Rates of biogeochemical phosphorus and copper redistribution in young floodplain soils

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Abstract. Nutrients and trace metals in river-floodplain systems may originate from anthropogenic activities and/or geogenic sources. Here, we analyze a soil chronosequence (2 to approximately 600 years) on a floodplain at the Danube River (Austria) to quantify the rates of P and Cu redistribution among biogeochemical pools during early soil formation under temperate continental climate. While bulk and clay mineralogy remained unchanged over the studied age gradient, we found considerable (mostly non-linear) redistribution of P and Cu among biogeochemical pools. The calcium-associated P and Cu fractions decreased rapidly during the initial decades of soil formation. The dissolution of calcium-associated P was mirrored by marked accumulation of organic P. Copper incorporated within resistant minerals showed a relative enrichment with soil age. The mean dissolution rates of calcium-associated (primary mineral) P decreased exponentially with increasing soil age from \( \sim 1.6 \, \text{g m}^{-2} \text{yr}^{-1} \) over \( \sim 15 \) years to \( \sim 0.04 \, \text{g m}^{-2} \text{yr}^{-1} \) over \( \sim 550 \) years, and were almost an order of magnitude higher than rates reported for tropical environments. Our study demonstrates that on riverine floodplains, rapid biogeochemical transformations can occur within the first centuries of soil formation under temperate climatic conditions.

1 Introduction

The uppermost layer of earth’s crust progressively changes over time through the actions of weathering and soil formation. Soil studies across substrate age gradients (chronosequences; Huggett, 1998) have enhanced our understanding of weathering rates under various environmental conditions. Most chronosequence studies in fluvial environments have covered thousands to millions of years, and depending on the climatic regime, the following trends were observed with increasing soil age: mineralogical changes (Dorronsoro and Alonso, 1994) combined with specific surface area increase (White et al., 1996); pH decrease (Vidic and Lobnic, 1997); increasing clay accumulation, clay translocation, and rubification (Dorronsoro and Alonso, 1994; Engel et al., 1996; Leigh, 1996; Vidic and Lobnic, 1997); accumulation of pedogenic carbonate (Eash and Sandor, 1995; Nordt et al., 1998) and silicon (Kendrick and Graham, 2004); increase of Fe oxide contents (Dorronsoro and Alonso, 1994; Engel et al., 1996; Leigh, 1996) and crystallinity (Shaw et al., 2003; Kendrick and Graham, 2004).

By comparison, only few studies have covered the initial stages of weathering and soil formation on floodplains. Generally, they report rapid (decadal-scale) accumulation of soil organic C and N, which leveled off during the following centuries of pedogenesis (e.g. van Cleve et al., 1993; Kaye et al., 2003; Adair et al., 2004).

In previous studies on a young floodplain at the Danube River in Austria, we found trends of P transformation (Zehetner et al., 2008) and sorption (Lair et al., 2009a) as well as Cu and Cd retention (Graf et al., 2007; Lair et al., 2008) along with changes of Fe oxide crystallinity. More recently, we linked Fe oxide crystallinity to measured soil age (Lair et al., 2009b), which allows calculation of process rates. We then used this approach to estimate the rates of organic matter accretion during early pedogenesis in these soils (Zehetner et al., 2009).

Nutrients and trace metals may become pollutants in fluvial environments (e.g. Du Laing et al., 2009; Lair et al., 2009c). Besides anthropogenic pollutant sources (see for example Lair et al., 2009c), also geogenic sources may contribute to the contamination of river-floodplain systems. The most dramatic example of the latter is probably the arsenic...
calamity in parts of India and Bangladesh (e.g. Mukherjee and Bhattacharya, 2001).

To date, the release of geogenic nutrients and trace metals in river-floodplain systems is still poorly understood and rarely quantified. For an improved risk assessment in fluvial environments, it is therefore essential to enhance our knowledge on the rates of geogenic contaminant release and redistribution among biogeochemical pools of different mobility and bioavailability. In the present study, we selected P and Cu as proxies for nutrients and trace metals, respectively, and quantify their rates of redistribution among biogeochemical pools during the first centuries of floodplain soil formation, in which the soils are still in intimate contact with groundwater and river water.

