

Fractionation and Mobilization of Toxic Elements in Floodplain Soils from Egypt, Germany, and Greece: a Comparison Study¹

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Abstract—Determining the chemical fractions of toxic elements (TEs) in soils is important to evaluate their mobilization and bioavailability. In this study, samples from three representative floodplain soils located close to the Rivers Nile (Egypt), Elbe (Germany), and Pinios (Greece) were used to link the soil formation and properties to the geochemical fractions and mobilization of cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) in these soils. The Elbe soil showed the highest total concentration of the elements except for Ni, in which the Pinios soil had the highest amount. A significant amount (55–94%) of the elements was present in the Elbe soil in the potentially mobile (non-residual) fraction, while the amount of this fraction ranged between 9 and 39% in the Pinios soil and between 9 and 34% in the Nile soil. In the Elbe soil, most of the non-residual Ni, Pb, and Zn was associated with the Fe–Mn oxide fraction, while Cd was distributed in the soluble plus exchangeable fraction and Cu in the organic fraction. In the Nile and Pinios soils the Fe–Mn oxide fraction was the abundant pool for Cu, Ni, Pb, and Zn whereas Cd had the highest amount in the soluble plus exchangeable as well as in the carbonate fractions.

Keywords: floodplains, mobilization, sequential extraction, trace elements

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INTRODUCTION

In recent years, increasing agricultural, industrial and urban activities have led to a significant release of toxic elements (TEs) including cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) into environment. These TEs can contaminate soils and can be transferred into the food chain [21]. Soil, with its potential to filter and transform TEs, is concerned as a key factor for environmental health [16]. The TEs occur naturally in soils and some of them are essential micronutrients for plants. At elevated levels, TEs, however, may become potentially toxic. Because of the growing awareness of these problems, TEs in soils have received widespread scientific and legislative attention during the last years [18].

Knowledge about total concentrations of TEs in soils is essential for many geochemical applications; however, total TEs concentration alone is definitely not sufficient for an adequate assessment of the environmental impacts of metal contaminants. The toxicity and mobilization of TEs in soils depend on their specific chemical form, their binding state, the metal

properties, and soil properties [10, 27, 37, 44]. Therefore, the chemical fractionation of TEs should be taken into account in pollution studies since total concentrations in soils provide limited information on the mobilization of these elements [27, 37, 44]. Thus, assessment of the mobilization of TEs in soils using sequential extraction techniques is a key issue in many environmental studies [37, 44].

The distribution of TEs among specific fractions varies widely based on the element's chemical properties and soil characteristics such as pH, particle size distribution, total carbonates, Fe–Mn oxides, organic matter (OM), and mineralogical composition. Thus, TEs distribute in soils in various geochemical fractions, i.e. water-soluble, exchangeable, carbonate associated, Fe–Mn oxide-associated, organic-associated and residual forms. Water-soluble and exchangeable fractions are considered to be mobile; oxide-, carbonate- and organic matter- bound fractions may be potentially mobile; while the mineral fraction is mainly not available to either plants or microorganisms [20, 27, 37, 44, 20]. For environmental purposes, a subject of prime interest tends to be the amount of mobile fraction of TEs in the soils, since this fraction greatly influences plant growth and element uptake,

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the quality of ground waters, and the pollution status of waterways [29]. Therefore, it is important to evaluate the mobilization of TEs to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of TEs contaminants in soils.

Floodplain soils are formed by the periodical deposition of suspended sediments from river water during flood events [11, 34]. Because of their generally high fertility, some floodplain soils have also been intensively used for agriculture for a long time. Today, an additional considerable risk is associated with the often very high levels of TEs in floodplain soils [7, 9, 17, 31, 33, 38, 45].

Soils are dynamic systems and their formation is depended on the climate and the position in the landscape which determines the hydrological regime, soil biota, parent material and time. A number of studies have shown correlations between soil formation and properties [9]. The progress of soil formation may therefore influence the distribution of TEs in soils. During soil formation, the soil properties can change dramatically, impacting the fractions and mobilization of TEs. The agricultural floodplain soils of Egypt, Germany and Greece differ widely in their origin, development and properties and therefore it is expected TEs content and its distribution among the different geochemical fractions to differ significantly.

Previous studies have detected Mollic Fluvisols and Eutric Gleysols as the most contaminated soil types in floodplains along the Elbe River and have determined the geochemical fractions of TEs in these soils (e.g., [33, 37, 44]). In addition, Shaheen et al. [43] presented the geochemical fractions of Co, Ni, Se, V in floodplain soils at the lower course of the Nile Delta. However, considerable knowledge gaps exist about the fractionation of TEs in the floodplains at the Pinios River. Moreover, according to our knowledge the comparison between the geochemical fraction and mobilization of TEs in three representative floodplain soils originates from different regions under large variation of the soil forming factors and process is still limited. Therefore, the objective of this study was to quantify and compare the total concentrations of cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) as well as their geochemical fractions in three selected floodplain soils representing the fluvial sediments of the rivers Nile (Egypt), Elbe (Germany), and Pinios (Greece) in relation to basic soil properties.

MATERIALS AND METHODS

Sampling Sites

Three surface soil samples were collected from floodplains close to the Rivers Nile, Elbe and Pinios representing the fluvial soils in Egypt, Germany and Greece, respectively (Fig. 1).

The German study area is located in floodplains at the Central Elbe River in Germany. It has been served

as model region for common floodplains in Europe [17]. The sampling location is situated on stream kilometer 284, (51°54'51" N, 11°58'33" E) (Fig. 1). The long-term annual precipitation ranges from 470 to 570 mm and the mean annual air temperature is approximately 8.0°C [34]. The sampling location was selected after large-scale conventional soil mapping and several years of comprehensive field pedological research in the floodplains of the Elbe River [34, 35, 53]. The site is used as extensive grassland, pasture or fallow. The study site is periodically flooded mainly depending on snow melt (winter and spring) and heavy rainfalls (spring and summer).

The study site of the Egyptian soil is located in the Kafr El-Sheikh governorate at the north of the Egyptian Nile Delta. The Nile delta is located along the southern coast of the Mediterranean Sea (30°00'–31°40' N and 30°00'–32°30' E) (Fig. 1), which is under an arid climate with an annual precipitation of <100 mm [5]. More details about this soil are published in Shaheen et al. [45]. The site is used as agricultural soil for different field crops such as corn and vegetables in summer and wheat and/or beans in winter.

The Greek soil was a typical alluvial soil located in a place near to Pinios River very close to the city of Larissa. These soils are developed by the continuous deposition of soil materials carried by the Pinios River's waters which goes through a catchment area consisting mainly of calcareous rocks. The climate in the area is characterized by the low annual rainfall ranging from 400 to 500 mm, and high air temperature happened during the summer time (mean annual air temperature 15.5–16.5°C, mean maximum air temperature 43–46°C and mean annual minimum air temperature –0.2°C). Very often these soils flooded by the Pinios River's waters. They are productive soils cultivated mainly with corn, cotton, and alfalfa [13].

