

We thank all reviewers for their comments and suggestions, which were very helpful for improving our manuscript. Below are our detailed responses.

### **Anonymous Referee #1**

*Received and published: 13 October 2009*

*Overall a very interesting manuscript that deserves publication in the journal. Below are some points that would strengthen the manuscript. The conclusion and discussion sections should weigh natural versus anthropogenic influences. What are the consequences of your findings for floodplains as well as riverine fluxes and deposition of heavy metals and nutrients?*

*Do you think for your detailed studied profiles sources and sinks could be quantified in a mass balance? Figure 3 seems to suggest that.*

We compared the study sites inside and outside the flood control dike, concluded on anthropogenic P inputs over the last century and weighed these against geogenic sources (added in the Results and Discussion section). We extended the Conclusion section to address the consequences of our findings more explicitly.

Our P and Cu data cover the soil depth interval 0-10 cm of 6 sites along the chronosequence (soil age range from 2 to app. 500 years). We clarified this in the Study Area section and also in the captions of Figures 1, 3, 4 and 5. Unfortunately, we do not have P and Cu extraction data for the whole soil profiles, which would have allowed for mass balance calculations.

*The terms “fraction”, “biogeochemical pools” and “fractionations” should be clearly defined in the text and coordinated with each other.*

We checked the document and now use the term “biogeochemical pool” in a more general context and the term “fraction” in connection with Cu or P extracted with defined extracting agents.

*Can you exclude bioturbation by worms or reworking of the soil through flooding events? If so, this should be clearly stated in the text.*

In our study, we did not analyze whole soil profiles. Rather we used dated topsoil layers (0-10 cm depth) of each investigated site. A certain degree of reworking of soil material by flood events and bioturbation may have occurred. However, potential mixing of soil material of different age is accounted for by the dating method used.

*What role does biology play in the processes described? Would dissolution processes and profiles described be similar without plant cover?*

Plant cover certainly affects the redistribution and cycling of the studied elements (as discussed in the cited Walker and Syers paper). We now explicitly mention the role of primary succession in this process (Results and Discussion section).

9525

*L4: Why are P and N important? Also point this out in the introduction*

The reviewer probably meant P and Cu. In the Introduction, we had already mentioned that nutrients and trace metals, of which P and Cu are examples, may become pollutants in fluvial environments.

*L7 age gradient please provide number ranges*

We added the age range of the chronosequence.

*L8 please name the biogeochemical pools addressed*

The relevant biogeochemical pools are named in the second half of the Abstract.

*L9 name mechanism for transfer of Ca P to org P and reverse trend for Cu*

Following suggestions of reviewer 3, we realize that Cu in fraction D may not only originate from organic matter and therefore removed our previous explanation for the observed Cu trend.

L14 “almost an order of magnitude higher than tropical environments” provide Number

We added the range of dissolution rates measured.

L17 “can be exceedingly high in these ecosystems” in comparison to which ecosystems?

We rephrased the last sentence of the Abstract for more clarity.

9527

L29 early stages provide age range in years

We added the age range.

*End of chapter: provide reasoning why Cu and P are important parameters. Are they proxies for nutrients and heavy metals? If so, why were they chosen over say N and Cd? Perhaps they are important parameters for specific compartments, plants, mechanisms or processes? If so; which ones and which important role do they play. Also give a reason for why the study area was chosen and not elsewhere.*

P and Cu were selected as proxies for nutrients and trace metals, respectively. We added this in the last paragraph of the Introduction. P was selected because its sources are mostly geogenic as opposed to N. Moreover, in semi-terrestrial and aquatic ecosystems P is often the limiting nutrient.

Cu represents a micronutrient and was chosen because its known high affinity to organic matter.

The study area was selected because it is one of the last remnants of a semi-natural floodplain ecosystem in Central Europe.

9528

L16: briefly explain the chronosequence approach

The chronosequence approach had been defined at the beginning of the Introduction section (Huggett, 1998). We had also described our chronosequence, covering areas from young river islands to older areas outside the flood-control dike. We now also include the age range of the studied soils in the Study Area section.

