

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

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Referee #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.

General Comments

Comment 1: A comprehensive dataset from a New Zealand intertidal flat on solid-
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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

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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

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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 coarse 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

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measurements), the usage of microelectrodes is, we believe, more prone to errors. Our study sites were spread out over a large area (c. 100 km²) 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 significantly reduced. The language can be simplified and the figure axes of Figure 2,3,4, and 6 at normal print size are almost unreadable. The use of Figure 6 is also debatable. The authors use this figure to demonstrate that pH effects dominate the partitioning between Al/Fe-P and metastable Ca-P, something that can already be deduced from looking at Figure 4a. However, Figure 6 compares two different extraction methods, whereby one, the 'Morgan-P' is sensitive to natural pH effects (I am not quite clear why), whereas the others are not. This then leads to the confusing

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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."

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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

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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 to 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

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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: I.6: ... parallel incubation at varying pH: Please be more precise. I.10: "Differential dissolution was verified by standard addition experiments." This is not clear enough. I.26: The data acquisition from the Vietnam site is not detailed here. Since this is a comparative study, more information needs to be provided on the other site.

Response 13: I.6: "parallel incubation of sediment subsamples at varying pH in 0.01 M CaCl₂" was replaced by "parallel incubation of sediment subsamples at different pH values (approximate pH range 3 to 8) in 0.01 M CaCl₂".

I.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 μ mol 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)."

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

Comment 14: p.10239: I.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? I.21: delete ' between the sites' (repeat)

Response 14: We decided to replace "P-unenriched site" by "low P site" and "P-
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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.

I.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)."

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

Comment 15: p.10240: I.12/13: the authors claim that there is only a substantial effect above pH 6.6. This a conclusion based on their summed data treatment. However, the dissolution/desorption/precipitation dynamics of phosphorus should be compared per site in order to demonstrate net mobilization/immobilization. That is, per site there may be a strong redox control that controls mobility. Without information of the dissolved phosphate concentrations, the authors cannot come to this conclusion.

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."

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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-Pmeta 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-Pmeta 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-Pmeta. 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

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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 Ca²⁺ 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 Ca²⁺. 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 Ca²⁺:

"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, Ca²⁺ 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 Turczyn, 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 Ca²⁺ concentrations from land to sea may also contribute to the observed Ca-P for-

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mation."

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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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C6219/2014/bgd-11-C6219-2014->

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[supplement.pdf](#)

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