Dear Prof. Slomp,

Please find enclosed the revised version of our manuscript „ Authigenic apatite and octacalcium phosphate formation due to adsorption/precipitation switching across estuarine salinity gradients".

The revised version still stresses the importance of pH in Ca-P formation across salinity gradients but places more emphasis on the role of other factors, in particular the role of the redox state. We therefore considered it reasonable to also modify the title slightly. A point-by-point response to the referee comments and a list of all relevant changes is included below.

The manuscript was also revised to improve its clarity and conciseness. A record of all changes is provided in the marked-up manuscript version.

We are looking forward for publication of our manuscript in Biogeosciences.

Kind regards,

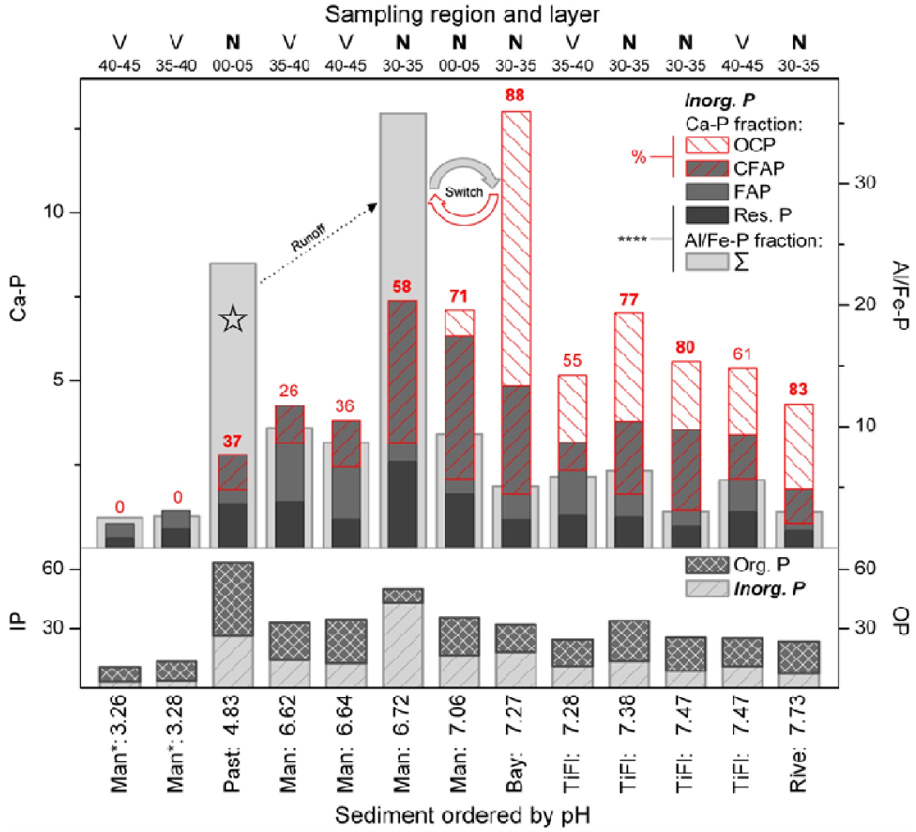
Julian Oxmann
Luitgard Schwendenmann

Referee #1

We thank the referee for providing feedback on the manuscript. The following section addresses each comment. The response is written in italics.

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 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 conveyer 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 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 dependence 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^{2+} *in the response to comment 17 of referee #3.*

<u>Comment 4</u>: 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. 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 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.

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. The response is written in italics.

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).

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 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, l.26 – p.10232, l.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 fine 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 comparison despite its significantly lower pH values (Sect. 3.4)."

Section 3.4: "To verify that the higher Ca-P_{meta} 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-P_{meta}) 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).

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 (~ pH<4) contained just detrital apatite (FAP), whereas slightly acidic sediments (~ 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^{2+}). 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 correlating with Al/Fe-P, and despite the ionic strength effects on Ca-P solubility. There may be, however, an effect of increasing Ca^{2+} 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).

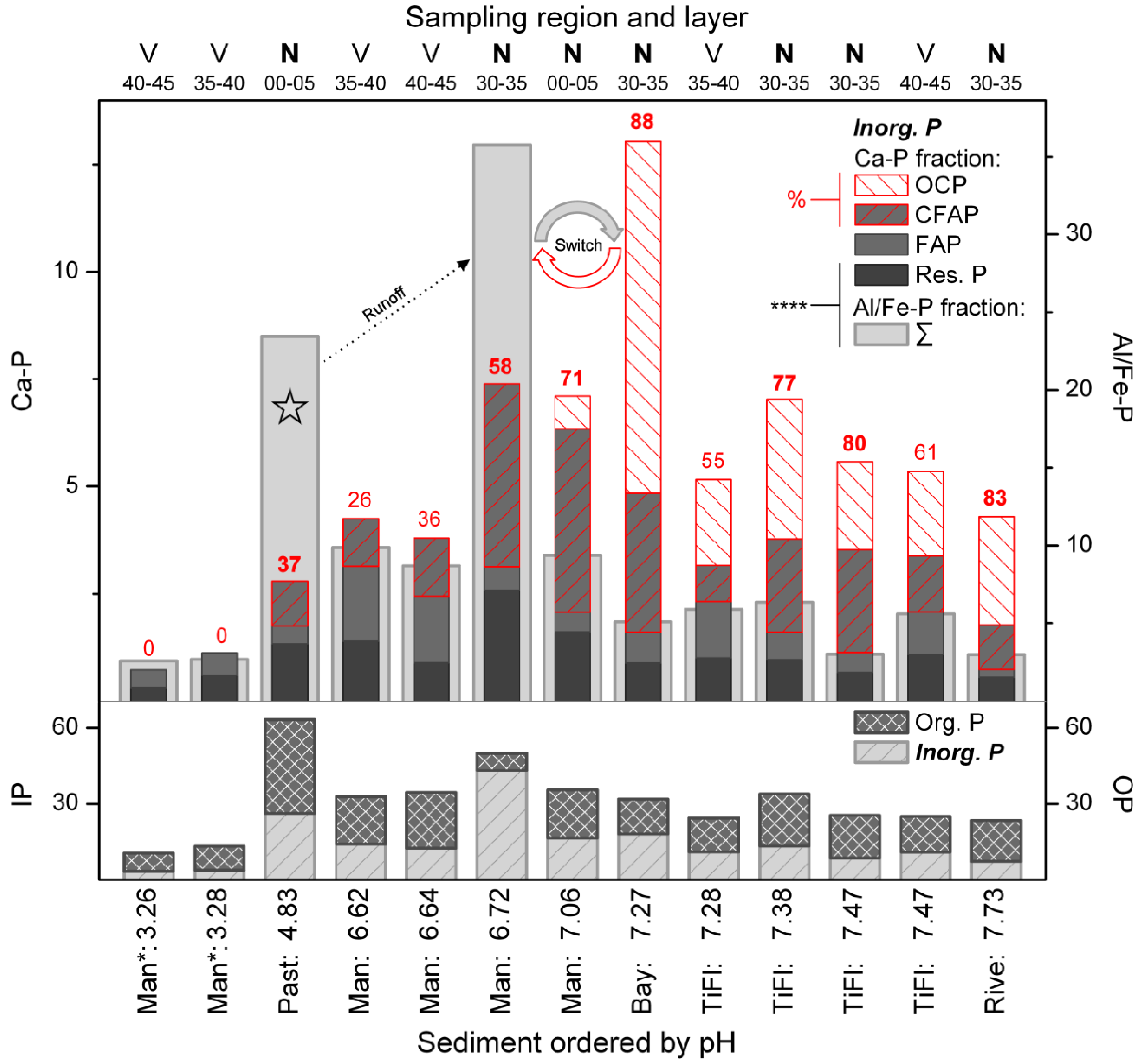
Comment 11: I suggest combining Sect.4.4 and Sect. 4.5 and the discussion here could be substantially shortened or better linked to the data presented. This may apply to other sections as well. For example, it's difficult to understand what's the focus of the paragraph (Page 10247-10248) and what's the 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.

Revised Fig. 5



Referee #3

We thank the referee for the constructive and detailed comments, which substantially helped in improving the quality of the manuscript. The following section addresses each comment. The response is written in italics.

General Comments

Comment 1: 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, 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).

Response 1: The referee raises some concern that the results may not generate fundamentally new insights into P speciation in the coastal zone. We would like to disagree. The separation and quantification of octacalcium phosphate provides fundamentally new insights. That is, high concentrations of octacalcium phosphate were found in the alkaline nearshore sediments, which have implications for P speciation and inorganic P accumulation in the coastal zone.

We would also like to point out that Figure 3 and 5 do not show the same data. While Fig. 3 shows changes in sediment phosphorus fractions (n=214 samples), Fig. 5 shows species distributions (n=13 samples). Figure 5 shows the importance of octacalcium phosphate for inorganic P speciation in the coastal zone.

Comment 2: 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.

> *Response 2: The referee suggests including more information about the pH control in the coastal zone (see also comment 18). We included a paragraph on the linkages between salinity and pH in the introduction:*
>
> *"Desorption and precipitation of phosphate along salinity gradients are influenced by redox potential (Eh) and pH (van Beusekom and de Jonge, 1997). Typically, Eh decreases and pH increases from land to the sea (Clarke, 1985; Huang and Morris, 2005; Sharp et al., 1982). Seawater inundation induces the Eh gradient by limiting oxygen diffusion into the sediment, thereby initiating anaerobic respiration. Sediments regularly inundated by seawater tend to have higher pH values than terrestrial soils because soils naturally acidify due to vegetation derived inputs (effects of enhanced carbonic acid production, root exudate release, litter decomposition, proton extrusion). Human activities such as N fertilization can also contribute to soil acidification (Fauzi et al., 2014; Hinsinger et al., 2009; Richardson et al., 2009). The acid generated is neutralized downstream by the high alkalinity of seawater."*
>
> *The pH range differences between the sites compared were marginal excluding the area of acid sulphate sediments at the Vietnam site (see also response 4 to referee #2). The correlations are, indeed, even more striking if datasets of both regions are considered thereby highlighting the similarities of both regions. Nevertheless, most correlations based on New Zealand data alone are highly significant (Table 1).*
>
> *We provide a reply on the issue of increasing calcium concentrations in response 17.*

Comment 3: 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 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.

> *Response 3: Cross-ecosystem studies of P speciation in the coastal zone are rare. Our objective was to include all ecosystems along the continuum from pasture to bay along three*

transects (Fig. 1). Our goal was to show that the physical-chemical sediment characteristics are the primary factors driving inorganic P speciation in the coastal zone.
The focus of this study was to investigate changes along the land-sea continuum. Thus we collected many samples across the landscape, but only a few samples of each core (= coarse vertical resolution). Due to the coarse vertical sampling resolution, we decided to collect samples of relatively long core sections to reduce vertical variability. Because laboratory data were obtained from 5 cm long core sections, the spatial averaging caused by the larger tip diameter of the electrodes was an advantage. We worked with microelectrodes (sulfide, pH, redox) during field trips, particularly in mangroves. If one aims to focus on large spatial scales (and not on e.g. micro-scale root measurements), the usage of microelectrodes is, we believe, more prone to errors. Our study sites were spread out over a large area (c. 100 km^2) and the electrodes were better suited than microelectrodes with respect to the sampling resolution.

We modified the text (p.10235; l.26) to provide a better description of the sampling approach: "Cores were divided into the following surface, intermediate and deeper sections: 0-5, 10-15, 30-35 and 35-40 cm. Longer core sections reduce vertical variability and were chosen for the relatively coarse vertical sampling, which allowed us to focus on geochemical changes along the land-sea continuum."

The referee criticizes that DIP concentrations were not assessed and states that mobilization is difficult to assess using the determination of solid phases alone. However, we would like to note that understanding P mobilization is difficult without knowing the solid-phase P composition. We used correlation analysis to determine the driving forces behind the solid-phase P speciation at the sites examined and we focused on the determination of the corresponding solid-phase composition, in particular the composition of calcium phosphates. Hence, this study did not focus on the mentioned efficiencies. If we had measured DIP, one could in turn raise concerns about the lack of parameters which are required to calculate saturation indices. We are interested in combining measurements of octacalcium phosphate on smaller spatial scales with measurements of dissolved analytes and aqueous geochemical modelling, but DIP measurements were not necessary for the conclusions drawn here.

Comment 4: The results description and parts of the discussion are at times too long-winded and can be signifcantly 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 longwinded 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.

Response 4: As suggested, we have increased the font size of the axis labels. We shortened the text (see comments 3 and 11 of referee #2). Figure 6 and the related section were removed in response to comment 12 of referee #2.
Soil tests for available P differ in their relative preference for extracting certain P fractions/species. Because concentrations of P fractions/species depend on the pH (e.g., Figs. 3 and 5), all these tests are to some degree dependent on the soil pH. Morgan is different from Olsen, Bray and M3P because it is more sensitive to increasing Ca-P and less sensitive to increasing Al/Fe-P. The latter are more sensitive to increasing Al/Fe-P and less sensitive to increasing Ca-P. We used these preferences to show the switch from Al/Fe-P to Ca-P at near-neutral soil pH. We did not call the validity of the Morgan's P test as such into question, yet concluded that the test likely overestimates plant-available P at high soil pH. This conclusion agrees well with results of other studies (see the references cited).

Specific Comments

Comment 5: p.10230, l.10: P status: Meaning unclear: speciation?

Response 5: P status has been replaced by "site-specific total P status".

Comment 6: p.10230, l.18-20: Simplify sentence.

Response 6: The sentence was rephrased "…at the high P site. Here, sediments contained on average 6-fold higher Ca-P_{meta} *levels compared with the low P site, although these sediments contained only 2-fold more total Ca-P than the low P sediments."*

Comment 7: p.10231, l.5-6 and l.19-20: 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).

Response 7: First paragraph was removed and the number of references reduced in line 19-20.

Comment 8: p.10233, l.12-16: Awkward sentence structure and vague. What factors are you referring to?

Response 8: The section was rephrased: "Authigenic Ca-P is widely dispersed in marine sediment, but its solubility in seawater remains difficult to predict. Because seawater is probably close to saturation with CFAP, both a possible formation and dissolution of CFAP in seawater cannot be rejected (Atlas and Pytkowicz, 1977; Faul et al., 2005; Lyons et al., 2011). In contrast, detrital fluorapatite (FAP) is unlikely to dissolve in seawater (Ruttenberg, 1990; Howarth et al., 1995)."

Comment 9: p.10234, l.12-15 and l.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.

Response 9: We believe that we addressed how our findings help to identify human perturbations and their effects on the P cycle throughout the discussion and conclusion section. For example, in the discussion we wrote (p.10245, l.14 – p.10246, l.2) "We hypothesize that more soluble Ca-P minerals accumulate relative to total Ca-P by anthropogenic P enrichment because the formation of sparingly soluble Ca-P minerals is too slow for balancing increased formation rates of thermodynamically less stable Ca-P minerals. This hypothesis is consistent with comparatively large amounts of metastable Ca-P, which apparently accumulated at the high P site due to external factors (Sect. 3.4, Table 3; Fig. 4c,d) (…) Results of both independent methods, which were significantly correlated (Table 4), therefore provide strong evidence for the proposed accumulation of thermodynamically less stable Ca-P by anthropogenic P inputs."
and (p.10245, l.7-11) "This site comparison therefore implies that fertilizer-derived P was largely included in the Al/Fe-P fraction (adsorbed P) of acidic upstream sediments. Phosphorus inputs by runoff or erosion to downstream environments apparently led to enhanced precipitation of Ca-P by increasing pH."

In addition to what we have written, we will include the following statement to clarify that less stable Ca-P may be a useful parameter to monitor anthropogenic accumulations of inorganic P.