9529

L1/2 how do the methods  $^{137}\text{Cs}$  and luminescence compare or is this a combined method in which one techniques contributes to the other?

$^{137}\text{Cs}$  dating is used for sediment layers deposited after the peak of bomb Cs (1960s). In our case, we used both bomb and Chernobyl Cs. OSL dating is used for sediment layers that have been covered with flood sediments for hundreds to thousands of years. A detailed description of the procedures is given in Lair et al. (2009b).

9530

*The entire methods section does not say anything about sampling. Can the authors provide a few lines about this?*

We made a separate subheading “Study sites and soil sampling” (Study Area section) in which the sampling procedure is described.

*The term “fractionation” in this manuscript seems to describe an analytical protocol to extract either P or metals. Could you replace it by “extraction” in order to avoid confusion with isotope fractionation (not true for P but for instance various Cu isotopes exist)*

We replaced “fractionation” by “extraction”.

9531

*Statistical analyses need some more references*

We included two references in the Statistical Analyses section.

*Probably IP and OP mean inorganic and organic phosphorous if not done previously spell out before first time use of abbreviation*

We had spelled out IP and OP in the Methods section.

*The description of Fig 3 is good but the authors seem to equal biogeochemical pools with age sections (probably corresponding to depth sections) of the soil. First it would be nice to see a correlation between depth and age and second perhaps compartments can be defined that correspond to age brackets. For instance younger soil within the grass root zone and older soils within the deeper root zone of larger plants. Do plants play a role or are there any other mechanisms for this age trend?*

In our study we did not analyze whole soil profiles. Our data cover the soil depth interval 0-10 cm of 6 sites along the chronosequence (soil age range from 2 to app. 500 years). We clarified this in the Study Area section and also in the captions of Figures 1, 3, 4 and 5.

9532

*First paragraph is a good comparison to other studies. Can these results be incorporated in one of the figures?*

Of the compared studies, only the study of Singleton and Lavkulich (1987) looks at a soil age range comparable to our study. We tried to include the data points of the Singleton and Lavkulich study into our Figure 3. However, this made Figure 3 too crowded and did not add more information beyond the detailed description already given in the manuscript.

*L19-21: Can you elaborate with a few lines how you calculated the dissolution rates?*

*This should then go into the methods section and could perhaps be substantiated with an example calculation*

We added the formula for the calculation of dissolution rates.

*Can you give a reason why the comparison to Krakatau was chosen? Would any comparison to a similar climatic zone be possible?*

The comparison to Krakatau was chosen as no other studies in climate zones similar to the conditions in our study area were available.

9533

*How much apatite is present in soils and background geology of your study area?*

The concentration of apatite was below 0.5%.

*(also on 9534) By Fractions A, B, and C etc do the authors rather mean zones or age sections of the soil?*

Fractions A, B, C etc refer to Cu in different biogeochemical pools (extracted with different extracting agents) as defined in the Methods section.

9534

*L20 high pH conditions ==> please provide number ranges*

This part was deleted.

9535

*How do you define “relatively dry”. This should be substantiated by precipitation heights and set in comparisons to other climates that should be named*

*The authors probably address the climate in the Danube valley near Vienna. This should be written out in case people only scan the conclusion*

We removed the word “relatively”. We had described the climatic conditions at our study area (T, PPT, PET) in the Study Area section. We added MAT and MAP in the Conclusion section.

*L5 biogeochemical pools: which ones? Can you name them?*

*Biogeochemical transformations can occur very rapidly. Can you substantiate this with number ranges and set into comparison with slower systems?*

The relevant biogeochemical pools are named in the following sentences of the Conclusion section.

We rephrased the last part of the Conclusions and mention the time frame more explicitly.

*Fig 1. Can the flow direction of the river be clearly indicated and an inset of a European map be provided?*

The flow direction is indicated by a white arrow and the river name was written in flow direction as usual in geographic maps. We replaced the inset map with another map showing a bigger part of Europe.