Soil Collection and Characterization

The collected samples were air-dried, ground to pass through a 2-mm sieve and analyzed for their basic physical and chemical properties according to the procedures referred by Sparks et al. [49]. Dithionite extractable iron (Fe_d) was extracted with 3M sodium citrate + 1 M sodium bicarbonate + 1 g sodium dithionite in a water bath heated at 85°C [28]. Associated Al and Mn measured in the same extracts. Oxalate extractable iron (Fe_o), aluminum (Al_o), and manganese (Mn_o) oxides content were extracted with 0.175 M ammonium oxalate + 0.1 M oxalic acid adjusted to pH 3.0. Alkaline soils were pre-treated with 1 M ammonium acetate (pH 5.5) to remove carbonates according to Loeppert and Inskeep [26]. The values of Fe, Al and Mn in the extractants were determined by atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia). Particle size analysis was performed according to Gee et al. [15] and Schlichting et al. [40].



Fig. 1. Map of the sampling locations.

Fractionation of Cd, Cu, Ni, Pb, and Zn

We have selected Cd, Cu, Ni, Pb, and Zn because they reveal relatively high concentrations as compared to other elements in the studied soils and their high ecotoxicological impact on the agro-ecosystem [37, 42, 44].

Fractionation of Cd, Cu, Ni, Pb, and Zn in the Nile and Pinios Soils

The chemical fractions of Cd, Cu, Ni, Pb, and Zn were determined by a sequential extraction method or five-step chemical fractionation based on the work of Tessier et al. [50] and proposed by Elliot et al. [12], Garcia-Delgado et al. [14], and Sánchez-Martín et al. [39] to characterize the partitioning of Cd, Cu, Ni, Pb,

and Zn in studied soils. The method used discriminates the elements into soluble plus exchangeable (F1: 1 M NH_4OAc (pH 7.0), easily mobilizable or carbonate bound (F2: 1 M NH_4OAc adjusted to pH 5 with HOAc), Fe-Mn oxide bound (F3: 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 0.1 M $\text{H}_2\text{C}_2\text{O}_4$), organically bound (F4: 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$), and residual fraction (F5: $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2$). Separation between steps was by decantation of the supernatant after centrifugation at 5000 rpm for 20 min. In order to determine the total metal concentrations 1 g soil was solubilized by acid digestion using $\text{HNO}_3 + \text{HCl} + \text{H}_2\text{O}_2$ [52]. Additionally, available form was extracted using DTPA [25]. The element concentrations were determined using an atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia).

Table 1. Classification and selected properties of the studied floodplain soils

Tested characteristics	Nile Soil	Pinios Soil	Elbe Soil
	Typic Ustifluent	Typic Xerofluent	Vertic Fluvaquent
Particle size distribution, %			
Sand (0.063–2 mm)	12	75	5
Silt (63–2 µm)	41	16	48
Clay (<2 µm)	47	9	47
Tested Basic characteristics			
pH (1 watetr : 1 soil)	7.87	7.75	4.05
EC, (dS/m)	0.782	0.184	1.03
OM, %	1.86	1.31	9.92
CEC, cmol _c kg ⁻¹	72.1	13.6	16.35
CaCO ₃ , %	1.5	10.45	16.35
Olsen-P, mg kg ⁻¹		18.8	7.81
Total oxides, g kg ⁻¹			
Fe	57.8	22.7	28.6
Mn	1.06	0.61	0.21
Al	52.8	37.8	–
CBD-extracted oxides, g kg ⁻¹			
Fe _d	10.8	2.96	6.90
Mn _d	0.92	0.25	0.01
Al _d	0.89	0.23	–
Oxalate-extracted oxides, g kg ⁻¹			
Fe _{ox}	2.54	1.12	6.30
Mn _{ox}	0.78	0.19	0.02
Al _{ox}	1.86	0.80	–
Active oxide ratio, OX/CBD			
Fe _o /Fe _d	0.235	0.378	0.913
Mn _o /Mn _d	0.848	0.760	2.000
Al _o /Al _d	2.089	3.478	–

pH (1 : 1 H₂O); EC; Electric conductivity; OM: Organic matter; CEC: Cation Exchange Capacity (cmolc kg⁻¹); TCE: Total CaCO₃ equivalent; Fe_d, Al_d, Mn_d: Citrate-bicarbonate-dithionate (CBD) extractable- Fe, Al, Mn; Fe_o, Al_o, Mn_o: Ammonium oxalate-oxalic acid extractable- Fe, Al, Mn; nd: not detected; (–): not measured.

Fractionation of Cd, Cu, Ni, Pb, and Zn in the Elbe soil

The soil was sequentially extracted to obtain the seven fractions of Cd, Cu, Ni, Pb and Zn according to Zeien and Brummer [56] and proposed by Rinklebe and Shaheen [37] and Shaheen and Rinklebe [44]. Briefly, 2 g of air dried soil (<2 mm) and 50 mL extracting agent were shaken (overhead 20 rotations min⁻¹) at 20°C. The soil was centrifuged for 10 min at 3000 g and filtered (592, Schleicher and Schuell, Dassel, Germany). The extracting agents and common interpretation of fractions were as follows: F1: 1 M NH₄NO₃ (Soluble plus exchangeable fraction), F2: 1 M NH₄-acetate (easily mobilizable fraction), F3: 0.1 M [NH₃ (OH)]Cl + 1 M NH₄-acetat (bound to Mn (hydr)oxides), F4: 0.025 M NH₄-EDTA (bound to soil organic matter (SOM)), F5: 0.2 M NH₄-oxalate buffer (bound by low crystalline Fe (hydr)oxides), F6: 0.2 M NH₄-oxalate buffer + ascorbic acid (bound by crystalline Fe (hydr) oxides), F7: Aqua Regia (residual fraction). The entire pool of Fe-Mn oxide fraction in the tabled data calculated from the summation of F3, F5 and F6 and presented as F3. Pseudototal concentrations of Cd, Cu, Ni, Pb, and Zn in separate soil samples were quantified after digestion using aqua regia (37% HCl 65% HNO₃, 3 : 1) (DIN ISO 11466, 1997).

Chemical Analysis and Quality Control

The total concentrations of Cu, Ni, Pb, and Zn in the digested soil samples and the concentrations of different element fractions after extractions of the soil were measured by inductively-coupled plasma with optical emission spectrometry (ICP-OES) and Cd by graphite furnace atomic absorption spectrometry (GF-AAS). Blanks, triplicate measurements of the elements in the extracts, and analysis of multi-element standards (Merck) were routinely included for quality control. Maximum allowable relative standard deviation between replicates was set to 10%. Origin Pro 7.5G (OriginLab Corporation, Northampton, USA) was used for creating the figures.

