Development of soil properties in a riverine floodplain with time – results from a chronosequence study in the National Park Donau-Auen in Austria

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Abstract
Recently, we established a chronological framework for fluvial deposits along a soil sequence at the Danube River near Vienna, Austria, using optically stimulated luminescence (OSL) dating. We identified fluvial deposits from different time periods ranging from the early last millennium BC to the 18\textsuperscript{th} century AD. We bridged the gap from the 18\textsuperscript{th} century AD to the present with fallout $^{137}$Cs dating, and developed a chronofunction model relating Fe oxide crystallinity ($\text{Fe}_o/\text{Fe}_d$) to deposition age along the studied soil sequence model relating Fe oxide crystallinity ($\text{Fe}_o/\text{Fe}_d$) to deposition age. This model allows age estimation of soil layers using routinely measured pedological characteristics ($\text{Fe}_o/\text{Fe}_d$). We examined specifically the build-up of soil organic matter, the redistribution of phosphorus among biogeochemical pools and the retention of pollutants related to soil development. We found rapid C accumulation during the initial 100 years of soil formation, with rates exceeding those in northern peatlands by an order of magnitude. We showed that floodplain land use strongly affects soil C sequestration and pool allocation, and found that the distribution of different C pools reaches a steady state within less than a century. Our results demonstrate that continually rejuvenated soils on riverine floodplains are strong C sinks, but also show that intensive cultivation severely compromises their high C sequestration potential. The youngest soils were dominated by calcium-associated phosphorus (CAP), in less than 100 yrs of pedogenesis, CAP markedly decreased and organic phosphorus (OP) increased, and in less than 180 yrs, OP reached CAP levels. Adsorption properties of the floodplain soils changed, governed specifically by OC accumulation and Fe- oxide and hydroxide accumulation with time. The soil retention capacity for Cd and Cu increased with increasing soil age.

Key Words
Chronosequence, floodplain soils, phosphorus, pollutant retention, soil organic matter.

Introduction
Ecosystems progressively evolve through the actions of biogeochemical processes over time. Soil studies across substrate age gradients (chronosequences) have enhanced our understanding of directions and rates of biogeochemical processes under different environmental conditions (Huggett 1998). On riverine floodplains, most chronosequence studies have covered thousands to millions of years and quantified long-term pedogenic changes, such as clay accumulation and translocation, the formation of pedogenic carbonate and silica, as well as increases in Fe oxide contents and crystallinity. By contrast, biogeochemical processes acting at shorter time scales, such as organic matter (OM) dynamics, remain poorly understood in floodplain soils, and short-term rates of change have rarely been quantified. However, in light of global change, a better understanding of C dynamics is essential for an improved assessment of the role of riverine floodplains in the global C cycle and biogeochemical cycle of elements in general. The objective of our study was, therefore, to bridge this knowledge gap and quantify the rates of organic C accumulation, changes of C pools, dissolution of primary mineral phosphorus and changes in contaminant retention properties in a riverine floodplain in Central Europe that have experienced different land use history.

Methods
\textit{Study area}
The study area is located east of Vienna, Austria, in the National Park “Donau-Auen” (Figure 1). The area is situated in the tectonically active Vienna basin, which was formed in the Miocene when a subsidence of the basin occurred (Decker \textit{et al.} 2005). Later, the basin inverted and more than 200 m of surface uplift occurred. During the Alpine glaciations, the Danube River continuously incised into the uplifted Tertiary basin fill and accumulated melt-water terraces. The floodplain is morphologically subdivided into two terraces called “Younger part of today’s valley floor” (= alluvium) and “Higher and older part of today’s valley floor” (=
Marchfeld fluvial terrace). We selected eleven representative sites at different geomorphic positions. Sites 4 and 11 are located on the older Marchfeld fluvial terrace, sites 5-10 on the younger alluvium and sites 1-3 on islands in the Danube River (Figure 1). The present main channel of the Danube River was created by a river regulation starting in 1870 and was at that time free of any islands. Thus, the studied island sites have evolved within the past 130 years (Fiebig and Preusser 2007). From 1882 to 1905, a dike was constructed to protect the area north of the Danube River from recurrent flood events and disconnected sites 7-11 from the river for the past 100 years (Figure 1). The recent floodplain consists of up to 20 m gravel and at many places several meters of fine sediments on top. The river regulation induced a higher flow velocity in the main channel and led to the deposition of predominantly silt- and fine sand-sized particles on the islands (sites 1-3). By contrast, the soils in the floodplain (sites 4-11) have considerably finer textures (Lair et al. 2007). The deposited sediments are dominated by dolomite and show medium to low amounts of quartz, plagioclase, K-feldspar, chlorite, kaolinite and mica (Haslinger et al. 2006). Most of the soils classify as Fluvisols and show progressing development with age towards the Chernozem group (IUSS Working Group WRB 2006; Lair et al. 2007). The study area experiences a continental climate with hot summers and cold winters (mean annual temperature ~ 9°C, C, mean annual precipitation ~ 550 mm).