*Fig 2. Does the uncertainty stem from repeat analyses ?*

The uncertainty results from the dating accuracy (OSL, 137Cs) and curve fitting. This is described in Lair et al. (2009b).

*Fig 3. Are these data from one of the soil profiles (if so which one? And are the other profiles similar?) or from all 7 profiles taken? This should be pointed out.*

Our data cover the soil depth interval 0-10 cm of 6 sites along the chronosequence (soil age range from 2 to app. 500 years). We clarified this in the Study Area section and also in the captions of Figures 1, 3, 4 and 5.

*Fig 4. Why does the uncertainty decrease with age? Can this be explained in the text?*

*Also why do the dissolution rates change most drastically between 100 and 200 years?*

*Is it really exhaustion of soils > 200 a or do other mechanisms such as agglomeration or different binding properties play a role?*

The relative uncertainty in age estimation (relative to the estimated age) is highest for young soils and decreases with soil age. The calculation of the mean dissolution rates (see inserted formula in the revised manuscript) results in decreasing uncertainty with soil age (Figure 4). We included another possible mechanism for the initially high rates decreasing with soil age (i.e., different solubility of primary phosphates exhibiting different carbonate substitution), as suggested by reviewer 3.

*Fig 3 and 4 are you sure you mean g kg-1 on the y-axis not mg kg-1?*

The unit (g kg<sup>-1</sup>) is correct.

## **Anonymous Referee #2**

Received and published: 9 November 2009

*GENERAL COMMENTS* The paper discusses the highly relevant and very interesting issue of phosphorous copper biogeochemistry in floodplains. Both the topic and the quality of the paper fits the scope and standards of the Biogeosciences (BG) journal.

*The study brings novel data and improved understanding of the temporal redistribution of P and Cu. The paper uses the results of the highly recognised EU AuqaTerra Project.*

*A strong aspect of this work is that it builds on the previous extensive publication from the research group, but it is not a simple repetition, reformulation or summary of the former results, but a new study.*

*The length of the text and the quality of figures are proper for publication. References are appropriate and adequate.*

*SPECIFIC COMMENTS* The paper is written in adequate English and scientific language. No particular detailed comments seem to be relevant.

*SUGGESTION* Accept with no changes.

### **Anonymous Referee #3**

Received and published: 18 November 2009

*The paper, which is very well written, two key results of the investigation are discussed: What is the reason for the initially high dissolution rate of primary mineral P during weathering of soil deposited in the Danube floodplain? Why is mineral Cu not transformed into organic forms as found for P?*

*It was suggested that the high dissolution rate of phosphorus may be caused by the small grain size of primary P minerals. As the soil consists of a significant portion of clay, the explanation makes sense. In addition, there may be a second explanation.*

*Although most sedimentary and igneous phosphate rock minerals have a low reactivity in near neutral or alkaline conditions, there is a small group of so called 'reactive' phosphate rock types that have a much higher solubility than phosphate rock. The high reactivity of these specific phosphate rock types is explained in the difference in their molecular structure, whereby a large proportion of the phosphate ions is substituted by carbonates. It could be that such phosphate compounds were present explaining the high initial solubility of mineral P.*

We included this possible mechanism as an additional explanation for the initially high rates decreasing with soil age.

*Concerning copper, the authors do not find the same increase in organically bound Cu as for phosphorus. Organic matter bound Cu remained relatively constant over time. The authors explain this by the low Cu uptake by plants and microorganisms due to a high soil pH followed by a Cu solubility.*

*The Cu:P ratio in crops is around 1:4000, showing that much less copper is cycling through the biological system than phosphorus. If the initial Cu concentration in the fraction representing organically bound Cu is the same as in organic matter derived from plants, one may actually do not expect any more Cu bound to organic matter. It could be useful to check the initial Cu:P ratio in the fraction representing organically bound Cu and P.*

We checked the Cu : P ratios in the fractions in question and found values between 30 and 80, which are clearly below the values found in plants. We realize that Cu in fraction D may not only originate from organic matter and therefore removed our previous explanation for the observed Cu trend. We also adapted the Abstract and Conclusion sections accordingly.