2 Study area

2.1 Geological and climatic setting

The study area is located in the Danube floodplain downstream of Vienna, Austria (Fig. 1). During the Alpine glaciations, the Danube River has continuously incised into the uplifted Tertiary fill of the Vienna basin and accumulated meltwater terraces (Decker et al., 2005). The recent floodplain consists of up to 20 m gravel covered by fine sediments. The present main channel of the Danube River was created by a channelization between 1870 and 1875, and a flood-control dike was constructed between 1882 and 1905 (Lair et al., 2009c). The study area experiences a continental climate with hot summers and cold winters (Fig. 1). The mean annual temperature (MAT) is approximately 9°C, the mean annual precipitation (MAP) approximately 550 mm, and the mean annual potential evapotranspiration approximately 570 mm.

2.2 Study sites and soil sampling

We used a chronosequence approach to follow floodplain soil development. Our chronosequence included young river islands (e.g. site 1; Fig. 1 and Table 1), areas periodically inundated by flood events (e.g. sites 5, 6), and areas disconnected from the river for approximately 100 years through the flood-control dike (e.g. sites 7, 9, 10). We sampled three soil profiles at each site using an 80-mm core drill. Core samples were taken down to 60 cm and divided into 5 and 10-cm depth layers. The age of individual soil depth layers was estimated using a chronofunction that relates Fe oxides crystallinity to soil age measured with $^{137}$Cs and optically stimulated luminescence (Fig. 2; Lair et al., 2009b). The studied soil profiles revealed various episodes of sediment deposition and soil formation. Yet, the topsoil layers down to at least 20 cm depth showed relatively uniform deposition ages (Lair et al., 2009b). In the present study, we used composite samples from 0 to 10 cm depth, whose deposition ages ranged from 2 years (site 1) to approximately 600 years (site 10).

2.3 Basic soil characteristics

In the studied soils, bulk mineralogy revealed mixed contributions of calcite, dolomite, quartz, plagioclase, K-feldspar and mica, and clay mineralogy was dominated by illite and chlorite (Haslinger et al., 2006). Neither bulk mineralogy nor clay mineralogy showed a consistent age trend across the studied chronosequence. Likewise, the soils’ carbonate contents showed little variation and no consistent age trend (Zehetner et al., 2008; cf. Table 1). Soil pH varied in a narrow range (above neutral) between sites; however, organic C (OC) contents were strongly influenced by soil age and land use (Zehetner et al., 2009; cf. Table 1).

In the studied fluvial environment, soil grain size distribution showed marked differences between different geomorphic positions. The island soils had coarse textures with low clay contents (Lair et al., 2009b; cf. Fig. 1, Table 1), comparable to the grain size distribution of suspended flood sediments in the Danube main channel (Zehetner et al., 2008). Conversely, the soils on the floodplain had considerably finer textures (Lair et al., 2009b; cf. Fig. 1, Table 1). The observed differences are a result of different sedimentation conditions, with decreasing flow velocities of flood water allowing finer particles to settle.

3 Methods

3.1 Phosphorus extraction

Phosphorus extraction was performed according to the SMT protocol (Standards, Measurements and Testing Programme of the European Commission; Pardo et al., 2003) using air-dried, finely ground soil samples. (1) One 200-mg sample aliquot was extracted with 20 mL of 1 M NaOH for 16 h. A 10 mL aliquot of the supernatant was acidified with 4 mL of 3.5 M HCl to precipitate humic substances. After 16 h, NaOH-extractable inorganic P (IP) was determined in the remaining supernatant. The residue of the NaOH extraction was extracted with 20 mL of 1 M HCl for 16 h, and HCl-extractable IP was determined in the extract. This fraction represents calcium-associated (primary mineral/apatite) P (Williams et al., 1976, 1980). (2) A second 200-mg sample aliquot was extracted with 20 mL of 1 M HCl for 16 h, and the residue was placed in a porcelain crucible and calcined at 450°C for 3 h, then extracted again with 20 mL of 1 M HCl for 16 h to determine organic P (OP). Extracted phosphate was measured spectrophotometrically using the molybdenum blue method according to Murphy and Riley (1962) (detection limit: 0.3 mg P L$^{-1}$).
Table 1. Basic site and soil characteristics. Soil depth 0–10 cm, \( n = 3 \) except for clay and sand (\( n = 1 \)) and \( \Sigma P_{\text{extracted}} \) (\( n = 2 \)); BD = bulk density; OC = organic C; \( \Sigma P_{\text{extracted}} \) = sum of NaOH-extractable inorganic P, HCl-extractable inorganic P, and organic P (Pardo et al., 2003); \( \Sigma Cu_{\text{extracted}} \) = sum of 5 sequentially extracted Cu fractions according to Tessier et al. (1979). Letters \( a, b \) indicate significantly different means (0.05 level, Scheffé test). Values in parentheses are standard deviations.

