



An in-depth human health risk assessment of potentially toxic elements in highly polluted riverine soils, Příbram (Czech Republic)

Ndiye M. Kebonye · Peter N. Eze · Kingsley John · Prince C. Agyeman · Karel Němeček · Luboš Borůvka

Received: 25 May 2020 / Accepted: 8 March 2021 / Published online: 19 March 2021
© The Author(s), under exclusive licence to Springer Nature B.V. 2021

Abstract Environmental pollution by potentially toxic element (PTE) and the associated health risks in humans are increasingly becoming a global challenge. The current study is an in-depth assessment of PTEs including the often studied lead (Pb), manganese (Mn), zinc (Zn), arsenic (As) and the less-studied titanium (Ti), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba) and thorium (Th) in highly polluted floodplain topsoil samples from the Litavka River, Czech Republic. Soil chemical properties including carbon (C_{ox}) and reaction (pH_{H_2O}) together with iron (Fe) were assessed in the same soils. A portable X-ray fluorescence spectrometer (p-XRFS) (Delta Premium) was used to measure the PTEs and Fe contents of the soils. Soil organic carbon and reaction pH were determined following routine

laboratory procedures. The concentration level of each PTE was compared against world average and crustal values, with the majority of elements exceeding the aforementioned geochemical background levels. Distributions of the PTEs were mapped. Two pollution assessment indices including enrichment factor (EF) and pollution index (PI) levels were calculated and their means for Zn (43.36, 55.54), As (33.23, 43.59) and Pb (81.08, 103.21) show that these elements were enriched. Zn, As and Pb accounted for the high pollution load index (PLI) levels observed in the study. The EF and PI distribution maps corresponded with the concentration distribution maps for each PTE. On health risk assessment, hazard quotients (HQ) in different human groups varied. Children had the highest HQs for all PTEs than adults (women and men). PTEs with high HQ levels in distinct human groups were As, Zr and Pb. Zirconium is a less likely element to pose a health risk in humans. Nonetheless, it should be kept in check despite its low pollution occurrence.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10653-021-00877-3>.

N. M. Kebonye (✉) · K. John · P. C. Agyeman · K. Němeček · L. Borůvka

Department of Soil Science and Soil Protection, Faculty of Agrobiolgy, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 00 Prague-Suchdol, Prague, Czech Republic
e-mail: kebonye@af.czu.cz

P. N. Eze
Department of Earth and Environmental Science, Botswana International University of Science and Technology, Private Bag 16, Palapye, Botswana

Keywords Riverine soils · Secondary pollution · Potentially toxic elements · Health-risk assessment · Litavka River

Introduction

Soil is a valuable resource that continues to suffer owing to the rapid pollution associated with industrialization and modernization (Gholizadeh et al., 2015). Floodplain or riverine soils to be specific are prone to pollution by potentially toxic elements (PTEs) usually sourced from geogenic and/or anthropogenic sources (Frohne et al., 2014). Despite this, some people continue to use these soils for arable farming because of their high fertility (Rinklebe et al. 2019). The distribution and occurrence of PTEs in floodplain soils are affected by various factors including but not limited to terrain attributes (e.g., slope, elevation), soil physicochemical properties (particle size, carbon, pH), pollution sources (e.g., mining activities, metal smelting) and flooding events/ occurrences (Vaněk et al., 2008). Floodplain soils of the Litavka River, Czech Republic are heavily polluted as a result of combined historic lead-silver (Pb–Ag) mining and smelting activities as well as extreme flooding events that occurred varyingly between the years 1932 and 2002 (Borůvka & Vácha, 2006; Vaněk et al., 2008). According to several authors, this has resulted in secondary pollution of the Litavka River (Kotková et al., 2019; Navrátil et al., 2008; Nováková et al., 2015).

Many studies have assessed various aspects of PTE occurrence around the Litavka River area including their contents, speciation, mobility/migration and distribution (e.g., Borůvka & Drábek, 2004; Borůvka & Vácha, 2006; Borůvka et al., 1996; Dlouhá et al., 2013; Ettler et al., 2006; Kotková et al., 2019; Nováková et al., 2015; Vaněk et al., 2005, 2008). Most PTEs emphasized by these studies have included lead (Pb), cadmium (Cd), zinc (Zn) and arsenic (As). Potentially toxic element interactions with soil properties have been observed by several researchers, for example, a PTE-pH-dependent solubility pattern has been observed at pHs 4 and 10 as well as 5 and 11 in soils (Jalali & Najafi, 2018). Conversely, Romero-Baena et al. (2018) established PTEs absorption by clay fractions and co-precipitation by secondary mineralogical components in surface soils diversely sampled in Spain. Also, the complexations formed between organic and inorganic ligands with PTEs of cationic form plays a key role in their sorption–desorption, availability and toxicity in soils (Violante et al. 2010). According to Choppala et al. (2018), soil

organic matter (SOM) has different functional groups (e.g., carbonyls: C=O, alcohols: –OH) that can retain and reduce soluble chromium (Cr) in soils.

In another study on paddy soils, Cd and Zn enrichment were linked to the organic fraction in soils (Zhou et al., 2018). These properties distinctively play important roles in PTE distribution, behavior and occurrence for various soils (Rinklebe et al., 2019). Potentially toxic elements including rubidium (Rb), strontium (Sr), thorium (Th), titanium (Ti), barium (Ba) and zirconium (Zr) have received marginal attention when it comes to floodplain soils. Similar to the observation made by Rinklebe et al. (2019) concerning floodplain soils at the Elbe River (Germany), there is a dearth of research for the Litavka River floodplain soils especially the least studied PTEs, despite their equal capabilities to pollute as well as pose potential human health risks. Moreover, while considering most studies on human health risk owing to PTE(s) contamination of soils, few studies account for potential human health risks associated with least studied PTEs (e.g., Rb, Sr, Ti, and so on). Conversely, studies on potential human health risk assessment are somewhat limited in the Czech Republic. Again, floodplain soils for example those of the Litavka area belong to the most polluted soils in Europe and thus require detailed assessment and evaluation (Vácha et al., 2016). According to Bambas (1990) and Kotková et al. (2019), the area has polymetallic ore deposits made of Ag-bearing galena (PbS), antimonite (SbS), sphalerite (ZnS) and gangue materials that have continuously been mined until 1972 (Borůvka & Vácha, 2006; Ettler, Johan, et al., 2005; Ettler, Vaněk, et al., 2005). Mining and smelting activities (e.g., waste dumping, rupture of tailing ponds) associated with these deposits would later become an environmental problem (Kotková et al., 2019). Some of these environmental problems included continuous deposition and accumulation of PTEs in topsoils as well as secondary pollution (Žák et al., 2009) of the Litavka River as part of past flooding events (Kotková et al., 2019; Vaněk et al., 2008).

The potential health risks of the least studied PTEs in humans are not well documented on (Rinklebe et al. 2019). Per contra, the spatial variability and distribution of the least studied PTEs are rarely considered in soil studies and more explicitly for floodplain soils; thus, such deficiency asserts the novelty of the current study. This study comprehensively assessed PTE

contents of titanium (Ti), manganese (Mn), arsenic (As), rubidium (Rb), strontium (Sr), zirconium (Zr), barium (Ba), lead (Pb) and thorium (Th), soil chemical properties pH and carbon (C_{ox}) together with iron (Fe) levels for floodplains soils of the Litavka River area. Specific objectives were to: (i) determine selected PTE, Fe, pH and C_{ox} contents in floodplain soils; (ii) estimate PTE pollution levels using the indices of enrichment factor (EF), pollution index (PI) and pollution load index (PLI); (iii) map the distribution of PTE contents and pollution levels of the floodplain soils and; (iv) assess health risks [Average Daily Doses (ADD) and Hazard Quotients (HQ)] associated with each PTE in various human groups (i.e., children, women and men). The findings of this study are expected to aid policymakers, environmentalists and health experts in precise and firm decision making regarding human–PTE interactions.

Materials and methods

The geographical location of the study area

The study area is situated near the Litavka River area in the Central Bohemian Region, South West of Prague, Czech Republic (Fig. 1a, b). This is approximately between northings – 1,078,000 to – 1,080,000 and eastings – 777,800 to – 777,400. It has temperate climatic conditions characterized by mean annual temperature and rainfall amount ranging between 6.5–7.5 °C and 600–800 mm, respectively (Borůvka & Vácha, 2006; Kotková et al., 2019). Predominant soil types in the area are Fluvisols (FL) covered by various grass species (Kotková et al., 2019). Water availability from the Litavka River has attracted a lot of irrigation and agricultural activities in the area, which is also famous for its historic mining activities.

Soil sampling and laboratory analysis

A total of 158 topsoil samples were collected during the year 2018. Sampling followed combined grid and transect sampling designs (Fig. 1). Bulk soils were collected from a depth of 0 to 25 cm through a manual auger and packaged in plastic Ziploc bags with sample identity labels. All samples were subsequently air-dried at room temperature, disaggregated and sieved

(< 2 mm) to remove all debris (e.g., rock fragments, large roots, plastics). Organic carbon (denoted by C_{ox} in the study) levels were determined through the Walkley–Black chromic acid wet oxidation method with consequent titration while pH levels in water suspension (denoted by pH_{H₂O}) were measured using a pH meter in a soil: water ratio of 1:2 (w/v). The C_{ox} levels were presented in weight percentage (%) form. Several researchers have intensively studied the area as well as provided soil textural data and cation exchange capacity (CEC) measurements obtained from soil samples collected within the area (e.g., Ettler, Johan, et al., 2005; Ettler, Vaněk, et al., 2005; Vaněk et al., 2005, 2008; Tremlová et al., 2017).

