Fractionation of Cd, Cu, Ni, Pb, and Zn in floodplain soils from Egypt, Germany and Greece

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Abstract. Trace elements are potentially toxic to human life and the environment. Element toxicity depends on chemical associations in soils. Therefore, determining the chemical form of an element in soils is important to evaluate its mobility and bioavailability. Initial soil development in river floodplains influences soil properties, processes and therefore behavior of trace elements. In this study, three different floodplain soils sampled at three rivers (Nile/Egypt, Elbe/Germany and Penios/Greece) were used to link soil development and properties to the geochemical fractions and mobility of some trace elements. Sequential extraction was used to fractionate five trace elements (Cd, Cu, Ni, Pb and Zn) into five operationally defined groups: water soluble + exchangeable, carbonate, Fe-Mn oxide, organic, and residual. German soil showed the highest total concentration of the studied elements (except Ni). The Greek soil had the greatest amount of Ni. The residual fraction was the abundant pool for the studied elements examined in the Egyptian and Greek soils while the non-residual fraction was the dominant pool for all elements in the German soil. A significant amount (71-94%) of all elements was present in German soil in the potentially available fraction: non-residual fraction, while the amount of this fraction ranged between 9 and 39 % in Greek soil and between 9 and 34 % in Egyptian soil. These suggest that the potential availability of the studied trace elements was extremely high in German soil compared to the Egyptian and Greek soil. In the German soil, most of the non-residual Cd, Ni and Zn were bounded with the Fe-Mn oxide fraction, while Cu and Pb distributed in the organic fraction. While in the Egyptian and Greek soils Fe-Mn oxide fraction was the abundant pool for the studied elements except for Cd, in which the exchangeable and the carbonate fractions had the greatest amount of Cd. Assuming that mobility and bioavailability of these elements are related to their solubility and geochemical forms, and that they decrease in the order of extraction sequence, the apparent mobility and potential bioavailability for the studied elements in the soils were: Cu > Cd > Ni ≥ Pb = Zn in Egyptian soil, Cd > Cu > Pb> Ni = Zn in Greek soil and Cd > Zn> Pb> Cu > Ni in German soil.

Key Words: Trace Elements; Speciation; Potential Availability; Floodplain Soils

Introduction

Trace elements, such as Cd, Cu, Ni, Pb and Zn, are potential soil pollutants. Soils consist of heterogeneous mixtures of organic and inorganic solid components as well as a variety of soluble substances. Therefore, metal distribution among specific forms varies widely based on the metal's chemical properties and soil characteristics (Hooda, 2010). Thus, it is important to evaluate the mobility of trace elements to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of trace elements in soils (Singh et al. 2005). The evaluation of metal distribution in the various organic and mineral phases found in soils may be more useful for the prediction of metal behavior, including solubility, mobility, bioavailability and thus toxicity (Kapata-Pendias, 2011). It is, therefore, important to find appropriate extraction methods for the quantification of elements bound to specific phases of soils. Therefore, sequential extraction procedures were developed aiming to predict retention, mobility and bioavailability of trace elements in soils. The agricultural

floodplain soils of Egypt, Germany and Greece differ widely in their origin, development and properties and therefore it is expected trace elements content and its distribution among the different chemical fractions differ also widely (Du Laing et al. 2009). Our objective was to investigate concentrations of total Cd, Cu, Ni, Pb, and Zn elements and their speciation in the different chemical fractions in three soil samples representing the fluvial sediments of the rivers Nile, Elbe, and Penios in relation to the basic soil properties.

Materials and Methods

Soil selection and characterization
Three surface soil samples were selected from the floodplain close to the rivers Nile, Elbe and Penios representing the fluvial soils in Egypt, Germany and Greece. The selected samples, 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. (1996). Total free iron oxides (Fe_d) were extracted with 3M sodium citrate + 1 M sodium bicarbonate + 1 g sodium dithionite in a water bath heated at 85 C^o (Mehra and Jackson, 1960). Associated Al and Mn measured in the same extracts.. Some properties of the studied soils are presented in Table 1. Total elements form was digested and extracted using HNO_3 + HCL + H_2O_2 according to USEPA (1995).