"Less stable Ca-P may thus be a useful parameter to monitor anthropogenic accumulations of inorganic P in coastal regions. Because physical-chemical sediment characteristics influence Ca-P formation, an important caveat is the between-site comparability of data. In this study, there was between-site comparability of both the sediment characteristics and the general response of each of the P fractions and P species to the sediment characteristics at different depth intervals along the land-sea continuum (Fig. 3a, b; Fig. 4 a, b; Fig. 5)."

Comment 10: 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.

Response 10: see response 3

Comment 11: p.10236: Line 16. What is 'semi-selective': Awkward term.

Response 11: "by preferential extraction of this fraction" has been substituted for "by semi-selective extraction"

Comment 12: p.10236: Line 22: ... predominantly more ... : meaning more than what?

Response 12: "preferentially extracts more soluble Ca-P phases" has been substituted for "extracts predominantly more soluble Ca-P phases"

Comment 13: p.10237: The methods description is not clear enough. Example: l.6: ... parallel incubation at varying pH: Please be more precise. l.10: "Differential dissolution was verified by standard addition experiments." This is not clear enough. l.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.

Response 13: l.6: "parallel incubation of sediment subsamples at varying pH in 0.01 M $CaCl_2$*" was replaced by "parallel incubation of sediment subsamples at different pH values (approximate pH range 3 to 8) in 0.01 M* $CaCl_2$*".*

l.10: We modified this section to provide a more detailed description of the methodology: "Differential dissolution was verified by standard addition experiments. For these experiments, reference compounds were added to the sediment subsamples before incubation using polyethylene caps loaded with 2 µmol P g^{-1} *(ultra-micro balance XP6U; Mettler Toledo GmbH, Greifensee, Switzerland). Reference compounds included OCP, hydroxylapatite (HAP), various CFAP specimens, FAP and biogenic apatite. Methodology, instrumentation and the suite of reference minerals are described in Oxmann and Schwendenmann (2014)."*

l.26: We provided more information on the Saigon River Delta site (see response to comment 4 of referee #2).

Comment 14: p.10239: l.16: "P-unenriched site": Awkward term and ill-defined. What does this mean? How do you know that this is not enriched in P. What is your reference level? l.21: delete ' between the sites' (repeat)

Response 14: We decided to replace "P-unenriched site" by "low P site" and "P-enriched site" by "high P site", except four passages at which it is more informative to use the local classification system for the high P site.

l.16: As described in Section 4.1, the Firth of Thames site was classified as P-enriched (according to the New Zealand classification system) due largely to the agriculture, which constitutes the main P source (Sect. 4.1; see also Supplementary Table S3). In contrast, the remote region in the Saigon River Delta was not in use for agriculture and Ho Chi Minh City (c. 50 km from the study site) was not a major source of P-input based on water samples taken from the Saigon River and Dong Tranh River (Schwendenmann et al., unpublished data).

We modified the text to provide additional information (see also response to comment 4 of referee #2): "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 of 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)."*

l.21: We removed "between the sites".

Comment 15: p.10240: l.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.

Response 15: Here we referred (i) to Fig. 3 that shows values for individual sediments (not summed data); and (ii) to the solid-phase speciation in individual sediments (not to net mobilization/immobilization per site). To further back up our assumption that a release of P adsorbed to ferric iron compounds did not occur in sediments with pH < 6.6, we included information about critical levels for reduction of ferric iron (p.10243, l.16 – p.10244, l.4):

"The maximum amount of adsorbed P at pH 6.6 also indicated that Eh, which showed the maximum decline at ~ pH 6.6 (Fig. 3d), did not cause significant desorption of P at this pH. Below this pH, Al/Fe-P did not decline with Eh (cf. Fig. 3b and d) and these parameters were not correlated (Table 1), suggesting that a release of P adsorbed to ferric iron compounds did not occur in the corresponding sediments. Yet, both Eh and Al/Fe-P decreased above pH 6.6 (cf. Fig. 3b and 3d) and were correlated in this range (Table 1). 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. 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.
Critical redox potentials reported for reduction of ferric iron compounds are around 300 mV at pH 5 and 100 mV at pH 7 (Gotoh and Patrick, 1974; Husson, 2013; Yu et al., 2007). These levels match very well with critical Eh levels for desorption of Fe-(hydr)oxide-bound P, including a similar pH dependence of those levels (compare Delaune et al., 1981 with Gotoh and Patrick, 1974). As Fig. 3d shows, Eh values that did not correlate with Al/Fe-P (sediments with pH < 6.6) were above the critical Eh level, whereas Eh values that correlated with Al/Fe-P (sediments with pH > 6.6) were below the critical Eh level. This implies that reductive dissolution and related desorption of P could have contributed to the downstream transition from Al/Fe-P to Ca-P. Interestingly, the physicochemically induced P redistributions largely agreed with those from the low P site despite considerable differences of P fraction concentrations between both sites (Fig. 3a,b). This suggests that the effects of physical-chemical sediment characteristics were independent of the site-specific total P status."

Comment 16: p.10240, l.23/24: I disagree with the assessment method: In order to understand 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.

Response 16: Our results suggest that Ca-P forms at the expense of adsorbed P along the salinity gradient and that this formation depends on physical-chemical sediment characteristics (Sect. 3.2 and 4.3; Fig. 3). Comparing the New Zealand and Vietnam sites, which differed in P but had similar physical-chemical sediment characteristics, revealed that total P, Al/Fe-P, Ca-P and $Ca\text{-}P_{meta}$ *were largely elevated at the P-rich site compared with the low P site. Anthropogenically-enriched sediments contained on average 6-fold higher concentrations of* $Ca\text{-}P_{meta}$ *compared with the low-P sediments, although these sediments contained only 2-fold more total Ca-P. This implies that more soluble Ca-P minerals accumulate relative to total Ca-P by anthropogenic P enrichment because the formation of sparingly soluble Ca-P minerals is too slow for balancing increased formation rates of thermodynamically less stable Ca-P minerals.*

The reason for the high P levels is obviously the high fertilizer application rate, which constitutes by far the main P source to the watershed (Fertilizer: 37 Gg P yr^{-1}*; Atmosphere and Weathering: 4 Gg P* yr^{-1}*). Hence, this is likely also the reason for the excessive accumulation of* $Ca\text{-}P_{meta}$*. A key advantage of this study is that trends in anthropogenic nutrient enrichment in the watershed are well documented in several studies (see e.g. Sect. 4.1 and references therein).*

Comment 17: 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.

Response 17: The mechanisms of redox-driven phosphate desorption (p.10232, l.10-24) and pH-induced changes in the saturation state (p.10232, l.25 – p.10233, l.16) from landward to seaward sites as well as the underlying mechanisms were described in detail (and in a similar way as suggested by the referee) in the introduction and discussion (e.g., p.10242, l.14-21; p.10243, l.3-8).

Regarding the effects of higher salinities and changes in the saturation state with respect to calcium phosphates by increasing pH and Ca^{2+} *concentrations (see also comment 2): We would like to note that the apparent Ca-P solubility increases strongly with salinity (with increasing ionic strength) and that this effect is contrary to facilitating effects of pH and* Ca^{2+}*. We modified the text (p.10248, l.13-20) to something very similar to the referee's suggestion and added information on the effect of* Ca^{2+}*:*

"In general, the established Ca-P precipitation in sediments along salinity gradients provides some insight into the relevance of factors influencing this precipitation such as changes in salinity, dissolved phosphate and pH. In fact, as the ionic strength increases with increasing salinity for a given phosphate concentration and pH, the apparent Ca-P solubility increases strongly (Atlas, 1975). Yet, increasing Ca-P concentrations imply that the salt effect may be more than offset by the rise in pH, redox-driven phosphate desorption from iron oxyhydroxides and other potential factors in interstitial waters along salinity gradients. For example, Ca^{2+} *concentrations generally increase from land to sea and, hence, increase the saturation state with respect to calcium phosphates (normal seawater and sediment pore-water: c. 10 mM; river water, global average: c. 0.4 mM; soil pore-water, average of temperate region soils: 1.5 mM; Girard, 2004; Lerman and Wu, 2008; Lower et al., 1999; Rengel, 2006; Sun and Turchyn, 2014). Although the correlation of salinity with Al/Fe-P was not significant, the correlation with Ca-P was decreased but still significant (Table 1), indicating that increasing* Ca^{2+} *concentrations from land to sea may also contribute to the observed Ca-P formation."*

Comment 18: 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.

Response 18: see our response to comment 2.

Comment 19: 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.

Response 19: We have revised this section (see also comment 11 of referee #2).

Comment 20: p.10247: l.20/21: ... to be largely generated where they are observed": Phrasing not clear enough;

Response 20: The sentence has been removed in response to comment 19.

Comment 21: 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.

Response 21: We removed this section.

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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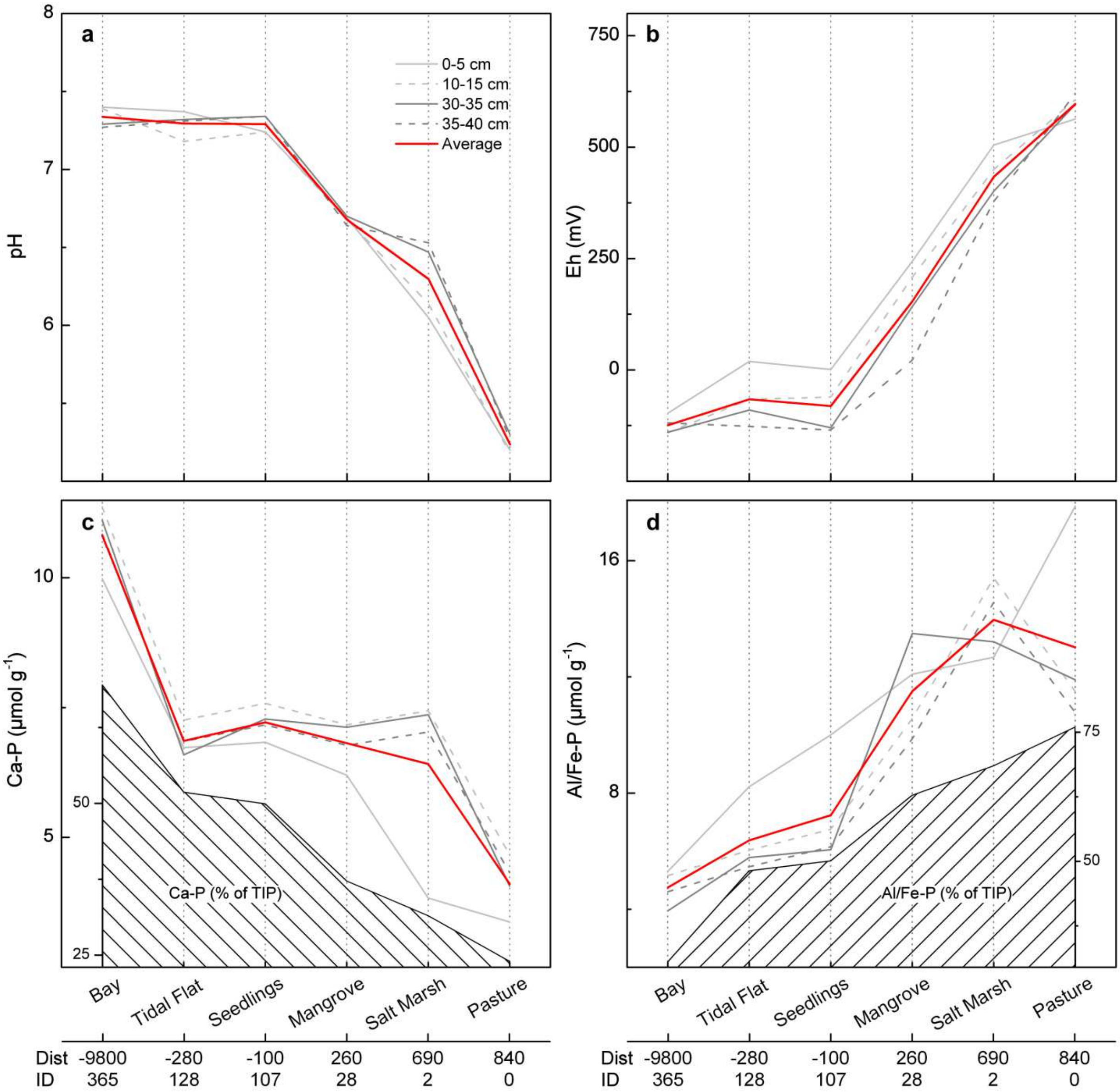
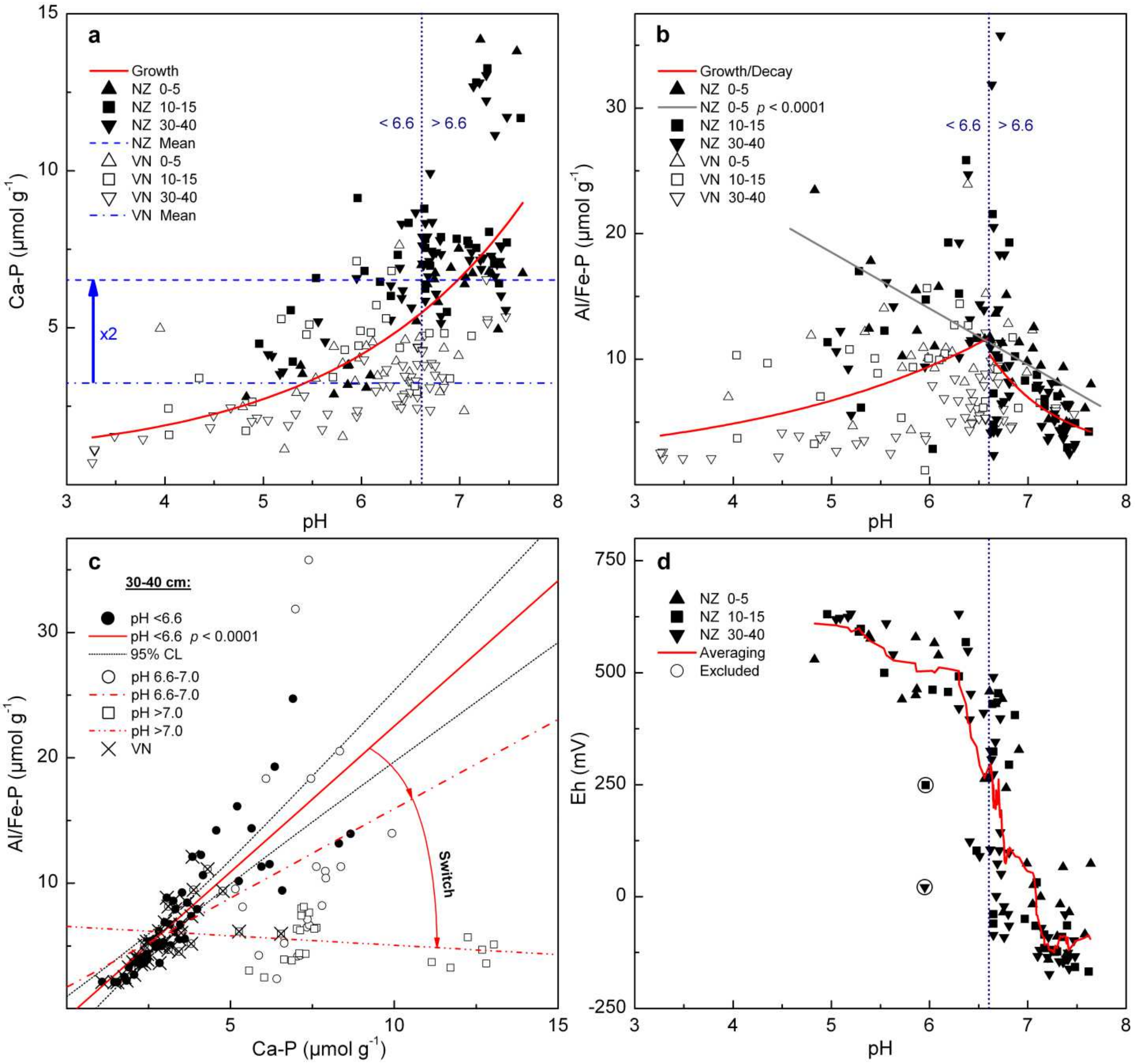
Revised figures (in response to comment 4 of referee #3)

