supervision, Investigation, Project administration, Writing – review & editing. R.K.: Supervision, Investigation, Resources, Writing – review & editing. J.Č.: Investigation, Methodology, Writing - review & editing. V.P.: Conceptualization, Writing – original draft, Investigation, Methodology, Validation, Project administration, Funding acquisition.

Declarations

Competing interests The authors declare no competing interests.

References

Andersen MK, Refsgaard A, Raulund-Rasmussen K, Strobel BW, Hansen HCB (2002) Content, distribution, and solubility of cadmium in Arable and forest soils. Soil Sci Soc Am J 66:1829. https://doi.org/10.2136/sssaj2002.1829

Andersen MK, Raulund-Rasmussen K, Strobel BW, Hansen HCB (2004) The effects of tree species and site on the solubility of Cd, Cu, Ni, Pb and Zn in soils. Water Air Soil Pollut 154:357–370. https://doi.org/10.1023/B:WATE.0000022991.59456.01

Andronikov AV, Novak M, Oulehle F, Chrastny V, Sebek O, Andronikova IE, Stepanova M, Sipkova A, Hruska J, Myska O, Chuman T, Veselovsky F, Curik J, Prechova E, Komarek A (2021) Catchment runoff in industrial areas exports legacy pollutant zinc from the topsoil rather than geogenic Zn. Environ Sci Technol 55:8035–8044. https://doi.org/10.1021/acs.est.1c01167

Augusto L, Bonnaud P, Ranger J (1998) Impact of tree species on forest soil acidification. For Ecol Manage 105(1–3):67–78. https://doi.org/10.1016/S0378-1127(97)00270-3

Augusto L, Ranger J, Binkley D, Rothe A (2002) Impact of several common tree species of European temperate forests on soil fertility. Ann for Sci 59:233–253. https://doi.org/10.1051/forest:2002020

Augusto L, de Schrijver A, Vesterdal L, Smolander A, Prescott C, Ranger J (2015) Influences of evergreen gymnosperm and deciduous angiosperm tree species on the functioning of temperate and boreal forests. Biol Rev 90:444–466. https://doi.org/10.1111/brv.12119

Bai Y, Zhou Y, An Z, Du J, Zhang X, Chang SX (2022) Tree species identity and mixing ratio affected several metallic elements release from mixed litter in coniferous-broadleaf plantations in subtropical China. Sci Total Environ. https://doi.org/10.1016/j.scitotenv.2022.156143

Bates D, Mächler M, Bolker B, Walker S (2015) Fitting linear mixed-effects models using lme4. J Stat Softw 67(1): 1–48. https://doi.org/10.18637/jss.v067.i01

Berger TW, Berger P (2012) Greater accumulation of litter in spruce (*Picea abies*) compared to beech (*Fagus sylvatica*) stands is not a consequence of the inherent recalcitrance of needles. Plant Soil 358:349–369. https://doi.org/10.1007/s11104-012-1165-z

Berger TW, Untersteiner H, Schume H, Jost G (2008) Throughfall fluxes in a secondary spruce (*Picea abies*), a beech (*Fagus sylvatica*) and a mixed spruce-beech stand. For Ecol Manag 255:605–618. https://doi.org/10.1016/j.foreco.2007.09.030

Billett MF, Fitzpatrick EA, Cresser MS (1991) Long-term changes in the Cu, Pb, and Zn content of forest soil organic horizons from North-East Scotland. Water Air Soil Pollut 59:179–191. https://doi.org/10.1007/BF00283180

Borůvka L, Sáňka M, Šrámek V, Vácha R, Čechmánková J, Čupr P, Drábek O, Fadrhonsová V, Fraňková A, Hofman J Houška J (2015) Metodika hodnocení kontaminace lesních půd (Forest soil contamination assessment methodology). Certifikovaná metodika. Strnady, Výzkumný ústav lesního hospodářství a myslivosti. (in Czech)

Bosela M, Tumajer J, Cienciala E, Dobor L, Kulla L, Marčiš P, Popa I, Sedmák R, Sedmáková D, Sitko R, Šebeň V, Štěpánek P, Büntgen U (2021) Climate warming induced synchronous growth decline in Norway spruce populations across biogeographical gradients since 2000. Sci Total Environ 752:141794. https://doi.org/10.1016/j.scitotenv.2020.141794

Bruemmer GW, Gerth J, Herms U (1986) Heavy metal species, mobility and availability in soils. Zeitschrift Für Pflanzenernährung Und Bodenkunde 149:382–398. https://doi.org/10.1002/jpln.19861490404