Potentially toxic elements (Ti, Mn, Zn, As, Rb, Sr, Zr, Ba, Pb and Th), as well as iron (Fe) contents were obtained with a handheld portable X-ray Fluorescence Spectrometer (p-XRFS) (Delta Premium). All elemental measurements were converted to milligrams per kilogram (mg/kg). Each sample was measured three times with an average per element generated by the spectrometer at the end of each analysis. Several authors over the years have emphasized the efficiency of the p-XRFS in obtaining rapid and easy elemental measurements of soils (e.g., Eze et al., 2016; Mukhopadhyay et al., 2020; Paulette et al., 2015; Ravansari et al., 2020). Before analyzing the sieved soil samples with p-XRFS, they were pulverized to further reduce their particle sizes. The p-XRFS was operated according to the manufacturer's instructions (e.g., calibration, setting the time spent during analysis) to reduce any form of inconsistencies and deficiencies in the resulting output. For quality control and assurance, two standard reference materials (SRM), NIST 2711a and NIST 2709a were regularly measured alongside the soil analysis. Results for the recoveries are provided in the supplementary data (Table A6 and A7). The Department of Soil Science and Soil Protection at the Czech University of Life Sciences in Prague (CZU) provided the platform as well as equipment to perform all the analyses with full permission.

Soil pollution and health risk assessment

Numerous indices have been used to estimate pollution levels in soils (Kowalska et al., 2018). In the current study, the EF, PI and PLI were applied (Eq. 1, 2 and 3, respectively). The EF was used for its ability

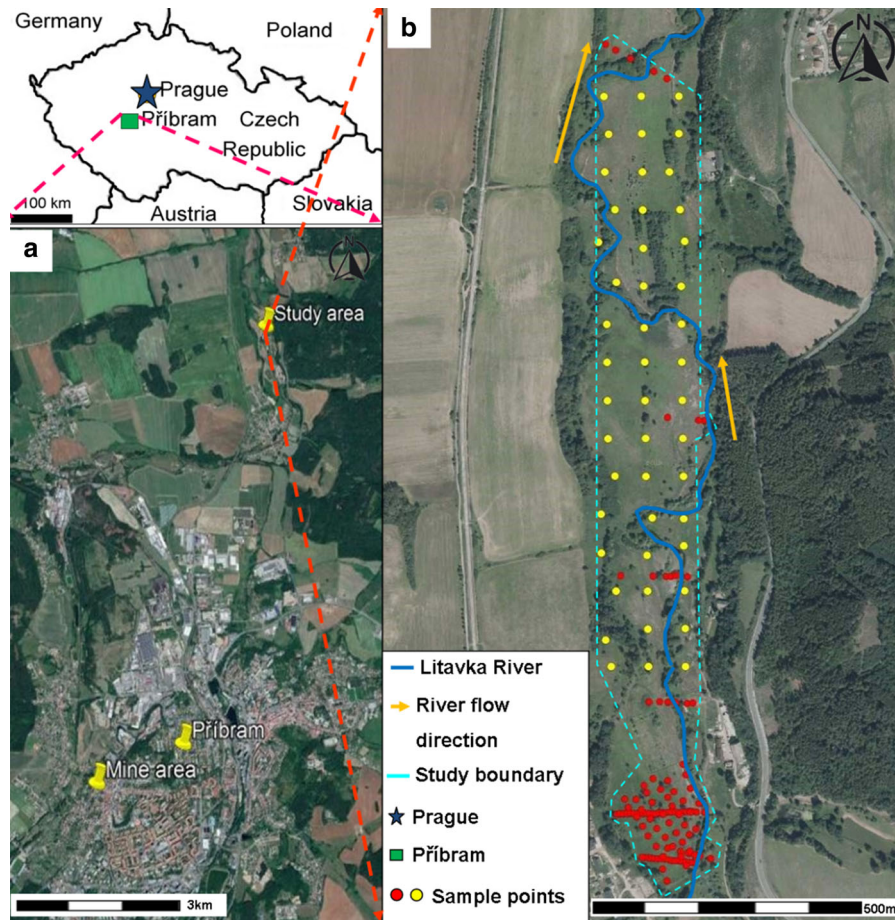


Fig. 1 **a** The study area relative to the Příbram town, Czech Republic and **b** location of all sampling points in red and yellow (Note: The colours represent two sampling campaigns in 2018).

Also a detailed sampling design providing the sample names can be found in the supplementary data denoted by figure A1)

to reduce elemental variability in soils, PI could evaluate the degree of pollution in topsoils and the PLI allowed for multiple PTEs to be combined while also utilizing already obtained PI values (Kowalska et al., 2018).

EF assessment

The EF is given by the equation:

$$EF = \frac{(C_x/C_a)_{\text{sample}}}{(C_x/C_a)_{\text{background}}} \quad (1)$$

where $(C_x/C_a)_{\text{sample}}$ represents the concentration (C) ratio between the element of interest “x” to iron (Fe) “a” in a topsoil sample, and $(C_x/C_a)_{\text{background}}$ is

the concentration ratio between the element of interest to a reference element in a local geochemical background (LGB) sample. The reason for using Fe as a reference element for normalization when calculating the EFs levels is because Fe is mainly of lithogenic origin and is a relatively stable element in soils. Further details on the selection of a reference element are provided by Kebonye and Eze (2019). The division of EF levels was in six main classes (Chai et al., 2017), < 1 (No enrichment (NE)), 1–3 (Minor enrichment (MiE)), 3–5 (Moderate enrichment (MoE)), 5–10 (Moderately severe enrichment (MoSE)), 10–25 (Severe enrichment (SE)), 25–50 (Very severe enrichment (VSE)) and > 50 (Extremely severe enrichment (ESE)). This study used world average values for

uncontaminated soils suggested by Kabata-Pendias, (2011) because of the unavailability of background values in the Czech Republic.

PI assessment

PI is given by the equation:

$$PI = \frac{(C_x)_{\text{sample}}}{(C_x)_{\text{background}}} \tag{2}$$

This evaluates the concentration ratio between the element of interest in a sample (C_x sample) and LGB (C_x background) of that same element (Kowalska et al., 2018). This time a reference or proxy element previously used in the EF assessment is excluded. In PI, the pollution classification is based on four main divisions, < 1 [No pollution (NP)], 1–3 [Moderate pollution (MP)], 3–6 [Considerable pollution (CP)] and > 6 [Very high pollution (VHP)] (Malkoc et al., 2010; Sayadi et al., 2015).

PLI assessment

PLI is computed through the equation:

$$PLI = (PI_1 * PI_2 * PI_3 * \dots * PI_n)^{\frac{1}{n}} \tag{3}$$

where each PI represents the ratio in Eq. 2 for individual PTEs 1, 2, ..., *n*. Their product is raised to the power 1 over *n*, “*n*” is the total number of PTEs studied. Significant pollution levels are PLI’s greater than 1 (PLI > 1) (Rinklebe et al., 2019).

Health risk assessment of children, women and men

Risk assessment for children (C), women (W) and men (M) exposed to topsoil pollution by PTEs were evaluated by first computing the ingestion ADDs (ADD_{ingestion} in mg/kg/day) for each human group (C, W and M) (Ge et al., 2019; Rinklebe et al., 2019) as follows:

$$ADD_{\text{ingestion}} = \frac{C_x * (IR * EFreq * ED * 10^{-6})}{(BW * AT)} \tag{4}$$

where C_x is the concentration of the element of interest in the soil as used in both EF and PI equations (mg/kg); *IR* being the soil ingestion rate expressed in mg/day (child: 200 mg and adult: 100 mg dust per day); *EFreq*

is the exposure frequency in days/year (child: 350 and adult: 250 days per year); *ED* as the exposure duration in years (child: 6 years and adult: 25 years); 10^{-6} for unit conversion in kg/mg; *BW* is the average body weight in kg (child: 15 kg, adult male: 68 kg and adult female: 58 kg); and *AT* as the average time (*ED* * 365 days) (child: 2190 days and adult: 9125 days). All these calculations were performed similarly by Rinklebe et al. (2019).

Secondly, ingestion HQ(s) for each element were computed according to the following equation:

$$HQ_{\text{ingestion}} = \frac{ADD_{\text{ingestion}}}{RfD_{\text{ingestion}}} \tag{5}$$

where $RfD_{\text{ingestion}}$ represents the oral reference dose (mg/kg/day) for each PTE. The *RfD*(s) for each element were *Ti* = 4 (EPA Region 9, 2008), *Mn* = 0.14, *Zr* = 0.00008 (EPA, 2019), *Zn* = 0.3, *As* = 0.0003, *Sr* = 600, *Ba* = 0.07, *Pb* = 0.0035 (Rinklebe et al., 2019), while those for *Rb* and *Th* were unavailable. HQs greater than 1 were considered indicative of a high likelihood of hostile health effects in either children or adults.

Data processing, visualization and statistical analysis

Data visualization was performed in R Studio 3.5 (R Core Team, 2019). These include boxplots for soil chemical property data (C_{ox} , Fe and pH_{H_2O}), PTE (*Ti*, *Mn*, *Zn*, *As*, *Rb*, *Sr*, *Zr*, *Ba*, *Pb* and *Th*) concentration and pollution (EF, PI and PLI), ADD and HQ levels. Potentially toxic element distribution maps depicting concentration and pollution levels were also made. A correlation matrix showing the relationship between PTEs and selected soil chemical properties was drawn.

Results and discussion

Soil chemical property levels

The soil Fe concentration levels ranged from 18,039 to 490,707 mg/kg (mean of 45,481 mg/kg). Carbon levels varied from 0.92 to 9.80% (mean 3.37%) which were slightly lower compared with soil carbon levels (4.9 to 11.6%) measured for floodplain soils at the

Elbe River (Germany) (Rinklebe & Langer, 2008). Soil pH_{H₂O} ranged from 4.64 to 7.23 (mean 6.23). Summary results for Fe, Cox and pH are available in the supplementary data (Fig. A3). In delineating pH_{H₂O} levels based on intensities, 0% of the samples were alkaline (pH of > 7.5), 29.7% were neutral (pH of 6.5–7.5) and 70.3% accounted for the acidic portion (pH of < 6.5) (Londo et al., 2006). Therefore, the majority of the soil samples were considered acidic. According to Chrzan (2016), acidic conditions favour the availability and mobility of certain elements in soils (e.g., copper, cadmium). In soils, iron occurs as Fe oxide particles (Langen & Hoberg, 1995). Between pHs of 6.0 to 7.0, these Fe oxide particles tend to have a high affinity for certain PTEs (e.g., Cd and Zn) compared to clay minerals (Garcia-Miragaya & Page, 1978; Trivedi & Axe, 2000). On the other hand, C_{ox} is known to influence metal solubility in soils (Gray & McLaren, 2006; Séguin et al., 2004).

