

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 #3

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Comments to Oxmann and Schwendenmann

General comments: A comprehensive dataset from a New Zealand intertidal flat on solid-phase P fractions extracted from sediments and soils of three transects. The authors applied tested methodology for P extractions that target Al/Fe-bound P, octacalcium-phosphate, carbonate apatite, and metastable C-P phases in soils and sediments. The overall goal was to assess solid-phase speciation changes in the land-to-sea continuum of a P-enriched estuary. These speciation changes would indicate the formation of stable P phases that could be buried and thus removed as nutrients,

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or whether the formation of labile phases that may be released from sediment and contribute to water column eutrophication. The data lead the authors to suggest a strong pH control on P speciation in sediment leading to the formation of metastable Ca-P phases in the Mangrove and intertidal sediment. The authors propose a speciation change around pH 6.5, above which P is desorbed from Al/Fe-P phases and is precipitated with Ca. This switch supposedly is, based on the type of measurements taken, to be more controlled by pH than Eh.

The general implications of this study could be better worked out in the discussion and conclusion sections. While this is a fine dataset, I have not learnt something fundamentally new about the transport and speciation of P in the coastal zone nor does the manuscript contain fundamentally new conclusions or conclusions relevant for coastal ecosystem management. The data are extensively described in the figures and tables, to the extent that one gets the impression that it is overdone. For example, figures 3 and 5 convey the same message since the same data are used in these figures. The figure can be omitted without a loss in overall manuscript clarity. As a matter of fact, Figure 4 is difficult to understand in the first place. I also think that the authors are too much guided by their environmental measurements than the obvious changes that are associated with the land-sea transition from pasture to permanently inundated sediment (see below).

In particular, I missed a discussion of the obvious salinity effects for the observed changes. An alkalinity increase is generally associated with a salinity increase in marine environments and will often drive up the pH and calcium concentrations. This is a ubiquitous phenomenon irrespective of whether a low-P or high-P system is considered. In fact, I suggest that the authors spend more time explaining why the Vietnam data set has a greater pH range than the New Zealand data set. Many of the correlations are much less obvious if the New Zealand data alone are considered.

Methods: what were the tip diameters of the sensors? How much are the measurements in the sediments affected by the sensors? This type of study should actually

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be conducted with microelectrodes rather than macrosensors. Why was such a course sampling resolution chosen for the depth intervals and why were certain depth intervals omitted? Why did the authors think that the same depth resolution should be applied to all samples? What were the dissolved phosphate concentrations in these sediments? Without information on the dissolved inorganic and even better dissolved organic phosphate a critical hypothesis concerning desorption and re-precipitation efficiency cannot be addressed. This is one of my major points of criticism with this manuscript. It tries to assess the potential dynamics of phosphorus from the perspective of the solid phases, which alone will be difficult when mobilization and transport need to be assessed.

The results description and parts of the discussion are at times too long-winded and can be significantly reduced. The language can be simplified and the figure axes of Figure 2,3,4, and 6 at normal print size are almost unreadable. The use of Figure 6 is also debatable. The authors use this figure to demonstrate that pH effects dominate the partitioning between Al/Fe-P and metastable Ca-P, something that can already be deduced from looking at Figure 4a. However, Figure 6 compares two different extraction methods, whereby one, the 'Morgan-P' is sensitive to natural pH effects (I am not quite clear why), whereas the others are not. This then leads to the confusing statement in the text that Morgan-P may not be a trustworthy extraction method in the first place (p.10250 first line). I am not sure that the non-linear behavior of an extraction method should be used to derive an environmental control parameter. This is too long-winded and complicated. To make it short, the point was made earlier in the text and didn't need to be reiterated. In addition, Figure 6a b use the same data with the only difference that they are split up into the acidic and alkaline samples in panel b.

Specific comments: Abstract: Line : 10: P status: Meaning unclear: speciation? Line 18-20: Simplify sentence

Introduction: The introduction is overloaded with references, which add to the impression that this study isn't overly novel. Reduce number of references to the most essential (lines 5-6 and lines 19-20). p.10233, lines 12-16. Awkward sentence structure

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and vague. What factors are you referring to? p.10234: lines 12-15 and 18-20. This sentence is the central motivation of this study, yet this issue is not really picked up again in the discussion and conclusion. The authors should make a better attempt at addressing how their findings help identify human perturbations and the effects on the P cycle in their study systems.

Materials and methods: Sampling resolution is very coarse in light of early diagenetic P cycling. What is the reasoning behind this coarse resolution? May be the authors wanted to explore pre-anthropogenic and anthropogenic differences in P inventories. If so, the sediment cores would have to be dated. In any case, an explanation has be given for the sampling resolution. p.10236: lines 5 and following: What was the tip diameter of these probes? Very steep gradients can be expected in the intertidal sediments that can be identified correctly only with high-resolution measurements. p.10236: Line 16. What is 'semi-selective': Awkard term. p.10236: Line 22: ... predominantly more ... : meaning more than what? p.10237: The methods description is not clear enough. Example: I.6: ... parallel incubation at varying pH: Please be more precise. I.10: "Differential dissolution was verified by standard addition experiments." This is not clear enough. I.26: The data acquisition from the Vietnam site is not detailed here. Since this is a comparative study, more information needs to be provided on the other site.

p.10239: I.16: "P-unenriched site": Awkard term and ill-defined. What does this mean? How do you know that this is not enriched in P. What is your reference level? I.21: delete ' between the sites' (repeat) p.10240: I.12/13: the authors claim that there is only a substantial effect above pH 6.6. This a conclusion based on their summed data treatment. However, the dissolution/desorption/precipitation dynamics of phosphorus should be compared per site in order to demonstrate net mobilization/immobilization. That is, per site there may be a strong redox control that controls mobility. Without information of the dissolved phosphate concentrations, the authors cannot come to this conclusion. p.10240, I.23/24: I disagree with the assessment method: In order to un-

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derstand the causes of an enrichment, an assessment of the P flux is necessary. P enrichment cannot be quantitatively understood in terms of the analysis of state variables such as pH and Eh. Instead, net dissolution, seaward transport, and precipitation need to be demonstrated.

p.10243: In the discussion, much is made of the speciation switch at pH 6.6. I recommend that the authors restructure their discussion and focus on the conditions that favor desorption/mobilization at the landward sites as opposed to the seaward sites and allow the reader to understand the P dynamics better. P dissolution likely occurs due to redox changes, but the low pH and low salinity makes it difficult for P to be immobilized as a Ca-P phase. Only at the seaward sites, where higher salinities increase the alkalinity and pH, is P precipitated as Ca-P phase. Here again, Eh conditions do not allow Fe/Al-P to be stable so that P can be fixed a Ca-P phase.

p.10244: As above, the authors should consider the causes for the higher pH. Understanding and discussion the pH regulation goes a long way to help the reader understand the dynamics of these systems.

p.10247-10248: the discussion of extraction methods targeting labile/non-labile Ca-P phases FAP and CFAP to allow distinctions of their detrital and authigenic origin is complicated and not easy to follow. Try to simplify this section. p.10247: l.20/21: ... to be largely generated where they are observed": Phrasing not clear enough;

Section 4.6. See above my comments on the use of Figure 4.6. Again, this discussion rather confuses the reader. The apparent pH effect has been worked out in the previous sections, which makes this section not very necessary. Consider omitting it for the sake of clarity.

If these structural changes and improvements of the data presentation and discussion are made this will be ultimately a good manuscript. Looking forward to seeing a revised version.

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