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 (Fe₂O₃) were extracted with 3M sodium citrate + 1 M sodium bicarbonate + 1 g sodium dithionite in a water bath heated at 85°C (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 HNO₃ + HCL + H₂O₂ according to USEPA (1995).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Egyptian soil</th>
<th>Greek soil</th>
<th>German soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classification</td>
<td>Ustifluvent</td>
<td>Xerofluvent</td>
<td>Ustifluvent</td>
</tr>
<tr>
<td>Particle size distribution, %</td>
<td>12</td>
<td>75</td>
<td>31</td>
</tr>
<tr>
<td>Sand</td>
<td>41</td>
<td>16</td>
<td>43</td>
</tr>
<tr>
<td>Silt</td>
<td>47</td>
<td>9</td>
<td>26</td>
</tr>
</tbody>
</table>

**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 |
| CaCO₃, %    | 1.5  | 10.45 | 0    |
| CBD-extracted oxides, g kg⁻¹ | 10.8 | 2.96 | 19.0 |
| Fe          | 0.92 | 0.25 | 8.9  |
| Mn          | 0.89 | 0.23 | -    |
| Al          | 2.54 | 1.12 | 18.2 |
| pH (1:1 H₂O); EC; Electric conductivity (µS/cm); OM: Organic matter; CEC: Cation Exchange Capacity (emol (+)/kg); Fe₂O₃, Al₂O₃, Mn₂O₃: Citrate-bicarbonate-dithionite extractable-Fe, Al, Mn; Fe, Al, Mn, Ammonium oxalate-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-Martin 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 NH₄OAc (pH 7.0), easily mobilizable or carbonate bound (F2: 1 M NH₄OAc adjusted to pH 5 with HOAc), Fe–Mn oxide bound (F3: 0.175 M (NH₄)₂C₂O₄ and 0.1 M H₂C₂O₄), organically bound (F4: 0.1 M Na₂P₂O₇), an F5: residual fraction = total concentration minus ΣF1 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 dry 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 NH₄NO₃ (mobile fraction),
- F2: 1 M NH₄-acetate (easily mobilizable fraction),
- F3: 0.1 M [NH₄(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: residual fraction = total concentration minus ΣF1 to F6.

The whole pool of Fe-Mn oxide fraction in the fractionation 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...
progressing development and reported that cadmium was not detected in the Egyptian and Greek soils. In this distributed in the organic fraction, while the same fraction remained in weakly bound fractions in both original and 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

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Egyptian floodplain</th>
<th>Greek floodplain</th>
<th>Germanic floodplain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg Cd</td>
<td>% of total</td>
<td>mg Cd</td>
</tr>
<tr>
<td>F1</td>
<td>0.15</td>
<td>8.8</td>
<td>0.02</td>
</tr>
<tr>
<td>F2</td>
<td>0.12</td>
<td>7.1</td>
<td>0.35</td>
</tr>
<tr>
<td>F3</td>
<td>0.04</td>
<td>2.4</td>
<td>0.21</td>
</tr>
<tr>
<td>F4</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>F5</td>
<td>1.39</td>
<td>81.7</td>
<td>0.92</td>
</tr>
<tr>
<td>Total</td>
<td>1.70</td>
<td>1.5</td>
<td>1.50</td>
</tr>
</tbody>
</table>

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.

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, which increased potential Cu mobility and bioavailability in these soils.

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-Pendas, 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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