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Calcium phosphate formation due to pH-induced adsorption/precipitation switching along salinity gradients

J. F. Oxmann¹ and L. Schwendenmann²

¹GEOMAR Helmholtz Centre for Ocean Research Kiel, Marine Biogeochemistry, 24148 Kiel, Germany

²School of Environment, The University of Auckland, Auckland 1010, New Zealand

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Correspondence to: J. F. Oxmann (joxmann@geomar.de)

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Abstract

Mechanisms governing phosphorus (P) speciation in coastal sediments remain unknown due to the diversity of coastal environments and poor analytical specificity for P phases. We investigated P speciation along 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 P-unenriched site. To improve analytical specificity, 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). Sediment pH primarily affected P fractions across ecosystems and independent of the P status. Increasing pH caused a pronounced downstream transition from adsorbed Al/Fe-P to mineral Ca-P. Downstream decline in Al/Fe-P was counterbalanced by the precipitation of Ca-P. This marked upstream-to-downstream switch occurred at near-neutral sediment pH and was enhanced by increased P loads. Accordingly, the site comparison indicated two location-dependent accumulation mechanisms at the P-enriched site, which mainly resulted in elevated Al/Fe-P at pH < 6.6 (upstream; adsorption) and elevated Ca-P at pH > 6.6 (downstream; precipitation). Enhanced Ca-P precipitation by increased loads was also evident from disproportional accumulation of metastable Ca-P (Ca-P_{meta}). 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. Species concentrations showed that these largely elevated Ca-P_{meta} levels resulted from transformation of fertilizer-derived Al/Fe-P to OCP and CFAP due to decreasing acidity from land to the sea. Formation of OCP and CFAP results in P retention in coastal zones, which may lead to substantial inorganic P accumulation by anthropogenic P input in near-shore sediments.

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1 Introduction

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, 1990, 2004; 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).

Desorption and precipitation of P along salinity gradients are influenced by redox potential (Eh) and pH (Sundareshwar and Morris, 1999; van Beusekom and de Jonge, 1997; DeLaune et al., 1981). Typically, pH increases and Eh decreases from land to the sea (Clarke, 1985; Huang and Morris, 2005; Paludan and Morris, 1999; Sharp et al., 1982; Spiteri et al., 2008; Sundareshwar and Morris, 1999). These pH and Eh changes facilitate P desorption from riverine particulate matter and generally account for the non-conservative behavior of 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 a significant amount of adsorbed inorganic P (Al/Fe-(hydr)oxide-bound P), which can be partly released to solution (e.g. 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

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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). The Al/Fe-P fraction of oxidized, acidic sediment usually comprises relatively large proportions of adsorbed P. Phosphate desorption induced by pH and Eh changes generally results in progressively decreasing concentrations of this sedimentary P fraction 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 levels in sediment from upper to lower zones involve critical levels for reduction of ferric iron compounds (pH-dependent; 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 ($\sim \text{pK}_2$, 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).

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 lowest phosphate concentrations in equilibrium

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with adsorbed P at acidic pH to lowest 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 downstream as a consequence of enhanced precipitation (Andrieux-Loyer et al., 2008; Coelho et al., 2004; Paludan and Morris, 1999; Sutula et al., 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; Faul et al., 2005; Lyons et al., 2011), detrital fluorapatite (FAP) is unlikely to dissolve in these environments (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). In view of the slow or inhibited direct nucleation (Golubev et al., 1999; Gunnars et al., 2004; Martens and Harriss, 1970), species of the apatite group may form in sediment by transformation of previously precipitated metastable precursors that are less susceptible to inhibitory effects of Mg^{2+} such as OCP (Oxmann, 2014; Oxmann and Schwendenmann, 2014). Hence, rapidly precipitating precursor phases (e.g. days to weeks for OCP; Bell and Black, 1970) may allow for successive crystallization until the thermodynamically favoured but

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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 sediment (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 occasionally increase relative to total Ca-P in response to increased P inputs. This human alteration to the solid-phase P speciation due to diagenetic processing of increased P loads 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 P-enriched site (Firth of Thames, New Zealand). We then compared the findings with data from a P-unenriched coastal site (Saigon River Delta, Vietnam) to identify similarities between temperate and tropical coastal regions and 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).