Table 1.Classification and selected properties of the studied soils

Characteristics	Egyptian soil	Greek soil	German soil
Classification	Typic Ustifluvent	Typic Xerofluvent	Typic Ustifluvent
Particle size distribution, %			
Sand	12	75	31
Silt	41	16	43
Clay	47	9	26
Tested Basic characteristics			
pH	7.87	7.75	6.98
EC	782.0	184.5	221.0
OM, %	1.86	1.31	16.1
CEC	72.1	13.6	35.9
$CaCO_3$, %	1.5	10.45	0
CBD-extracted oxides, g kg^{-1}			
Fe	10.8	2.96	19.0
Mn	0.92	0.25	8.9
Al	0.89	0.23	-
Oxalate-extracted oxides, g kg^{-1}			
Fe	2.54	1.12	18.2
Mn	0.78	0.19	0.60
Al	1.86	0.8	-

pH (1:1 H_2O); EC; Electric conductivity (µS/cm); OM: Organic matter; CEC: Cation Exchange Capacity (cmol(+)/kg); Fe_d, Al_d, Mn_d: Citrate-bicarbonate-dithionate 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 trace elements in Egyptian and Greek soil samples
The chemical forms of the metals were determined by a sequential extraction method or five-step chemical

fractionation based on the work of Tessier et al. (1979) and proposed by Elliott et al. (1990), Sánchez-Martín et al., (2007) and Shaheen and Tsadilas (2011) to characterize the partitioning of trace metals in studied soils. The method used discriminates the metals into water soluble and 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 $(NH_4)_2C_2O_4$ and 0.1 M $H_2C_2O_4$), organically bound (F4: 0.1 M $Na_4P_2O_7$), an F5: residual fraction = total concentration minus Σ F1 to F4. Separation between steps was by decantation of the supernatant after centrifugation at 5000 rpm for 20 min. Metal and oxides concentrations of samples were determined using an atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia).

Fractionation of trace elements German soil samples
The soil samples were sequentially extracted to obtain the seven fractions of Cd, Cu, Ni, Pb and Zn (Zeien and Brummer 1989). Briefly, 2 g of air dried soil (<2 mm) and 50 mL extracting agent were shaken (over head 20 rotations min^{-1}) at 20 °C. The samples were centrifuged for 10 min at 3000 x g and filtered. The extracting agents and common interpretation of fractions are as follows:
F1: 1 M NH_4NO_3 (mobile fraction), F2: 1 M NH_4-acetate (easily mobilizable fraction), F3: 0.1 M $[NH_3 (OH)]Cl$ + 1 M NH_4 -acetat (bound to Mn (hydr)oxides), F4: 0.025 M NH_4 -EDTA (bound to soil organic matter (SOM)), F5: 0.2 M NH_4–oxalate buffer (bound by low crystalline Fe (hydr)oxides), F6: 0.2 M NH_4–oxalate buffer + ascorbic acid (bound by crystalline Fe (hydr) oxides), F7: residual fraction = total concentration minus Σ F1 to F6. The whole pool of Fe-Mn oxide fraction in the tabled data calculated from the summation of F3, F5 and F6 and presented as F3. The metal concentrations were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, JY 238, Jobin Yvon, France).

Results and Discussion

The sequential extraction is useful to assess the potential mobility and bioavailability of heavy metals in the soils. The chemical fractions are operationally defined). Assuming that bioavailability is related to solubility, then metal bioavailability decreases in the order: water soluble > exchangeable > carbonate > Fe-Mn oxide > organic > residual (Ma and Rao, 1997). This order is just a generalization and offers qualitative information about metal bioavailability. Based on the above information, we can further assume that metals in the non-residual fractions are more bioavailable than metals associated with the residual fraction. The non-residual fraction is the sum of all fractions except the residual fraction.

Cadmium
The three studied soils showed high variation in the total concentration and distribution of Cd among the different fractions. German soil contained high concentration of

total Cd (7.9 mg kg^{-1}) and was highly contaminated compared to the Egyptian (1.7 mg kg^{-1}) and Greek soil (1.5 mg kg^{-1}). In the Egyptian and Greek soils, Cd was mostly concentrated in the residual fraction, while in the German soil it was concentrated in the non residual fractions (Table 2). The percentage of total Cd in the residual fraction were 6.3, 61.3 and 81.8 % in German, Greek and Egyptian soils respectively. These data mean that, in the German soil the percentage of Cd in the non-residual fractions was much greater than that of the residual fractions.