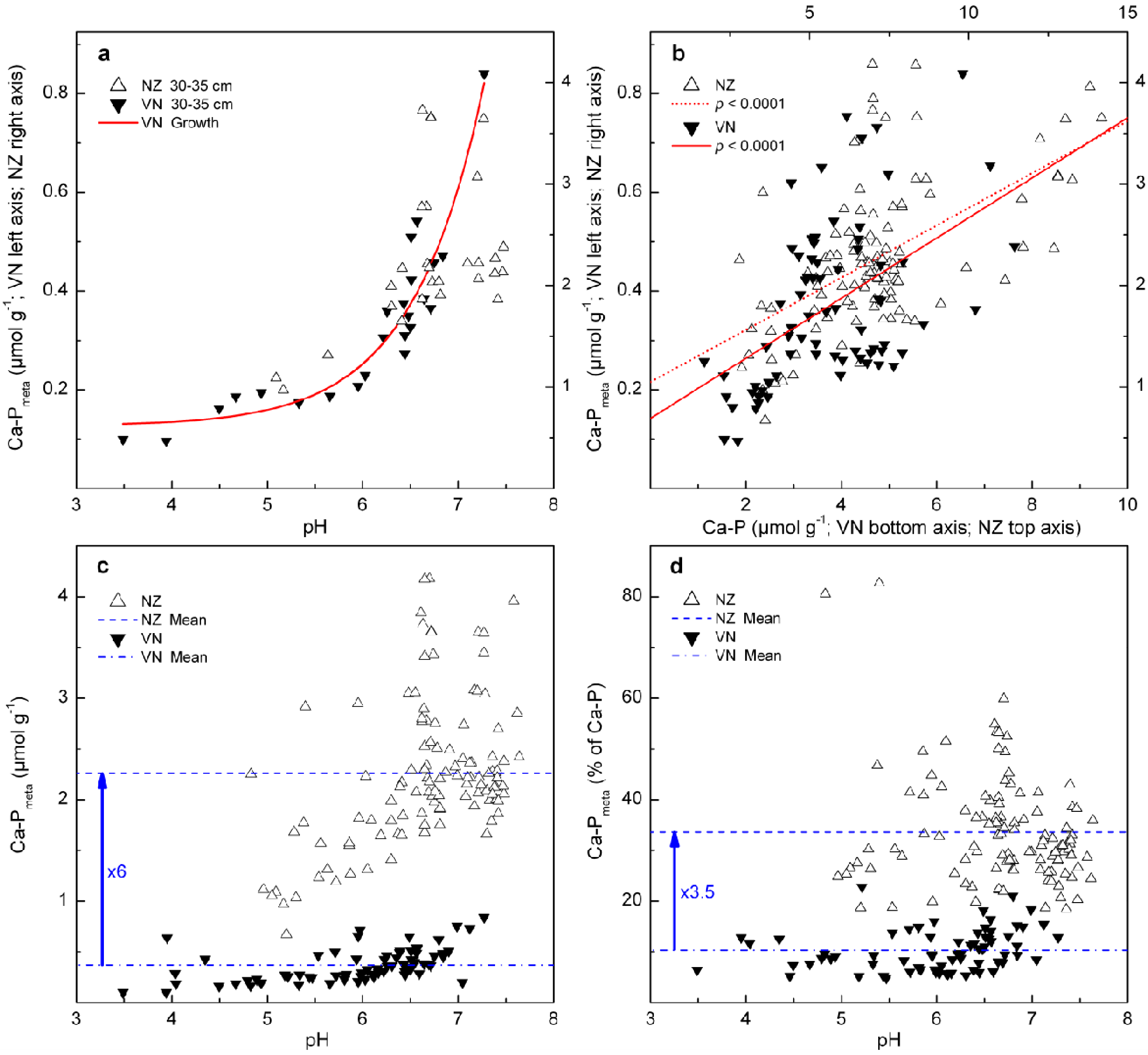
Revised Fig. 2



Revised Fig. 3



Revised Fig. 4



List of relevant changes

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
Throughout			Inserted	high P site	R. #3 / Comment 14
Throughout			Deleted	P-enriched site	R. #3 / Comment 14
Throughout			Inserted	low P site	R. #3 / Comment 14
Throughout			Deleted	P-unenriched site	R. #3 / Comment 14
Abstract	1	20	Inserted	site-specific total	R. #3 / Comment 5
Abstract	1	22	Inserted	This switch occurred at near-neutral sediment pH and has possibly been enhanced by redox-driven phosphate desorption from iron oxyhydroxides.	R. #2 / Comment 2
Abstract	1	22	Deleted	This marked upstream-to-downstream switch occurred at near-neutral sediment pH and was enhanced by increased P loads.	R. #2 / Comment 2
Abstract	1	28	Inserted	Here, sediments contained on average 6-fold higher Ca-P$_{meta}$ levels compared with the low P site, although these sediments contained only 2-fold more total Ca-P than the low P sediments.	R. #3 / Comment 6
Abstract	1	28	Deleted	The average Ca-P$_{meta}$ concentration was six-fold, whereas total Ca-P was only twofold higher at the P-enriched site compared to the P-unenriched site.	R. #3 / Comment 6
Introduction	2	2	Inserted	Desorption and precipitation of phosphate along salinity gradients are influenced by redox potential (Eh) and pH (van Beusekom and de Jonge, 1997). Typically, Eh decreases and pH increases from land to the sea (Clarke, 1985; Huang and Morris, 2005; Sharp et al., 1982). Seawater inundation induces the Eh gradient by limiting oxygen diffusion into the sediment, thereby initiating anaerobic respiration. Sediments regularly inundated by seawater tend to have higher pH values than terrestrial soils because soils naturally acidify due to vegetation derived inputs (effects of enhanced carbonic acid production, root exudate release, litter decomposition, proton extrusion). Human activities such as N fertilization can also contribute to soil acidification (Fauzi et al., 2014; Hinsinger et al., 2009; Richardson et al., 2009). The acid generated is neutralized downstream by the high alkalinity of seawater.	R. #3 / Comment 2&18
Introduction	2	2	Deleted	Anthropogenic P inputs more than doubled the global P flux to marine environments (Meybeck et al., 1982; Bennett et al., 2001). In some regions the fluxes have increased to more than ten times their pre-agricultural levels (Howarth et al., 1995). A large proportion of this terrestrial input to marine systems is retained in estuaries and near-shore marine environments (Dürr et al., 2010; Howarth et al., 1995; Ruttenberg, 2004; Ruttenberg, 1990; Slomp, 2011; Teodoru et al., 2007). The primary anthropogenic P source to this reservoir originates from manure and fertilizer P, which is mainly lost from agricultural systems in the form of erosion-derived particulate P (Kronvang et al., 2007; McDowell et al., 2003;	R. #2 / Comment 3 R. #3 / Comment 7

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
				Jordan et al., 2008). Coastal environments may be particularly vulnerable to excessive P loads because physical-chemical changes along salinity gradients facilitate transformations of P and thereby lead to sharp increases in dissolved reactive P (DRP) concentrations (Correll, 1998; Howarth et al., 1995; Mindy and Greenhalch, 2009; Townsend and Porder, 2011).	
Introduction	2	3	Deleted	Sundareshwar and Morris, 1999	R. #3 / Comment 7
Introduction	2	3	Deleted	DeLaune et al., 1981	R. #3 / Comment 7
Introduction	2	4	Deleted	Paludan and Morris, 1999	R. #3 / Comment 7
Introduction	2	4	Deleted	Spiteri et al., 2008; Sundareshwar and Morris, 1999	R. #3 / Comment 7
Introduction	2	17	Deleted	Thus, DRP levels are usually higher than expected from oceanic and riverine endmembers (Sharp et al., 1982; Spiteri et al., 2008; van der Zee et al., 2007). These relationships hold true for effects on adsorbed P in sediment and related pore water chemical changes (e.g. Jordan et al., 2008). Hence, non-conservative mixing is also a result of similar processes in the benthic boundary layer. Accordingly, P desorption from sediment by elevated pH values was shown to enhance eutrophication (Gao et al., 2012; Seitzinger, 1991).	R. #2 / Comment 3
Introduction	3	16	Inserted	Authigenic Ca-P is widely dispersed in marine sediment, but its solubility in seawater remains difficult to predict. Because seawater is probably close to saturation with CFAP, both a possible formation and dissolution of CFAP in seawater cannot be rejected (Atlas and Pytkowicz, 1977; Faul et al., 2005; Lyons et al., 2011). In contrast, detrital fluorapatite (FAP) is unlikely to dissolve in seawater (Ruttenberg, 1990; Howarth et al., 1995).	R. #3 / Comment 8
Introduction	3	16	Deleted	Due to factors that allow for widespread, dispersed formation and persistence of more soluble authigenic Ca-P in marine environments (possibly even in the water column; Faul et al., 2005; Lyons et al., 2011), detrital fluorapatite (FAP) is unlikely to dissolve in these environments (Ruttenberg, 1990; Howarth et al., 1995).	R. #3 / Comment 8
Materials & M.	5	13	Inserted	Longer core sections reduce vertical variability and were chosen for the relatively coarse vertical sampling because the focus of this study was on geochemical changes along the land-sea continuum.	R. #3 / Comment 3
Materials & M.	5	32	Deleted	semi-selective	R. #3 / Comment 11
Materials & M.	5	32	Inserted	preferential	R. #3 / Comment 11
Materials & M.	6	2	Inserted	preferentially	R. #3 / Comment 12
Materials & M.	6	2	Deleted	predominantly	R. #3 / Comment 12
Materials & M.	6	12	Deleted	varying pH	R. #3 / Comment 13

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
Materials & M.	6	12	Inserted	different pH values (approximate pH range 3 to 8)	R. #3 / Comment 13
Materials & M.	6	17	Inserted	For these experiments, reference compounds were added to the sediment subsamples before incubation using polyethylene caps loaded with 2 µmol P g−1 (ultra-micro balance XP6U; Mettler Toledo GmbH, Greifensee, Switzerland).	R. #3 / Comment 13
Materials & M.	6	34	Deleted	Data of the Firth of Thames site were compared with those of a contrasting P-unenriched site of the Saigon River Delta (Oxmann et al., 2008; 2010). The site was located c. 50 km from Ho Chi Minh City and was not significantly influenced by anthropogenic P input (remote location; no agriculture). It comprised an area exhibiting physical-chemical sediment characteristics very similar to those of the Firth of Thames site and an area of acid sulphate sediments (analysed separately; Sect. 3.4).	R. #2 / Comment 4 R. #3 / Comment 13 R. #3 / Comment 13
Materials & M.	6	34	Inserted	Concentrations of P fractions and proportions 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 used 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 comparison despite its significantly lower pH values (Sect. 3.4).	R. #2 / Comment 4 R. #3 / Comment 13 R. #3 / Comment 14
Results	8	15	Inserted	strongly	R. #2 / Comment 5
Results	8	15	Deleted	exponentially	R. #2 / Comment 5
Results	8	17	Deleted	between the sites	R. #3 / Comment 14
Results	8	18	Deleted	linear	R. #2 / Comment 5
Results	8	18	Inserted	continuous	R. #2 / Comment 5
Results	8	30	Deleted	exponentially	R. #2 / Comment 5
Results	8	30	Inserted	strongly	R. #2 / Comment 5
Results	8	33	Deleted	This suggests a pH-induced switch towards Ca-P predominance (see arrows in Fig. 3c)	R. #2 / Comment 6
Results	8	34	Deleted	In contrast to the substantial pH effects, a potential reduction-mediated P desorption was restricted to pH>6.6. The Al/Fe-P fraction declined with decreasing Eh only in that pH range (cf. Fig. 3b,d; Table 1).	R. #2 / Comment 6

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
Results	9	2	Deleted	exponentially	R. #2 / Comment 5
Results	9	2	Inserted	strongly	R. #2 / Comment 5
Results	9	2	Inserted	Firth of Thames cross-dataset correlations in Table 1	R. #2 / Comment 7
Results	9	4	Inserted	Table 1	R. #2 / Comment 7
Results	9	10	Inserted	To verify that the higher $\text{Ca-P}_{\text{meta}}$ concentrations were not a consequence of site-specific differences in vegetation or physical-chemical sediment 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).	R. #2 / Comment 4 R. #3 / Comment 13
Results	9	10	Deleted	To verify that the higher $\text{Ca-P}_{\text{meta}}$ concentrations were not generated by differences in pH and Eh values we restricted the comparison to mangrove plots with similar pH and Eh values at both sites (Table 3).	R. #2 / Comment 4 R. #3 / Comment 13
Discussion	11	14	Modified	The maximum amount of adsorbed P at pH 6.6 also indicated that Eh, which showed the maximum decline at ~ pH 6.6 (Fig. 3d), did not cause significant desorption of P at this pH. Below this pH, Al/Fe-P did not decline with Eh (cf. Fig. 3b and d) and these parameters were not correlated (Table 1), suggesting that a release of P adsorbed to ferric iron compounds did not occur in the corresponding sediments. Yet, both Eh and Al/Fe-P decreased above pH 6.6 (cf. Fig. 3b and 3d) and were correlated in this range (Table 1). 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. The decreasing amount of adsorbed P at near-neutral to alkaline pH 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. Critical redox potentials reported for reduction of ferric iron compounds are around 300 mV at pH 5 and 100 mV at pH 7 (Gotoh and Patrick, 1974; Husson, 2013; Yu et al., 2007). These levels match very well with critical Eh levels for desorption of Fe-(hydr)oxide-bound P, including a similar pH dependence of those levels (compare Delaune et al., 1981 with Gotoh and Patrick, 1974). As Fig. 3d shows, Eh values that did not correlate with Al/Fe-P (sediments with pH < 6.6) were above the critical Eh threshold, whereas Eh values that correlated with Al/Fe-P (sediments with pH > 6.6) were below the critical Eh threshold. This implies that reductive dissolution and related desorption of P could have contributed to the downstream transition from Al/Fe-P to Ca-P. Interestingly, the physicochemically induced P redistribution largely agreed with that from the low P site despite considerable differences of P fraction concentrations between both sites (Fig. 3a,b). This suggests that the effects of physical-chemical sediment characteristics were independent of the site-specific total P status.	R. #3 / Comment 15