Analyses
At each study site (Figure 1), we took three soil samples at the corners of an equilateral 15-m triangle using an 80-mm core drill. The samples were divided into the depth layers 0-5, 5-10 and 10-20 cm. At ploughed sites (sites 4, 8, 11), we took composite 0-20 cm cores. Suspended sediments from the 20 highest flood events between 1990 and 2006 were retrieved from a sediment trap located in the Danube’s main channel upstream of the studied floodplain. Depth profiles of fallout $^{137}$Cs were used to assess short-term sedimentation, and optically stimulated luminescence (OSL) dating was used to attribute sediment deposits to time periods between the early last millennium BC and the 18th century AD. Total C was quantified by dry combustion, and carbonate C was measured gas-volumetrically. Organic C was calculated as the difference of total and carbonate C. Phosphorus fractionation was performed in duplicate according to the SMT protocol (Pardo et al. 2003). Sequential extraction was used to fractionate copper and cadmium in original and spiked soils in order to study the long-term and short-term behaviour of copper and cadmium retention (Vanek et al. 2005).

Results
In our soils the ratio of oxalate to dithionite-extractable iron ($\text{Fe}_o/\text{Fe}_d$), which indicates the degree of iron oxide crystallinity and can be a reliable indicator of soil maturity (e.g. McFadden and Hendricks 1985) progressively decreased from ratios greater than 0.5 to values less than 0.2 with increasing soil age (Figure 2A). We linked the observed $\text{Fe}_o/\text{Fe}_d$ ratios to the radiometric and OSL ages in a chronofunction (Figure 2A), which allows to approximately date soil layers that lack an independent age control. The soil ages calculated with this chronofunction accurately reflected their geomorphological position, resulted in consistent age trends with depth and highlighted the active morphodynamics of the studied floodplain.
Organic C contents and accumulation rates across the studied soil age gradient showed distinct trends (Figure 2B and C). The suspended river sediments and young island soils contained relatively little OC. However, within 50 to 100 years of soil formation, the topsoil OC contents at forest and grassland sites showed a steep increase, which continuously levelled off during the following 300 to 500 years. The grassland topsoils accumulated higher amounts of OC than the forest topsoils. The OM in young (<5-yr-old) sediment deposits contained almost no hydrolyzable components and relatively little humic acids, but already a sizeable fraction of microbial biomass C and comparatively high proportions of DOC and non-oxidizable OM (Zehetner et al. 2009a). After a few decades of soil formation, OM composition changed dramatically. The fraction of microbial biomass C remained more or less constant, but humic acids and hydrolyzable OM significantly increased (p<0.01; Scheffé’s test) while DOC and non-oxidizable OM became less dominant (data not shown). This rapidly established pool distribution remained essentially unchanged throughout the studied soil chronosequence.

Total phosphorus (TP) averaged 732 mg/kg, and biogeochemical fractionation yielded important primary mineral contributions (CAP ~80% of TP). The TP concentrations of the floodplain soils were in the range of the Danube sediments and showed little variation along the chronosequence (Zehetner et al. 2008). However, the distribution of P among biogeochemical fractions changed considerably in less than 600 yrs of soil development (Figure 2D). The youngest soils (<20 yrs) were dominated by CAP, as was observed for the Danube sediments. In less than 100 yrs of pedogenesis, CAP markedly decreased and OP increased, and in less than 200 yrs, OP reached CAP levels. This shows that while P biogeochemistry in very young floodplain soils is strongly related to the river sediments, significant transformations can occur in less than 200 yrs of soil development in the dry and temperate climate of Central Europe (Zehetner et al. 2009). Copper partitioning among defined geochemical fractions was mainly determined by soil pH and the contents of carbonates, organic matter and Fe-/Mn-oxides and hydroxides. Copper retained in original soils was found in more strongly bound fractions, whereas sorption of freshly added copper was primarily influenced by the presence of carbonates. Beyond the effect of progressing soil formation, variations in organic carbon...
contents due to different land use history affected the copper retention capacity of the investigated soils (Graf et al. 2007). Cadmium remained in weakly bound fractions in both original and spiked soils, representing an entirely different behaviour than observed for copper. Correlation analysis revealed the involvement of different sorption surfaces in soil, with no single soil constituent determining cadmium retention behaviour. Nevertheless, in the calcareous soils of the Danube floodplain, we found increased cadmium retention and decreased portions of readily desorbable cadmium with progressing soil development (Lair et al. 2008).

**Conclusion**
Our analyses show that the floodplain development towards a terrestrial ecosystem in the National Park Donau-Auen is accompanied by considerable changes in the soil environment, such as increasing organic matter content, changes in nutrient content and Fe-oxide crystallinity as well as a general increase in the retention capacity for (cationic) pollutants. In the studied floodplain, OC accumulation rates seem to be larger than in most other soil ecosystems. Other soil properties like phosphorus forms and heavy metal retention properties undergo quite rapid changes as well and are partly linked to the observed OC dynamics.

**Acknowledgement**
This work was supported by the European Union FP6 Integrated Project AquaTerra (Project no. GOCE 505428) under the thematic priority ‘sustainable development, global change and ecosystems’.

**References**