

## ***Interactive comment on “Calcium phosphate formation due to pH-induced adsorption/precipitation switching along salinity gradients” by J. F. Oxmann and L. Schwendenmann***

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Referee #1

We thank the referee for providing feedback on the manuscript. The following section addresses each comment.

Comment 1: This paper contributes to understanding the fate and transformation of particulate phosphorus (PP) in transit from land to marine ecosystems. Research on this topic has been hindered by the difficulty of distinguishing different forms of PP. This

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study applies methods previously developed by the authors to estimate concentrations of metastable authigenic calcium-phosphate minerals, notably octacalcium phosphate (OCP). Like most methods for characterizing PP forms, this method separates different PP forms based on different extractions. Comparing sediments in pasture, salt marsh, mangrove, tidal flat, tidal river, and bay, the study found that PP content was similar among the locations but that the dominant form of PP changed with pH with calcium bound forms (Ca-P) dominant in alkaline sediment and PP adsorbed to Al and Fe (Al/Fe-P) dominant in acid sediment. The proportion of OCP in Ca-P was highest at near neutral pH. From this the authors suggest that the OCP may be a transitional Ca-P form that precipitates as Al/Fe-P is converted to Ca-P. I wonder whether apparent OCP accumulation might also indicate the reverse transition.

Response 1: We addressed the reverse transformation from OCP to adsorbed P in response to changing physical-chemical conditions on p.10243 (l.11-15). This transformation is also shown in Fig. 5 (see arrows). Largest changes occur upstream from the high-OCP sediments and not further offshore. If OCP-rich sediment is transported to more acidic upstream environments, OCP will likely dissolve and the phosphate released will be adsorbed by the more oxidized sediment (sediment, which is located in the "Fe conveyor belt"; see reference cited in comment 3). The reverse transformation would partly explain the maximum amount of adsorbed P at pH 6.6 (see Fig. 3b).

Comment 2: The paper implies that sediments are being transported along an elevation gradient from pasture to marsh to mangroves to tidal flat to bay sediments. Tidal river sediments were also sampled but it is unclear how the authors fit rivers into the transport sequence. The results for tidal river sediments were not plotted on figure 2, which shows the sequence arranged by elevation as in the transects in figure 1. Why not add the tidal river data to figure 2? I think that particles eroding from upland soils would be carried in overland flow to freshwater streams and rivers, then to tidal rivers and finally to the estuarine environments including mangroves and marshes, which can trap suspended sediment entering with the flood tide. Some sediment in mangroves

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and marshes may originate from resuspension of sediments that had been deposited in tidal rivers or in the bay. If so, PP in marshes and mangroves might transition from predominantly Ca-P to Al/Fe-P after deposition and subsequent oxidation.

Response 2: Results from the river plots were not included in Figure 2 as the distance from transects was up to c. 5 km (Fig. 1). Further, the elevation (and thus inundation duration) along the transects is a function of the relative position (e.g. distance from mangrove seaward margin; Fig. 2) within the landscape. River plots do not fit into this sequence. Results from the river plots are shown in Fig. 5. We addressed possible effects of sediment re-suspension and transport to upstream environments in the Discussion Section (p.10243, l.11-15).

Comment 3: This study did not find an effect of salinity on PP concentration or composition but some other studies have found that increase in sulfide production with increasing salinity in anoxic sediment leads to decrease in Fe bound P and a decline in PP (e.g. Caraco et al. 1990). Jordan et al. (2008) and Hartzell et al. (2010) found that such effects over salinities ranging from 0-11 were unrelated to pH, which ranged from 6.8 to 8.3, and that Ca-P remained a minor component of PP relative to Fe-P throughout this range. In contrast, the present study compared inundated sediments with salinities ranging from 11-39 and found a switch to Ca-P dominance of PP above pH 6.6. The authors should consider whether the importance of salinity depends on the salinity range. The relative abundance of Fe, S, and Ca in the sediments is likely important and would be worth comparing among studies.

Response 3: Effects of pH and Eh on P desorption are difficult to distinguish using field surveys (addressed in the manuscript: see comment 4). Controlled laboratory experiments showed that critical Eh levels for the reduction of ferric iron compounds in soils are pH dependent (Gotoh and Patrick, 1974). Controlled Laboratory experiments with estuarine sediment indicated that critical Eh levels for desorption of Fe-(hydr)oxide-bound P are similar to the critical levels observed by Gotoh and Patrick (1974) and that these levels were also pH dependent (Delaune et al., 1981). The pH depen-

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dence of these critical Eh levels was similar for both soil and sediment. Hence, pH and Eh together influence the reduction of ferric iron compounds and release of P in both sediments and soils. These effects appear to be independent of the salinity range (see also response to comment 15 of referee #3). We provide a reply on the issue of downstream-increasing Ca<sup>2+</sup> in the response to comment 17 of referee #3.