<table>
<thead>
<tr>
<th>Site</th>
<th>Land use</th>
<th>Inundation frequency (^{(1)}) (yr (^{-1}))</th>
<th>Soil age (^{(2)}) (yr)</th>
<th>BD (g cm(^{-3}))</th>
<th>Sand (^{(3)}) (%)</th>
<th>Clay (^{(3)}) (%)</th>
<th>pH (H(_2)O) (^{(3)})</th>
<th>OC (^{(4)}) (%)</th>
<th>CaCO(_3) (^{(3)}) (%)</th>
<th>( \Sigma P_{\text{extracted}} ) (mg kg(^{-1}))</th>
<th>( \Sigma Cu_{\text{extracted}} ) (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Woodland</td>
<td>130–150</td>
<td>2(^{#})</td>
<td>1.06 (0.07)</td>
<td>40.5</td>
<td>11.3</td>
<td>7.29 (0.08)</td>
<td>0.79 (0.16)</td>
<td>19.0 (3.3)</td>
<td>684 (100)(^{a})</td>
<td>21.5 (6.4)(^{a})</td>
</tr>
<tr>
<td>5</td>
<td>Forest</td>
<td>5–10</td>
<td>18 (6)</td>
<td>1.59 (0.23)</td>
<td>22.0</td>
<td>27.1</td>
<td>7.35 (0.07)</td>
<td>2.66 (0.15)</td>
<td>25.1 (1.3)</td>
<td>714 (2)(^{a})</td>
<td>35.4 (1.4)(^{b})</td>
</tr>
<tr>
<td>6</td>
<td>Grassland</td>
<td>1–2</td>
<td>140 (80)</td>
<td>1.96 (0.13)</td>
<td>13.0</td>
<td>29.8</td>
<td>7.29 (0.10)</td>
<td>3.28 (0.31)</td>
<td>26.5 (1.5)</td>
<td>602 (52)(^{a})</td>
<td>27.0 (1.5)(^{a, b})</td>
</tr>
<tr>
<td>7</td>
<td>Grassland</td>
<td>0</td>
<td>131 (77)</td>
<td>1.80 (0.16)</td>
<td>16.3</td>
<td>30.1</td>
<td>7.34 (0.01)</td>
<td>4.18 (0.51)</td>
<td>26.4 (0.4)</td>
<td>670 (21)(^{a})</td>
<td>n.d.</td>
</tr>
<tr>
<td>9</td>
<td>Forest</td>
<td>0</td>
<td>332 (75)</td>
<td>0.97 (0.06)</td>
<td>15.6</td>
<td>38.0</td>
<td>7.50 (0.16)</td>
<td>3.10 (0.29)</td>
<td>25.1 (1.5)</td>
<td>690 (4)(^{a})</td>
<td>25.7 (2.2)(^{a})</td>
</tr>
<tr>
<td>10</td>
<td>Grassland</td>
<td>0</td>
<td>505 (91)</td>
<td>0.89 (0.15)</td>
<td>19.0</td>
<td>30.4</td>
<td>7.44 (0.02)</td>
<td>5.87 (0.34)</td>
<td>18.8 (1.2)</td>
<td>761 (12)(^{a})</td>
<td>29.4 (2.3)(^{a, b})</td>
</tr>
</tbody>
</table>