RESULTS AND DISCUSSION

Characterization of the Studied Soils

Classification of the studied soils and their basic properties are presented in (Table 1). The three soils are classified as Entisols [48]. The Nile soil is a Typic Ustifluent, the Pinios soil a Typic Xerofluent, and the Elbe soil is classified as Vertic Fluvaquent. The soils exhibited different particle size distribution and

chemical properties. The diverse geological nature of these deposits is reflected in the wide variation of clay content, carbonates content, and the forms of Fe, Al and Mn oxides. The Pinios soil is characterized by a sandy texture while the Nile and the Elbe soils are dominated by silt and clay. The Nile and Pinios soils were alkaline with pH values ranging from 7.8 to 7.9, while the Elbe soil was acidic with pH value 4.1. The Nile soil showed the highest cation exchange capacity ($72.1 \text{ cmol c kg}^{-1}$) followed by the Elbe (16.4) and the Pinios soils (13.6). The Nile and Pinios soils were poor in OM content compared to the Elbe soil. Enrichment of the Elbe soil by OM could be explained by the prolonged sedimentation of OM-rich colloids and particles at restricted aerobic decomposition during the flooding conditions [36]. The Pinios soil had the highest total calcium carbonate content (0.5%) followed by the Nile soil, while no carbonates were detected in the acidic Elbe soil. Total Fe, Al, and Mn concentrations differed largely between the soil (Table 1). The Nile soil showed the highest total concentrations of Fe, Al and Mn compared to the two other soils. In the Nile and Pinios soils, the Fe_o and Mn_o concentrations were low compared to Fe_d and Mn_d suggesting that the majority of Fe and Mn existed in crystalline forms. On the other hand, Al_o values were higher than those of Al_d suggesting that Al oxides mainly existed in amorphous form. However, in the Elbe soil, the amorphous iron (Fe_o) was very close to Fe_d , while Mn_o values were higher than those of Mn_d suggesting that Mn oxides mainly existed in amorphous form. Thus, the active ratios (Fe_o/Fe_d and Mn_o/Mn_d) of these oxides differed between the studied soils, where the Elbe soil showed the highest active Fe and Mn ratios followed by Pinios and Nile soils (Table 1). A number of studies have shown correlations between soil development and soil properties such as pH, carbonate content, clay mineralogy, soil organic matter composition or extractable Fe-, Mn- and Al-oxides [9]. The progress of soil formation may therefore significantly influence TEs distribution in soils. Consequently, the large differences in these properties were expected to affect TEs mobilization and distribution by fractions.

Total Concentrations and Fractions of Cd, Cu, Ni, Pb, and Zn Total Concentrations

The Elbe soil showed the highest total concentration of the studied elements (except Ni), in which the Pinios soil had the greatest amount of this element (Table 2). Such high total TEs concentrations in samples from soils closer to the Elbe River were described previously [7, 37, 44]. Furthermore, the total TEs concentrations in the Elbe soil were in the range of those documented for other floodplain soils along the river Elbe and its catchment [7, 37, 44]. Concentrations of the studied TEs (except Pb) were lower than the mean concentrations of topsoils reported for the Elbe soil [22]. However, according to the critical con-

centrations in soils as referred by Kabata-Pendias [21], the total concentrations of Cu, Pb, and Zn in the Elbe soil were found to be within the critical range concentrations. The Pinios soil showed total Ni higher than the critical concentration. The three soils had total Cd lower than the critical concentrations.

High total TEs concentration in the Elbe soil compared to the Nile and Pinios soils are considered to be due to the discharge of contaminated waters into the Elbe River by these elements mainly caused by anthropogenic activities. In this respect, it was reported that, during the last century large amounts of TEs from anthropogenic and geogenic sources have been accumulated in floodplain soils of the Elbe River ecosystem [33, 37, 44]. These TEs were carried along with the river water and sediments, and originate from various sources in the catchment area such as industrial or mining activities, agricultural non-point sources, mining, or natural, geogenic processes [31, 34]. Large portions of these contaminants are sorbed to suspended particulate matter and can sediment in the riverbed [11]. On the other hand the high total concentrations of Ni in the Pinios and Nile soils as compared to the Elbe soil might be explained by the increase of Ni-bearing clay minerals in the Pinios and Nile soils. We did not determine clay mineralogy of the soils under consideration, but previous studies showed that similar fluvial soils from Egypt and Greece contain appreciable amounts of serpentine, vermiculite, smectite, and different ferromagnesian minerals [1, 41].

Fractions of Cd, Cu, Ni, Pb, and Zn

The sequential extraction used in this study is useful to indirectly assess the potential mobility and mobilization of the studied elements in the soils. The chemical fractions are operationally defined by an extraction sequence that follows the order of decreasing solubility [2]. Assuming that the potential mobility is related to solubility, then element mobilization decreases in the order: water soluble > exchangeable > carbonate > Fe-Mn oxide > organic > residual [27, 37, 44]. This order offers qualitative information about element bioavailability. Based on the above information, we can further assume that elements in the non-residual fractions are potential mobile than elements associated with the residual fraction. The non-residual fraction is the summation of the extracted fractions except the residual fraction [37, 44]. The non-residual fraction is often considered as the potential hazardous fraction to organisms because this fractions bond much less strongly with soil phases than residual fraction [57]. Additionally, the mobilization of TEs in soils will be assessed using the mobile fraction ($\text{MF} = \text{F1} + \text{F2}$) [37, 44]. The high MF values have been interpreted as symptoms of relatively high lability and biological availability of TEs in soils [27, 37, 44]. The concentrations of element content in each fraction are expressed as mg kg^{-1} and as an extraction percentage, reflecting

Table 2. Chemical fractions of Cd, Cu, Ni, Pb, and Zn in the studied floodplain soils