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
Discussion	11	35	Inserted	site-specific total	R. #3 / Comment 5
Discussion	12	25	Inserted	site-specific total	R. #3 / Comment 5
Discussion	13	12	Inserted	This conclusion is supported by other studies which have indicated that the Morgan test preferentially extracts more soluble Ca-P phases, whereas most other available P tests preferentially extract adsorbed P (cf. Ahmad et al., 1968; Curran, 1984; Curran and Ballard, 1984; Dabin, 1980; Herlihy and McCarthy, 2006). (inserted due to removal of Sect. 4.6)	R. #2 / Comment 12 R. #3 / Comment 21
Discussion	13	21	Inserted	Less stable Ca-P may thus be a useful parameter to monitor anthropogenic accumulations of inorganic P in coastal regions. Because physical-chemical sediment characteristics influence Ca-P formation, an important caveat is the between-site comparability of data. In this study, there was between-site comparability of both the sediment characteristics and the general response of each of the P fractions and P species to the sediment characteristics at different depth intervals along the land-sea continuum (Fig. 3a, b; Fig. 4 a, b; Fig. 5).	R. #3 / Comment 9
Discussion	14	14	Deleted	Other naturally occurring mineral phases of Ca-P with a higher solubility than detrital FAP include, for example, biogenic apatite, HAP and calcium-carbonate-phosphates (e.g. CFAP, carbonate hydroxylapatite; e.g. Avnimelech, 1983). Howarth et al. (1995) proposed that the suggested rapid CFAP formation in surface layers of non-upwelling sediments (Ruttenberg and Berner, 1993), which was derived from authigenic P fractions (extracted with pH 4 acetate buffer; SEDEX method; Ruttenberg, 1992), may be biased by biogenic apatite. Slomp (2011) similarly suggested that the occurrence of more amorphous, not operationally defined authigenic Ca-P phases causes overestimates of operationally defined Ca-P phases and that, on the other hand, long-term diagenesis of authigenic Ca-P can cause overestimates of detrital Ca-P. We found large solubility differences between FAP and CFAP in sediment (Oxmann and Schwendenmann, 2014), which agree with notable differences between solubilities of laboratory synthesized FAP and CFAP detected by Jahnke (1984). The pH at which differential dissolution of FAP and CFAP occurred during addition experiments for validation of the CONVEX method agrees with a pH of 4, at which best separation of FAP and CFAP is attained in the SEDEX acetate buffer (Ruttenberg, 1992). It is important to note that several CFAP specimens with different degrees of carbonate substitution as well as biogenic apatite were distinguishable from FAP in these addition experiments. We therefore believe that the SEDEX method gives a reliable estimate of continental-derived FAP and that the method reliably distinguishes this detrital FAP from more soluble Ca-P. More soluble Ca-P, however, may include CFAP and OCP, both of which can be expected to be largely generated where they are observed. However, the assumption that less stable Ca-P phases, which dissolve in acetate buffer of pH 4, did only form at sampling sites may be misleading. Given the possibility that some CFAP or other less stable Ca-P phases do not readily dissolve in alkaline seawater (Faul et al., 2005; Lyons et al., 2011; Sheldon, 1981; see also Gulbrandsen et al., 1984 as cited in Slomp, 2011), yet in the pH 4 acetate	R. #2 / Comment 11 R. #3 / Comment 19

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
				buffer of the SEDEX method (~ 4 pH units difference), some of this more soluble Ca-P may be of allochthonous origin. To define the entire ‘non-detrital’ Ca-P fraction (i.e. Ca-P phases other than FAP; separated by e.g. pH 4 acetate buffer) in marine sediment as being an oceanic sink for SRP (i.e. authigenically precipitated from seawater) assumes that, contrary to detrital FAP, ‘non-detrital’ Ca-P of terrestrial sources completely dissolves before or after entering the marine environment. From the downstream formation of OCP that occurred despite higher solubility of OCP compared to CFAP and on the basis of several recent findings, we speculate that this assumption is likely inaccurate and needs further evaluation, at least for specific near-shore marine environments. Pertinent recent findings include, for example, (i) large amounts of less stable Ca-P in soil and parent rock (determined by the SEDEX method or comparable sequential extractions with acetate buffer; Alt et al., 2013; Hansen et al., 2004) that could enter the marine realm, e.g. through erosion processes; (ii) apparent occurrence or even formation of less stable Ca-P in terrestrial and marine waters (also confirmed by the SEDEX method; Faul et al., 2005; Lyons et al., 2011; Slomp, 2011; Sutula et al., 2004); and (iii) common Ca-P formation in intertidal sediments (confirmed by several independent methods; see Sect. 4.2).	
Discussion	14	15	Modified	In general, the established Ca-P precipitation in sediments along salinity gradients provides some insight into the relevance of factors influencing this precipitation such as changes in salinity, dissolved phosphate and pH. In fact, as the ionic strength increases with increasing salinity for a given phosphate concentration and pH, the apparent Ca-P solubility increases strongly (Atlas, 1975). Yet, increasing Ca-P concentrations imply that the salt effect may be more than offset by the rise in pH, redox-driven phosphate desorption from iron oxyhydroxides and other potential factors in interstitial waters along salinity gradients. For example, Ca^{2+} concentrations generally increase from land to sea and, hence, increase the saturation state with respect to calcium phosphates (normal seawater and sediment pore-water: *c*. 10 mM; river water, global average: *c*. 0.4 mM; soil pore-water, average of temperate region soils: 1.5 mM; Girard, 2004; Lerman and Wu, 2008; Lower et al., 1999; Rengel, 2006; Sun and Turchyn, 2014). Although the correlation of salinity with Al/Fe-P was not significant, the correlation with Ca-P was decreased but still significant (Table 1), indicating that increasing Ca^{2+} concentrations from land to sea may also contribute to the observed Ca-P formation.	R. #3 / Comment 17
Discussion	14	34	Deleted	Although P redistributions may strongly differ between sediments and soils (e.g. effects of the redox state and ionic strength), the fundamental processes operating on P speciation are comparable. This fact is reflected, for example, in the extensive direct utilization or adaptation of soil P methods for sedimentological studies. It is therefore appropriate to identify potential similarities between sediments and soils in terms of P speciation as described below, especially when analysing transformations from freshwater to seawater environments.	R. #2 / Comment 11
				4.6 Adsorption/precipitation switching in terrestrial soil	R. #2 / Comment 12

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
				It is well-known that P availability and, hence, P composition differs substantially between acidic (mainly Al/Fe-(hydr)oxide-bound P) and calcareous soils (mainly Ca-P of varying solubility; e.g. Batjes, 2011). Thus soil pH, in particular the distinction between acidic and calcareous soils, is empirically the best predictor of appropriate soil tests for available P (e.g. Batjes, 2011). Correlations between two soil tests should diverge at a specific soil pH provided that (i) pH-driven adsorption/precipitation processes strongly influenced P speciation of soils analysed; and (ii) one P test extracts more soluble Ca-P (Morgan test) and the other mainly adsorbed P (most available P tests) (cf. Ahmad et al., 1968; Curran, 1984; Curran and Ballard, 1984; Dabin, 1980 and references therein; Herlihy and McCarthy, 2006). Figure 6 shows that the Morgan test is indeed fundamentally different from other methods used to determine available P. Available P tests were significantly correlated with each other except Morgan P (Ca-Pmeta; all correlations non-significant; Fig. 6a). However, by separating those data into acidic and neutral to alkaline soils we found that all correlations with Morgan P were statistically significant (Fig. 6b). Hence, the divergence between correlations of P tests with pH equals the pH of the proposed switch from adsorption to Ca-Pmeta precipitation. While the pH-related divergence can certainly not be explained by a similar pH of specific extraction solutions (Morgan: 4.8; Olsen: 8.5; Bray: 1.6; M3P: 2.5) it agrees with decreasing amounts of adsorbed P (Figs. 5, 3b) and the onset of OCP precipitation at near-neutral pH (Figs. 5; S2a,b). These P redistributions in soils and the described redistributions in particulate matter (Sutula et al., 2004) imply that the proposed switch is not necessarily dependent on changes of the ambient redox conditions. Furthermore, the comparable switch for sediments (this study) and soils with quite different characteristics (Fig. 6; Bair and Davenport, 2012; Curran, 1984) may indicate that the underlying pH-induced transformation is a very common mechanism. The Morgan test is evidently an unreliable indicator for the determination of P availability in sample sets with both acidic and alkaline substrates (Fig. 6a). Permanently alkaline environments are usually characterized by lower P availability than slightly acidic environments due to decreasing Ca-P solubility with pH (Figs. 2a,c; 3a; 5; S2a,b) and lower amounts of Al/Fe-P (Figs. 3b; 5), whereas Morgan P continuously increases with pH across the pH range (Figs. 4a,c). This conclusion is consistent with known overestimates of plant-available P by the Morgan test at high soil pH (Aura, 1978; Foy et al., 1997). Hence, despite highest Morgan test values for bay sediments (Ca-Pmeta; Table S1) the availability of P is likely lower in permanently alkaline environments thereby mitigating coastal eutrophication. Because limited P availability is generally negatively correlated with P mobility, this positive effect comes at the expense of an increased P accumulation at the coastal zone.	R. #3 / Comment 21
Conclusions	15	3	Inserted	The decrease in Eh and increase in Ca2+ concentrations from land to the sea likely contribute to this switch.	R. #2 / Comment 10
Conclusions	15	14	Inserted	site-specific total	R. #3 / Comment 5
Table	24	14	Inserted	Ca-P vs. Salinity 112 0.39824 1.4E-05	R. #2 / Comment 10

Section	P.	L.	Type	What has been inserted, deleted or modified	Referee / Comment
Caption	29	8	Inserted	(NZ values in bold).	R. #2 / Comment 9
Figure and caption	29	15	Deleted	Figure 6. Influence of soil pH on Al/Fe-(hydr)oxide-bound P (Al/Fe-P) and calcium-bound P (Ca-P) as derived from correlations between Morgan P and other available P tests (Olsen P, Bray P and Mehlich M3P). All correlations were non-significant ($p > 0.05$) for the entire pH range (a) due to extraction of different P fractions (Morgan P: mainly metastable Ca-P; other available P tests: mainly Al/Fe-P). By separating data into acidic and neutral-alkaline soils all correlations were significant (b; $p < 0.05$). Data from (i) Bair and Davenport (2012), excluding a heavily fertilized sample (Morgan P ten times higher than the second highest Morgan P value) and a sample with high carbonate content despite low pH; and (ii) from Curran (1984), excluding an OM sample (forest floor). Values for Mehlich P only from Bair and Davenport (2012) due to different Mehlich tests (Bair and Davenport: M3P; Curran: M2P). Note the significant correlations in 5b despite very different soils: developed in marine clay, native, garden, manured and unfertilized agriculture, pasture, P-fertilized and unfertilized forest; different horizons; varying pH.	R. #3 / Comment 4 R. #2 / Comment 12

Authigenic apatite and octacalcium phosphate formation due to adsorption/precipitation switching across estuarine salinity gradients

Short title: Calcium phosphate formation across salinity gradients

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Abstract

Mechanisms governing phosphorus (P) speciation in coastal sediments remain largely unknown due to the diversity of coastal environments and poor analytical specificity for P phases. We investigated P speciation across salinity gradients comprising diverse ecosystems in a P-enriched estuary. To determine P load effects on P speciation we compared the high P site with a low P site. Octacalcium phosphate (OCP), authigenic apatite (carbonate fluorapatite; CFAP) and detrital apatite (fluorapatite) were quantitated in addition to Al/Fe-bound P (Al/Fe-P) and Ca-bound P (Ca-P). Gradients in sediment pH strongly affected P fractions across ecosystems and independent of the site-specific total P status. We found a pronounced switch from adsorbed Al/Fe-P to mineral Ca-P with decreasing acidity from land to sea. This switch occurred at near-neutral sediment pH and has possibly been enhanced by redox-driven phosphate desorption from iron oxyhydroxides. The seaward decline in Al/Fe-P was counterbalanced by the precipitation of Ca-P. Correspondingly, two location-dependent accumulation mechanisms occurred at the high P site due to the switch, leading to elevated Al/Fe-P at pH < 6.6 (landward; adsorption) and elevated Ca-P at pH > 6.6 (seaward; precipitation). Enhanced Ca-P precipitation by increased P loads was also evident from disproportional accumulation of metastable Ca-P ($Ca\text{-}P_{meta}$) at the high P site. Here, sediments contained on average 6-fold higher $Ca\text{-}P_{meta}$ levels compared with the low P site, although these sediments contained only 2-fold more total Ca-P than the low P sediments. Phosphorus species distributions indicated that these elevated $Ca\text{-}P_{meta}$ levels resulted from transformation of fertilizer-derived Al/Fe-P to OCP and CFAP in near-shore areas. Formation of OCP and CFAP results in P retention in coastal zones and can thus lead to substantial inorganic P accumulation in response to anthropogenic P input.

Gelöscht: pH-induced

Gelöscht: along

Gelöscht: along

Gelöscht: estuarine

Gelöscht: along

Gelöscht: P-unenriched site. To improve analytical specificity, octacalcium

Gelöscht: Sediment

Gelöscht: primarily

Gelöscht: Increasing pH caused

Gelöscht: downstream transition

Gelöscht: . Downstream

Gelöscht: This marked upstream-to-downstream switch occurred at near-neutral sediment pH and was enhanced by increased P loads. Accordingly, the site comparison indicated

Gelöscht: -enriched

Gelöscht: , which mainly resulted in

Gelöscht: <

Gelöscht: upstream

Gelöscht: >

Gelöscht: downstream

Gelöscht:). The

Gelöscht: concentration was six-fold, whereas

Gelöscht: was only twofold higher at the P-enriched site compared to the P-unenriched site. Species concentrations showed

Gelöscht: largely

Gelöscht: due to decreasing acidity from land to the sea.

Gelöscht: , which may

Gelöscht: by

Gelöscht: in near-shore sediments

1 Introduction

Desorption and precipitation of phosphate along salinity gradients are influenced by redox potential (Eh) and pH (van Beusekom and de Jonge, 1997). Typically, Eh decreases and pH increases from land to the sea (Clarke, 1985; Huang and Morris, 2005; Sharp et al., 1982). Seawater inundation induces the Eh gradient by limiting oxygen diffusion into the sediment, thereby initiating anaerobic respiration. Sediments regularly inundated by seawater tend to have higher pH values than terrestrial soils because soils naturally acidify due to vegetation derived inputs (effects of enhanced carbonic acid production, root exudate release, litter decomposition, proton extrusion). Human activities such as N fertilization can also contribute to soil acidification (Fauzi et al., 2014; Hinsinger et al., 2009; Richardson et al., 2009). The acid generated is neutralized downstream by the high alkalinity of seawater.

Changes in pH and Eh facilitate phosphorus (P) desorption from particulate matter and generally account for the non-conservative behavior of dissolved reactive P (DRP) during admixing of water along salinity gradients. Particulate P includes a significant amount of inorganic P, which mainly consists of calcium-bound P (Ca-P; detrital and authigenic) and aluminium/iron-bound P (Al/Fe-P). The Al/Fe-P fraction contains adsorbed inorganic P (Al/Fe-(hydr)oxide-bound P), which can be partly released to solution (e.g. Slomp, 2011). The Al/Fe-P fraction of oxidized, acidic sediment usually comprises relatively large proportions of adsorbed P. Phosphate desorption induced by pH and Eh gradients generally results in progressively decreasing concentrations of the Al/Fe-P from upper to lower intertidal zones (Andrieux-Loyer et al., 2008; Coelho et al., 2004; Mortimer, 1971; Jordan et al., 2008; Paludan and Morris, 1999; Sutula et al., 2004).

Decreasing Eh in sediment from upper to lower zones involve critical levels for reduction of ferric iron compounds (e.g. Gotoh and Patrick, 1974). These critical levels facilitate desorption of Fe-(hydr)oxide-bound P due to less efficient sorption of P by iron in the Fe(II) state compared to the Fe(III) state (Hartzell and Jordan, 2012; Sundareshwar and Morris, 1999). Desorption from metal (hydr)oxides with increasing pH (Oh et al., 1999; Spiteri et al., 2008), on the other hand, is driven by the decreasing surface electrostatic potential with increasing pH (Barrow et al., 1980; Sundareshwar and Morris, 1999). This effect may be partly offset by the increasing proportion of the strongly sorbing divalent phosphate ion (HPO_4^{2-}) with increasing pH until pH 7 (~ pK_2, which decreases with salinity increase; Atlas, 1975). In the alkaline pH range, however, this offset is less pronounced thus allowing stronger desorption (Bolan et al., 2003; Bowden et al., 1980; Haynes, 1982). Similarly, studies on soils attributed desorption with pH to increasing competition between hydroxyl- and phosphate ions for sorption sites, or to less sorption sites due to Al hydroxide precipitation (Anjos and Roswell, 1987; Smyth and Sanchez, 1980).