While soil acts as the main sink for PTEs, various reactions between PTEs and soil constituents affect their complexation, speciation, mobility as well as solubility (Scokart et al., 1983; Uchimiya et al., 2020). Potentially toxic elements in soil occur in two main forms: solid and solution forms. The solid form represents the immobile or the harmless form of PTEs, while the latter is the mobile or very harmful form (Ogundiran & Osibanjo, 2009). Organic and inorganic ligands act as binding sites of the solid forms of these PTEs, thus rendering them immobile (Ogundiran & Osibanjo, 2009). However, these PTEs may be made available with slight changes in soil reaction (pH), cation exchange capacity (CEC) and redox potential (Eh) levels. Meanwhile, the solution form of these PTEs may occur in ionic form (e.g., Pbn⁺) or as soluble complexes of organic and inorganic ligands (COOH⁻, SO₄²⁻ and so on) (McLean & Bledsoe, 1992). Moreover, it is worth noting that low soil pH increases PTEs solubility while higher pH levels result in a reduction (Rieuwerts et al., 1998). The more the amount of PTE in solution forms in soils, the higher the chances of absorption by plants and subsequent release of same elements to humans and animals in the food chain—phytotoxicity.

Concentrations and distribution of PTEs in studied soils

Ti, Mn, Zn, As, Rb, Sr, Zr, Ba, Pb and Th levels ranged from 2454.67–6466.33, 471.33–77,280.00, 64.67–17,861.00, 9.13–1248.67, 35.87–95.00, 47.57–185.33, 79.33–480.67, 416.33–1814.67, 54.83–9241.00 and 8.90–25.33 mg/kg, their mean levels were 4676.33, 4363.36, 3887.57, 297.75, 61.24, 71.93, 275.63, 666.08, 2786.76 and 16.51 mg/kg (Fig. 2), respectively. In descending order, mean concentration levels were such that Ti > Mn > Zn > Pb > Ba > As > Zr > Sr > Rb > Th. The majority of PTE average concentration levels in the study were higher than both crustal and world average values (CAV and WAV) provided by Kabata-Pendias (2011) which indicated some level of contribution from mining and smelting activities around the area (refer to supplementary data, Fig. A2). The extremely high values of Pb, Zn and As compared to CAV and WAV in this study are worth mentioning because these are considered important environmental pollutants. Several studies confirm high pollutant emissions associated with historical smelting activities in the area (e.g., Ettler et al., 2010; Ettler, Johan, et al., 2005; Ettler, Vaněk, et al., 2005; Vurm, 2001).

The soil PTEs level distribution varied extensively (Fig. 3), an occurrence reflecting variations in the degree of anthropogenic influence (i.e., historic mining and smelting activities) and probably the way of sedimentation of the alluvium deposit in the area. The distribution of Pb, Zn, and As concentration levels were similar (Fig. 3). These findings coincided with those obtained by Van Nguyen et al. (2016) who studied similar elements in different land-use soils of Northern Vietnam. These elements are usually present in most anthropogenically sourced pollutants released in soil environments (e.g., mine tailings, organic and inorganic fertilizers, sewage sludge, fossil fuels).

PTE interactions with soil chemical properties

In this study, Ti showed a positive linear relationship with Rb and Zr, respectively (refer to supplementary data, Fig. A4). Both Ti and Zr tend to present similar behaviors in soils. Some authors (e.g., Kebonye & Eze, 2019) have used both Ti and Zr as reference elements for computing EF levels in semi-arid soils because they are stable and can resist weathering

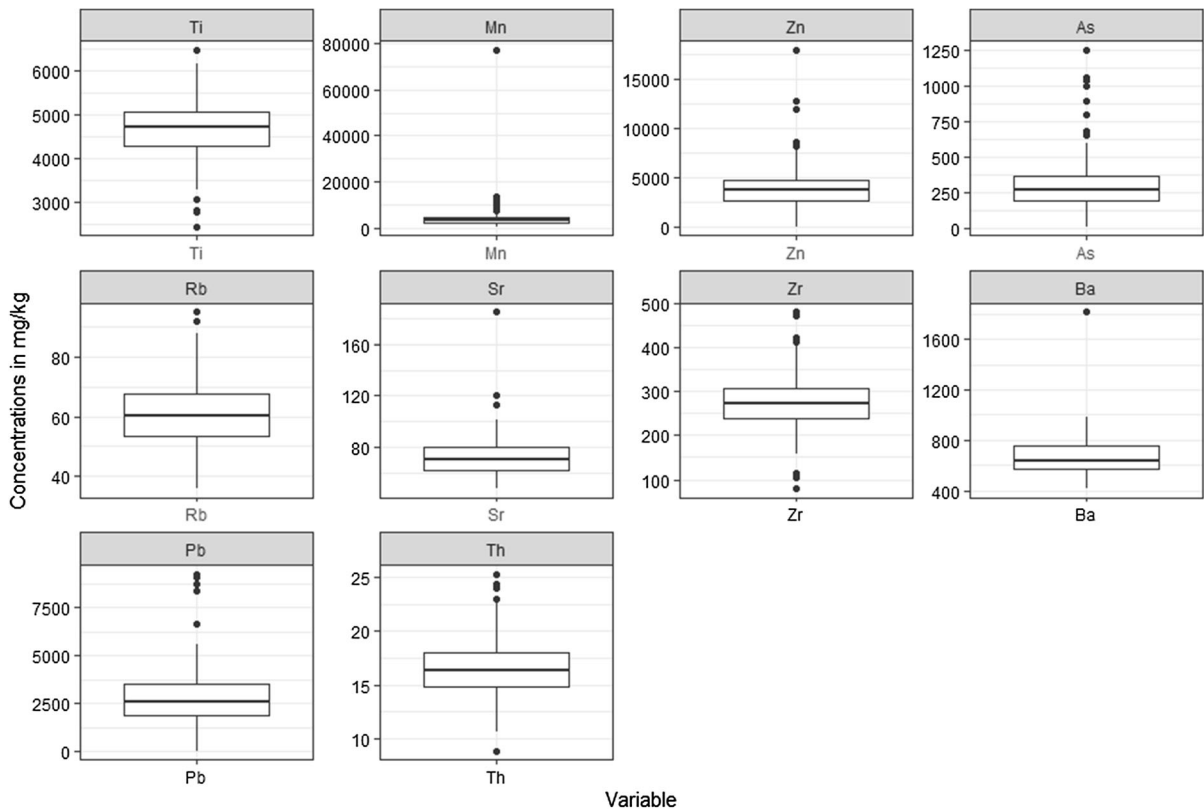


Fig. 2 PTE concentration levels in studied soils in mg/kg ($n = 158$). (Black upper and lower dots represent the upper and lower outliers, respectively, extreme upper and lower lines are the first and third quartile (Q1 and Q3) and the mid-line is the mean value)

effect. The simultaneous use of Ti, Rb and Zr in soil genesis research has been reported by Kabata-Pendias (2011). Zinc exhibited a significant positive relationship with As and Pb while As also strongly interacted with Pb (refer to supplementary data, Fig. A4). The results may suggest some level of co-existence in geochemical processes as well as similarities in sources between these significantly correlating PTEs in soils. Other studies verify the same outcome regarding these PTEs (As, Zn and Pb) in soil (e.g., Abraham et al., 2018; Fan et al., 2019). Other correlations between PTEs included Mn/Ba ($r = 0.769$), Rb/Zr ($r = 0.57$) and Rb/Th ($r = 0.50$) (refer to supplementary data, Fig. A4).

Strontium was the only element that showed a significant positive correlation with C_{ox} for the study soils (refer to supplementary data, Fig. A4). These results are in agreement with Kabata-Pendias, (2011) who emphasized the dependency of Sr on soil organic matter (SOM). Kebonye et al. (2020) observed similar interaction for semi-arid soils through structural

equation model estimates. This result may require further research to assess aspects relating to Sr biogeochemistry in floodplain soils. In the current study, C_{ox} did not show much positive correlation with often studied PTEs like Pb, Zn and As. Nevertheless, it is noteworthy that C_{ox} just like colloidal soil constituents can retain these PTEs (Rinklebe et al. 2019). Manganese and Ba were strongly positively correlated as well (refer to supplementary data, Fig. A4), a situation that might indicate that Ba had much preference for Mn than Fe. Thus, alike to results by Rinklebe et al. (2019), Mn oxides may have provided a strong binding site.

Soil pollution levels

A summary of the soil EF, PI and PLI statistics is presented in boxplots of Fig. 4. Mean values of EF levels decreased in the following sequence: Pb (81.08) > Zn (43.36) > As (33.23) > Mn (6.21) > Th (1.57) > Ba (1.23) > Zr (0.96) > Rb

(0.80) > Ti (0.59) > Sr (0.37). Each of the element means ranged in the following enrichment categories: Pb (ESE), Zn (VSE), As (VSE), Mn (MoSE), Th (MiE), Ba (MiE), Zr (NE), Rb (NE), Ti (NE) and Sr (NE), respectively. For PI, mean values decreased in the same order as EF levels. Each element mean PI value as well as pollution category was Pb (103.21,

Fig. 4 a EF, b PI and c PLI levels in studied soils ($n = 158$) (Note: Red dotted lines represent sequential pollution categories, respectively. Black upper and lower dots represent the upper and lower outliers, respectively, extreme upper and lower lines are the first and third quartile (Q1 and Q3) and the mid-line is the mean value)