Fractions	Nile Soil		Pinios Soil		Elbe Soil	
	mg kg ⁻¹	% of ΣF1–F5	mg kg ⁻¹	% of ΣF1–F5	mg kg ⁻¹	% of ΣF1–F5
Cd						
F1	0.08	4.65	0.02	1.33	0.75	52.45
F2	0.12	6.98	0.35	23.33	0.24	16.78
F3	0.07	4.07	0.21	14.00	0.25	17.49
F4	—	0.00	—	0.00	0.10	6.99
F5	1.45	84.30	0.92	61.34	0.09	6.29
ΣF1–F5	1.72	100.0	1.50	100.0	1.43	100.0
Total	1.81		1.68		1.85	
% Recovery	95.0		89.3		77.3	
Cu						
F1	0.14	0.21	0.11	0.37	1.91	1.70
F2	0.17	0.26	0.23	0.77	2.44	2.17
F3	18.46	28.14	9.27	31.22	33.76	30.08
F4	3.25	4.96	1.32	4.45	43.02	38.32
F5	43.71	66.63	18.88	63.59	31.13	27.73
ΣF1–F5	65.60	100.0	29.70	100.0	112.26	100.0
Total	67.46		31.92		119.70	
% Recovery	97.24		93.04		93.78	
Ni						
F1	0.27	0.37	0.15	0.06	4.82	13.94
F2	0.43	0.60	1.27	0.55	0.31	0.90
F3	6.58	9.18	14.06	6.06	11.24	32.50
F4	0.58	0.81	4.43	1.91	2.75	7.95
F5	63.75	89.04	212.34	91.45	15.46	44.71
ΣF1–F5	71.60	100.0	232.2	100.0	34.58	100.0
Total	74.27		236.41		29.05	
% Recovery	96.41		98.22		119.04	
Pb						
F1	1.06	3.84	0.38	1.79	14.48	8.28
F2	0.48	1.75	2.05	9.53	24.29	13.89
F3	1.20	4.36	1.12	5.21	72.69	41.58
F4	0.00	0.00	0.72	3.35	46.92	26.83
F5	24.76	90.05	17.23	80.13	16.47	9.42
ΣF1–F5	27.50	100.0	21.50	100.0	174.85	100.0
Total	30.56		22.78		188.55	
% Recovery	89.99		94.38		92.73	
Zn						
F1	0.14	0.15	0.07	0.17	21.78	18.20
F2	0.28	0.31	0.27	0.62	2.47	2.06
F3	6.51	7.16	2.83	6.59	39.63	33.12
F4	1.58	1.73	0.56	1.30	3.43	2.87
F5	82.45	90.65	39.27	91.32	52.35	43.75
ΣF1–F5	90.95	100.0	43.00	100.0	119.66	100.0
Total	92.49		45.64		110.00	
% Recovery	98.33		94.22		108.78	

F1: Soluble + Exchangeable fraction; F2: Carbonate fraction; F3: Fe/Mn Oxide fraction; F4: Organic fraction; F5: Residual fraction; bdl: Below Detection Limit.

individual fraction removal relative to the total concentration which represents 100% (Table 2, Figs. 2 and 3).

Cadmium

The studied soils showed high variation in the distribution of Cd among the different geochemical frac-

tions (Fig. 2). In the Nile and Pinios soils, Cd was mostly concentrated in the residual fraction, while in the Elbe soil it was concentrated in the non-residual fractions. The percentages of total Cd in the residual fraction were 6.3, 61.3 and 84.3% in the Elbe, Pinios and Nile soils, respectively. These data demonstrate that, in the Elbe soil the percentage of Cd in the non-

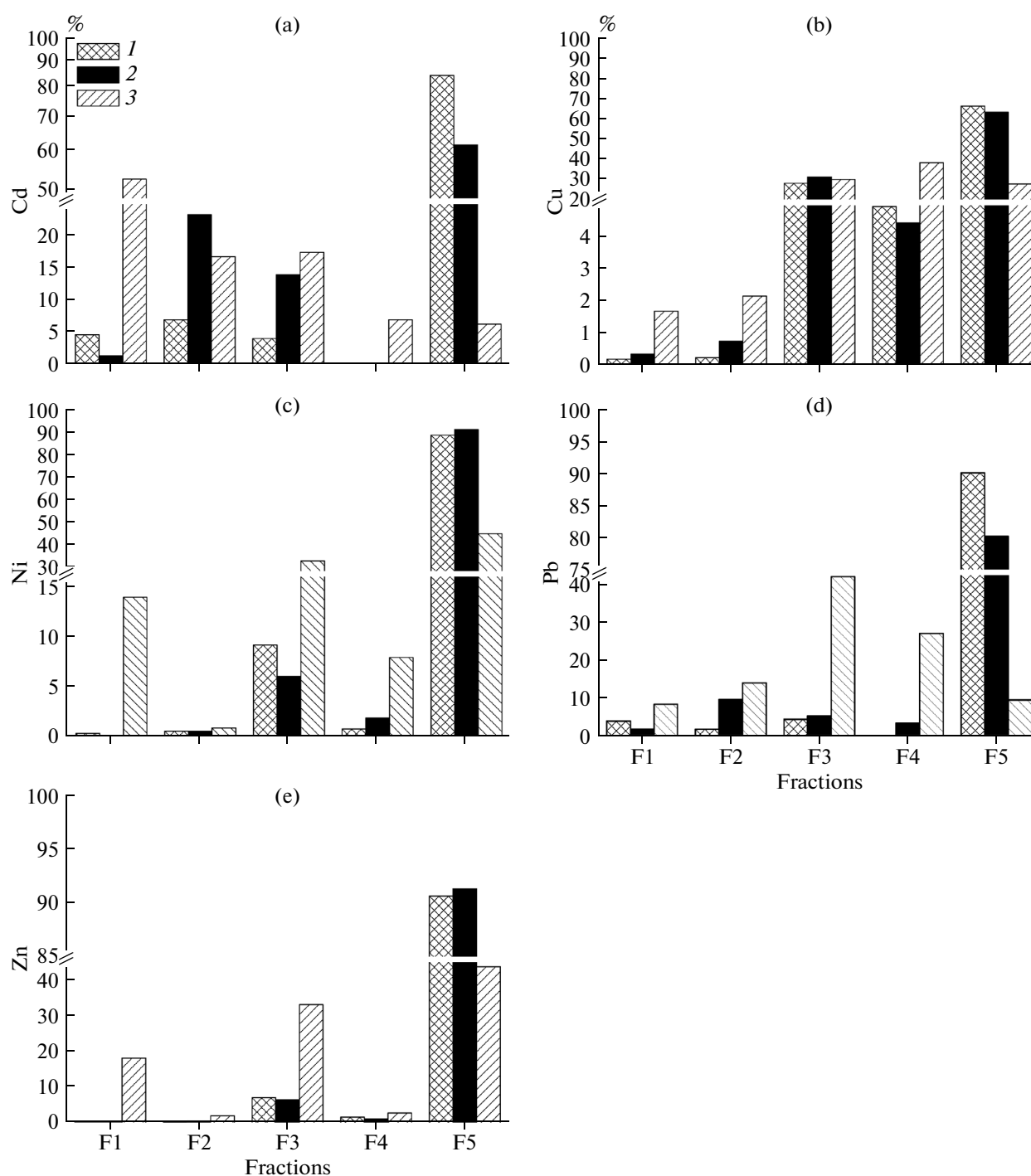


Fig. 2. Chemical fractions of Cd, Cu, Ni, Pb and Zn (% of ΣF1-F5) in floodplain soils from Egypt, Germany and Greece.

residual fractions (93.7%) was much greater than that of the residual fractions (Fig. 3). Among the non-residual fractions, the soluble plus exchangeable fraction contained the largest amount of Cd in Elbe River soil compared to the Nile and Pinios soils, in which the carbonate fractions have the highest amount of Cd (Fig. 2, Table 2). Increasing the soluble plus exchangeable fraction of Cd in the Elbe soil may be explained by

its high acidity, while increasing of the carbonate Cd fraction in the Pinios and Nile soils could be explained by their high alkalinity and carbonate content. Furthermore, our data showed that about 4–17% of the total Cd was distributed in oxide fraction in the soils and only 7% of Cd in the Elbe soil was in the organic fraction, while the same fraction was not detected in the Nile and Pinios soils.