Table 2: Chemical fractions of studied elements in fluvial sediments from Egypt, Germany and Greece

Fractions	Egyptian floodplain		Greek floodplain		Germanic floodplain	
	mg kg^{-1}	% of total	mg kg^{-1}	% of total	mg kg^{-1}	% of total
Cd						
F1	0.15	8.8	0.02	1.3	0.1	1.3
F2	0.12	7.1	0.35	23.3	2.2	27.8
F3	0.04	2.4	0.21	14.0	2.7	34.1
F4	0.00	0.0	0.00	0.0	2.4	30.3
F5	1.39	81.7	0.92	61.3	0.5	6.3
Total	1.70		1.50		7.9	
Cu						
F1	0.14	0.21	0.11	0.37	1.9	1.1
F2	0.17	0.26	0.23	0.77	3.0	1.8
F3	18.5	28.1	9.3	31.2	31.9	18.9
F4	3.3	4.9	1.3	4.5	99.6	59.1
F5	43.7	66.6	18.9	63.5	32.0	19.0
Total	65.6		29.7		168.	
Ni						
F1	0.27	0.37	0.15	0.06	0.2	0.30
F2	0.43	0.60	1.27	0.55	1.3	1.95
F3	6.58	9.18	14.0	6.06	34.2	51.3
F4	0.58	0.81	4.43	1.91	11.3	16.9
F5	63.7	89.0	212.	91.4	19.6	29.4
Total	71.6		232.		66.6	
Pb						
F1	1.06	3.84	0.38	1.79	0.5	0.50
F2	0.48	1.75	2.05	9.53	1.3	1.29
F3	1.20	4.36	1.12	5.21	25.8	25.6
F4	0.00	0.00	0.72	3.35	57.7	57.2
F5	24.7	90.0	17.2	80.1	15.5	15.3
Total	27.5		21.5		100.	
Zn						
F1	0.14	0.15	0.07	0.17	9.5	1.10
F2	0.28	0.31	0.27	0.62	87.6	10.2
F3	6.51	7.16	2.83	6.59	453	52.7
F4	1.58	1.73	0.56	1.30	214	24.9
F5	82.4	90.6	39.2	91.3	96.3	11.1
Total	90.9		43.0		861	

F1: water soluble and exchangeable; F2: carbonate bound; F3: Fe–Mn oxide bound; F4: organically bound; F5: residual fraction; ∑F1-F4: non-residual fraction

Among the nonresidual fractions, the Fe-Mn oxide fraction contained the greatest amount of Cd in German soil compared to the Egyptian and Greek soils, in which the soluble + exchangeable and the carbonate fractions, respectively, had the greatest amount of Cd (Table 2). Also, data showed that about 30 % of the total Cd was distributed in the organic fraction, while the same fraction was not detected in the Egyptian and Greek soils. In this respect, Lair et al. (2008) studied distribution of cadmium among geochemical fractions in floodplain soils of progressing development and reported that cadmium remained in weakly bound fractions in both original and

spiked soils. Increasing the non residual fraction in German soil compared to the Egyptian and Greek soils suggests that Cd in this German soil was potentially bioavailable because the metals present in the exchangeable fraction are usually thought to be readily available for plant uptake.