Gelöscht: Anthropogenic P inputs more than doubled the global P flux to marine environments (Meybeck et al., 1982; Bennett et al., 2001). In some regions the fluxes have increased to more than ten times their pre-agricultural levels (Howarth et al., 1995). A large proportion of this terrestrial input to marine systems is retained in estuaries and near-shore marine environments (Dürr et al., 2010; Howarth et al., 1995; Ruttenberg, 2004; Ruttenberg, 1990; Slomp, 2011; Teodoru et al., 2007). The primary anthropogenic P source to this reservoir originates from manure and fertilizer P, which is mainly lost from agricultural systems in the form of erosion-derived particulate P (Kronvang et al., 2007; McDowell et al., 2003; Jordan et al., 2008). Coastal environments may be particularly vulnerable to excessive P loads because physical-chemical changes along salinity gradients facilitate transformations of P and thereby lead to sharp increases in dissolved reactive P (DRP) concentrations (Correll, 1998; Howarth et al., 1995; Mindy and Greenhalch, 2009; Townsend and Porder, 2011).¶

Gelöscht: P

Gelöscht: Sundareshwar and Morris, 1999;

Gelöscht: ; DeLaune et al., 1981).

Gelöscht: and Eh decreases

Gelöscht: Paludan and Morris, 1999;

Gelöscht: 1982; Spiteri et al., 2008; Sundareshwar and Morris, 1999). These

Gelöscht: changes

Gelöscht: riverine

Gelöscht: a significant amount of

Gelöscht: Slomp, 2011). Thus, DRP levels are usually higher than expected from oceanic and riverine endmembers (Sharp et al., 1982; Spiteri et al., 2008; van der Zee et al., 2007). These relationships hold true for effects on adsorbed P in sediment and related pore water chemical changes (e.g. Jordan et al., 2008). Hence, non-conservative mixing is also a result of similar processes in the benthic boundary layer. Accordingly, P desorption from sediment by elevated pH values was shown to enhance eutrophication (Gao et al., 2012; Seitzinger, 1991).

Gelöscht: changes

Gelöscht: this sedimentary

Gelöscht: fraction

Gelöscht: levels

Gelöscht: pH-dependent;

Release of P adsorbed on Al/Fe-(hydr)oxide facilitates Ca-P formation at higher pH (Heggie et al., 1990; Ruttenberg and Berner, 1993; Slomp, 2011) which, in turn, causes P removal from the adsorbed P fraction. Consequently, desorption at higher pH does not necessarily increase soluble P (van Cappelen and Berner, 1988; Reddy and Sacco, 1981). This agrees with a switch from low phosphate concentrations in equilibrium with adsorbed P at acidic pH to low phosphate concentrations in equilibrium with mineral Ca-P under alkaline conditions (e.g. Murrmann and Peech, 1969). Low equilibrium concentrations under alkaline conditions are a result of the decreasing solubility of Ca-P phases, such as carbonate fluorapatite (CFAP) and octacalcium phosphate (OCP), with increasing pH (Hinsinger, 2001; Murrmann and Peech, 1969). Precipitation of Ca-P may therefore mitigate a desorption-derived P release from sediment (e.g. van Beusekom and de Jonge, 1997). Similarly, Ca-P precipitation is likely to result in the occasionally observed and apparently conflicting decrease of available P by liming to neutral or alkaline pH (Bolan et al., 2003; Haynes, 1982; Naidu et al., 1990). Accordingly, concentrations of Ca-P usually increase seaward as a consequence of enhanced precipitation (Andrieux-Loyer et al., 2008; Coelho et al., 2004; Paludan and Morris, 1999; Sutula et al., 2004).

Gelöscht: lowest

Gelöscht: lowest

Gelöscht: downstream

Gelöscht: 2004). Due to factors that allow for widespread, dispersed formation and persistence of more soluble authigenic Ca-P in marine environments (possibly even in the water column

Gelöscht: ; Faul et al., 2005; Lyons et al., 2011), detrital fluorapatite (FAP) is unlikely to dissolve in these environments (Ruttenberg, 1990; Howarth et al., 1995

Authigenic Ca-P is widely dispersed in marine sediment, but its solubility in seawater remains difficult to predict. Because seawater is probably close to saturation with CFAP, both a possible formation and dissolution of CFAP in seawater cannot be rejected (Atlas and Pytkowicz, 1977; Faul et al., 2005; Lyons et al., 2011). In contrast, detrital fluorapatite (FAP) is unlikely to dissolve in seawater (Ruttenberg, 1990; Howarth et al., 1995). In addition to the dependence on species-specific saturation states (Atlas, 1975; Gunnars et al., 2004), the occurrence of Ca-P minerals depends on their formation kinetics (Atlas and Pytkowicz, 1977; Gulbrandsen et al., 1984; Gunnars et al., 2004; Jahnke et al., 1983; Schenau et al., 2000; Sheldon, 1981) and inhibitors such as Mg^{2+} ions (Golubev et al., 1999; Gunnars et al., 2004; Martens and Harriss, 1970). In general, the first solid to form is the one which is thermodynamically least favored (Ostwald step rule; see Morse and Casey, 1988; Nancollas et al., 1989).

Gelöscht: In view of the

Given slow or inhibited direct nucleation (Golubev et al., 1999; Gunnars et al., 2004; Martens and Harriss, 1970), species of the apatite group may form by transformation of metastable precursors that are less susceptible to inhibitory effects of Mg^{2+} such as OCP (Oxmann, 2014; Oxmann and Schwendenmann, 2014). Precursor phases form more readily (e.g. days to weeks for OCP; Bell and Black, 1970) and can promote successive crystallization until the thermodynamically favoured but kinetically slow apatite formation occurs (ten to some thousand years; Schenau et al., 2000; Jahnke et al., 1983; Gulbrandsen et al., 1984). Several studies presented field and experimental evidence for this mode of apatite formation in

Gelöscht: in sediment

Gelöscht: previously precipitated

Gelöscht: Hence, rapidly precipitating precursor

Gelöscht: may allow for

sediment systems (Gunnars et al., 2004; Jahnke et al., 1983; Krajewski et al., 1994; Oxmann and Schwendenmann, 2014; Schenau et al., 2000; van Cappellen and Berner, 1988). A systematic comparison of P K-edge XANES (X-ray absorption near edge structure spectroscopy) fingerprints from reference materials and marine sediment particles also provided evidence for the occurrence of OCP in sediment (Oxmann, 2014). However, despite significant progress in the determination of different matrix-enclosed Ca-P phases it is not yet clear whether specific conditions at certain locations facilitate successive or direct crystallization of apatite (Slomp, 2011).

Provided more soluble Ca-P minerals such as OCP or less stable CFAP form in coastal environments, these minerals might mirror short-term changes of human alterations to the P cycle. Conversely, sparingly soluble apatite minerals may reflect long-term changes due to slow precipitation. Hence, the proportion of more soluble Ca-P should increase relative to total Ca-P in response to increased P inputs. This human alteration to the solid-phase P speciation may have implications for P fluxes and burial. To better describe P transformations from terrestrial to marine systems and to track the fate of anthropogenic P inputs, we analysed effects on P fractions and species across different ecosystems of a high P site (Firth of Thames, New Zealand). We then compared the findings with results from a low P site (Saigon River Delta, Vietnam) to distinguish speciation differences related to increased P loads. Octacalcium phosphate, authigenic apatite and detrital apatite were determined using a recently validated conversion-extraction method (CONVEX; Oxmann and Schwendenmann, 2014).

Gelöscht: occasionally

Gelöscht: due to diagenetic processing of increased P loads

Gelöscht: -enriched

Gelöscht: data

Gelöscht: -unenriched coastal

Gelöscht: to identify similarities between temperate and tropical coastal regions and

2 Materials and methods

2.1 Study area, Firth of Thames, New Zealand

The Firth of Thames, a meso-tidal, low wave energy estuary of the Waikato region's rivers Waihou and Piako, is located at the southern end of the Hauraki Gulf (37°S, 175.4°E; Fig. 1). It is the largest shallow marine embayment in New Zealand (800 km^2; $<$ 35 m depth). The tides are semidiurnal with a spring tide range of 2.8 m and a neap tide range of 2.0 m (Eisma, 1997). The southern shore of the bay (~ 7800 ha) is listed as a wetland of international importance under the Ramsar Convention. The Firth of Thames encompasses large tidal flats (up to 4 km wide) and extensive areas of mangroves (*Avicennia marina*) at the southern end of the embayment (Brownell, 2004). Mangroves have been expanding seawards leading to a 10-fold increase in area since the mid of the last century (Swales et al., 2007). Mangrove expansion has been related to sediment accumulation and nutrient enrichment but may also coincide with climatic conditions (Lovelock et al., 2010; Swales et al., 2007). The upper

Gelöscht: large

coastal intertidal zone is covered by salt marshes. Behind the levee *c.* 1.3 million ha is used for pastoral agriculture (~ half of the total area of the Waikato region; Hill and Borman, 2011; Fig. 1a).

2.2 Sampling, field measurements and sample preparation

We established 28 plots along three transects (Fig. 1b,c). Transects extended across the entire tidal inundation gradient and across different ecosystems including bay (n=4), tidal flat (n=6), mangrove (n=9), salt marsh (n=6) and pasture (n=3). Transects were at least 300 m from rivers to exclude areas affected by sediment aeration. Five additional plots were located along rivers. Sediment cores were taken during low tide using a polycarbonate corer (one core per plot; length: 40 cm; diameter: 9 cm). Immediately after core sampling, sediment pH, redox potential (Eh) and temperature were measured *in-situ* at 0-5, 10-15, 30-35 and 35-40 cm depth intervals. Cores were divided into the following surface, intermediate and deeper sections: 0-5, 10-15, 30-35 and 35-40 cm. Longer core sections reduce vertical variability and were chosen for the relatively coarse vertical sampling because the focus of this study was on geochemical changes along the land-sea continuum. Samples were kept on ice and subsequently frozen until further processing. After thawing roots were removed from the sediment samples. Subsamples were then taken for particle size and salinity analysis. The remaining material was dried, ground and sieved (37°C; < 300 µm mesh; PM 100; Retsch, Haan, Germany) for P and nitrogen analyses.

Gelöscht: at

Temperature, pH and Eh were measured with a Pt-100 temperature sensor, sulfide resistant SensoLyt SEA/PtA electrodes, and pH/Cond340i and pH 3310 mV-meters (WTW, Weilheim, Germany). The mV-meters were connected to a computer with optoisolators (USB-isolator; Serial: 289554B; Acromag Inc., Wixom, USA) for data visualization and logging (MultiLab pilot; WTW, Weilheim, Germany). Topographic elevation at the plots was measured with a total station (SET530R; Sokkia Co., Atsugi, Japan) relative to a reference point and converted to geo-referenced elevation using a global navigation satellite system (Trimble R8; Trimble Navigation Ltd., Sunnyvale, USA). Inundation duration was calculated from measured elevation above mean sea level and local tide tables (Waikato Regional Council, Hamilton East, New Zealand).

2.3 Sediment analyses

Phosphorus fractions and total P were analysed using three different methods. (i) The relative proportion of more soluble Ca-P was determined by preferential extraction of this fraction using the Morgan test method (Morgan, 1941); (ii) Al/Fe-P and Ca-P fractions were determined by sequential extraction of P after Kurmies (Kurmies, 1972); and (iii) total P (TP)

Gelöscht: semi-selective

Gelöscht: analysis

Gelöscht: quantitated

was analysed after Andersen (1976) as modified by Ostrofsky (2012). The Morgan test, commonly used to determine available P, preferentially extracts more soluble Ca-P phases using a pH 4.8 buffered acetic acid (see Sect. 4.4). Hence, the term ‘metastable Ca-P’ (Ca-P_{meta}) is used for Morgan P in this paper. The method of Kurmies includes initial wash steps with KCl/EtOH to eliminate OCP precipitation prior to the alkaline extraction and Na_2SO_4 extractions to avoid re-adsorption. It therefore provides an accurate means of determining Al/Fe-P and Ca-P using NaOH and H_2SO_4, respectively (Fig. S2c; steps 2a-3c). Total inorganic P (TIP) was defined as the sum of inorganic P fractions (Ca-P, Al/Fe-P). Organic P was calculated by subtracting TIP from TP.

Gelöscht: predominantly

Gelöscht: by

Gelöscht: ; 4.6

Gelöscht: phenomena

Gelöscht: determination

Octacalcium phosphate, CFAP (authigenic apatite) and FAP (detrital apatite) were quantitated using the CONVEX method (Oxmann and Schwendenmann, 2014). This method employs a conversion procedure by parallel incubation of sediment subsamples at different pH values (approximate pH range 3 to 8) in 0.01 M $CaCl_2$ for differential dissolution of OCP, CFAP and FAP (Fig. S2c). The concentration of OCP, CFAP and FAP is determined by the difference of Ca-P concentrations before and after differential dissolution of OCP, CFAP and FAP, respectively. These Ca-P concentrations are determined by the method of Kurmies. Differential dissolution was verified by standard addition experiments. For these experiments, reference compounds were added to the sediment subsamples before incubation using polyethylene caps loaded with 2 µmol P g^{-1} (ultra-micro balance XP6U; Mettler Toledo GmbH, Greifensee, Switzerland). Reference compounds included OCP, hydroxylapatite (HAP), various CFAP specimens, FAP and biogenic apatite. Methodology, instrumentation and the suite of reference minerals are described in Oxmann and Schwendenmann (2014). CONVEX analysis was conducted for seven sediment samples (differential dissolution shown in Fig. S2a,b), which covered the observed pH gradient and included sediments from each ecosystem. The sum of OCP and CFAP represents more soluble Ca-P (similar to Ca-P_{meta}) and was termed ‘Ca-$P_{OCP+CFAP}$’. Phosphate concentrations in chemical extracts were determined after Murphy and Riley (1962) using a UV-Vis spectrophotometer (Cintra 2020; GBC Scientific Equipment, Dandenong, Australia).

Gelöscht: varying pH

Gelöscht: quantitated

Particle size was analysed using laser diffractometry (Mastersizer 2000; Malvern Instruments Ltd., Malvern, UK; sediment dispersed in 10% sodium hexametaphosphate solution). Salinity was determined by means of a TetraCon 325 electrode (WTW, Weilheim, Germany; wet sediment to deionized water ratio: 1:5). Nitrogen content was measured using a C/N elemental analyzer (TruSpec CNS; LECO soil 1016 for calibration; LECO Corp., St. Joseph, USA).

Concentrations of P fractions and proportions 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

Gelöscht: Data

Gelöscht: -unenriched

Gelöscht: of

Gelöscht: *c.* 50 km from Ho Chi Minh City

Can Gio close to the South China Sea and was not significantly influenced by anthropogenic P inputs. The region is not used 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 comparison despite its significantly lower pH values (Sect. 3.4)..

Gelöscht: input (remote location; no

Gelöscht:). It comprised an area exhibiting

Gelöscht: very

Gelöscht: to those of the Firth of Thames site and an

Gelöscht: (

Gelöscht: ; Sect. 3.4).

3 Results

3.1 Particle size, pH and Eh

Inundation duration ranged from 365 days/year in the bay to 0 days/year in the pastures (Table S1). Clay, silt and sand fractions varied between 0-20%, 60-80% and 0-30%, respectively (not shown). Particle size distribution differed only slightly among transects. In contrast, considerable differences in particle size distribution were found along transects with higher silt and lower sand contents in mangrove plots. Salinity decreased from the bay (32‰) to tidal flats (21‰). Highest values were measured in the mangroves (35‰), which declined to 25‰ in the salt marshes and 0‰ in the pastures (Table S1). Sediment humidity ranged between 60% and 70% in the bay, tidal flat and mangrove fringe plots and decreased to 20-30% in the pastures (not shown).

Gelöscht: pasture

Sediment pH ranged from 5.18 in the pastures to 7.4 in the bay (Fig. 2a,b; Table S1). Redox potential varied between 621 mV in the pastures and -141 mV in the bay (Fig. 2a,b; Table S1). This pronounced and relatively constant pH increase and Eh decrease towards the bay was closely correlated with inundation duration (Fig. 2a,b; $p < 0.0001$). While systematic differences among depth intervals were less apparent for pH, Eh typically decreased with increasing sediment depth (Fig. 2b).