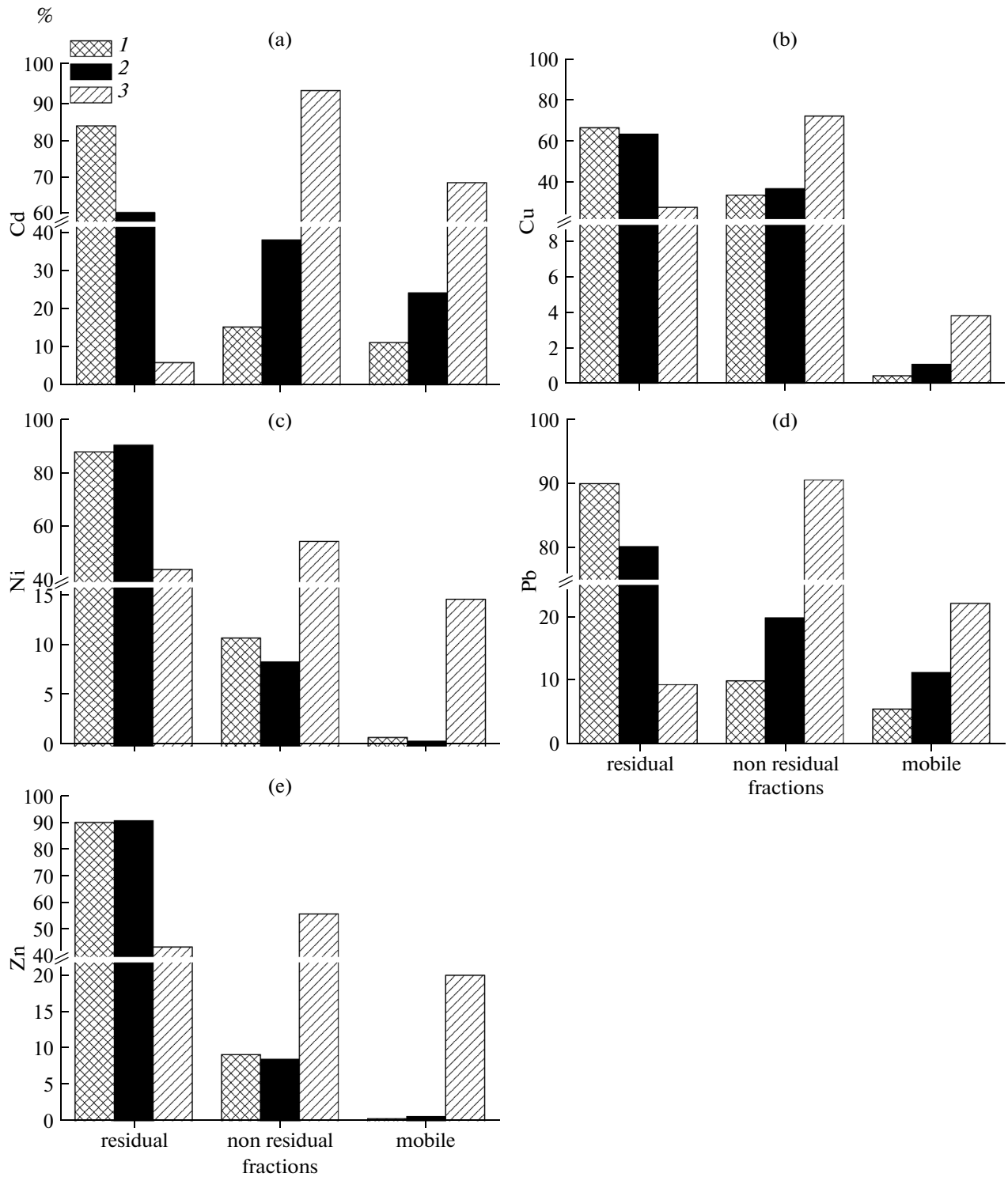


Fig. 3. Distribution of Cd, Cu, Ni, Pb and Zn (% of total) among the residual, non-residual, and mobile fraction in floodplain soils from Egypt, Germany and Greece.

Data in Fig. 3 showed that the MF of Cd was the dominant non-residual fraction in the soils especially in the Elbe soil. This suggests that Cd in the studied soils especially in the Elbe soil was potentially mobile

because the metals present in the MF are usually thought to be readily available for plant uptake [37, 44, 45]. In this respect, Lair et al. [23] studied the distribution of Cd among geochemical fractions in floodplain

soils and reported that Cd remained in weakly bound fractions in both original and spiked soils. Additionally, [54] it was reported that Cd has the highest mobilization of the elements studied since it presented the highest content in the first fraction (mobile) followed by Mn, Zn, Pb Cu, and Fe, respectively. This indicated that Cd formed weak complexes and was easily removed at the initial stages of the extraction. Those results indicate that the potential release of Cd may be harmful for the ecosystem particularly with view to the transfer of Cd in the food chain via plants and/or groundwater.

Copper

The data of Table 2 show that most of the Cu in the Nile and Pinios soils was present in the residual fraction (63–67%), while only 28% of the total Cu was distributed in the residual fraction in the Elbe soil (Fig. 3). Although Cu was found in the non-residual fractions in the three soils, a small percentage of Cu (0.47–3.8%) was associated with the MF. These results confirm that, Cu is specifically adsorbed or fixed in soils, making it one of the TEs which move the least [47]. The Fe-Mn oxide Cu was the dominant non residual fraction in the Nile and Pinios soils (28–31%) followed by the organic fraction (<5%). On the other hand, the organic fraction was dominant (38%) in the Elbe soil followed by Fe-Mn oxide Cu (30%) as shown in Fig. 2. These results concluded that, Cu distribution in various chemical fractions depended on the total Cu content of the studied soils. As the total Cu concentration in the Elbe soil is higher compared to the two other soils, the percent of total Cu in the soluble + exchangeable, carbonate, and organic fractions increased. Increasing the organic fraction of Cu in the Elbe soil may be explained by its high content of total organic carbon. The major association of Cu with the organic fraction in the Elbe soil may be due to high formation constants of organic-Cu complexes. Our results were consistent with those of Ma and Rao [27] who found significant amount of Cu in soils associated with the organic fraction and forms specific complexes with soil organic matter. The association of a significant amount of Cu with organic fractions was also observed by others who found that the MF accounted for less than 0.5% of the total soil Cu [2, 44].