Comment 4: In the present study the switch from predominance of Al/Fe-P to Ca-P occurred over a pH range of about 6.1 to 7.6 that corresponded to an Eh range from 500 to -200 (Fig. 3). Because both pH and Eh change together it is difficult to know which one is the driving variable. The saline sediments with low pH and high (oxidizing) Eh were found in mangroves and salt marshes. It is very unusual to find oxidizing sediment in such environments, especially down to 40cm. The salt marsh in this study was very infrequently inundated compared to most salt marshes. Saturated anoxic sediments allow accumulation of peat in most mangroves and salt marshes, which is critical to their accretion in pace with rising sea level. Increasing water saturation restricts oxygen penetration into the sediments, which stimulates sulfate reduction, which, in turn, raises pH. The pasture soil does not seem comparable to inundated sediments as a representative of freshwater conditions for the purpose of investigating the effect of salinity. Unlike the inundated sediment, pasture soil is subject to leaching of dissolved ions (importantly Ca), which plays an important role in P diagenesis. Similarly, the mangrove and salt marsh sediments in this study, which are apparently high in the intertidal zone, may not be analogous to the inundated sediments. In a way, differences in inundation confound the comparison of different salinities, pH, and Eh. As mentioned, pH and Eh levels are set by effect of water saturation limiting oxygen penetration into the soil. The authors should discuss the differences of P diagenesis in terrestrial soils versus intertidal and subtidal sediments.

Response 4: The first point has been addressed in the Discussion Section (p.10243, l.19-25): "Because the drop in Al/Fe-P correlated also with an increase in pH (Table 1, Fig. 3b), effects of pH and Eh on P desorption could not be distinguished above pH 6.6.

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The decreasing amount of adsorbed P above pH 6.6 may therefore be due to (i) charge changes of metal (hydr)oxides with pH (Oh et al., 1999; Spiteri et al., 2008; Barrow et al., 1980; Sundareshwar and Morris, 1999); (ii) less efficient sorption by iron in the Fe(II) state compared to the Fe(III) state (e.g. Sundareshwar and Morris, 1999); or (iii) a combination of charge changes and Fe reduction." Regarding the plot locations (and related physical-chemical properties) and spatial vegetation cover ("apparently high in the intertidal zone"): Mangrove plots included plots at the mangrove seaward margin (Fig. 1) at low elevation. Further, mangrove sediments were reduced in all the layers investigated (Table S1; see e.g. main classes according to Eh in Husson, 2013). However, transects extended across the entire tidal inundation gradient and, thus, some sediment samples (including the salt marsh sediments) were only moderately reduced or even oxidized. Further, inundation duration at mangrove plots ranged from 0.7% to 22% (percent of time) and was close to usual inundation tolerance thresholds of mangroves, indicating a usual pattern of the vegetation distribution. Finally, the referee comments that some samples (pasture and bay sediments) may not be comparable with others. Even if we exclude the pasture, the bay or both from the correlation analysis, results do not change significantly. This cross-ecosystem study revealed significant correlations between P fractions/species and physical-chemical sediment characteristics, indicating that physicochemically induced transformations are similar for the different ecosystems investigated. Further, the correlations occurred despite the large range in salinity. Mechanisms controlling P transformations (e.g. redox-driven P adsorption/desorption; pH-driven P dissolution/precipitation) are similar for both soils and sediments. We would like to note that the surface sediment of the pasture showed a different pH dependence of the Al/Fe-P fraction compared with other sediments; a fact that is not surprising given the high fertilizer application rates.

Comment 5: The authors compare their study of the sediments in Saigon Delta, Vietnam, as an example of less P enriched sediment. Comparing only one P enriched site vs. one unenriched site does not give much confidence that the differences are due to the degree of P enrichment, because so many other things can differ between

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two sites. However, this is still an interesting comparison, the PP analysis methods were the same, and the patterns are consistent with expectations. The authors should also note that the salinity ranges were similar in both studies. The low pH observed in the Saigon Delta sediments caused by sulfide oxidation may result from unusual circumstances, but this expands the range over which the comparisons may be made.

Response 5: We agree that conducting such a study across a range of sites with varying P content would strengthen our case. However, our study is unique in the sense that the same methods were applied at two sites with strongly contrasting P status. Based on the reviewers' comments we included further information on the site conditions of the Vietnam Delta site to show that the sites were similar in their physicochemical site conditions (see response to comment 4 of referee #2).

#### References

Husson, O.: Redox potential (Eh) and pH as drivers of soil/plant/microorganism systems: a transdisciplinary overview pointing to integrative opportunities for agronomy, *Plant Soil*, 362, 389-417, 2013.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C6207/2014/bgd-11-C6207-2014-supplement.pdf>

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Interactive comment on Biogeosciences Discuss., 11, 10229, 2014.

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