Gelöscht: pasture

Gelöscht: pasture

3.2 Phosphorus fractions: Transformations

Ecosystem-averaged Ca-P concentrations varied considerably and ranged from 3.37 µmol g^{-1} (pastures, 0-5 cm) to 11.37 µmol g^{-1} (bay, 10-15 cm) (Fig. 2c,d; Table S1). In contrast, Al/Fe-P was highest in the pastures (17.9 µmol g^{-1}; 0-5 cm) and lowest in the bay (3.94 µmol g^{-1}; 30-35 cm). On average, the lowest Ca-P and highest Al/Fe-P concentrations were measured in 0-5 cm depth (Fig. 2c,d). Averaged percentages of Ca-P (% of TIP) steadily increased and

Gelöscht: pasture

Gelöscht: pasture

Gelöscht:) in the bay.

averaged percentages Al/Fe-P (% of TIP) steadily decreased from pastures to bay (Fig. 2c,d). Along the marked downstream transition from Al/Fe-P (2.7-fold decrease) to Ca-P (2.6-fold increase) the average drop in Al/Fe-P from pastures to bay approximately matched the average Ca-P increase (-8.27 vs. +6.73 µmol g^{-1}; averages across all plots and depth intervals of each ecosystem; Table S1). Furthermore, mean Al/Fe-P concentrations in the different systems were negatively correlated with those of Ca-P (r = -0.66, $p < 0.001$; Table S1). In addition, the decline in Al/Fe-P with depth was counterbalanced by the Ca-P increase with depth (-1.16 vs. +1.18 µmol g^{-1}; Table S1). Pastures were excluded from estimating these changes with depth because here the large loss of Al/Fe-P with depth was not counterbalanced by Ca-P (apparent surface runoff: -6.00 vs. +0.69 µmol g^{-1}; Table S1).

3.3 Phosphorus fractions: P load, pH and Eh effects

Mean sediment Ca-P concentration at the high P site was approximately twice the level of Ca-P at the low P site (Fig. 3a). Mean sediment Al/Fe-P concentration was approximately 30% higher at the high P site compared to the low P site. However, at both sites Ca-P increased strongly with pH (Fig. 3a). Al/Fe-P showed a peak at ~ pH 6.6 (Fig. 3b). Thus, despite large differences in P fraction concentrations between the two sites pH dependencies of both fractions were similar, except for Al/Fe-P concentrations in 0-5 cm depth. Concentrations of Al/Fe-P in this depth range showed a continuous decrease with pH at the high P site due to high Al/Fe-P levels in acidic surface sediment of the pastures (linear regression in Fig. 3b; Table 1; r = -0.81, $p < 0.0001$).

In sediments with pH $<$ 6.6 the average concentration of Al/Fe-P was 70% higher at the high P site than at the low P site (Table 2; Fig. 3b). Despite these largely elevated levels of Al/Fe-P at topographically higher areas, Al/Fe-P was only slightly increased (13%) in the lower intertidal zones and the bay (pH $>$ 6.6; Table 2; Fig. 3b). Calcium phosphate in contrast showed the opposite pattern of enrichment at the high P site. In comparison to the low P site the average concentration of Ca-P was only 49% higher in the upper intertidal zones and pastures (pH $<$ 6.6) but increased by 88% in the lower intertidal zones and the bay (pH $>$ 6.6; Table 2; Fig. 3a).

Although Ca-P and Al/Fe-P clearly showed opposite trends along the three transects of the high P site (Fig. 2c,d), both fractions increased strongly with pH below pH 6.6 (Fig. 3a,b). Both fractions were positively correlated at pH $<$ 6.6 (shown in Fig. 3c for lower depth of both sites). At pH $>$ 6.6, however, Ca-P increased further, whereas Al/Fe-P abruptly decreased (cf. Fig. 3a and b). Because this switch occurred in the landward to seaward direction, it is in agreement with the observed Ca-P increase and Al/Fe-P decrease towards the bay (Fig. 2c,d).

Gelöscht: pasture
Gelöscht: pasture
Gelöscht: The pasture was
Gelöscht: in sediments of
Gelöscht: -enriched
Gelöscht: in
Gelöscht: -unenriched
Gelöscht: in sediments of
Gelöscht: -enriched
Gelöscht: -unenriched
Gelöscht: concentrations
Gelöscht: exponentially
Gelöscht: concentrations
Gelöscht: In summary
Gelöscht: between the sites
Gelöscht: linear
Gelöscht: -enriched
Gelöscht: pasture
Gelöscht: <
Gelöscht: -enriched
Gelöscht: -unenriched
Gelöscht: zone
Gelöscht: >
Gelöscht: -enriched
Gelöscht: -unenriched
Gelöscht: upstream environments
Formatiert: Englisch (USA)
Gelöscht: <
Gelöscht: zone
Gelöscht: >
Gelöscht: -enriched
Gelöscht: exponentially
Gelöscht: <
Gelöscht: >
Gelöscht: This suggests a pH-induced switch towards Ca-P predominance (see arrows in Fig. 3c).
Gelöscht: downstream
Gelöscht: 2c,d). In contrast to the substantial pH effects, a potential reduction-mediated P desorption was restricted to pH>6.6. The Al/Fe-P fraction declined with decreasing Eh only in that pH range (cf. Fig. 3b,d; Table 1

3.4 Metastable calcium phosphate

Metastable Ca-P (Ca-P$_{meta}$) 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). Yet sediments of the high P site contained on average 6-fold higher concentrations of Ca-P$_{meta}$ compared with the low P site (Fig. 4c). In contrast, sediments of the high P site contained only 2-fold more total Ca-P than those of the low P site (Fig. 3a). On average, Ca-P$_{meta}$ comprised *c.* 35% of total Ca-P at the high P site and only 10% at the low P site (Fig. 4d).

Gelöscht: exponentially

Gelöscht: the concentration of Ca-P$_{meta}$ in

Gelöscht: -enriched

Gelöscht: was six

Gelöscht: to

Gelöscht: -unenriched

Gelöscht: was only twofold higher compared to

Gelöscht: -unenriched

Gelöscht: -enriched

Gelöscht: -unenriched

To verify that the higher Ca-P$_{meta}$ concentrations were not a consequence of site-specific differences in vegetation or physical-chemical sediment 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). This adjustment did not change the results. The difference in Ca-P$_{meta}$ concentrations between mangrove plots of the two sites was just as disproportionate when compared to the difference in total Ca-P concentrations between those plots (six-fold vs. twofold). The portion of Ca-P$_{meta}$ was still *c.* 35% at the high P site and 10% at the low P site (Table 3). Moreover, the proportion of Ca-P$_{meta}$ to total Ca-P was equally low for an area of acid sulphate sediments of the low P site (10%) despite its very different average pH and Eh values (Table 3). In summary, comparatively large amounts of metastable Ca-P accumulated at the high P site.

Gelöscht: generated by

Gelöscht: in pH and Eh values

Gelöscht: with

Gelöscht: pH

Gelöscht: Eh values

Gelöscht: By doing this, previous figures

Gelöscht: -enriched

Gelöscht: -unenriched

Gelöscht: equal

Gelöscht: two areas

Gelöscht: -unenriched

Gelöscht: their

Gelöscht: -enriched

3.5 Octacalcium phosphate and authigenic apatite

Distributions of OCP, authigenic apatite and detrital apatite were related to the pH at both sites. Strongly acidic sediments (~ pH < 4) contained just detrital apatite (FAP), whereas slightly acidic sediments (~ pH 4-7) contained also authigenic apatite (CFAP). Octacalcium phosphate was additionally present in alkaline mangrove, river, bay and tidal flat sediments. Hence, the concentration of more soluble Ca-P$_{OCP+CFAP}$ (hatched area in Fig. 5) significantly increased with pH (r = 0.88, $p < 0.0001$; Table 4). However, the portion of Ca-P$_{OCP+CFAP}$ as a percentage of total Ca-P was significantly larger (70.5 ± 17.5%; numbers above columns in Fig. 5) for sediments of the high P site compared to the low P site (29.5 ± 26.0%), t(11) = 3.346, $p = 0.0065$. This larger portion of Ca-P$_{OCP+CFAP}$ provided supporting evidence for the larger portion of Ca-P$_{meta}$ in sediments of the high P site (cf. Sect. 3.4). Overall, more soluble Ca-P determined by the two independent methods (CONVEX method: Ca-P$_{OCP+CFAP;}$ Morgan test: Ca-P$_{meta}$) yielded comparable results. Accordingly, corresponding values obtained by the two methods were significantly correlated (r = 0.74, $p < 0.05$; Table 4).

Gelöscht: Concentrations

Gelöscht: largely affected by

Gelöscht: in sediments of

Gelöscht: <

Gelöscht: -enriched

Gelöscht: -unenriched

Gelöscht: -enriched

4 Discussion

4.1 Phosphorus status, Firth of Thames

The Firth of Thames sediments were high in P compared to the Saigon River Delta site and sediments from other coastal areas (Table 3; Table S3; Figs. 3 and 4). Total P concentrations measured along the three transects are classified as 'enriched' (> 16 µmol P g^{-1}) and 'very enriched' (> 32 µmol P g^{-1}) according to the New Zealand classification system (Robertson and Stevens, 2009; Sorensen and Milne, 2009). This is due largely to high P fertilizer application rates, which constitute the main P source (~ 90%) to the watershed (Waikato region; Total input: 41 Gg P yr^{-1}; Fertilizer: 37 Gg P yr^{-1}; Rate: 28 kg P ha^{-1} yr^{-1}; Atmosphere and Weathering: 4 Gg P yr^{-1}; Parfitt et al., 2008). A significant increase in TP is correlated with intensification of pastoral farming and contributes to the deterioration of the river water quality by surface runoff (Vant and Smith, 2004). Further, elevated levels of P and nitrogen in ground water at coastal farmlands agreed with specific fertilizer application rates (Brownell, 2004). The application rates and previous findings strongly suggest that the P accumulation measured in this study was largely related to P fertilization practices. Hence, the Firth of Thames site is characterized by anthropogenic P enrichment.

Gelöscht: provide

Gelöscht: for the high P inputs

4.2 Phosphorus fractions

Phosphorus fractions showed a strong and continuous increase of Ca-P and decrease of Al/Fe-P with increasing inundation duration (Fig. 2). These changes were driven by pH and Eh gradients (Fig. 2). Salinity had no detectable effect on Al/Fe-P (Table 1), similar to findings of Maher and DeVries (1994). Both an increase in Ca-P (decreasing solubility of calcium phosphates with increasing pH; Lindsay et al., 1989; Hinsinger, 2001) and a decline in Al/Fe-P (desorption of P from metal (hydr)oxides with increasing pH or decreasing Eh; e.g. Mortimer, 1971) commonly occur across estuarine inundation gradients. A similar seaward redistribution of sediment P fractions has been observed, for example, in marsh systems in Portugal (Coelho et al., 2004) and South Carolina (Paludan and Morris, 1999), estuarine zones of a French river (Andrieux-Loyer et al., 2008) and an estuarine transect from the Mississippi River to the Gulf of Mexico (Sutula et al., 2004). In the latter case, the opposing landward-to-seaward changes in sediments (Sutula et al., 2004) were mirrored by similar changes in corresponding samples of surface water particulate matter. Furthermore, the same trends were observed along a continuum from agricultural soils across hard-water stream sediments to lake sediments (Noll et al., 2009).

Gelöscht: from pasture to bay

Gelöscht: Similar upstream-to-downstream changes in

Gelöscht: have

Gelöscht: at

Gelöscht: upstream

Gelöscht: downstream

The pH dependence of the solubility of Ca-P phases was mirrored by the increase in Ca-P with decreasing acidity (Fig. 3a). In contrast, concentrations of Al/Fe-P showed a maximum amount of adsorbed P at pH 6.6 (Fig. 3b) and therefore agreed with the commonly occurring maximum P availability at pH 6.5 in agricultural soils (e.g. Chapin III et al., 2011). This maximum P availability is caused by the highest P solubility in equilibrium with various P minerals at pH 6.5 (Lindsay et al., 1989). Considering that low amounts of P are precipitated with Ca, Fe and Al at pH 6.5 (e.g. Chapin III et al., 2011), large amounts of soluble reactive P could be available for adsorption on metal (hydr)oxides. Further, Ca-P phases predominated in alkaline downstream environments and could undergo dissolution and subsequent adsorption after upstream transport by tides (cf. 2a,c,d; De Jonge and Villerius; 1989). If these phases are transported to close locations of ~ pH 6.5 and subsequently dissolve, the phosphate released can be adsorbed on more oxidized sediment, thereby contributing to the elevated Al/Fe-P concentrations at this pH.

The maximum amount of adsorbed P at pH 6.6 also indicated that Eh, which showed the maximum decline at ~ pH 6.6 (Fig. 3d), did not cause significant desorption of P at this pH. Below this pH, Al/Fe-P did not decline with Eh (cf. Fig. 3b and d) and these parameters were not correlated (Table 1), suggesting that a release of P adsorbed to ferric iron compounds did not occur in the corresponding sediments. Yet, both Eh and Al/Fe-P decreased above pH 6.6 (cf. Fig. 3b and 3d) and were correlated in this range (Table 1). 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. The decreasing amount of adsorbed P at near-neutral to alkaline pH 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.

Critical redox potentials reported for reduction of ferric iron compounds are around 300 mV at pH 5 and 100 mV at pH 7 (Gotoh and Patrick, 1974; Husson, 2013; Yu et al., 2007). These levels match very well with critical Eh levels for desorption of Fe-(hydr)oxide-bound P, including a similar pH dependence of those levels (compare Delaune et al., 1981 with Gotoh and Patrick, 1974). As Fig. 3d shows, Eh values that did not correlate with Al/Fe-P (sediments with pH < 6.6) were above the critical Eh threshold, whereas Eh values that correlated with Al/Fe-P (sediments with pH > 6.6) were below the critical Eh threshold. This implies that reductive dissolution and related desorption of P could have contributed to the downstream transition from Al/Fe-P to Ca-P. Interestingly, the physicochemically induced P redistribution largely agreed with that from the low P site despite considerable differences of P fraction concentrations between both sites (Fig. 3a,b). This suggests that the effects of physical-chemical sediment characteristics were independent of the site-specific total P status.

Gelöscht: ; Sect. 4.5

Gelöscht: and adsorb, they contribute

Gelöscht:

Gelöscht: below

Gelöscht: at

Gelöscht: >

Gelöscht: in this range

Gelöscht: above

Gelöscht: 6.6

Gelöscht: However,

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Gelöscht: Al/

Gelöscht: -P across

Gelöscht: pH range

Gelöscht: a possible reduction-mediated decline in Al/Fe-P was restricted to pH>6.6. Thus, pH exerted strong control on inorganic

Gelöscht: fractions and therefore largely accounted for

Gelöscht: these pH-driven

Gelöscht: redistributions

Gelöscht: those

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Gelöscht: In summary,

Gelöscht: dominating effect

Gelöscht: the pH was therefore

Gelöscht: of the diverse coastal sites

4.3 Transformation of phosphorus fractions

The increase in Ca-P along transects, which correlated with an equivalent decrease in Al/Fe-P, strongly suggests that Ca-P formed at the expense of adsorbed P along the salinity gradient. By plotting Al/Fe-P and Ca-P concentrations on a pH scale (Fig. 3a,b) it became evident that the downstream transition from Al/Fe-P to Ca-P was related to a pronounced switch from P adsorption to Ca-P precipitation at ~ pH 6.6 (see also Fig. 3c). Above this pH, reduction processes are less important for P desorption (Reddy and DeLaune, 2008), P adsorption is usually less pronounced (Murrmann and Peech, 1969) and thermodynamically less stable Ca-P phases such as octacalcium phosphate (OCP) may form (Bell and Black, 1970; Oxmann and Schwendenmann, 2014).