Lead

In the Nile and Pinios soils, Pb was mostly concentrated in the residual fraction, while in the Elbe soil it was concentrated in the non-residual fractions (Table 2). The percentages of total Pb in the non-residual fraction were about 90, 20 and 10% in Elbe, Pinios and Nile soil, respectively (Fig. 3). Among the non-residual fractions, Fe-Mn oxide fraction contained the largest amount of Pb in the Elbe (42%) and Nile soils (4.4%) followed by the organic fraction

(27%) in the Elbe and soluble + exchangeable fraction in the Nile soil. While in the Pinios soil, carbonate fraction had the greatest amount of Pb (Fig. 2). The increase of the oxide fraction in the Elbe and Nile soils might be explained by the higher active iron rations in these soils than the Pinios soil. In addition, the increase of the carbonate fraction in the Pinios soil might be due to its high content of total calcium carbonates as compared to the Elbe and Nile soils (Table 1). Similar findings have been reported in the study of Li et al. [24] in which a low percentage of soluble and exchangeable fractions of Pb (1.8%) were observed [24]. This is consistent with results obtained by several authors who found that Fe and Mn hydrous oxides are important scavengers of Pb [2]. In this respect, Nogueira et al. [30] reported that Pb was the element found associated to more stable amorphous and crystalline fractions and not to the exchangeable fraction. Lead usually shows high affinity to the oxide and residual fractions [47], where it is strongly bound and thus decreases its mobilization and soil availability to plants [46].

The MF of Pb in the Elbe soil was high compared to the Nile and Pinios soils. The percentages of total Pb in the mobile fraction were 22.2, 11.3, and 5.6% in the Elbe, Pinios, and Nile soils, respectively (Fig. 3).

Nickel

The Elbe soil showed -unlike the other tested elements- lower concentration of total Ni than the Nile and Pinios soil (Table 2). However, like, Cd and Cu most of the total Ni in the Nile and Pinios soils was present in the residual fraction (>89%), while only 45% of the total Ni was fractionated in the residual fraction in the Elbe soil (Fig. 3). These results are consistent with the observations of Ma and Rao [27] who suggested that a majority of the Ni in soils and sediments was detrital in nature. Also, our results were in agreement with Doelsch et al. [8] who demonstrated that the residual fraction was the dominating binding form of Ni which can be regarded as hard-reactive concerning metal dynamics. In this respect Xaio et al. [55] studied the fractionation of Ni in cropland soils from reclaimed tidal wetlands in Pearl River estuary, South China and found that the total proportion of exchangeable and carbonate bound Ni contributed less than 6.6% of the total Ni, while similar to Cr, the residual form was predominant, having a proportion of >68% in all the soils sampled.

The Fe-Mn oxide fraction was the dominant non residual fraction in the three studied soils by a percent around 32, 9 and 6% of total Ni in the Elbe, Nile and Pinios soils, respectively followed by the organic fraction in the Nile and Pinios soils and the soluble + exchangeable fraction in the Elbe soil (Fig. 2). According to Kabata-Pendias [21], Ni is geochemically siderophilic and will join metallic Fe wherever such a phase occurs. During weathering process, Ni is

easily mobilized and then is co-precipitated mainly with Fe oxides. The high affinity of Ni to react and be bound to Fe oxides were reported by others [32, 58].

The Elbe soil showed the highest MF of Ni compared to the Nile and Pinios soils. The percentages of total Ni in the MF were 14.8, 0.61 and 0.97% in the Elbe, Pinios and Nile soils respectively (Fig. 3). Increasing the mobile fraction of Ni in the Elbe soil may be explained by its low pH value. These results confirm the immobilization of Ni making it one of the TEs which show low availability. Hseu [19] found that low Ni concentrations were associated with the exchangeable plus carbonate fraction that are considered as readily bio-available. Antic-Mladenovic et al. [4] speculate that an amount of Ni can potentially be mobilized either by reducing dissolution of oxides or oxidative degradation of soil organic matter.

Zinc

Like the other elements, in the Nile and Pinios soils, Zn was mostly concentrated in the residual fraction, while in the Elbe soil it was concentrated in the non-residual fractions. The percent of total Zn in the non-residual fraction were around 57, 10, and 9% in the Elbe, Nile and Pinios soils, respectively (Table 2). The higher percentage of Zn in the residual fraction in the Nile and Pinios soils probably reflects the greater tendency for Zn to become unavailable once it was in soils. Similar Zn results were reported by [6, 29].

Among the non-residual fractions, the Fe-Mn oxide contained the highest amount of Zn in the studied soils containing about 33% in the Elbe soil followed by the soluble plus exchangeable fraction, and 7% in the Nile and Pinios soils followed by the organic fraction (Table 2, Fig. 2). This may be partially due to the high stability constants of Zn oxides. Several other scientists have also found that Zn is associated with Fe-Mn oxides [29, 44].

The MF of Zn in the Elbe soil was high compared to the Nile and Pinios soils. Xian [54] found that the sum of the exchangeable and the carbonate-bound forms were strongly correlated with Zn uptake by cabbage plants (*Brassicu oleruceu*). The MF of Zn was 20.2, 0.8, and 0.5% in the Elbe, Pinios and Nile soil, respectively (Fig. 3), which indicates that the Zn in the Elbe soil may be highly available for plants compared to the Nile and Pinios soils.

CONCLUSIONS

The influence of soil formation, and properties as well as the linked flooding regime on the geochemical fractions and mobilization of selected trace elements is documented based on properties of soils from three river floodplain ecosystems (Nile/Egypt, Elbe/Germany and Pinios/Greece). In the Nile and Pinios soils, the Cd, Cu, Ni, Pb, and Zn distributed mostly in the residual fraction indicating that the greater con-

centrations of these metals are immobile. A significant percentage of total Cu and Cd were associated with the non-residual fractions and therefore, they should be evaluated when studying the pollution levels of trace metals in those soils. In the Elbe soil, the non-residual fraction was the most dominant particularly for Cd, Pb, and Cu suggesting high potential mobility compared to the Nile soil and the Pinios soil. The soil origin, progress of soil formation, and soil properties seem to be significant factors influence the TEs distribution in the soils studied. The results presented in the paper might contribute to regional geochemical research and provide important information on the reactivity of the mentioned trace elements in floodplain soils. Further studies on the vertical distribution of different geochemical fractions of the studied elements and others in complete soil profiles from the studied soils along the Rivers Elbe, Nile, and Pinios are needed for a comprehensive understanding of the geochemical processes determining pollutant distributions and potential mobility in floodplain soils originating from different regions.