(1) C. Baumgartner (National Park Donau-Auen GmbH, personal communication, 2009)
(2) according to Lair et al. (2009b)
(3) determined according to Soil Survey Staff (2004)
(4) calculated as the difference of total and carbonate C; total C quantified by dry combustion (Tabatabai and Bremner, 1991)
\(^{#}\) deposited during a 100-year-return flood in 2002

3.2 Copper extraction

Sequential extraction of Cu was conducted according to the protocol developed by Tessier et al. (1979) and slightly modified by Vanek et al. (2005), in which 1.00 g of soil is sequentially subjected to the following extraction steps. (A) 8 mL of 1 M MgCl\(_2\) at pH 7 (exchangeable, weakly sorbed); (B) 8 mL of 1 M NaOAc at pH 5 (sorbed or carbonate-bound); (C) 20 mL of 0.04 M NH\(_2\)OH-HCl in 25% HOAc (strongly bound to easily reducible Mn oxides and amorphous Fe oxides); (D) 3 mL of 0.02 M HNO\(_3\) and 5 mL of 30% H\(_2\)O\(_2\) at pH 1.5 (very strongly bound or incorporated into organic matter or other oxidizable species); (E) 20 mL of 65% HNO\(_3\) at 140°C for at least 3 h (incorporated within resistant minerals). After each extraction step, an aliquot of the supernatant was removed with a pipette and stored in a polyethylene bottle to which 0.5 mL of 65% HNO\(_3\) was added for sample preservation. The remainder of the extract was discarded, and the residue was washed with 4 mL of distilled-deionized water, which was discarded after centrifuging. Extracted Cu was measured with flame atomic absorption spectroscopy (detection limit: 0.01 mg L\(^{-1}\)).

3.3 Statistical analyses

Statistical analyses were performed using the SPSS 16 software package for Windows (Bühl, 2008). Correlations between variables were calculated with the Pearson correlation coefficient. One-way analysis of variance (ANOVA) with Scheffé’s post-hoc test was used for comparison of means (Mann, 2007).
Fig. 2. Chronofunction model relating iron oxide crystallinity (Fe$_{ox}$/Fe$_{d}$) to soil age measured with $^{137}$Cs and optically stimulated luminescence (Lair et al., 2009b); Fe$_{ox}$=oxalate-extractable Fe; Fe$_{d}$=dithionite-extractable Fe.

4 Results and discussion

4.1 Temporal redistribution of phosphorus among biogeochemical pools

The sum of extracted P (NaOH-extractable IP, HCl-extractable IP, OP) did not change significantly within 600 years of pedogenesis and varied between approximately 600 and 750 mg kg$^{-1}$ (Table 1), which is comparatively high and characteristic of young and slightly weathered soils (Cross and Schlesinger, 1995). We did not find elevated soil P levels in areas between the river and the flood-control dike compared to areas outside the dike (Table 1, Fig. 1), which shows that anthropogenic P release during the last century has not resulted in increased P levels on the recent floodplain. The majority of P in the studied soils is likely of geogenic origin.

The distribution of P among biogeochemical pools showed distinctive changes with soil age (Fig. 3). In the young soils, HCl-extractable IP was the dominant fraction with minor portions of OP and NaOH-extractable IP (Fig. 3). However, during the initial 100 years of soil formation, HCl-extractable IP dissolved rapidly while OP increased markedly. The trends of OP and HCl-extractable IP intersect after approximately 150 years and continuously level off during the following centuries of pedogenesis. Conversely, NaOH-extractable IP did not show a significant age trend and remained at low levels throughout the chronosequence (Fig. 3). The trend of dissolving primary mineral P (HCl-extractable IP) and concomitant build-up of OP through primary succession in the early stages of soil formation corresponds with Walker and Syers’ (1976) conceptual model of P transformation during pedogenesis and with the observations of Crews et al. (1995) across a chronosequence in Hawaii. In the latter study, primary mineral P comprised about 80% of total P at a 300-yr-old site, about 60% at a 2100-yr-old site, and decreased to 1% after 20 000 years of pedogenesis. Unfortunately, the initial several hundred years of weathering and soil formation were not well resolved in this study. In a chronosequence study on Vancouver Island (MAT=9.2°C, MAP=3200 mm), Singleton and Lavkulich (1987) observed an exponential decline of primary mineral P from about 350 mg kg$^{-1}$ in the sandy parent sediments to about 10 mg kg$^{-1}$ in the upper 10 cm of a 550-yr-old soil. In our study, we found a similar exponential dissolution pattern of HCl-extractable IP with a loss of approximately 300 mg kg$^{-1}$ over approximately 600 years (Fig. 3), albeit under much drier climatic conditions.

