

# ***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 #2

We thank the referee for the constructive suggestions, which have led to a significant improvement of our manuscript. The following section addresses each comment.

In response to referee #3, "P-enriched site" and "P-unenriched site" have been replaced by "high P site" and "low P site", respectively (see response to comment 14 of referee #3).

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## General Comments

Comment 1: This paper presented interesting data for P speciation along salinity gradient in the Firth of Thames estuary and discussed the mechanisms controlling the P transformation and the effects of anthropogenic P inputs on P transformation – formation of less stable Ca-P. However I found that the paper could be better structured: there is a lot of redundancy in the paper, for example, some parts in the Results section can be moved to discussion (see specific comments). The discussion part is difficult to follow as a lot of less relevant information is presented but not really serves the arguments of the paper. I suggest the author better streamline the manuscript and keep focus on the central theme (see also specific comments below).

Response 1: We have restructured and shortened the text (see comments 3, 8, 11, 12), in particular in the discussion section (shortened by 30%). The redundancy between the results and discussion section has been eliminated.

## Specific Comments

Comment 2: Abstract: (Line 12-13) "This marked upstream-to-downstream switch occurred at near-neutral pH was enhanced by increased P loads" – This sentence is a little misleading, or not fully discussed in the paper to make it conclusive, if true. My understanding, from the data, is that Al/Fe-P in the P-enriched system is higher and this leads to more transformation of Al/Fe-P to Ca-P with increasing pH ("upstream-to-downstream switch"). However only by comparing the percentage of Al/Fe-P is transformed to Ca-P downstream between P-enriched and P-unenriched systems may lead to such conclusion.

Response 2: We rephrased the statement.

Comment 3: Introduction: The introduction reviews the speciation of sediment phosphorus, the mechanism of non-conservative behavior of DRP levels caused by desorption of P from sediments, and the possible controlling mechanisms. The useful

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references provided are appreciated. However I feel that it's a little long and could be shortened. I would suggest holding the details for OCP formation kinetics (and/or their indication for P input) for discussion (also see comments below).

Response 3: We shortened the introduction by removing the first paragraph and removing several statements from the second paragraph (p.10231, 1.26 – p.10232, 1.4). However, it is important to keep the statements on formation kinetics as they provide the necessary background for our hypothesis that the proportion of more soluble Ca-P occasionally increases relative to total Ca-P in response to increased P inputs.

Comment 4: (Page 10238, line 0-5) "It comprised an area exhibiting physical-chemical sediment characteristic very similar to those of the Firth of Thames site. . . (analyzed separately; Sect. 3.4)" – I couldn't find the analyses in Sect. 3.4. More information about the physical-chemical sediment characteristic for the Saigon River Delta is needed otherwise it's not convincing that these two systems are comparable.

Response 4: As suggested we provide more information on the Saigon River Delta site in Section 2.3 and 3.4.

Section 2.3: "Concentrations of P fractions and portions of more soluble Ca-P phases in sediments of the Firth of Thames site were compared with those of a contrasting low P site in the Saigon River Delta (Oxmann et al., 2008; 2010). The site was located in the UNESCO Biosphere Reserve Can Gio close to the South China Sea and was not significantly influenced by anthropogenic P inputs. The region is not in use for agriculture and the Saigon River downriver from Ho Chi Minh City (c. 50 km from the study site) did not contain high levels of P (Schwendenmann et al., unpublished data). In contrast, the physical-chemical sediment characteristics measured at the two sites were comparable. For example, pH, Eh and salinity showed similar gradients along the land-to-sea transects of both sites and these parameters had similar ranges and mean values for mangrove sediments of both sites (Sect. 3.4). An area of acid sulphate sediments at the low P site was analysed separately and confirmed results of the site

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comparison despite its significantly lower pH values (Sect. 3.4)."

Section 3.4: "To verify that the higher Ca-Pmeta concentrations were not caused by site-specific differences related to ecosystem compositions or physical-chemical conditions we restricted the comparison to mangrove plots, which showed similar ranges and mean values of pH, Eh and salinity at both sites (Firth of Thames: pH 5.8-7.1, -160-450 mV, 25-50‰ ; Saigon River Delta: pH 5.7-7.0, -180-400 mV; 25-40‰ ; Table 3)."