Copper
German soil contained high concentration of total Cu (168.4 mg kg^{-1}) compared to the Egyptian (65.6 mg kg^{-1}) and Greek soil (29.7 mg kg^{-1}). Like, Cd most of the Cu in the Egyptian and Greek soil soils was present in the residual fraction (> 63 %), while only 19 % of the total Cu was fractionated in the residual fraction in German soil. Ma and Rao (1997) found a majority of the Cu in soils and sediments to be associated with the residual fraction. Although Cu was found in all non residual fractions in the three soils, a small percentage of Cu (0.47- 1.8%) was associated with the water soluble+exchangeable and carbonate fractions, while Fe-Mn oxide fraction was the dominant non residual in the Egyptian and Greek soil soils and the organic fraction was the dominant one in German soil. In the case of German soil, the greatest percentage of Cu was associated with the organic fraction (59%) due to the high organic carbon content. Although Cu was found in all non residual fractions in the three soils , it was mostly concentrated in the Fe-Mn oxide fraction in the Egyptian and Greek soils. Our results were consistent with that of Ma and Rao (1997) who found significant amount of Cu in soils associated with the organic fraction. The major association of Cu with the organic fraction in these soil may be due to high formation constants of organic-Cu complexes. As the total Cu concentration in the German soils increased, the percent of total Cu in the water soluble+ exchangeable, carbonate, and organic fractions increased and Cu in the Fe-Mn oxide and residual fractions decreased. This suggests that as the extent of Cu contamination in soils increased, more Cu was associated with the nonresidual fractions, which increased potential Cu mobility and bioavailability in these soils.

Nickel
Unlike the other tested elements, German soil showed lower concentration of total Ni than the Egyptian and Greek soil (Table 2). However, like, Cd and Cu, most of the total Ni in the Egyptian and Greek soil soils was present in the residual fraction (> 89 %), while only 29 % of the total Ni was fractionated in the residual fraction in German soil. These results are consistent with the observations of Tessier et al. (1980), who suggested that a majority of the Ni in soils and sediments was detrital in nature. The Fe-Mn oxide fraction was the dominant non residual fraction in all three soils by a percent around 51, 9 and 6 % of total Ni in German, Egyptian and Greek soils respectively.

Lead
German soil contained high concentration of total Pb (100.8 mg kg^{-1}) compared to the Egyptian (27.5 mg kg^{-1}) and Greek soil (21.5 mg kg^{-1}). In the Egyptian and Greek soils, Pb was mostly concentrated in the residual fraction,

while in the German soil it was concentrated in the non residual fractions (Table 2). The percentage of total Pb in the residual fraction were 15.3, 80.1 and 90.1 % in German, Greek and Egyptian soils respectively. Among the nonresidual fractions, the organic fraction contained the greatest amount of Pb in German soil (57%) followed by Fe-Mn oxide (25%) compared to the Egyptian and Greek soils, in which the Fe-Mn oxide and carbonate fraction, respectively, had the greatest amount of Pb.

Zinc

Total concentration of Zn in German soil (862 mg kg^{-1}) was higher than Egyptian (91 mg kg^{-1}) and Greek soils (43 mg kg^{-1}). The normal Zn concentration in soils is 70 to 400 mg kg^{-1} (Kabata-Pendias, 2011). These data showed that, the Egyptian and Greek soil were not contaminated with Cu, whereas the German soil was contaminated with Zn. Like the other elements, in the Egyptian and Greek soils, Zn was mostly concentrated in the residual fraction; while in the German soil was concentrated in the non residual fractions (Table 2). The percentage of total Zn in the residual fraction were 11.2, 90.6 and 91.3 % in German, Egyptian and Greek soils respectively. Among the nonresidual fractions, the Fe-Mn oxide contained the greatest amount of Pb in all soils containing about 53 % in German soil , and 7% in the Egyptian and Greek soils.

Conclusion

A sequential extraction procedure was used to fractionate Cd, Cu, Ni, Pb and Zn present in three surface floodplain soil samples close to the rivers Nile, Elbe and Penios in Egypt, Germany and Greece. Different geochemical fractions are operationally defined by an extraction sequence that generally follows the order of decreasing solubility. The residual fraction was the abundant pool (61-91%) for the studied elements examined in the Egyptian and Greek studied soils. However, in German soil, a significant percentage (71-94%) of total elements was associated with the nonresidual fractions. Therefore, they should be evaluated when studying the pollution levels of heavy metals in soils. These results suggest that the potential availability of the studied trace elements was extremely high in German soil compared to the both other. A major portion (36-80%) of Cu and (19 -94 %) of Cd was associated with the organic, Fe-Mn oxide, and carbonate fractions in the soils studied, indicating that this metals was potentially more bioavailable than other elements examined. Among the three soils tested, German soil were the most contaminated soils with the five trace elements studied.

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