4.2 Dissolution kinetics of primary mineral phosphorus

The HCl-extractable IP contents of the studied island soils (mean ± standard deviation: 590±80 mg kg$^{-1}$) closely matched those of 20 suspended flood sediment samples collected in the Danube main channel between 1990 and 2006 (581±59 mg kg$^{-1}$; Zehetner et al., 2008). For the present study, we calculated mean area-based dissolution rates of HCl-extractable IP using the mean HCl-extractable IP content of the island soils (site 1) as starting point and bulk density for weight-to-volume conversion:
[(HCl-extractable IP)_{site1} – (HCl-extractable IP)_{site}] \times BD_{site} \times D_{site} \div (\text{soil age})_{site}

where BD is soil bulk density and D is the layer thickness (10 cm).

The mean HCl-extractable IP dissolution rates decreased exponentially with increasing soil age (Fig. 4). Schlesinger et al. (1998) determined HCl-extractable IP release rates from volcanic ash of between 0.05 and 0.22 g m\(^{-2}\) yr\(^{-1}\) during 110 years of tropical weathering on Krakatau (MAT=27\(^\circ\)C, MAP=2500–3000 mm). At a soil age of approximately 100 years, we estimate the mean HCl-extractable IP dissolution rates in the Danube floodplain soils at approximately 0.50 g m\(^{-2}\) yr\(^{-1}\) (Fig. 4), i.e. almost an order of magnitude higher than on Krakatau.

The high pH values of the studied soils (pH>7; Table 1) do not favour apatite dissolution, which generally increases with decreasing pH (e.g. Guidry and Mackenzie, 2003; Chaïrat et al., 2007); nor do the relatively dry climatic conditions, as apatite dissolution has been reported to be several times faster at far-from-equilibrium conditions (which would be expected in a high-leaching environment) compared to near-equilibrium conditions (Guidry and Mackenzie, 2003). But what is the cause for the high dissolution rates of primary mineral P in the Danube floodplain soils? The latter authors concluded that apatite dissolution was surface-controlled rather than diffusion-controlled. Indeed, close relationships have been reported between apatite surface area and dissolved P in soil-water extracts (Kuo et al., 2009), and apatite dissolution rates have been found to be inversely related to grain size (Abu-Hilal et al., 2008). A reason for the rapid primary mineral P dissolution during the initial 100 years of soil formation in our study area could therefore lie in the fine grain sizes on the Danube floodplain (Table 1), which are the result of sedimentation under low flood water velocities. Between 200 and 600 years of soil formation, the mean HCl-extractable IP dissolution rates decreased to between 6 and 2% of the initial rates (Fig. 4), reflecting the exhaustion of readily soluble (fine-grained) primary mineral P sources. An additional explanation for the initially high rates decreasing with soil age could be different solubilities of primary phosphates exhibiting different degrees of carbonate substitution (Guidry and Mackenzie, 2003).

**4.3 Temporal redistribution of copper among biogeochemical pools**

The sum of the five sequentially extracted Cu fractions (Tessier et al., 1979) varied between approximately 20 and 35 mg kg\(^{-1}\) (i.e. in the average range of non-polluted soils; Alloway, 1999), with no consistent age trend but significant differences between study sites (Table 1). These differences are likely due to slight variations in the Cu contents of the parent sediments. In the following, we therefore did not compare absolute amounts of extracted Cu fractions between sites, but rather followed their relative distribution across the studied chronosequence (Fig. 5).

