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Interactive Comment

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

Anonymous Referee #1

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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 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,

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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.

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 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.

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

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abundance of Fe, S, and Ca in the sediments is likely important and would be worth comparing among studies.

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.

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 two sites. However, this is still an interesting comparison, the PP analysis methods were the

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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.

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