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REFERENCES

1. M. Ahmad, A. R. Usman, S. S. Lee, S. Kim, J. Joo, J. E. Yang, and Y. S. Ok, "Egg shell and coral wastes as low cost sorbents for the removal of Pb²⁺, Cd²⁺ and Cu²⁺ from aqueous solutions," *J. Ind. Eng. Chem.* **18**, 198–204 (2012).
2. P. Akkajit and C. Tongcumpou, "Fractionation of metals in cadmium contaminated soil: Relation and effect on bioavailable cadmium," *Geoderma* **156**, 126–132 (2010).
3. B. J. Alloway, "Soil processes and the behaviour of metals," in *Heavy Metals in Soils* (Blackie Academic and Professional, London, 1995), pp. 11–37.
4. S. Antic-Mladenovic, J. Rinklebe, T. Frohne, J. Stärk, R. Wennrich, Z. Tomić, and V. Licina, "Impact of controlled redox conditions on nickel in a serpentine soil," *J. Soils Sediments* **11**, 406–415 (2011).
5. P. G. Appleby, H. H. Birks, and R. J. Flower, "Radiometrically determined dates and sedimentation rates for recent sediments in nine North African wetland lakes," *Aquat. Ecol.* **35**, 347–367 (2001).

6. M. A. Ashraf, M. J. Maah, and I. Yusoff, "Chemical speciation and potential mobility of heavy metals in the soil of former tin mining catchment," *Sci. World J.*, (2012). doi: 10.1100/2012/125608
7. I. Devai, J. Patrick, W. H. Neue, H. DeLaune, R. D. Kongchum, and J. Rinklebe, "Methyl mercury and heavy metal content in soils of rivers Saale and Elbe (Germany)," *Anal. Lett.* **38**, 1037–1048 (2005).
8. E. Doelsch, G. Moussard, and H. Saint Macary, "Fractionation of tropical soil borne heavy metals – comparison of two sequential extraction procedures," *Geoderma* **143**, 168–179 (2008).
9. C. Dorransoro and P. Alonso, "Chronosequence in Almar River fluvial-terrace soil," *Soil Sci. Soc. Am. J.* **5**, 910–925 (1994).
10. G. Du Laing, "Analysis and fractionation of trace elements in soils," in *Trace Elements in Soils*, Ed. by P. S. Hooda (Chichester, UK, Wiley, 2010), pp. 53–80.
11. G. Du Laing, J. Rinklebe, B. Vandecasteele, E. Meers, and F. M. Tack, "Trace metal behavior in estuarine and riverine floodplain soils and sediments: a review," *Sci. Total Environ.* **407**, 3972–3985 (2009).
12. H. A. Elliott, B. A. Dempsey, and M. J. Maille, "Content and fractionation of heavy metals in water treatment sludges," *J. Environ. Qual.* **19**, 330–334 (1990).
13. E. Evangelou, P. Dalias, C. Giourg, and C. D. Tsadilas, "Effect of land-use history on soil carbon and nitrogen in a Mediterranean catchment," *Commun. Soil Sci. Plant Anal.* **45**, 2331–2340 (2014).
14. M. Garcia-Delgado, M. Rodriguez-Cruz, L. Lorenzo, M. Arienzo, and M. Sanchez-Martin, "Seasonal and time variability of heavy metal content and of its forms in sewage sludges from different wastewater treatment plants," *Sci. Total Environ.* **382**, 82–92 (2007).
15. G. W. Gee and J. W. Bauder, "Particle size analysis," in *Methods of Soil Analysis: Physical and Mineralogy Methods, Part 1*, Ed. by A. Klute, et al. (American Society of Agronomy, Madison, WI, 1986), pp. 383–412.
16. M. Graf, G. J. Lair, F. Zehetner, and M. H. Gerzabek, "Geochemical fractions of copper in soil chronosequences of selected European floodplains," *Environ. Pollut.* **148**, 788–796 (2007).
17. K. Henle, F. Dziock, F. Foeckler, K. Follner, V. Hüsing, A. Hettrich, M. Rink, S. Stab, and M. Scholz, "Study design for assessing species environment relationships and developing indicator systems for ecological changes in floodplains – the approach of the RIVA Project," *Int. Rev. Hydrobiol.* **91**, 292–313 (2006).
18. P. S. Hooda, *Trace Elements in Soils* (Chichester, UK, Wiley, 2010).
19. Z. Hseu, "Concentration and distribution of chromium and nickel fractions along a serpentinitic toposequence," *Soil Sci.* **171**, 341–353 (2006).
20. C. Kabala and B. R. Singh, "Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter," *J. Environ. Qual.* **30**, 485–492 (2001).
21. A. Kabata-Pendias, *Trace Elements in Soils and Plants* (CRC Press, Boca Raton, 2011).
22. F. Kruger and A. Grongroft, "The difficult assessment of heavy metal contamination of soils and plants in Elbe River floodplains," *Acta Hydrochim. Hydrobiol.* **31**, 436–443 (2003).
23. G. Lair, M. Graf, F. Zehetner, and M. Gerzabek, "Distribution of cadmium among geochemical fractions in floodplain soils of progressing development," *Environ. Pollut.* **156**, 207–214 (2008).
24. Q. Li, Z. F. Wu, B. Chu, N. Zhang, S. S. Cai, and J. H. Fang, "Heavy metals in coastal wetland sediments of the Pearl River estuary, China," *Environ. Pollut.* **149**, 158–164 (2007).
25. W. L. Lindsay and W. A. Norvell, "Development of a DTPA soil test for zinc, iron, manganese and copper," *Soil Sci. Soc. Am. J.* **42**, 421–428 (1978).
26. R. H. Loeppert and W. P. Inskeep, "Iron," in *Methods of Soil Analysis: Chemical Methods, Part 3*, Ed. by D. G. Sparks, et al. (American Society of Agronomy, Madison, WI, 1996), pp. 639–664.
27. L. Q. Ma and G. N. Rao, "Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils," *J. Environ. Qual.* **26**, 259–264 (1997).
28. O. P. Mehra and M. L. Jackson, "Iron oxides removal from soils and clays by dithionate-citrate system buffered with sodium bicarbonate," *Clays Clay Miner.* **7**, 317–327 (1960).
29. F. Nannoni, G. Protano, and F. Riccobono, "Fractionation and geochemical mobility of heavy elements in soils of a mining area in northern Kosovo," *Geoderma* **16**, 63–73 (2011).
30. T. A. R. Nogueira, W. J. Melo, I. M. Fonseca, S. A. Marcussi, G. M. P. Melo, and M. O. Marques, "Fractionation of Zn, Cd, and Pb in a tropical soil after nine-year sewage sludge applications," *Pedosphere* **20**, 545–556 (2010).
31. M. Overesch, J. Rinklebe, G. Broll, and H. Neue, "Metals and arsenic in soils and corresponding vegetation at Central Elbe River floodplains (Germany)," *Environ. Pollut.* **145**, 800–812 (2007).
32. M. Rajaie, N. Karimian, and J. Yasrebi, "Nickel transformation in two calcareous soil textural classes as affected by applied nickel sulfate," *Geoderma* **144**, 344–351 (2008).
33. J. Rinklebe, PhD Thesis (Agricultural Faculty, Martin Luther University Halle, Wittenberg, Germany, 2004).
34. J. Rinklebe, C. Franke, and H.-U. Neue, "Aggregation of floodplain soils as an instrument for predicting concentrations of nutrients and pollutants," *Geoderma* **141**, 210–223 (2007).
35. J. Rinklebe, C. Franke, and H.-U. Neue, "Verbreitung, Eigenschaften und Klassifikation von Auenböden-Auenbodenformen als Indikatoren für Nähr- und Schadstoffkonzentrationen," in *Entwicklung von Indikationssystemen am Beispiel der Elbaue* (Ulmer Verlag, Stuttgart, 2009), pp. 130–153.
36. J. Rinklebe and U. Langer, "Microbial diversity in three floodplain soils at the Elbe River (Germany)," *Soil Biol. Biochem.* **38**, 2144–2151 (2006).
37. J. Rinklebe and S. M. Shaheen, "Assessing the mobilization of cadmium, lead, and nickel using a seven-step sequential extraction technique in contaminated floodplain soil profiles along the Central Elbe River, Germany," *Water, Air, Soil Pollut.* **225** (8), 2039 (2014). doi: 10.1007/s11270-014-2039-1