Burt R (2004) Soil Survey Investigation Report No. 42. USDA

CHMI (2021a). Denní data dle zákona 123/1998 Sb (Daily dates according to law 123/1998 Sb). [WWW Document]. Czech Hydrometeorological Institute. (in Czech) URL https://www.chmi.cz/historicka-data/pocasi/denni-data/Denni-data-dle-z.-123-1998-Sb

CHMI (2021b). Průměrné koncentrace za roky 2016–2020: Olomoucký kraj (Average concentrations for the years 2016–2020: Olomouc Region). [WWW Document]. Czech Hydrometeorological Institute. (in Czech) URL https://www.chmi.cz/files/portal/docs/uoco/isko/ozko/20petileti/png/olomoucky_CZ.html

ČHMÚ (2022a). Pětiletý průměr 2016–2022a. Olovo roční průměr (Lead annual average). [WWW Document]. Czech Hydrometeorological Institute. (in Czech) URL https://www.chmi.cz/files/portal/docs/uoco/isko/ozko/20petileti/png/Pb/20Pb_regM.png

ČHMÚ (2022b) Pětilený průměr 2016–2020. Kadmium roční průměr (Cadmium annual average). [WWW Document]. Czech Hydrometeorological Institute. (in Czech) URL https://www.chmi.cz/files/portal/docs/uoco/isko/ozko/20petileti/png/Cd/20Cd_regM.png

Chrastný V, Vaněk A, Teper L, Cabala J, Procházka J, Pechar L, Drahota P, Penížek V, Komárek M, Novák M (2012) Geochemical position of Pb, Zn and Cd in soils near the Olkusz mine/smelter, South Poland: effects of land use, type of contamination and distance from pollution source. Environ Monit Assess 184:2517–2536. https://doi.org/10.1007/s10661-011-2135-2

Cools N, Vesterdal L, de Vos B, Vanguelova E, Hansen K (2014) Tree species is the major factor explaining C: N ratios in European forest soils. For Ecol Manage 311:3–16. https://doi.org/10.1016/j.foreco.2013.06.047

Coûteaux M-M, Bottner P, Berg B (1995) Litter decomposition, climate and litter quality. Trends Ecol Evol 10:63–66. https://doi.org/10.1016/S0169-5347(00)88978-8

de Schrijver A, Geudens G, Augusto L, Staelens J, Mertens J, Wuyts K, Gielis L, Verheyen K (2007) The effect of forest type on throughfall deposition and seepage flux: a review. Oecologia 153:663–674. https://doi.org/10.1007/s00442-007-0776-1

Durmaz B, Sanin FD (2001) Effect of carbon to nitrogen ratio on the composition of microbial extracellular polymers in activated sludge. Water Sci Technol 44:221–229. https://doi.org/10.2166/wst.2001.0626

Egli M, Fitze P, Oswald M (1999) Changes in heavy metal contents in an acidic forest soil affected by depletion of soil organic matter within the time span 1969–93. Environ Pollut 105:367–379. https://doi.org/10.1016/S0269-7491(99)00040-8

Fang H, Baret F, Plummer S, Schaepman-Strub G (2019) An overview of global leaf area index (LAI): methods, products, validation, and applications. Rev Geophys 57:739–799. https://doi.org/10.1029/2018RG000608

Frey B, Stemmer M, Widmer F, Luster J, Sperisen C (2006) Microbial activity and community structure of a soil after heavy metal contamination in a model forest ecosystem. Soil Biol Biochem 38:1745–1756. https://doi.org/10.1016/j.soilbio.2005.11.032

Helmisaari H-S, Derome J, Fritze H, Nieminen T, Palmgren K, Salemaa M, Vanha-Majamaa I (1995) Copper in Scots pine forests around a heavy-metal smelter in south-western Finland. Water Air Soil Pollut 85:1727–1732. https://doi.org/10.1007/BF00477229

Hernandez L, Probst A, Probst JL, Ulrich E (2003) Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Sci Total Environ 312:195–219. https://doi.org/10.1016/S0048-9697(03)00223-7

Holm PE, Rootzén H, Borggaard OK, Møberg JP, Christensen TH (2003) Correlation of cadmium distribution coefficients to soil characteristics. J Environ Qual 32:138–145. https://doi.org/10.2134/jeq2003.1380

Hothorn T, Bretz F, Westfall P (2008) Simultaneous inference in general parametric models. Biom J 50:346–363. https://doi.org/10.1002/bimj.200810425