Gelöscht:

A similar switch has been suggested for observed fraction changes with increasing sediment depth in non-upwelling continental margin environments, but from organic P to authigenic Ca-P (Ruttenberg and Berner, 1993). This switch was partly explained by the redox state, which could be the controlling parameter for diagenetic redistribution and related downcore changes of P fractions in marine environments. The main difference between the P redistribution in this study and results of Ruttenberg and Berner (1993) relates to the P source to the formation of authigenic Ca-P. Our results show strong interactions between inorganic P forms, with Al/Fe-P being a significant P source for Ca-P. In contrast to these strong interactions between Al/Fe-P and Ca-P all correlations with organic P were not significant.

Gelöscht: redistributions

Gelöscht: redistributions

Gelöscht: data indicate

Gelöscht:

However, the P redistribution along marine sediment cores may strongly differ from that across intertidal zones. The marked fraction changes suggest that the pH regulates an alternative switch between Al/Fe-P and Ca-P at the coastal sites investigated here. This pH-driven P redistribution could be a common mechanism at coastal pH gradients because it took place along different transects, comprising diverse ecosystems, and it was independent of the site-specific total P status (Fig. 3a,b). Hence, this mechanism could also be important for processes of P accumulation by increased P loads, as discussed next.

Gelöscht: redistributions

Gelöscht: those

Gelöscht: coastal sites.

4.4 Phosphorus accumulation processes

The anthropogenic P input at the high P site caused two different location-dependent accumulation mechanisms, which mainly resulted in elevated Al/Fe-P at pH < 6.6 (landward) and elevated Ca-P at pH > 6.6 (seaward). The between-site comparison (high vs. low P site) therefore implies that fertilizer-derived P was largely included in the Al/Fe-P fraction (adsorbed P) of acidic landward sediments. Phosphorus inputs by runoff or erosion to downstream areas apparently led to enhanced precipitation of Ca-P by increasing pH. The accumulation pattern in this site comparison therefore corresponds to location-dependent

Gelöscht: -enriched

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Gelöscht: upstream

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Gelöscht: downstream). This

Gelöscht: upstream

Gelöscht: environments

transformations between Al/Fe-P and Ca-P, which are to be expected from the P redistribution at individual sites (Sect. 4.3).

Gelöscht: P redistributions

We hypothesize that more soluble Ca-P minerals accumulate relative to total Ca-P due to anthropogenic P inputs because the formation of sparingly soluble Ca-P minerals is too slow for balancing increased formation rates of thermodynamically less stable Ca-P minerals. This hypothesis is consistent with comparatively large amounts of metastable Ca-P, which apparently accumulated at the high P site due to external factors (Sect. 3.4, Table 3; Fig. 4c,d). Our findings showed that Morgan's weakly acidic acetate-acetic acid solution preferentially extracts metastable Ca-P phases. Because sparingly soluble Ca-P minerals, such as detrital apatite, are unlikely to dissolve in Morgan's solution (pH 4.8; cf. Ruttenberg, 1992), the correlations between Morgan P (Ca-P_{meta}) and Ca-P ($p < 0.0001$ at both sites; Fig. 4b) are attributable to more soluble Ca-P minerals. This conclusion is supported by other studies which have indicated that the Morgan test preferentially extracts more soluble Ca-P phases, whereas most other available P tests preferentially extract adsorbed P (cf. Ahmad et al., 1968; Curran, 1984; Curran and Ballard, 1984; Dabin, 1980; Herlihy and McCarthy, 2006).

Gelöscht: by

Gelöscht: enrichment

Gelöscht: -enriched

Gelöscht: In agreement with several studies (Sect. 4.6) our

Gelöscht: mainly

Our hypothesis is also consistent with concentrations of OCP, CFAP and FAP, which were separately determined for sediments of both sites (Fig. 5). Sediments of the high P site showed a significantly larger portion of $\text{Ca-P}_{OCP+CFAP}$ compared to the low P site. Results of both independent methods, which were significantly correlated (Table 4), therefore provide strong evidence for the proposed accumulation of thermodynamically less stable Ca-P by anthropogenic P inputs. Less stable Ca-P may thus be a useful parameter to monitor anthropogenic accumulations of inorganic P in coastal regions. Because physical-chemical sediment characteristics influence Ca-P formation, an important caveat is the between-site comparability of data. In this study, there was between-site comparability of both the sediment characteristics and the general response of each of the P fractions and P species to the sediment characteristics at different depth intervals along the land-sea continuum (Fig. 3a, b; Fig. 4 a, b; Fig. 5).

Gelöscht: -enriched

Gelöscht: -unenriched

A dominant proportion of more soluble Ca-P was contributed by OCP in alkaline sediments (Fig. 5). These OCP concentrations therefore suggest authigenic apatite formation by initial precipitation of OCP in alkaline mangrove, river, bay and tidal flat sediments. Octacalcium phosphate has been suggested to occur in surface marine sediment using XANES (Oxmann, 2014; µXANES spectra of Brandes et al., 2007), which requires minimal sample preparation and is minimally affected by common sample matrices. Results of the CONVEX method, which was validated by the matrix effect-free method of standard addition (Oxmann and Schwendenmann, 2014), therefore agree with field and experimental evidence for the occurrence of OCP in sediment (see also Gunnars et al., 2004; Jahnke et al., 1983; Krajewski

Gelöscht: <#>Octacalcium phosphate and authigenic apatite¶

et al., 1994; Morse and Casey, 1988; Nancollas et al., 1989; Schenau et al., 2000; van Cappellen and Berner, 1988).

We conclude that OCP plays a crucial role in the redistribution of sediment P (see arrows in Figure 5), including the pH-dependent switch from adsorbed P to Ca-P in the landward to seaward direction; the potential reverse transformation after upstream transport; and the pH-dependent accumulation processes. Further, apatite formation by successive crystallization is possibly mainly restricted to alkaline sediments. Octacalcium phosphate is an important intermediate in the formation of apatite in alkaline environments, including calcareous soil (Alt et al., 2013; Beauchemin et al., 2003; Grossl and Inskeep, 1992), lake sediment (e.g. Avnimelech, 1983) and marine sediment (see above references). In agreement with the high OCP concentrations found in this study (Fig. 5), solid-state NMR and XANES spectroscopy based studies implied that OCP does not only belong to the most commonly reported but also to the most prevalent inorganic P forms in alkaline environments (Beauchemin et al., 2003; Kizewski et al., 2011; Oxmann, 2014).

In general, the established Ca-P precipitation in sediments across salinity gradients provides some insight into the relevance of factors influencing this precipitation such as changes in salinity, dissolved phosphate and pH. In fact, as the ionic strength increases with increasing salinity for a given phosphate concentration and pH, the apparent Ca-P solubility increases strongly (cf. Atlas, 1975). Yet, increasing Ca-P concentrations imply that the salt effect is usually more than offset by the rise in pH, redox-driven phosphate desorption from iron oxyhydroxides and other potential factors in interstitial waters across salinity gradients. For example, Ca^{2+} concentrations generally increase from land to sea and, hence, increase the saturation state with respect to calcium phosphates (normal seawater and sediment pore-water: *c.* 10 mM; river water, global average: *c.* 0.4 mM; soil pore-water, average of temperate region soils: *c.* 1.5 mM; Girard, 2004; Lerman and Wu, 2008; Lower et al., 1999; Rengel, 2006; Sun and Turchyn, 2014). Although the correlation of salinity with Al/Fe-P was not significant, the correlation with Ca-P was decreased but still significant (Table 1), indicating that increasing Ca^{2+} concentrations from land to sea may also contribute to Ca-P formation.

Our results imply that when P enters the marine environment, enhanced Ca-P formation takes place in near-shore environments. Given the possibility that CFAP or other less stable Ca-P phases do not readily dissolve in alkaline seawater (Faul et al., 2005; Lyons et al., 2011; Sheldon, 1981; see also Gulbrandsen et al., 1984 as cited in Slomp, 2011), some non-detrital Ca-P at sites further offshore could be derived from Ca-P-generating areas of the lower intertidal zone or even from freshwater environments (see e.g. Raimonet et al., 2013).

Gelöscht:

Gelöscht: this precursor

Gelöscht: P redistributions

Gelöscht: downstream

Gelöscht: ¶

Gelöscht: and references therein

Gelöscht: and references therein

Gelöscht: Other naturally occurring mineral phases of Ca-P with a higher solubility than detrital FAP include, for example, biogenic apatite, HAP and calcium-carbonate-phosphates (e.g. CFAP, carbonate hydroxylapatite; e.g. Avnimelech, 1983). Howarth et al. (1995) proposed that the suggested rapid CFAP formation in surface layers of non-upwelling sediments (Ruttenberg and Berner, 1993), which was derived from authigenic P fractions (extracted with pH 4 acetate buffer; SEDEX method; Ruttenberg, 1992), may be biased by biogenic apatite. Slomp (2011) similarly suggested that the occurrence of more amorphous, not operationally defined authigenic Ca-P phases causes overestimates of operationally defined Ca-P phases and that, on the other hand, long-term diagenesis of authigenic Ca-P can cause overestimates of detrital Ca-P.

Gelöscht: We found large solubility differences between FAP and CFAP in sediment (Oxmann and Schwendenmann, 2014), which agree with notable differences between solubilities of laboratory synthesized FAP and CFAP detected by Jahnke (1984). The pH at which differential dissolution of FAP and CFAP occurred during addition experiments for validation of the CONVEX method agrees with a pH of 4, at which best separation of FAP and CFAP is attained in the SEDEX acetate buffer (Ruttenberg, 1992). It is important to note that several CFAP specimens with different degrees of carbonate substitution as well as biogenic apatite were distinguishable from FAP in these addition experiments. We the ... [1]

Formatiert: Englisch (Großbritannien)

Gelöscht: along

Gelöscht: apparent Ca-P solubility

Gelöscht: strongly

Gelöscht: (

Gelöscht: may be

Gelöscht: P desorption, the rise in pH and other potential factors in interstitial waters along salin ... [2]

Gelöscht: the intertidal zone. Some

Gelöscht: Although P redistributions may strongly differ between sediments and soils ... [3]

4.5 Conclusions

Our results show a pH-induced switch from P adsorption to Ca-P precipitation at near-neutral pH, which apparently leads to inorganic P accumulation in near-shore sediments. The decrease in Eh and increase in Ca^{2+} concentrations from land to the sea likely contribute to this switch. Further, this P redistribution is apparently driven by OCP formation and enhanced by anthropogenic P inputs. Hence, a significant proportion of authigenic Ca-P may be derived from anthropogenic sources in some coastal regions.

The proposed mechanism, including relatively rapid formation of an apatite precursor, explains several independent observations: the downstream transition from Al/Fe-P to Ca-P at ~ pH 6.6; the Ca-P formation at the expense of adsorbed P; the large increase of Ca-P$_{meta}$ with increasing pH; the dominant proportion of OCP in alkaline sediments; the pH-dependent accumulation mechanisms of Al/Fe-P and Ca-P; and the accumulation of Ca-P$_{meta}$ and Ca-P$_{OCP+CFAP}$ at the high P site. The suggested switch appears to be a very common mechanism because it was observed across different ecosystems and it was independent of the site-specific total P status. Further evidence that this mechanism operates in different environments comes from similar downstream transitions reported by several studies.

Less stable Ca-P is mainly formed and buried during sedimentation rather than being allochthonous material. Hence, CFAP and OCP act as diagenetic sinks for P at the investigated sites and are mainly responsible for the accumulation of inorganic P in the lower intertidal zone and bay. Some authigenic Ca-P, however, could be dissolved when physical-chemical conditions change or after upstream transport by tides. Some of it could also be resuspended and transported further offshore, similar to detrital FAP. In general, OCP formation may mitigate a desorption-derived P release from sediment and seems to occur when P adsorption is usually less pronounced – that is, under alkaline conditions.

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Gelöscht: <#>Adsorption/precipitation switching in terrestrial soil¶
It is well-known that P availability and, hence, P composition differs substantially between acidic (mainly Al/Fe-(hydr)oxide-bound P) and calcareous soils (mainly Ca-P of varying solubility; e.g. Batjes, 2011). Thus soil pH, in particular the distinction between acidic and calcareous soils, is empirically the best predictor of appropriate soil tests for available P (e.g. Batjes, 2011). Correlations between two soil tests should diverge at a specific soil pH provided that (i) pH-driven adsorption/precipitation processes strongly influenced P speciation of soils analysed; and (ii) one P test extracts more soluble Ca-P (Morgan test) and the other mainly adsorbed P (most available P tests) (cf. Ahmad et al., 1968; Curran, 1984; Curran and Ballard, 1984; Dabin, 1980 and references therein; Herlihy and McCarthy, 2006). Figure 6 shows that the Morgan test is indeed fundamentally different from other methods used to determine available P. Available P tests were significantly correlated with each other except Morgan P (Ca-P$_{meta}$; all correlations non-significant; Fig. 6a). However, by separating those data into acidic and neutral to alkaline soils we found that all correlations with Morgan P were statistically significant (Fig. 6b). Hence, the divergence between correlations of P tests with pH equals the pH of the proposed switch from adsorption to Ca-P$_{meta}$ precipitation. While the pH-related divergence can certainly not be explained by a similar pH of specific extraction solutions (Morgan: 4.8; Olsen: 8.5; Bray: 1.6; M3P: 2.5) it agrees with decreasing amounts of adsorbed P (Figs. 5, 3b) and the onset of OCP precipitation at near-neutral pH (Figs. 5; S2a,b). These P redistributions in soils and the described redistributions in particulate matter (Sutula et al., 2004) imply that the proposed switch is not necessarily dependent on changes of the ambient redox conditions. Furthermore, the comparable switch for sediments (this study) and soils with quite different characteristics (Fig. 6; Bair and Davenport, 2012; Curran, 1984) may indicate that the underlying pH-induced transformation is a very common mechanism.¶
The Morgan test is evidently an unreliable indicator for the determination of P availability in sample sets with both acidic and alkaline substrates (Fig. 6a). ... [4]

Gelöscht: findings indicate

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Gelöscht: ; the comparable pH-driven switch in various soils.

Gelöscht: the analogue pH dependence in very different soils and

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Table 1. Correlations between physical-chemical sediment characteristics and P fractions at the transects of the Firth of Thames, New Zealand.

Gelöscht: P-enriched

Correlation			n	Subset[1]	r	*p* [2]
pH	vs.	Eh	112		-0.83561	2.2E-30
Ca-P	vs.	pH	112		0.60525	1.6E-12
Ca-P	vs.	Ca-P_{meta}	112		0.57074	5.0E-11
Al/Fe-P	vs.	Eh	112		0.54742	4.2E-10
Al/Fe-P	vs.	pH	28	0-5 cm	-0.81043	1.7E-07 [3]
Ca-P_{meta}	vs.	pH	112		0.44885	6.9E-07
Al/Fe-P	vs.	pH	112		-0.43497	1.6E-06[3]
Al/Fe-P	vs.	Eh	77	pH > 6.6	0.50890	2.3E-06
Al/Fe-P	vs.	Eh	28	Surface	0.75979	2.7E-06
Al/Fe-P	vs.	pH	77	pH > 6.6	-0.48749	6.9E-06
Ca-P	vs.	Salinity	112		0.39824	1.4E-05
Ca-P_{meta}	vs.	Eh	112		-0.26717	4.4E-03
Ca-P	vs.	Al/Fe-P	112		-0.26236	5.2E-03 [4]
Al/Fe-P	vs.	Eh	35	pH < 6.6	0.15496	NS
Al/Fe-P	vs.	Ca-P_{meta}	112		0.09103	NS
Al/Fe-P	vs.	Salinity	112		-0.13359	NS

Al/Fe-P: Al/Fe-bound P; Ca-P: calcium-bound P; Ca-P_{meta}: metastable Ca-P

[1] Blank rows indicate complete sample set analysed

[2] All correlations with organic P non-significant

[3] Surface layer showed a stronger correlation between Al/Fe-P and pH than the complete data set because other depth intervals showed a peak at pH 6.6 (see Fig. 3c).