38. J. Rinklebe, A. Stubbe, H.-J. Staerk, R. Wennrich, and H.-U. Neue, "Factors controlling the dynamics of As, Cd, Zn, Pb in alluvial soils of the Elbe River (Germany)," in *Proceedings of Environmental Science and Technology* (American Science, New Orleans, 2005), Vol. 2, pp. 265–270.
39. M. Sánchez-Martín, M. García-Delgado, L. Lorenzo, M. Rodríguez-Cruz, and M. Arienzo, "Heavy metals in sewage sludge amended soils determined by sequential extractions as a function of incubation time of soils," *Geoderma* **142**, 262–273 (2007).
40. E. Schlichting, H.-P. Blume, and K. Stahr, *Bodenkundliches Praktikum* (Blackwell, Berlin, 1995).
41. I. D. Sgouras, C. D. Tsadilas, N. Barbayiannis, and N. Danalatos, "Physicochemical and mineralogical properties of red Mediterranean soils from Greece," *Commun. Soil Sci. Plant Anal.* **38**, 695–711 (2007).
42. S. M. Shaheen, "Sorptions and lability of cadmium and lead in different soils from Egypt and Greece," *Geoderma* **153**, 61–68 (2009).
43. S. M. Shaheen, M. E. Abo-Waly, and R. A. Ali, "Classification, characterization, and management of some agricultural soils in the North of Egypt," in *Developments in Soil Classification, Land Use Planning and Policy Implications: Innovative Thinking of Soil Inventory for Land Use Planning and Management of Land Resources*, Ed. S.A. Shahid, et al. (Springer-Verlag, Dordrecht, 2013), pp. 417–447.
44. S. M. Shaheen and J. Rinklebe, "Geochemical fractions of chromium, copper, and zinc and their vertical distribution in soil profiles along the Central Elbe River, Germany," *Geoderma* **228–229**, 142–159 (2014).
45. S. M. Shaheen, J. Rinklebe, T. Frohne, J. White, and R. DeLaune, "Biogeochemical factors governing Co, Ni, Se, and V dynamics in periodically flooded Egyptian north Nile delta rice soils," *Soil Sci. Soc. Am. J.* **78**, 1065–1078 (2014).
46. M. I. Sheppard and D. H. Thibault, "Desorption and extraction of selected heavy metals from soils," *Soil Sci. Soc. Am. J.* **56**, 415–423 (1992).
47. M. L. Silva and G. C. Vitti, "Fractionation of heavy metals in polluted soil before and after rice cultivation," *Quim. Nova* **31**, 1385–1391 (2008).
48. Soil Survey Staff, *Key of Soil Taxonomy*, 10th ed. (USDA-NRCS Government Printing Office, Washington DC, 2010).
49. D. L. Sparks, A. L. Page, P. A. Helmke, R. H. Loppert, P. N. Soltanpour, M. A. Tabatabai, C. T. Johnston, and M. E. Summner, *Methods of Soil Analysis: Chemical Methods. Part 3* (American Society of Agronomy, Madison, WI, 1996).
50. A. Tessier, P. G. C. Campbell, and M. Bisson, "Sequential extraction procedure for the speciation of particulate trace metals," *Anal. Chem.* **51**, 844–851 (1979).
51. C. D. Tsadilas, V. Samaras, and D. Dimoyiannis, "Phosphate sorption by red Mediterranean soils from Greece," *Commun. Soil Sci. Plant Anal.* **27**, 2279–2293 (1996).
52. United States Environmental Protection Agency (USEPA), *Test Method for Evaluating Solid Waste, Report Number SW-846* (USEPA Office of Solid Waste, Economic, Methods, and Risk Analysis Division, Washington DC, 1986).
53. K. Wälder, O. Wälder, J. Rinklebe, and J. Menz, "Estimation of soil properties with geostatistical methods in floodplains," *Arch. Agron. Soil Sci.* **54**, 275–295 (2008).
54. X. Xian, "Effect of chemical forms of cadmium, zinc, and lead in polluted soils on their uptake by cabbage plants," *Plant Soil* **113**, 257–264 (1989).
55. R. Xiao, J. Bai, H. Gao, L. Huang, C. Huang, and P. Liu, "Heavy metals (Cr and Ni) distribution and fractionation in cropland soils from reclaimed tidal wetlands in Pearl River estuary, South China," *Proc. Environ. Sci.* **13**, 1684–1687 (2012).
56. H. Zeien and G. W. Brummer, "Chemische Extraktion zur Bestimmung von Schwermetallbindungsformen in Boden," *Mitt. Dtsch. Bodenkundl. Ges.* **59**, 505–510 (1989).
57. X. Zhong, S. Zhou, Q. Zhu, and Q. Zhao, "Fraction distribution and bioavailability of soil heavy metals in the Yangtze River delta—a case study of Kunshan city in Jiangsu Province, China," *J. Hazard. Mater.* **198**, 13–21 (2011).
58. D. Zimmer, K. Kiersch, C. Baum, R. Meissner, G. Muller, P. Jand, and P. Leinweber, "Scale-dependent variability of as and heavy metals in a River Elbe floodplain," *Clean – Soil, Air, Water* **39**, 328–337 (2011).