Kabała C, Singh BR (2006) Distribution and forms of cadmium in soils near a copper smelter. Pol J Environ Stud 15:90–97

Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, Berlin. https://doi.org/10.1007/978-3-540-32714-1

Kandziora-Ciupa M, Ciepał R, Nadgórska-Socha A, Barczyk G (2016) Accumulation of heavy metals and antioxidant responses in *Pinus sylvestris* L. needles in polluted and non-polluted sites. Ecotoxicology 25:970–981. https://doi.org/10.1007/s10646-016-1654-6

Kelly JJ, Häggblom MM, Tate RL (2003) Effects of heavy metal contamination and remediation on soil microbial communities in the vicinity of a zinc smelter as indicated by analysis of microbial community phospholipid fatty acid profiles. Biol Fertil Soils 38:65–71. https://doi.org/10.1007/s00374-003-0642-1

Kushwaha A, Hans N, Kumar S, Rani R (2018) A critical review on speciation, mobilization and toxicity of lead in soil-microbe-plant system and bioremediation strategies. Ecotoxicol Environ Saf 147:1035–1045. https://doi.org/10.1016/j.ecoenv.2017.09.049

Li F, Fan Z, Xiao P, Oh K, Ma X, Hou W (2009) Contamination, chemical speciation and vertical distribution of heavy metals in soils of an old and large industrial zone in Northeast China. Environ Geol 57:1815–1823. https://doi.org/10.1007/s00254-008-1469-8

Liénard A, Colinet G (2016) Assessment of vertical contamination of Cd, Pb and Zn in soils around a former ore smelter in Wallonia. Belgium Environ Earth Sci. https://doi.org/10.1007/s12665-016-6137-9

Luo K, Liu H, Zhao Z, Long J, Li J, Jiang C, Rao C (2019) Spatial distribution and migration of cadmium in contaminated soils associated with a geochemical anomaly: a case study in Southwestern China. Pol J Environ Stud 28:3799–3807. https://doi.org/10.15244/pjoes/94847

McBride MB (1989) Reactions controlling heavy metal solubility in soils. Springer, New York, pp 1–56. https://doi.org/10.1007/978-1-4613-8847-0_1

McLaren RG, Clucas LM, Taylor MD, Hendry T (2004) Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge 2 leaching of metals. Soil Research 42(4):459. https://doi.org/10.1071/SR03168

Mihaljevič M, Ettler V, Šebek O, Drahota P, Strnad L, Procházka R, Zeman J, Sracek O (2010) Alteration of arsenopyrite in soils under different vegetation covers. Sci Total Environ 408:1286–1294. https://doi.org/10.1016/j.scitotenv.2009.12.003

Novák M, Emmanuel S, Vile MA, Erel Y, Véron A, Pačes T, Wieder RK, Vaněček M, Štěpánová M, Břízová E, Hovorka J (2003) Origin of lead in eight central european peat bogs determined from isotope ratios, strengths, and operation times of regional pollution sources. Environ Sci Technol 37:437–445. https://doi.org/10.1021/es0200387

Novotný R, Buriánek V, Šrámek V, Hunová I, Skorepová I, Zapletal M, Lomský B (2017) Nitrogen deposition and its impact on forest ecosystems in the Czech Republic–change in soil chemistry and ground vegetation. iForest Biogeosci for 10:48–54. https://doi.org/10.3832/ifor1847-009

Novotný R, Pecina V, Černý J, Valtera M, Juřička D (2021) Influence of Norway spruce and European beech on Cd, Cu, Pb and Zn content in the surface horizons of forest soils in the area of the Jeseníky Mountains. Zprávy Lesnického Výzkumu 66:86–94

Pecina V, Valtera M, Trávníčková G, Komendová R, Novotný R, Brtnický M, Juřička D (2021) Vertical Distribution of Mercury in

Forest Soils and Its Transfer to Edible Mushrooms in Relation to Tree Species. Forests 12:539. https://doi.org/10.3390/f12050539

Pecina V, Valtera M, Drápela K, Novotný R, Vahalík P, Komendová R, Brtnický M, Juřička D (2022) Influence of beech and spruce on potentially toxic elements-related health risk of edible mushrooms growing on unpolluted forest soils. Sci Rep 12:5407. https://doi.org/10.1038/s41598-022-09400-9

Prescott CE, Grayston SJ (2013) Tree species influence on microbial communities in litter and soil: current knowledge and research needs. For Ecol Manage 309:19–27. https://doi.org/10.1016/j.foreco.2013.02.034