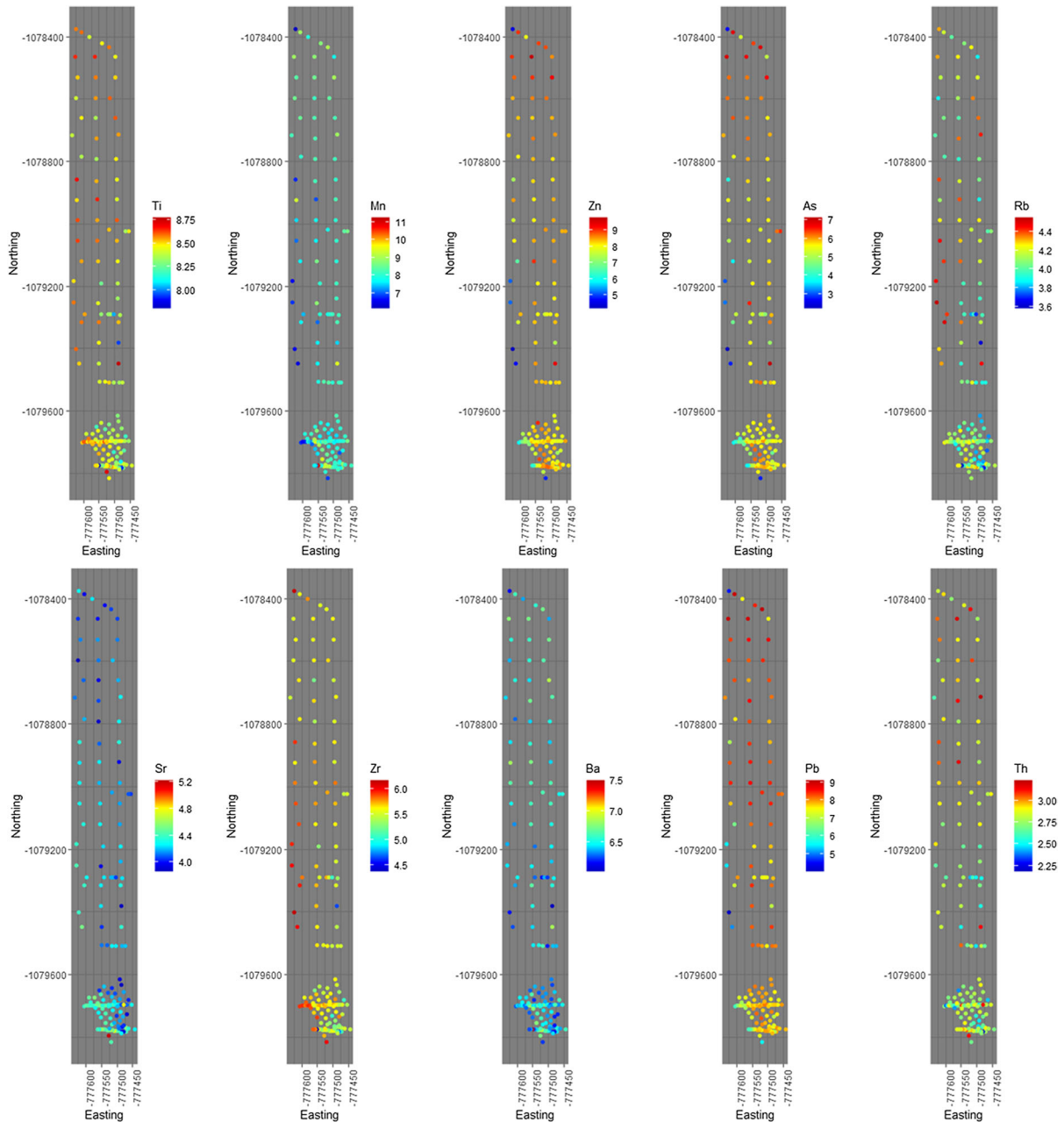
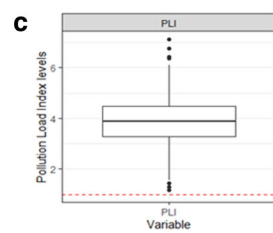
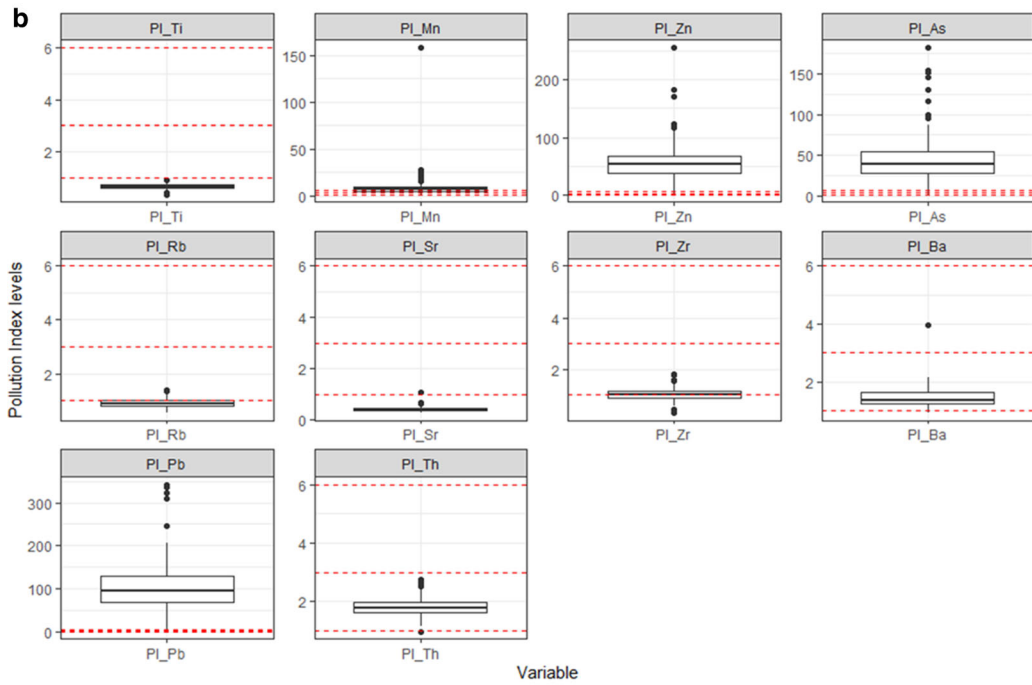
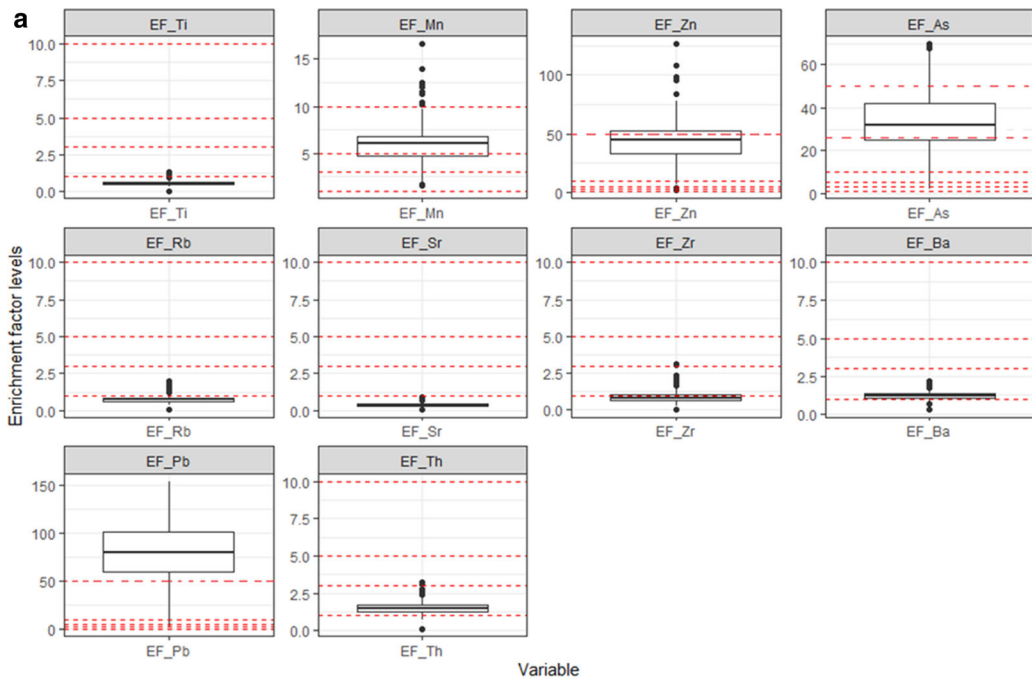


Fig. 3 Distribution of PTE concentration levels in the floodplain soils ($n = 158$) (Note: Concentration levels are in logarithm scale to ease colour gradient visualization)