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 km²; < 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 large 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 coastal intertidal zone is covered by salt marshes. Behind the levee ca. 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 at 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 sections: 0–5, 10–15, 30–35 and 35–40 cm. Samples were kept

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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; PM₁₀₀; Retsch, Haan, Germany) for P and nitrogen analyses.

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 semi-selective extraction analysis using the Morgan test method (Morgan, 1941); (ii) Al/Fe-P and Ca-P fractions were quantitated by sequential extraction of P after Kurmies (Kurmies, 1972); and (iii) total P (TP) was analysed after Andersen (1976) as modified by Ostrofsky (2012). The Morgan test, commonly used to determine available P, extracts predominantly more soluble Ca-P phases by pH 4.8 buffered acetic acid (see Sects. 4.4, 4.6). 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 Na₂SO₄ extractions to avoid re-adsorption phenomena. It therefore provides an accurate means of Al/Fe-P and Ca-P determination using NaOH and H₂SO₄, respectively (Fig. S2c; steps 2a-3c). Total inorganic P (TIP) was

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defined as the sum of inorganic P fractions (Ca-P, Al/Fe-P). Organic P was calculated by subtracting TIP from TP.

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 varying pH in 0.01 M CaCl₂ 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 quantitated by the method of Kurmies. Differential dissolution was verified by standard addition experiments. 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).

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).

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 ca. 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

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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).

3 Results

3.1 Particle size, pH and Eh

5 Inundation duration ranged from 365 days yr⁻¹ in the bay to 0 days yr⁻¹ in the pasture (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).

15 Sediment pH ranged from 5.18 in the pasture to 7.4 in the bay (Fig. 2a, b; Table S1). Redox potential varied between 621 mV in the pasture 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).

20 3.2 Phosphorus fractions: transformations

Ecosystem-averaged Ca-P concentrations varied considerably and ranged from 3.37 μmol g⁻¹ (pasture, 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 pasture (17.9 μmol g⁻¹; 0–5 cm) and lowest (3.94 μmol g⁻¹; 30–35 cm) in the bay. On average, the lowest Ca-P and highest

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Al/Fe-P concentrations were measured in 0–5 cm depth (Fig. 2c, d). Averaged percentages of Ca-P (% of TIP) steadily increased and averaged percentages Al/Fe-P (% of TIP) steadily decreased from pasture 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 pasture to bay approximately matched the average Ca-P increase (-8.27 vs. $+6.73 \mu\text{mol g}^{-1}$; 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. $+1.18 \mu\text{mol g}^{-1}$; Table S1). The pasture was 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. $+0.69 \mu\text{mol g}^{-1}$; Table S1).

3.3 Phosphorus fractions: P load, pH and Eh effects

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

In sediments with $\text{pH} < 6.6$ the average concentration of Al/Fe-P was 70% higher at the P-enriched site than at the P-unenriched 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 zone and the bay ($\text{pH} > 6.6$; Table 2;

Fig. 3b). Calcium phosphate in contrast showed the opposite pattern of enrichment at the P-enriched site. In comparison to the P-unenriched site the average concentration of Ca-P was only 49 % higher in upstream environments (pH < 6.6) but increased by 88 % in the lower intertidal zone 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 P-enriched site (Fig. 2c, d), both fractions increased exponentially 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). This suggests a pH-induced switch towards Ca-P predominance (see arrows in Fig. 3c). Because this switch occurred in the downstream direction, it is in agreement with the observed Ca-P increase and Al/Fe-P decrease towards the bay (Fig. 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 ($\text{Ca-P}_{\text{meta}}$) increased exponentially with pH (Fig. 4a), similar to Ca-P (Fig. 3a), and correlated with Ca-P at both sites (Fig. 4b). Yet the concentration of $\text{Ca-P}_{\text{meta}}$ in sediments of the P-enriched site was six-fold higher compared to the P-unenriched site (Fig. 4c). In contrast, total Ca-P was only twofold higher compared to the P-unenriched site (Fig. 3a). On average, $\text{Ca-P}_{\text{meta}}$ comprised ca. 35 % of total Ca-P at the P-enriched site and only 10 % at the P-unenriched site (Fig. 4d).