Comment 5: Be careful about using the term "linear" (Page 10239, line 23) and "exponentially" (Page 10240, line 6) given the large spread of the data, especially for the Al/Fe-P vs. pH plot.

Response 5: These terms were deleted.

Comment 6: (Page 10240, line 9- 15) I suggest moving this to discussion (or remove if similar statement has been made in discussion).

Response 6: We deleted these sentences except for the second sentence, which we believe is important here.

Comment 7: (Page 10240, line 17) "Metastable Ca-P increase exponentially with pH (Fig. 4a)": state that this is only for sediments at 30- 35 cm. How about other depth? Is this statement still true?

Response 7: Other depth layers also show an increase in metastable Ca-P with pH (cross-dataset correlations are given in Table 1) and the increase appears to be exponential in all the layers. We nevertheless excluded the term exponential (see comment 5) and rephrased as follows: "Metastable Ca-P (Ca-Pmeta) increased strongly with pH (Fig. 4a; Firth of Thames cross-dataset correlations in Table 1), similar to Ca-P (Fig. 3a), and correlated with Ca-P at both sites (Fig. 4b; Table 1)."

Comment 8: (Page 10241, line 6- 10) I suggest remove this to avoid redundancy (explanations of results could go to discussion).

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Response 8: We agree that the first sentence of Sect. 3.5 can be removed. However, the following two phrases are describing results and are not explanations of results ("Strongly acidic sediments ( $\sim$  pH<4) contained just detrital apatite (FAP), whereas slightly acidic sediments ( $\sim$  pH 4-7) contained also authigenic apatite (CFAP). Octacalcium phosphate was additionally present in alkaline mangrove, river, bay and tidal flat sediments.").

Comment 9: Sect. 3.5 and Fig. 5: Figure is confusing as different sites and sediments from different depths are mixed together. It looks like Ca-P decrease when pH >7.3, as opposed to what's stated in the paper: "The concentrations of more soluble Ca-P significantly increased with pH". Just need to be consistent between data and description.

Response 9: We modified Fig. 5 by replacing standard font with bold font for sediments of the Firth of Thames site (caption modified accordingly).

Comment 10: (Page 10242, line 16) I am surprised that salinity had no detectable correlation as the pH and Eh gradients are along with the salinity gradient. Also in Table 1 only Al/Fe-P vs. Salinity is shown. How about Ca-P vs. Salinity?

Response 10: We did not detect a correlation between Al/Fe-P and salinity (Table 1). Overall, the gradient of increasing salinity from pasture to bay was different from the relatively continuous gradients observed for pH, Ca-P, Eh and Al/Fe-P (steady increase/decrease; Fig. 2) in that the salinity peaked in the intertidal zone (Sect. 3.1; Table S1). It is questionable whether salinity effects can facilitate Ca-P formation. Increased salinity can also inhibit the formation of Ca-P because solubility of Ca-P increases strongly with salinity (with increasing ionic strength). This fact should be kept in mind when considering Ca-P formation due to potential salinity effects (increased P desorption, increased Ca<sup>2+</sup>). There is a decreased but still significant correlation between Ca-P and salinity, which may be a non-causal correlation. It would be difficult to argue that salinity facilitated Ca-P formation via P desorption, despite not correlat-

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ing with Al/Fe-P, and despite the ionic strength effects on Ca-P solubility. There may be, however, an effect of increasing Ca<sup>2+</sup> concentrations on Ca-P formation along the continuum, which would also explain the correlation between Ca-P and salinity (see response 17 to referee 3).

Comment 11: I suggest combining Sect.4.4 and Sect. 4.5 and the discussion here could be substantially shortened or better linked to the data presented. This may apply to other sections as well. For example, it's difficult to understand what's the focus of the paragraph (Page 10247- 10248) and what's the functionality of the paragraph for the story line and the central theme. This is not a review paper so to avoid distraction discussion should be focus on the findings/implications of this paper based on the data presented; only those references relevant to arguments of this paper is needed.

Response 11: As suggested we combined sections 4.4 and 4.5 and shortened the text.

Comment 12: Sect. 4.6: I feel that this section should go to intro section, or removed as it does not serve the interests of the manuscript as stated in the introduction.

Response 12: We removed this section.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C6213/2014/bgd-11-C6213-2014-supplement.pdf>

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

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