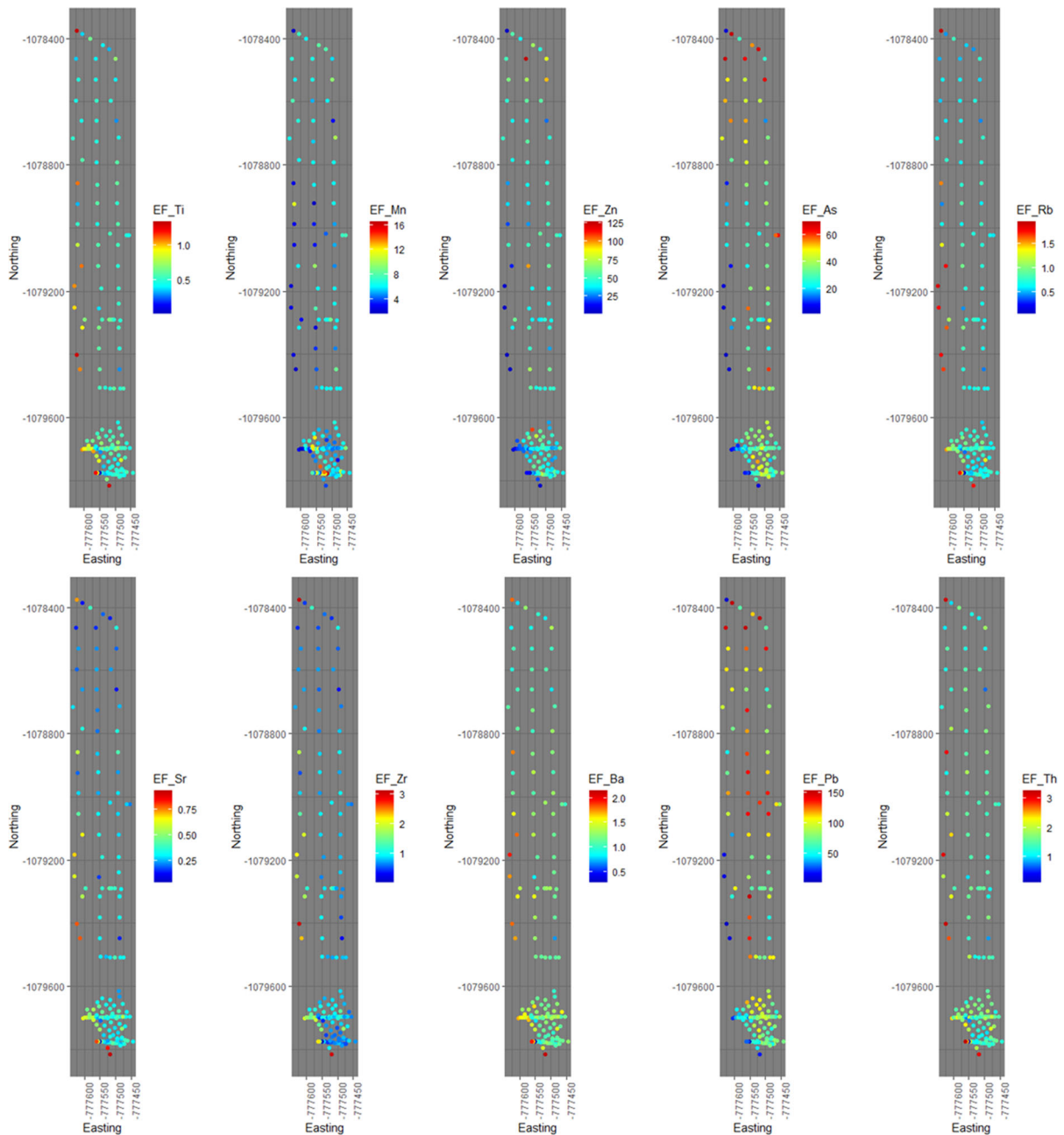


Fig. 5 Distribution of EF levels in study soils ($n = 158$)

VHP), Zn (55.54, VHP), As (43.59, VHP), Mn (8.94, VHP), Th (1.79, MP), Ba (1.45, MP), Zr (1.03, MP), Rb (0.90, NP), Ti (0.66, NP), Sr (0.41, NP), respectively. According to PLI levels, all soil samples were considered significantly polluted (Fig. 4c). It is worth mentioning that the PLI (individual value per sample) is a computation of several PTEs studied. Therefore, if

most PTEs were not enriched, PLI levels would be expected to be low (Rinklebe et al., 2019).

Zinc, As and Pb mean EF levels were somehow enriched. These elements together with Mn were also confirmed to be enriched based on mean PI levels. Both EF and PI levels suggest some deposition of PTEs in the study soils which is also justifiable in

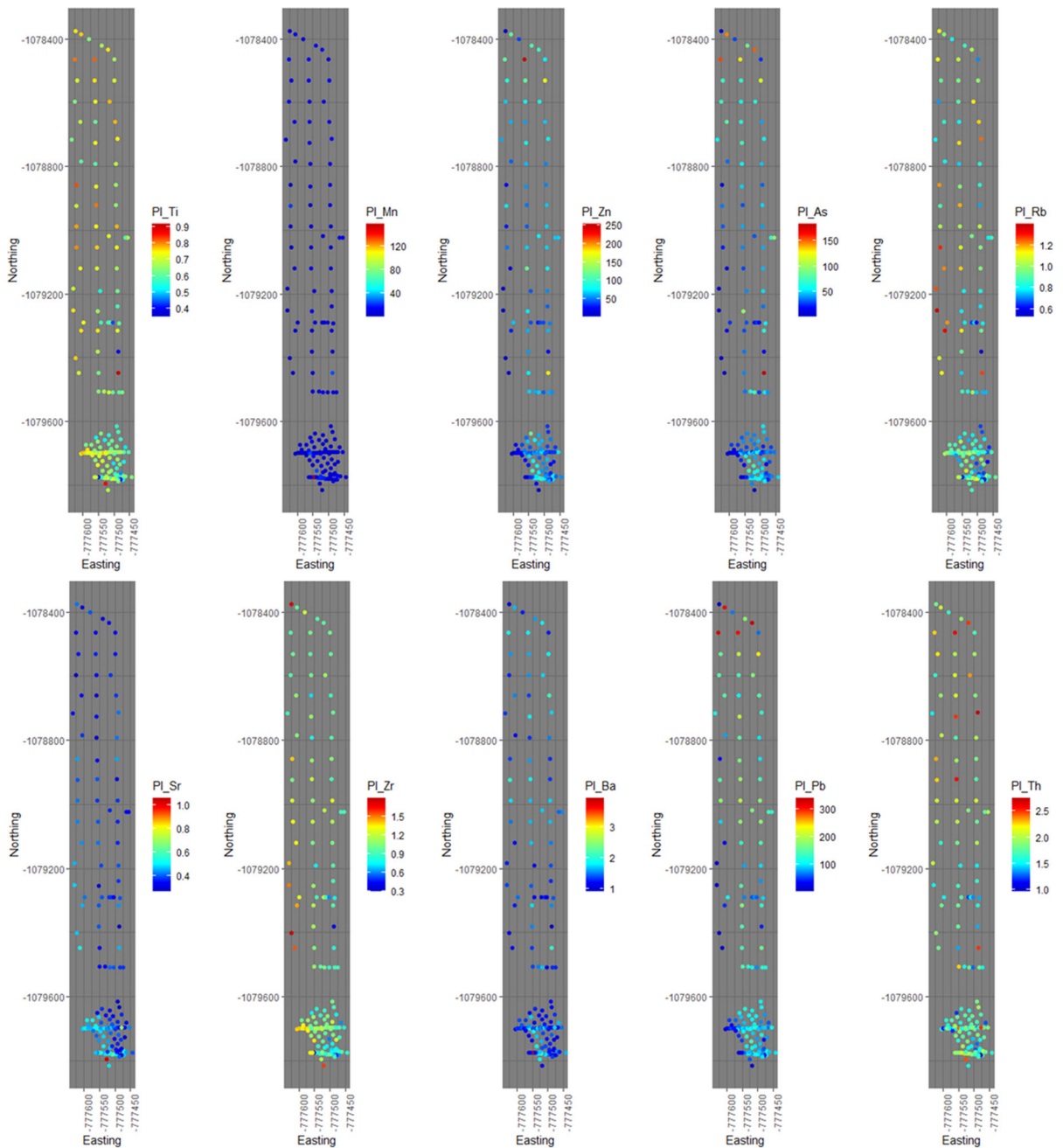


Fig. 6 Distribution of PI levels in study soils ($n = 158$)

previous studies of the same locality and the vicinity (e.g., Borůvka & Vácha, 2006; Borůvka et al., 1996; Ettler et al., 2006; Kozák et al., 1995; Vaněk et al., 2005). In other parts of the world, floodplain soils continue to accumulate PTEs as a result of anthropogenic activities (e.g., industrial, mining and

municipal effluents) (e.g., Barać et al., 2016; Devai et al., 2005; Jiménez-Ballesta et al., 2017). Barium and Th EF and PI mean levels indicated that the elements had minor enrichment (MiE) and were moderately polluted (MP) (Fig. 4a, b). At least one sample was considerably polluted (CP) with Ba (Fig. 4b). The

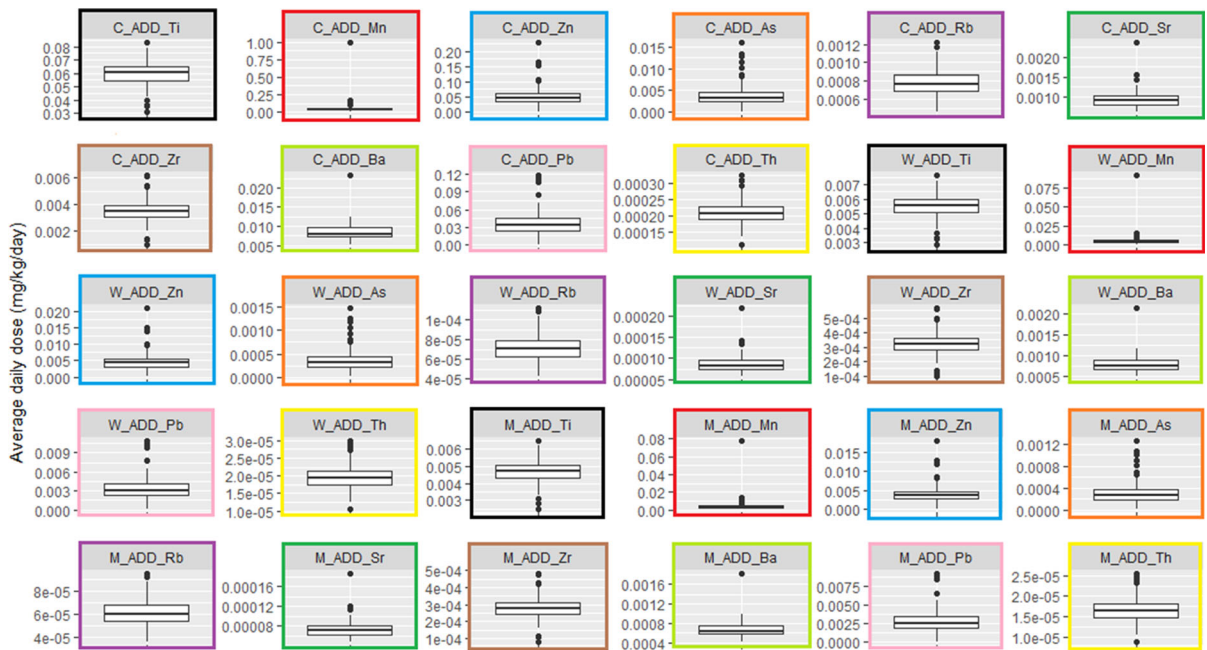


Fig. 7 Distribution of ADD comparisons per element between different human groups in mg/kg/day ($n = 158$) (Similar colours represent same element ADD levels in children: C, women: W and men: M. Black upper and lower dots represent the upper and

lower outliers, respectively, extreme upper and lower lines are the first and third quartile (Q1 and Q3) and the mid-line is the mean value)

majority of the samples were within the non-enrichment (NE) (Fig. 4a) and moderately polluted (MP) (Fig. 4b) regions for Zr. These results suggested that Zr is non-anthropogenically sourced (agreeing with Jiménez-Ballesta et al., 2017 and Kabata-Pendias, 2011).