Probst A, Hernandez L, Probst JL (2003) Heavy metals partitioning in three French forest soils by sequential extraction procedure. Journal De Physique IV (proceedings) 107:1103–1106. https://doi.org/10.1051/jp4:20030493

Ransedokken Y, Asplund J, Ohlson M, Nybakken L (2019) Vertical distribution of soil carbon in boreal forest under European beech and Norway spruce. Eur J Forest Res 138(2):353–361. https://doi.org/10.1007/s10342-019-01176-4

R Core Team (2021) R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria

Römkens PFAM, Salomons W (1998) Cd, Cu and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. Soil Sci 163:859–871. https://doi.org/10.1097/00010694-199811000-00003

Rothe A, Huber C, Kreutzer K, Weis W (2002) Deposition and soil leaching in stands of Norway spruce and European beech: results from the Höglwald research in comparison with other European case studies. Plant Soil 240:33–45. https://doi.org/10.1023/A:1015846906956

Ruan X-L, Zhang G-L, Ni L-J, HE Y (2008) Distribution and migration of heavy metals in undisturbed forest soils: a high-resolution sampling method. Pedosphere 18:386–393. https://doi.org/10.1016/s1002-0160(08)60029-6

Sucharová J, Suchara I, Hola M, Reimann C, Boyd R, Filzmoser P, Englmaier P (2011) Linking chemical elements in forest floor humus (Oh-horizon) in the Czech Republic to contamination sources. Environ Pollut 159:1205–1214. https://doi.org/10.1016/j.envpol.2011.01.041

Sucharová J, Suchara I, Hola M, Marikova S, Reimann C, Boyd R, Filzmoser P, Englmaier P (2012) Top-/bottom-soil ratios and enrichment factors: What do they really show? Appl Geochem 27:138–145. https://doi.org/10.1016/j.apgeochem.2011.09.025

Svendsen ML, Steinnes E, Blom HA (2007) Vertical and horizontal distributions of Zn, Cd, Pb, Cu, and Hg in uncultivated soil in the vicinity of a zinc smelter at Odda, Norway. Soil and Sediment Contam 16:585–603. https://doi.org/10.1080/15320380701623644

Taiz L, Zeiger E (2010) Plant physiology, 5th edn. Sinauer Associates Inc., Sunderland

Tang X, Wu Y, Lan Z, Han L, Rong X (2021) Analysis of the spatial distribution of heavy metals in an area of farmland in Sichuan province. China Environ Earth Sci 80:321. https://doi.org/10.1007/s12665-021-09612-8

Vacek Z, Prokůpková A, Vacek S, Bulušek D, Šimůnek V, Hájek V, Králíček I (2021) Mixed vs. monospecific mountain forests in response to climate change: structural and growth perspectives of Norway spruce and European beech. For Ecol Manag 488:119019. https://doi.org/10.1016/j.foreco.2021.119019

Vannier C, Didon-Lescot J-F, Lelong F, Guillet B (1993) Distribution of sulphur forms in soils from beech and spruce forests of Mont Lozère (France). Plant Soil 154:197–209. https://doi.org/10.1007/BF00012525

Wang L, Li Y, Prasher SO, Yan B, Ou Y, Cui H, Cui Y (2019) Organic matter, a critical factor to immobilize phosphorus, copper, and zinc during composting under various initial C/N ratios. Biores Technol 289:121745. https://doi.org/10.1016/j.biortech.2019.121745

Wieczorek J, Baran A, Urbański K, Mazurek R, Klimowicz-Pawlas A (2018) Assessment of the pollution and ecological risk of lead and cadmium in soils. Environ Geochem Health 40:2325–2342. https://doi.org/10.1007/s10653-018-0100-5

Yuncu B, Sanin FD, Yetis U (2006) An investigation of heavy metal biosorption in relation to C/N ratio of activated sludge. J Hazard Mater 137:990–997. https://doi.org/10.1016/j.jhazmat.2006.03.020

Zapletal M (2012) Atmospheric deposition of nitrogen and sulphur in relation to critical loads of nitrogen and acidity in the Czech Republic. J for Sci 52:92–100. https://doi.org/10.17221/4490-JFS

Zapletal M, Kuňák D, Chroust P (2007) Chemical characterization of rain and fog water in the Cervenohorske sedlo (Hruby Jesenik Mountains, Czech Republic). Water Air Soil Pollut 186:85–96. https://doi.org/10.1007/s11270-007-9467-0