Fraction A (exchangeable, weakly sorbed Cu) ranged from 1 to 3% of total extracted Cu and did not show a significant age trend (Fig. 5). Fraction B (sorbed or carbonate-bound Cu) made up between 8 and 13% of total extracted Cu in the youngest soils, however, decreased rapidly during the initial years of soil formation. The decreasing trend continuously leveled off during the following centuries of pedogenesis (Fig. 5). This exponential decrease closely matches the dissolution pattern of HCl-extractable IP, described in Sect. 4.1 (Fig. 3), which shows that carbonate-bound Cu and HCl-extractable IP may be associated with one another in recently deposited sediments, or at least similar processes may be operating in their dissolution.

Fraction C (Cu strongly bound to easily reducible Mn oxides and amorphous Fe oxides) accounted for 11 to 19% of total extracted Cu and did not change consistently with soil age (Fig. 5). Fraction D (Cu very strongly bound or incorporated into organic matter or other oxidizable species) made up a considerable portion of total extracted Cu, ranging from 30 to 39%, and did not show a significant age trend either (Fig. 5). While OP accumulation mirrored HCl-extractable IP dissolution (Fig. 3) and essentially followed the accumulation of OC (Table 1), Cu in fraction D did not increase along with the dissolution of carbonate-bound Cu and the accumulation of OC across the chronosequence. A reason for this could be that Cu in fraction D may not only originate from organic matter.
Fig. 5. Distribution of copper among biogeochemical pools along the floodplain soil chronosequence (0–10 cm depth); Cu extraction according to Tessier et al. (1979): (A) 1 M MgCl₂ (exchangeable, weakly sorbed), (B) 1 M NaOAc (sorbed or carbonate-bound), (C) 0.04 M NH₄OH·HCl in 25% HOAc (strongly bound to easily reducible Mn oxides and amorphous Fe oxides), (D) 0.02 M HNO₃ +30% H₂O₂ (very strongly bound or incorporated into organic matter or other oxidizable species), (E) 65% HNO₃ at 140°C (incorporated within resistant minerals); trend lines were fitted to fractions that showed a statistically significant age trend ($p < 0.05$), i.e. fractions B and E, respectively.

Fraction E (Cu incorporated within resistant minerals) was the dominant fraction in all studied soils (41 to 55% of total extracted Cu) and showed a linear increase with soil age (Fig. 5). This increase represents a relative enrichment of immobile Cu (at a rate of 0.017% yr⁻¹) due to the stability of the minerals extracted in this fraction. In the course of weathering and soil formation, Cu may so become enriched relative to more mobile elements. For example, Poulton and Raiswell (2000) found Cu enrichment (relative to Al) in the sediments of eight world rivers, which, the authors concluded, was likely caused by accumulation of residual Cu in weathered topsoil layers that supply the riverine particulate load.

5 Summary and conclusions

Six hundred years of weathering under dry continental climate (MAT=9°C, MAP=550 mm) have not resulted in notable changes of bulk or clay mineralogy. However, we found considerable (mostly non-linear) redistribution of P and Cu among biogeochemical pools. Calcium-associated P (HCl-extractable IP) and Cu (fraction B) decreased rapidly during the initial decades of soil formation, with trends continuously leveling off in the following centuries. The dissolution of calcium-associated P was accompanied by accumulation of OP. Copper incorporated within resistant minerals (fraction E) showed a relative enrichment with soil age. Mean dissolution rates of calcium-associated (primary mineral) P decreased exponentially with increasing soil age, and the initial rates (first century of pedogenesis) were almost an order of magnitude higher than rates reported for tropical environments. A reason for this could lie in the fine grain sizes on the Danube floodplain, providing readily soluble (fine-grained) primary mineral P sources.

Our results demonstrate that under moderate weathering conditions, considerable biogeochemical redistribution can take place within the first centuries of floodplain soil formation. Rapid dissolution of calcium-associated fractions mobilizes nutrients and metals and makes them temporarily bioavailable and susceptible for solute transport in the soil-groundwater-river system. This process supplies P for primary production, which is a prerequisite for the rapid C accretion observed in such ecosystems (Zehetner et al., 2009).

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