Regarding the remaining elements (Ti, Rb and Sr), mean EF (0.59, 0.80 and 0.37) and PI (0.66, 0.90 and 0.41) levels, respectively, indicated that the soils were non-polluted (NE, NP). However, Ti and Rb EF levels for certain samples signified minor enrichment (MiE). Ti, Rb and Sr could have been enriched rather with heavy anthropogenic activities associated with specific mining of these elements, paint making, radioactive waste handling steel and glazed ceramic production (e.g., Maina et al., 2016; Simonin et al., 2016; Timofeeva et al., 2018). Other than these, most Ti, Rb and Sr soil enrichment is largely associated with weathering and pedogenesis of the site-specific lithology (Egli & Fitze, 2000; Horbe & Anand, 2011; Kabata-Pendias, 2011; Wang et al., 2009). This is because these elements tend to have a strong affinity for silicate minerals. The EF and PI distribution maps (Figs. 5 and 6) of each PTE somehow coincided with

the respective concentration level distribution maps although it was not clear based on the colour gradients (Fig. 3). Further details regarding the EF and PI level distribution of the study samples can be observed from the boxplots in Figs. 4a and 4b. PLI levels were widely distributed (refer to supplementary data, Fig. A5). Remarkably, some of the highest PLI levels were observed on the topmost sample points (e.g., L24, L27, L111 and L127) of the distribution map (refer to supplementary data, Fig. A5). These very sample points (i.e., L24, L27, L111 and L127) constituted some of the highest Pb and As concentration levels, thus, an explanation as to why they yielded high PLI levels.

Health risk assessment

Average daily dose (ADD)

ADDs per PTE in both children and adults (women and men) are summarized through boxplots (Fig. 7). General mean ADDs per PTE for children and adults (women and men) decreased in this order: Ti > Mn > Zn > Pb > Ba > As > Zr > Sr > Rb > Th,

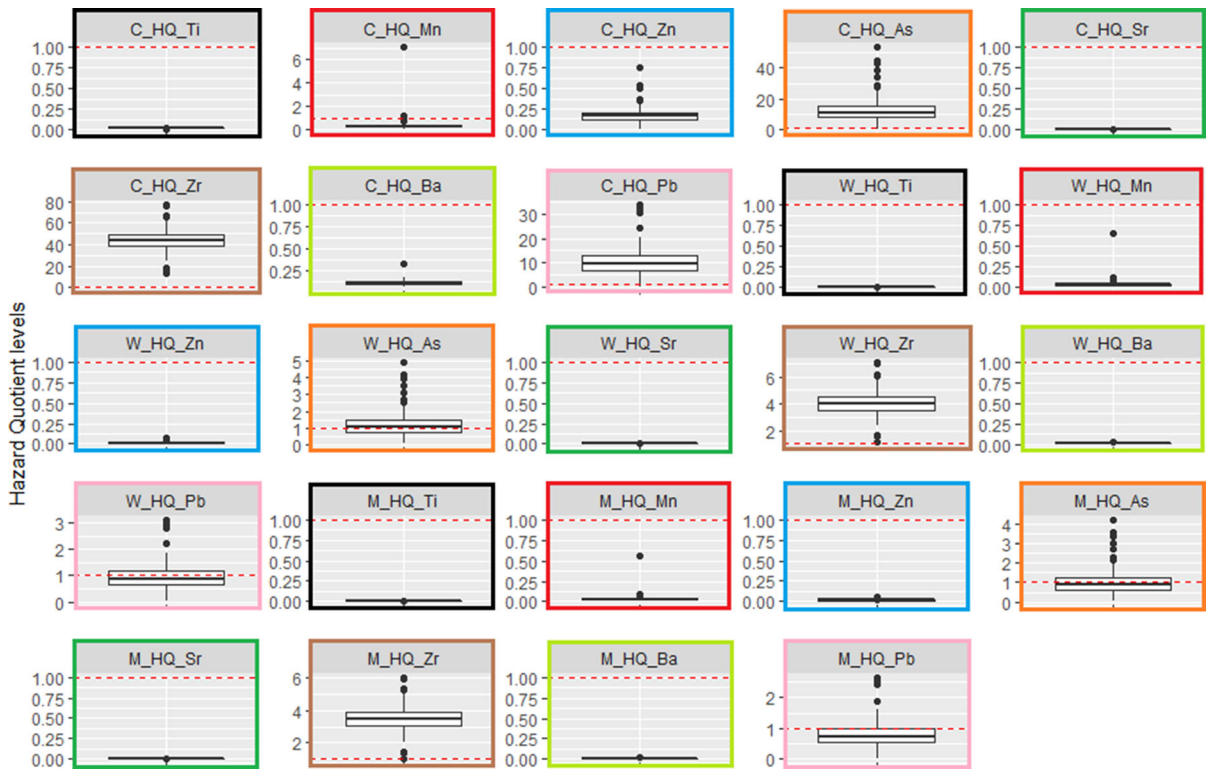


Fig. 8 HQ levels per element between different human groups ($n = 158$). (Red dotted line represents the baseline level by which if crossed there may be a high probability of occurrence of adverse effects) (Similar colours represent same element HQ

levels in children: C, women: W and men: M. Black upper and lower dots represent the upper and lower outliers, respectively, extreme upper and lower lines are the first and third quartile (Q1 and Q3) and the mid-line is the mean value)

respectively. Generally, ADDs per element in children were higher than those corresponding for adults.

Hazard quotients (HQ)

The results of the HQs which were used to assess health risks in children, women and men are shown in Fig. 8. Mean elemental HQs in children ranged between 1.53×10^{-6} to 4.41×10^1 while in women and men they ranged from 1.42×10^{-7} to 4.07×10^0 as well as 1.21×10^{-7} to 3.47×10^0 , respectively. Children had the highest mean HQ for each PTE compared to adults (Fig. 8). Based on the HQ levels, it showed that children are at a higher exposure risk for most of these PTEs compared to adults, and these results are in agreement with related studies (Rinklebe et al., 2019; Mensah et al., 2020; Jadoon et al., 2020). According to Jadoon et al. (2020), children are at higher risk of exposure to these PTEs because of activities related with hand to mouth practices (e.g.,

finger-licking, unlimited eating from the ground). HQ mean levels for As and Zr (i.e., for all human groups) were all higher than the threshold of 1 as well as that of Pb in children. The topsoils pose health risk with regards to As and Zr in all human groups and particularly Pb in children. This study effectively identified PTEs of potential health risk in humans for floodplain soils of the Litavka River area.

Potential effects of PTEs with high HQs on human and animal health

Arsenic, lead and zirconium

Both Pb and As are considered non-essential elements in the body. Thus, the excessive intake or exposure to Pb and As may be detrimental in both humans and animals alike (Mandal, 2017). Arsenic causes various forms of cancer that usually affect several body parts including but not limited to the skin, bladder and lungs

(Kadirvel et al., 2007). Furthermore, other less severe complications that have been observed in As exposed people include anaemia, swelling of legs, liver fibrosis and a burning feeling in the eyes (Mandal, 2017). On the other hand Pb intake can cause damage to most systems in the body and worse off result in death (Zhang et al., 2019). In addition to death, Pb may reduce cognitive development in children (Li et al., 2020). In animals, acute As exposure causes severe abdominal pains accompanied by intense vomiting and diarrhoea. Subsequent effects include circulatory system failure which may eventually lead to death within a short time (Mandal, 2017). Similar to humans, Pb also causes damage to most systems in animals (Hampton et al., 2018). Zirconium is considered toxic at very high concentration levels usually as a result of occupational exposure (Vetrimurugan et al., 2017).

General study recommendations

Regarding people (locals)

Regular community awareness and education campaigns are a necessity to ensure successful intervention (WHO 2020). If people (i.e., locals) can fully understand the risks of exposure, modes of exposure and ways of reducing possible exposure, this would allow them to better respond to the situation. Intermittent testing of locals by health officials would ensure early detection of likely symptoms that could be used as possible indicators of poisoning associated with PTEs (e.g., skin-related ailments) may be helpful. Parents should always keep a close eye on little children as they are the most vulnerable group. Already, because of the high As and Zr HQ levels, locals should try and reduce their dietary intake for some foodstuffs that may contain these elements in their inorganic form. For instance, mussels and selected seaweeds usually contain high levels of inorganic As (Edmonds & Francesconi, 1993).

Regarding the study floodplain soils

There is a need for larger investments and research in line with modern precision mapping techniques such as Digital Soil Mapping (DSM). These are expected to help facilitate intermittent identification of PTE hotspots within affected areas. Thus, several remediation techniques could later be tested at each hotspot area

for possible PTE remediation. For example, remediation techniques involving: containment (e.g., encapsulation), extraction and removal (e.g., Phytoremediation), as well as solidification and stabilization (e.g., Vitrification) (Liu et al., 2018). In some instances, low-cost amendments have somehow proven effective in the immobilization of certain PTEs in floodplain soils of Germany (Shaheen & Rinklebe, 2015).

Conclusions

The highest PTE enrichment levels of the Litavka River floodplain soils were observed for Pb, Zn and As according to the EF and PI indices. These elements constituted high PLI levels in the riverine soils from Pířbram. Generally, EF and PI distribution maps align well with PTE concentration level maps. Ti in all human groups (children and adults: women and men) had the highest ADD levels of all PTEs studied, with the lowest ADD levels belonging to Th in all groups. Children had the uppermost ADD levels for all PTEs than adults (women and men). Therefore, they were at greater health risk than women and men according to HQ levels obtained for all PTEs. Arsenic, Zr and Pb mean HQ levels were the only elements to exceed the health risk threshold of 1 which meant greater health risks associated with these elements for affected human groups. Because of this, there is an intermittent need to monitor the concentration level changes for these specific PTEs in the study soils as well as their potential health risks in all human groups, particularly in children because of their vulnerability. The current study was able to provide more insight into the less studied PTEs (Ti, Sr, Zr, Rb and Th) in floodplain soils of the Czech Republic. Moreover, we were able to capture preliminary aspects required for soil pollution management like mapping the distribution of these elements (e.g., their concentration and pollution levels). This information is expected to contribute to the understanding of human–PTE interactions as obtained in highly polluted soils.