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). By doing this, previous figures did not change. The difference in $\text{Ca-P}_{\text{meta}}$ 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 $\text{Ca-P}_{\text{meta}}$ was still ca.

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35% at the P-enriched site and 10% at the P-unenriched site (Table 3). Moreover, the proportion of Ca-P_{meta} to total Ca-P was equal for two areas of the P-unenriched site (10%) despite their very different average pH and Eh values (Table 3). In summary, comparatively large amounts of metastable Ca-P accumulated at the P-enriched site.

3.5 Octacalcium phosphate and authigenic apatite

Concentrations of OCP, authigenic apatite and detrital apatite were largely affected by the pH in sediments of both sites. Strongly acidic sediments (\sim pH < 4) contained just detrital apatite (FAP), whereas slightly acidic sediments (\sim pH 4–7) contained also authigenic apatite (CFAP). Octacalcium phosphate was additionally present in alkaline mangrove, river, bay and tidal flat sediments. 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 ($70.5 \pm 17.5\%$; numbers above columns in Fig. 5) for sediments of the P-enriched site compared to the P-unenriched site ($29.5 \pm 26.0\%$), $t(11) = 3.346$, $p = 0.0065$. This larger portion of Ca-P_{OCP+CFAP} provided supporting evidence for the larger portion of Ca-P_{meta} in sediments of the P-enriched 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).

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” ($> 16 \mu\text{mol}$

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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 provide the main P source (~ 90%) for the high P inputs 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.

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 from pasture to bay (Fig. 2). These changes were driven by pH and Eh gradients (Fig. 2). Salinity had no detectable effect (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. Similar upstream-to-downstream changes in sediment P fractions have been observed, for example, at 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 upstream-to-downstream changes in sediments (Sutula et al., 2004) were mirrored by similar changes in corresponding samples of surface water particulate matter. Furthermore,

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the same trends were observed along a continuum from agricultural soils across hard-water stream sediments to lake sediments (Noll et al., 2009).

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. Fig. 2a, c, d, Sect. 4.5, De Jonge and Villerius, 1989). If these phases are transported to close locations of ~pH 6.5 and subsequently dissolve and adsorb, they contribute 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 below this pH. Yet, both Eh and Al/Fe-P decreased at pH > 6.6 (cf. Fig. 3b and d) and were correlated in this range (Table 1). Because the drop in Al/Fe-P correlated also with an increase in pH in this range (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 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.

However, pH apparently affected both Ca-P and Al/Fe-P across the pH range, whereas a possible reduction-mediated decline in Al/Fe-P was restricted to pH > 6.6. Thus, pH exerted strong control on inorganic P fractions and therefore largely accounted for the downstream transition from Al/Fe-P to Ca-P. Interestingly, these pH-

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driven P redistributions largely agreed with those from the P-unenriched site despite considerable differences of P fraction concentrations between both sites (Fig. 3a, b). In summary, the dominating effect of the pH was therefore independent of the P status 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 switch from P adsorption to Ca-P precipitation at \sim 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). 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 redistributions and related downcore changes of P fractions in marine environments. The main difference between P redistributions in this study and results of Ruttenberg and Berner (1993) relates to the P source to the formation of authigenic Ca-P. Our data indicate 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. However, P redistributions along marine sediment cores may strongly differ from those across intertidal zones. The marked fraction changes suggest that the pH regulates an alternative switch between Al/Fe-P and Ca-P at the investigated coastal sites. This pH-driven P redistribution could be a common mechanism at coastal pH gradients because it took place along different transects, comprising

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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 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

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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). 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, the apparent Ca-P solubility increases strongly with increasing salinity for a given phosphate concentration and pH (Atlas, 1975). Yet, increasing Ca-P concentrations imply that the salt effect may be more than offset by P desorption, the rise in pH and other potential factors in interstitial waters along salinity gradients.