[4] Note that r and *p* values of Ca-P vs. Al/Fe-P strongly depend on selected pH intervals (cf. Fig. 3c).

NS: Non-significant

Table 2. Phosphorus fractions at different pH intervals in sediments of the high P site (Firth of Thames) and low P site (Saigon River Delta).[1]

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Gelöscht: -unenriched sediments of the

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Site	n		pH		Ca-P µmol/g		Al/Fe-P µmol/g	
	<6.6	>6.6	<6.6	>6.6	<6.6	>6.6	<6.6	>6.6
High P	35	72	5.9	7.0	5.92	7.69	13.65	8.90
Low P	66	23	6.0	6.9	3.55	4.10	8.03	7.89
% Increase					+49	**+88**	**+70**	+13

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Ca-P: calcium-bound P (mean); Al/Fe-P: Al/Fe-bound P (mean)

[1] The analysis was restricted to sediments at overlapping pH intervals for both sites (pH ≤ 6.6: 4.83-5.99; pH ≥ 6.6: 6.01-7.47) to compare the increase for similar mean pH values at the lower (average pH ~6) and upper (average pH ~7) pH intervals.

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Table 3. Phosphorus fractions in mangrove sediments of the high P site (Firth of Thames) and low P site (Saigon River Delta).

Mangrove site	n	pH	Eh mV	Ca-P µmol/g	Al/Fe-P µmol/g	Ca-P_{meta} µmol/g	Ca-P_{meta} (% of Ca-P)
High P	48	6.8	95	6.91	10.44	2.35	34
Low P	64	6.4	66	3.85	8.36	0.40	10
Low P_{acid}[1]	(32)	(5.0)	(240)	(2.78)	(6.26)	(0.27)	(10)
% Increase[2]				**+80** (+150)	**+25** (+65)	**+482** (+800)	**+240** (+240)

Ca-P: calcium-bound P (mean); Al/Fe-P: Al/Fe-bound P (mean); Ca-P_{meta}: metastable Ca-P (mean)

[1] Area of acid sulphate sediments in mangroves of the low P site

[2] Percentages of P fraction increase at the high P site in comparison to the low P site, which had similar pH and Eh values. Values for a comparison of the high P site with an area of acid sulphate sediments (Low P_{acid}) in parentheses.

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Gelöscht: P-unenriched$_{acid}$[1]

Gelöscht: -unenriched

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Gelöscht: P-unenriched$_{acid}$

Table 4. Correlation coefficients (for $p < 0.05$) between concentrations of P fractions, OCP, CFAP, FAP and pH in sediments analysed for particular Ca-P species.[1]

	Al/Fe-P	Res. P	pH	FAP	CFAP	OCP	Ca-P	OCP+ CFAP	Ca-P$_{meta}$
Res. P	0.88****								
pH	^{2}	-							
FAP	-	-	-						
CFAP	-	0.69**	-	-					
OCP	-	-	-	-	-				
Ca-P	^{2}	-	0.68*	-	0.77**	0.81***			
OCP+CFAP	-	-	0.88****	-	0.65*	0.67*	0.79**		
Ca-P$_{meta}$	-	-	-	-	0.84**^{3}	-	0.76*^{3}	0.74*^{3}	
TIP	0.95****	0.91****	-	-	0.66*	-	-	-	0.69*^{3}

TIP: total inorganic P; Al/Fe-P: Al/Fe-bound P; Ca-P: calcium-bound P; Ca-P$_{meta}$: metastable Ca-P; OCP: octacalcium phosphate; CFAP: carbonate fluorapatite; FAP: fluorapatite; Res. P: residual P

NS = non-significant; * = 0.05 level; ** = 0.01 level; *** = 0.001 level; **** = 0.0001 level

[1] Species distributions shown in Fig. 5

[2] See Fig. 3 for correlations among Ca-P, Al/Fe-P and pH using a larger set of fraction data

[3] n = 9; for all other correlations n=13

Figure 1. Study area. (a) Location of the Firth of Thames, North Island, New Zealand. The area of the catchment area which is predominantly used for pastoral agriculture (1.3 million ha) is shown in green. (b) Firth of Thames transects across different ecosystems. (c) Plots (n=28) along transects were located in the following ecosystems: bay (dark blue), tidal flat (blue), mangrove (light green), salt marsh (green) and pasture (dark green). Tidal flat plots close to mangrove forests included mangrove seedlings. Five additional plots were located at rivers (grey). Isolines indicate elevations in meters below mean sea level. Google Earth images for areas from pasture to tidal flat in c.

Figure 2. Physical-chemical sediment characteristics (a: pH; b: Eh) and sediment phosphorus fractions (c: Ca-P; d: Al/Fe-P) across ecosystems at the Firth of Thames. Each depth interval includes average values of several plots of each ecosystem across the entire site (all transects; see Table S1 for the number of averaged data and their values). Mean values of all depth intervals (112 samples) are also shown for each parameter. Mean fraction concentrations in % of total inorganic P (TIP) are given in c and d. X-axis labels include mean distance (Dist, meters, mangrove seaward margin is set as zero) and mean inundation durations (ID, days/year). r and *p* values for correlations among these parameters are given in Table 1.

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Figure 3. Changes of sediment phosphorus fractions (Al/Fe-P; Ca-P) as a function of pH and Eh variations at transects at the Firth of Thames (NZ) and Saigon River Delta (VN) site. (a) Ca-P increase with pH (exponential; both sites, all samples). Mean Ca-P concentration of Firth of Thames samples *c*. twice that of Saigon River Delta samples. (b) Al/Fe-P peak at ~ pH 6.6 due to increase below and decrease above that value (exponential; both sites, all samples). (c) Linear regressions between Al/Fe-P and Ca-P at deeper depths (30-35, 35-40 cm) for different pH intervals (cf. Fig. 3a, b). Arrows indicate switch from Al/Fe-P to Ca-P with increasing pH (seaward direction). (d) Eh vs. pH (NZ; all samples). Different symbols denote surface (0-5 cm), intermediate (10-15 cm) and deeper depth intervals (30-35, 35-40 cm) in a, b and d. Symbols for VN data marked with cross in c. Smoothing by averaging 10 adjacent Eh values of pH sorted data in d. See text for linear regression in b.

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Figure 4. Accumulation and pH dependence of metastable Ca-P ($\text{Ca-P}_{\text{meta}}$) along transects at the Firth of Thames (NZ) site compared to the Saigon River Delta (VN) site. (a) Increase of $\text{Ca-P}_{\text{meta}}$ with pH (exponential; 30-35 cm). (b) Linear regressions of $\text{Ca-P}_{\text{meta}}$ vs. total Ca-P (all plots and depths; NZ: r = 0.57, $p < 0.0001$; VN: r = 0.50, $p < 0.0001$). (c) $\text{Ca-P}_{\text{meta}}$ vs. pH (all plots and depths). Mean $\text{Ca-P}_{\text{meta}}$ concentration at the Firth of Thames site *c*. six times that

of the Saigon River Delta site. (d) Ca-$\mathrm{P_{meta}}$ in % of total Ca-P vs. pH (all plots and depths). Mean percentage *c*. 3.5 times higher for the Firth of Thames site. Note different axis ranges for the two sites in a and b.

Figure 5. Phosphorus species distributions in sediments across different ecosystems at the Firth of Thames (NZ) and Saigon River Delta (VN) site ordered by pH (all concentrations in µmol P g^{-1}). The sampling site (N: NZ, New Zealand; V: VN, Vietnam) and depth interval (cm) is given at the top axis. The portion of more soluble Ca-$\mathrm{P_{OCP+CFAP}}$ (hatched area) is given as a percentage of total Ca-P above columns (NZ values in bold). A typical decrease of adsorbed P and increase of OCP with increasing pH from 6.7 to 7.3 suggests a reversible transformation in that range (arrows; adsorption/precipitation switch). Strong Al/Fe-P predominance in acidic surface sediment of the pasture is denoted (star). Org. P: total organic P; Inorg. P: total inorganic P; OCP: octacalcium phosphate; CFAP: carbonate fluorapatite; FAP: fluorapatite; Res. P: residual P; Man*: strongly acidic mangrove; Man: mangrove; Past: pasture; TiFl: tidal flat; Rive: river. Residual P correlated with Al/Fe-P at a significance level of 0.0001 (asterisks). See Table 4 for further correlations among these species distributions.

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Figure 6. Influence of soil pH on Al/Fe-(hydr)oxide-bound P (Al/Fe-P) and calcium-bound P (Ca-P) as derived from correlations between Morgan P and other available P tests (Olsen P, Bray P and Mehlich M3P). All correlations were non-significant ($p > 0.05$) for the entire pH range (a) due to extraction of different P fractions (Morgan P: mainly metastable Ca-P; other available P tests: mainly Al/Fe-P). By separating data into acidic and neutral-alkaline soils all correlations were significant (b; $p < 0.05$). Data from (i) Bair and Davenport (2012), excluding a heavily fertilized sample (Morgan P ten times higher than the second highest Morgan P value) and a sample with high carbonate content despite low pH; and (ii) from Curran (1984), excluding an OM sample (forest floor). Values for Mehlich P only from Bair and Davenport (2012) due to different Mehlich tests (Bair and Davenport: M3P; Curran: M2P). Note the significant correlations in 5b despite very different soils: developed in marine clay, native, garden, manured and unfertilized agriculture, pasture, P-fertilized and different unfertilized forest; different horizons; varying pH.

Seite 14: [1] Gelöscht JFOxmann 09.11.2014 11:43:00

We found large solubility differences between FAP and CFAP in sediment (Oxmann and Schwendenmann, 2014), which agree with notable differences between solubilities of laboratory synthesized FAP and CFAP detected by Jahnke (1984). The pH at which differential dissolution of FAP and CFAP occurred during addition experiments for validation of the CONVEX method agrees with a pH of 4, at which best separation of FAP and CFAP is attained in the SEDEX acetate buffer (Ruttenberg, 1992). It is important to note that several CFAP specimens with different degrees of carbonate substitution as well as biogenic apatite were distinguishable from FAP in these addition experiments. We therefore believe that the SEDEX method gives a reliable estimate of continental-derived FAP and that the method reliably distinguishes this detrital FAP from more soluble Ca-P. More soluble Ca-P, however, may include CFAP and OCP, both of which can be expected to be largely generated where they are observed. However, the assumption that less stable Ca-P phases, which dissolve in acetate buffer of pH 4, did only form at sampling sites may be misleading. Given the possibility that some CFAP or other less stable Ca-P phases do not readily dissolve in alkaline seawater (Faul et al., 2005; Lyons et al., 2011; Sheldon, 1981; see also Gulbrandsen et al., 1984 as cited in Slomp, 2011), yet in the pH 4 acetate buffer of the SEDEX method (~ 4 pH units difference), some of this more soluble Ca-P may be of allochthonous origin.

To define the entire 'non-detrital' Ca-P fraction (i.e. Ca-P phases other than FAP; separated by e.g. pH 4 acetate buffer) in marine sediment as being an oceanic sink for SRP (i.e. authigenically precipitated from seawater) assumes that, contrary to detrital FAP, 'non-detrital' Ca-P of terrestrial sources completely dissolves before or after entering the marine environment. From the downstream formation of OCP that occurred despite higher solubility of OCP compared to CFAP and on the basis of several recent findings, we speculate that this assumption is likely inaccurate and needs further evaluation, at least for specific near-shore marine environments. Pertinent recent findings include, for example, (i) large amounts of less stable Ca-P in soil and parent rock (determined by the SEDEX method or comparable sequential extractions with acetate buffer; Alt et al., 2013; Hansen et al., 2004) that could enter the marine realm, e.g. through erosion processes; (ii) apparent occurrence or even formation of less stable Ca-P in terrestrial and marine waters (also confirmed by the SEDEX method; Faul et al., 2005; Lyons et al., 2011; Slomp, 2011; Sutula et al., 2004); and (iii) common Ca-P formation in intertidal sediments (confirmed by several independent methods; see Sect. 4.2).

Seite 14: [2] Gelöscht JFOxmann 09.11.2014 11:43:00

P desorption, the rise in pH and other potential factors in interstitial waters along salinity gradients

Seite 14: [3] Gelöscht **JFOxmann** **09.11.2014 11:43:00**

Although P redistributions may strongly differ between sediments and soils (e.g. effects of the redox state and ionic strength), the fundamental processes operating on P speciation are comparable. This fact is reflected, for example, in the extensive direct utilization or adaptation of soil P methods for sedimentological studies. It is therefore appropriate to identify potential similarities between sediments and soils in terms of P speciation as described below, especially when analysing transformations from freshwater to seawater environments.

Seite 15: [4] Gelöscht **JFOxmann** **09.11.2014 11:43:00**

Adsorption/precipitation switching in terrestrial soil

It is well-known that P availability and, hence, P composition differs substantially between acidic (mainly Al/Fe-(hydr)oxide-bound P) and calcareous soils (mainly Ca-P of varying solubility; e.g. Batjes, 2011). Thus soil pH, in particular the distinction between acidic and calcareous soils, is empirically the best predictor of appropriate soil tests for available P (e.g. Batjes, 2011). Correlations between two soil tests should diverge at a specific soil pH provided that (i) pH-driven adsorption/precipitation processes strongly influenced P speciation of soils analysed; and (ii) one P test extracts more soluble Ca-P (Morgan test) and the other mainly adsorbed P (most available P tests) (cf. Ahmad et al., 1968; Curran, 1984; Curran and Ballard, 1984; Dabin, 1980 and references therein; Herlihy and McCarthy, 2006). Figure 6 shows that the Morgan test is indeed fundamentally different from other methods used to determine available P. Available P tests were significantly correlated with each other except Morgan P (Ca-P$_{meta}$; all correlations non-significant; Fig. 6a). However, by separating those data into acidic and neutral to alkaline soils we found that all correlations with Morgan P were statistically significant (Fig. 6b). Hence, the divergence between correlations of P tests with pH equals the pH of the proposed switch from adsorption to Ca-P$_{meta}$ precipitation. While the pH-related divergence can certainly not be explained by a similar pH of specific extraction solutions (Morgan: 4.8; Olsen: 8.5; Bray: 1.6; M3P: 2.5) it agrees with decreasing amounts of adsorbed P (Figs. 5, 3b) and the onset of OCP precipitation at near-neutral pH (Figs. 5; S2a,b). These P redistributions in soils and the described redistributions in particulate matter (Sutula et al., 2004) imply that the proposed switch is not necessarily dependent on changes of the ambient redox conditions. Furthermore, the comparable switch for sediments (this study) and soils with quite different characteristics (Fig. 6; Bair and Davenport, 2012;

Curran, 1984) may indicate that the underlying pH-induced transformation is a very common mechanism.

The Morgan test is evidently an unreliable indicator for the determination of P availability in sample sets with both acidic and alkaline substrates (Fig. 6a). Permanently alkaline environments are usually characterized by lower P availability than slightly acidic environments due to decreasing Ca-P solubility with pH (Figs. 2a,c; 3a; 5; S2a,b) and lower amounts of Al/Fe-P (Figs. 3b; 5), whereas Morgan P continuously increases with pH across the pH range (Figs. 4a,c). This conclusion is consistent with known overestimates of plant-available P by the Morgan test at high soil pH (Aura, 1978; Foy et al., 1997). Hence, despite highest Morgan test values for bay sediments (Ca-P_{meta}; Table S1) the availability of P is likely lower in permanently alkaline environments thereby mitigating coastal eutrophication. Because limited P availability is generally negatively correlated with P mobility, this positive effect comes at the expense of an increased P accumulation at the coastal zone.