Acknowledgements The first author, Mr. Ndiye M. Kebonye, would like to acknowledge the Ph.D. scholarship and internal grant no. SV20-5-21130 offered by the Czech University of Life Sciences, Prague (CZU). Also, we thank the Czech Science Foundation, Project nos. 17–277265 (Spatial prediction of soil properties and classes based on position in the landscape and

other environmental covariates) and 18–28126Y (Soil contamination assessment using hyperspectral orbital data) for the financial support. Moreover the Centre of Excellence (Centre of the investigation of synthesis and transformation of nutritional substances in the food chain in interaction with potentially risk substances of anthropogenic origin: comprehensive assessment of the soil contamination risks for the quality of agricultural products, NutRisk Centre), European project no. CZ.02.1.01/0.0/0.0/16_019/0000845 highly acknowledged.

Declarations

Conflict of interest The authors declare no conflicts of interest regarding this work.

References

Abraham, J., Dowling, K., & Florentine, S. (2018). Assessment of potentially toxic metal contamination in the soils of a legacy mine site in Central Victoria, Australia. *Chemosphere*, *192*, 122–132.

Bambas, J. (1990). Březohorský rudní revír (Ore district of Březové Hory). Publication of symposium on mining in Příbram scientific and technological aspects. VZ Kamenná Publications (**in Czech**).

Barać, N., Škrivanj, S., Bukumirić, Z., Živojinović, D., Manojlović, D., Barać, M., Petrović, R., & Ćorac, A. (2016). Distribution and mobility of heavy elements in floodplain agricultural soils along the Ibar River (Southern Serbia and Northern Kosovo). Chemometric investigation of pollutant sources and ecological risk assessment. *Environmental Science and Pollution Research*, *23*(9), 9000–9011.

Borůvka, L., & Drábek, O. (2004). Heavy metal distribution between fractions of humic substances in heavily polluted soils. *Plant, Soil and Environment*, *50*(8), 339–345.

Borůvka, L., & Vácha, R. (2006). Litavka river alluvium as a model area heavily polluted with potentially risk elements. In J.-L. Morel, G. Echevarria, & N. Goncharova (Eds.), *Phytoremediation of metal-contaminated soils* (pp. 267–298). Dordrecht: Springer.

Borůvka, L., HuanWei, C., Kozák, J., & Křištoufková, S. (1996). Heavy contamination of soil with cadmium, lead and zinc in the alluvium of the Litavka River. *Rostlinna výroba*, *42*(12), 543–550.

Chai, L., Li, H., Yang, Z., Min, X., Liao, Q., Liu, Y., Men, S., Yan, Y., & Xu, J. (2017). Heavy metals and metalloids in the surface sediments of the Xiangjiang River, Hunan, China: Distribution, contamination, and ecological risk assessment. *Environmental Science and Pollution Research*, *24*(1), 874–885.

Choppala, G., Kunhikrishnan, A., Seshadri, B., Park, J. H., Bush, R., & Bolan, N. (2018). Comparative sorption of chromium species as influenced by pH, surface charge and organic matter content in contaminated soils. *Journal of Geochemical Exploration*, *184*, 255–260.

Chrzan, A. (2016). Monitoring bioconcentration of potentially toxic trace elements in soils trophic chains. *Environmental Earth Sciences*, *75*(9), 786.

Devai, I., Patrick, W. H., Jr., Neue, H. U., DeLaune, R. D., Kongchum, M., & Rinklebe, J. (2005). Methyl mercury and heavy metal content in soils of rivers Saale and Elbe (Germany). *Analytical Letters*, *38*(6), 1037–1048.

Dlouhá, Š., Petrovský, E., Kapička, A., Borůvka, L., Ash, C., & Drábek, O. (2013). Investigation of polluted alluvial soils by magnetic susceptibility methods: A case study of the Litavka River. *Soil and Water Research*, *8*, 151–157.

Edmonds, J. S., & Francesconi, K. A. (1993). Arsenic in sea-foods: Human health aspects and regulations. *Marine Pollution Bulletin*, *26*(12), 665–674.

Egli, M., & Fitze, P. (2000). Formulation of pedologic mass balance based on immobile elements: A revision. *Soil Science*, *165*(5), 437–443.

EPA Region 9. (2008). Risk Assessment Issue Paper for: Derivation of interim oral and inhalation toxicity values for titanium (CAS No. 7440-32-6) and compounds, especially titanium dioxide (CAS No. 13463-67-7), but excluding titanium tetrachloride (CAS No. 7550-45-0), titanium dichloride and organic complexes of titanium such as titanocenes. DRAFT document; 95-019/05-26-95).

EPA. (2019). Regional screening levels (RSLs)—Generic tables. Retrieved from March 18, 2020 from <https://semsub.epa.gov/work/HQ/197025.pdf>.

Ettler, V., Johan, Z., Baronnet, A., Jankovský, F., Gilles, Ch., Mihaljevič, M., Šebek, O., Strnad, L., & Bezdička, P. (2005). Mineralogy of air-pollution-control residues from a secondary lead smelter: Environmental implications. *Environmental Science and Technology*, *39*, 9309–9316.

Ettler, V., Mihaljevič, M., Šebek, O., Molek, M., Grygar, T., & Zeman, J. (2006). Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic. *Environmental Pollution*, *142*, 409–417.

Ettler, V., Vaněk, A., Mihaljevič, M., & Bezdička, P. (2005). Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. *Chemosphere*, *58*(10), 1449–1459.

Ettler, V., Tejnecký, V., Mihaljevič, M., Šebek, O., Zuna, M., & Vaněk, A. (2010). Antimony mobility in lead smelter-polluted soils. *Geoderma*, *155*(3–4), 409–418.

Eze, P. N., Mosokomani, V. S., Udeigwe, T. K., & Oyedele, O. F. (2016). Quantitative geospatial dataset on the near-surface heavy metal concentrations in semi-arid soils from Maibele Airstrip North, Central Botswana. *Data in Brief*, *8*, 1448–1453.

Fan, S., Wang, X., Lei, J., Ran, Q., Ren, Y., & Zhou, J. (2019). Spatial distribution and source identification of heavy metals in a typical Pb/Zn smelter in an arid area of northwest China. *Human and Ecological Risk Assessment: An International Journal*, *25*(7), 1661–1687.

Frohne, T., Rinklebe, J., & Diaz-Bone, R. A. (2014). Contamination of floodplain soils along the Wupper River, Germany, with As Co, Cu, Ni, Sb, and Zn and the impact of pre-definite redox variations on the mobility of these elements. *Soil and Sediment Contamination: An International Journal*, *23*(7), 779–799.

- Garcia-Miragaya, J., & Page, A. L. (1978). Sorption of trace quantities of Cd by soils with different chemical and mineralogical composition. *Water, Air and Soil Pollution*, 9, 289–299.
- Ge, M., Liu, G., Liu, H., Yuan, Z., & Liu, Y. (2019). The distributions, contamination status, and health risk assessments of mercury and arsenic in the soils from the Yellow River Delta of China. *Environmental Science and Pollution Research*, 26(34), 35094–35106.
- Gholizadeh, A., Borůvka, L., Vašát, R., Saberioon, M., Klement, A., Kratina, J., Tejnecký, V., & Drábek, O. (2015). Estimation of potentially toxic elements contamination in anthropogenic soils on a brown coal mining dumpsite by reflectance spectroscopy: A case study. *PLoS ONE*, 10(2), e0117457.
- Gray, C. W., & McLaren, R. G. (2006). Soil factors affecting heavy metal solubility in some New Zealand soils. *Water, Air, and Soil Pollution*, 175(1–4), 3–14.
- Hampton, J. O., Laidlaw, M., Buenz, E., & Arnemo, J. M. (2018). Heads in the sand: Public health and ecological risks of lead-based bullets for wildlife shooting in Australia. *Wildlife Research*, 45(4), 287–306.
- Horbe, A. M. C., & Anand, R. R. (2011). Bauxite on igneous rocks from Amazonia and Southwestern of Australia: Implication for weathering process. *Journal of Geochemical Exploration*, 111(1–2), 1–12.
- Jadoona, S., Muhammad, S., Hilal, Z., Ali, M., Khan, S., & Khattak, N. U. (2020). Spatial distribution of potentially toxic elements in urban soils of Abbottabad city, (N Pakistan): Evaluation for potential risk. *Microchemical Journal*, 153, 104489.
- Jalali, M., & Najafi, S. (2018). Effect of pH on potentially toxic trace elements (Cd, Cu, Ni, and Zn) solubility in two native and spiked calcareous soils: experimental and modeling. *Communications in Soil Science and Plant Analysis*, 49(7), 814–827.
- Jiménez-Ballesta, R., García-Navarro, F. J., Bravo, S., Amorós, J. A., Perez-de-Los-Reyes, C., & Mejias, M. (2017). Environmental assessment of potential toxic trace element contents in the inundated floodplain area of Tablas de Daimiel wetland (Spain). *Environmental Geochemistry and Health*, 39(5), 1159–1177.
- Kabata-Pendias, A. (2011). *Trace elements in soils and plants* (4th ed., pp. 33487–32742). CRC Press.
- Kadirvel, R., Sundaram, K., Mani, S., Samuel, S., Elango, N., & Panneerselvam, C. (2007). Supplementation of ascorbic acid and tocopherol prevents arsenic-induced protein oxidation and DNA damage induced by arsenic in rats. *Human and Experimental Toxicology*, 26, 939–946.
- Kebonye, N. M., & Eze, P. N. (2019). Zirconium as a suitable reference element for estimating potentially toxic element enrichment in treated wastewater discharge vicinity. *Environmental Monitoring and Assessment*, 191(11), 705.
- Kebonye, N. M., Eze, P. N., Ahado, S. K., & John, K. (2020). Structural equation modeling of the interactions between trace elements and soil organic matter in semiarid soils. *International Journal of Environmental Science and Technology*, 17, 2205–2214.
- Kotková, K., Nováková, T., Tůmová, Š., Kiss, T., Popelka, J., & Faměra, M. (2019). Migration of risk elements within the floodplain of the Litavka River, the Czech Republic. *Geomorphology*, 329, 46–57.
- Kowalska, J. B., Mazurek, R., Gąsiorek, M., & Zaleski, T. (2018). Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination—A review. *Environmental Geochemistry and Health*, 40(6), 2395–2420.
- Kozák, J., Janků, J., & Jehlička, J. (1995). The problems of heavily polluted soils in the Czech Republic: A case study. In U. Förstner, W. Salomons, & P. Mader (Eds.), *Heavy metals* (pp. 287–300). Springer.
- Langen, M., & Hoberg, H. (1995). A description of the distribution of heavy metals in soils and sediments containing iron oxides and consequences for the decontamination process. In W. J. Van Den Brink, R. Bosman, & F. Arendt (Eds.), *Contaminated Soil'95* (pp. 513–514). Springer.
- Li, S. W., Li, M. Y., Sun, H. J., Li, H. B., & Ma, L. Q. (2020). Lead bioavailability in different fractions of mining-and smelting-contaminated soils based on a sequential extraction and mouse kidney model. *Environmental Pollution*, 262, 114253.
- Liu, L., Li, W., Song, W., & Guo, M. (2018). Remediation techniques for heavy metal-contaminated soils: Principles and applicability. *Science of the Total Environment*, 633, 206–219.
- Londo, A. J., Kushla, J. D., & Carter, R. C. (2006). Soil pH and tree species suitability in the south. *Southern Regional Extension Forestry*, 2, 1–5.
- Maina, D. M., Ndirangu, D. M., Mangala, M. M., Boman, J., Shepherd, K., & Gatari, M. J. (2016). Environmental implications of high metal content in soils of a titanium mining zone in Kenya. *Environmental Science and Pollution Research*, 23(21), 21431–21440.
- Malkoc, S., Yazıcı, B., & Savas Kopalal, A. (2010). Assessment of the levels of heavy metal pollution in roadside soils of Eskisehir, Turkey. *Environmental Toxicology and Chemistry*, 29(12), 2720–2725.
- Mandal, P. (2017). An insight of environmental contamination of arsenic on animal health. *Emerging Contaminants*, 3(1), 17–22.
- McLean, J.E., & Bledsoe, B.E. (1992). Behavior of metals in soils. Ground water issue. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC. EPA/540/S-92/018.
- Mensah, A. K., Marschner, B., Shaheen, S. M., Wang, J., Wang, S. L., & Rinklebe, J. (2020). Arsenic contamination in abandoned and active gold mine spoils in Ghana: Geochemical fractionation, speciation, and assessment of the potential human health risk. *Environmental Pollution*, 261, 114116.
- Mukhopadhyay, S., Chakraborty, S., Bhadoria, P. B. S., Li, B., & Weindorf, D. C. (2020). Assessment of heavy metal and soil organic carbon by portable X-ray fluorescence spectrometry and NixPro™ sensor in landfill soils of India. *Geoderma Regional*, 20, e00249.
- Navrátil, T., Rohovec, J., & Žák, K. (2008). Floodplain sediments of the 2002 catastrophic flood at the Vltava (Moldau) River and its tributaries: mineralogy, chemical composition, and post-sedimentary evolution. *Environmental Geology*, 56(2), 399–412.
- Nováková, T., Kotková, K., Elznicová, J., Strnad, L., Engel, Z., & Grygar, T. M. (2015). Pollutant dispersal and stability in a severely polluted floodplain: A case study in the Litavka River, Czech Republic. *Journal of Geochemical Exploration*, 156, 131–144.
- Ogundiran, M. B., & Osibanjo, O. (2009). Mobility and speciation of heavy metals in soils impacted by hazardous waste. *Chemical Speciation and Bioavailability*, 21(2), 59–69.

- Paulette, L., Man, T., Weindorf, D. C., & Person, T. (2015). Rapid assessment of soil and contaminant variability via portable X-ray fluorescence spectroscopy: Copşa Mică, Romania. *Geoderma*, 243, 130–140.
- R Core Team. (2019). R: A language and environment for statistical computing. R Foundation for Statistical Computing. Vienna, Austria. Retrieved from <https://www.r-project.org/>. (Verified on 13 May 2020).
- Ravansari, R., Wilson, S. C., & Tighe, M. (2020). Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. *Environment International*, 134, 105250.
- Rieuwerts, J. S., Thornton, I., Farago, M. E., & Ashmore, M. R. (1998). Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation and Bioavailability*, 10(2), 61–75.
- Rinklebe, J., & Langer, U. (2008). Floodplain soils at the Elbe River, Germany, and their diverse microbial biomass. *Archives of Agronomy and Soil Science*, 54(3), 259–273.
- Rinklebe, J., Antoniadis, V., Shaheen, S. M., Rosche, O., & Altermann, M. (2019). Health risk assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environment International*, 126, 76–88.
- Romero-Baena, A. J., González, I., & Galán, E. (2018). Soil pollution by mining activities in Andalusia (South Spain) – the role of mineralogy and geochemistry in three case studies. *Journal of Soils and Sediments*, 18(6), 2231–2247.
- Sayadi, M. H., Shabani, M., & Ahmadvpour, N. (2015). Pollution index and ecological risk of heavy metals in the surface soils of Amir-Abad Area in Birjand City. *Iran. Health Scope*, 4(1), ee21137.
- Scokart, P. O., Meeus-verdinne, K., & De Borger, R. (1983). Mobility of heavy metals in polluted soils near zinc smelters. *Water, Air and Soil Pollution*, 20, 451–463.
- Séguin, V., Gagnon, C., & Courchesne, F. (2004). Changes in water extractable metals, pH and organic carbon concentrations at the soil–root interface of forested soils. *Plant and Soil*, 260(1–2), 1–17.
- Shaheen, S. M., & Rinklebe, J. (2015). Impact of emerging and low cost alternative amendments on the (im) mobilization and phytoavailability of Cd and Pb in a contaminated floodplain soil. *Ecological Engineering*, 74, 319–326.
- Simonin, M., Richaume, A., Guyonnet, J. P., Dubost, A., Martins, J. M., & Pommier, T. (2016). Titanium dioxide nanoparticles strongly impact soil microbial function by affecting archaeal nitrifiers. *Scientific Reports*, 6(1), 1–10.
- Timofeeva, Y. O., Kosheleva, Y., Semal, V., & Burdukovskii, M. (2018). Origin, baseline contents, and vertical distribution of selected trace lithophile elements in soils from nature reserves, Russian Far East. *Journal of Soils and Sediments*, 18(3), 968–982.
- Tremlová, J., Sehnal, M., Száková, J., Goessler, W., Steiner, O., Najmanová, J., Horáková, T., & Tlustoš, P. (2017). A profile of arsenic species in different vegetables growing in arsenic-contaminated soils. *Archives of Agronomy and Soil Science*, 63(7), 918–927.
- Trivedi, P., & Axe, L. (2000). Modeling Cd and Zn sorption to hydrous metal oxides. *Environmental Science and Technology*, 34(11), 2215–2223.
- Uchimiya, M., Bannon, D., Nakanishi, H., McBride, M. B., Williams, M. A., & Yoshihara, T. (2020). Chemical speciation, plant uptake, and toxicity of heavy metals in agricultural soils. *Journal of Agricultural and Food Chemistry*, 68, 12856–12869.
- Van Nguyen, T., Ozaki, A., Nguyen Tho, H., Nguyen Duc, A., Tran Thi, Y., & Kurosawa, K. (2016). Arsenic and heavy metal contamination in soils under different land use in an estuary in Northern Vietnam. *International Journal of Environmental Research and Public Health*, 13(11), 1091.
- Vaněk, A., Borůvka, L., Drábek, O., Mihaljevič, M., & Komárek, M. (2005). Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry. *Plant, Soil and Environment*, 51(7), 316–321.
- Vaněk, A., Ettler, V., Grygar, T., Borůvka, L., Šebek, O., & Drábek, O. (2008). Combined chemical and mineralogical evidence for heavy metal binding in mining-and smelting-affected alluvial soils. *Pedosphere*, 18(4), 464–478.
- Vácha, R., Sánka, M., Skála, J., Čechmánková, J., & Horváthová, V. (2016). Soil contamination health risks in Czech proposal of soil protection legislation. In M. L. Larramendy & S. Soloneski (Eds.), *Environmental health risk* (1st ed., pp. 57–75). InTech.
- Vetrimurugan, E., Brindha, K., Elango, L., & Ndwandwe, O. M. (2017). Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta. *Applied Water Science*, 7(6), 3267–3280.
- Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of Soil Science and Plant Nutrition*, 10(3), 268–292.
- Vurm, K. (2001). *Dějiny příbramské hutě 1311–2000 (History of the Příbram Smelter 1311–2000)*. Příbram, Czech Republic. (in Czech).
- Wang, X., Cheng, G., Zhong, X., & Li, M. H. (2009). Trace elements in sub-alpine forest soils on the eastern edge of the Tibetan Plateau, China. *Environmental Geology*, 58(3), 635–643.
- World Health Organization (WHO). (2020). Arsenic. Retrieved April 23, 2020 from <https://www.who.int/news-room/fact-sheets/detail/arsenic>.
- Zhang, Y., Hou, D., O'Connor, D., Shen, Z., Shi, P., Ok, Y. S., Tsang, D. C., Wen, Y., & Luo, M. (2019). Lead contamination in Chinese surface soils: Source identification, spatial-temporal distribution and associated health risks. *Critical Reviews in Environmental Science and Technology*, 49(15), 1386–1423.
- Zhou, T., Wu, L., Luo, Y., & Christie, P. (2018). Effects of organic matter fraction and compositional changes on distribution of cadmium and zinc in long-term polluted paddy soils. *Environmental Pollution*, 232, 514–522.
- Žák, K., Rohovec, J., & Navrátil, T. (2009). Fluxes of heavy metals from a highly polluted watershed during flood events: a case study of the Litavka River, Czech Republic. *Water, Air and Soil Pollution*, 203(1–4), 343–358.