Our results imply that when P enters the marine environment, enhanced Ca-P formation takes place in the intertidal zone. 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). 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

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 (Fig. 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.

5 Conclusions

Our findings indicate 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. 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 P-enriched site; the comparable pH-driven switch in various soils. The suggested switch appears to be a very common mechanism because it was observed across different ecosystems and it was independent of the P status. Further evidence that this mechanism operates in different envi-

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ronments comes from the analogue pH dependence in very different soils and 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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Table 1. Correlations between physical-chemical sediment characteristics and P fractions at P-enriched transects of the Firth of Thames, New Zealand.

Correlation		<i>n</i>	Subset ^a	<i>r</i>	<i>p</i> ^b
pH	vs. Eh	112		-0.83561	2.2×10^{-30}
Ca-P	vs. pH	112		0.60525	1.6×10^{-12}
Ca-P	vs. Ca-P _{meta}	112		0.57074	5.0×10^{-11}
Al/Fe-P	vs. Eh	112		0.54742	4.2×10^{-10}
Al/Fe-P	vs. pH	28	0–5 cm	-0.81043	1.7×10^{-07c}
Ca-P _{meta}	vs. pH	112		0.44885	6.9×10^{-07}
Al/Fe-P	vs. pH	112		-0.43497	1.6×10^{-06c}
Al/Fe-P	vs. Eh	77	pH > 6.6	0.50890	2.3×10^{-06}
Al/Fe-P	vs. Eh	28	Surface	0.75979	2.7×10^{-06}
Al/Fe-P	vs. pH	77	pH > 6.6	-0.48749	6.9×10^{-06}
Ca-P _{meta}	vs. Eh	112		-0.26717	4.4×10^{-03}
Ca-P	vs. Al/Fe-P	112		-0.26236	5.2×10^{-03d}
Al/Fe-P	vs. Eh	77	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

^a Blank rows indicate complete sample set analysed

^b All correlations with organic P non-significant

^c 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).

^d 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

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Table 2. Phosphorus fractions at different pH intervals in P-enriched sediments of the Firth of Thames and P-unenriched sediments of the Saigon River Delta.^a

Site	<i>n</i>		pH		Ca-P $\mu\text{mol g}^{-1}$		Al/Fe-P $\mu\text{mol g}^{-1}$	
	< 6.6	> 6.6	< 6.6	> 6.6	< 6.6	> 6.6	< 6.6	> 6.6
P-enriched	35	72	5.9	7.0	5.92	7.69	13.65	8.90
P-unenriched	66	23	6.0	6.9	3.55	4.10	8.03	7.89
% Increase					+49	+88	+70	+13

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

^a 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 P-enriched mangrove sediments of the Firth of Thames and P-unenriched mangrove sediments of the Saigon River Delta.

Mangrove	<i>n</i>	pH	Eh mV	Ca-P $\mu\text{mol g}^{-1}$	Al/Fe-P $\mu\text{mol g}^{-1}$	Ca-P _{meta} $\mu\text{mol g}^{-1}$	Ca-P _{meta} (% of Ca-P)
P-enriched	48	6.8	95	6.91	10.44	2.35	34
P-unenriched	64	6.4	66	3.85	8.36	0.40	10
P-unenriched _{acid} ^a	(32)	(5.0)	(240)	(2.78)	(6.26)	(0.27)	(10)
% Increase ^b				+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)

^a Area of acid sulphate sediments in mangroves of the P-unenriched site

^b Percentages of P fraction increase at the P-enriched site in comparison to the P-unenriched site, which had similar pH and Eh values. Values for a comparison of the P-enriched site with an area of acid sulphate sediments (P-unenriched_{acid}) in parentheses.

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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.^a

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

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

^a Species distributions shown in Fig. 5

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

^c $n = 9$; for all other correlations $n = 13$

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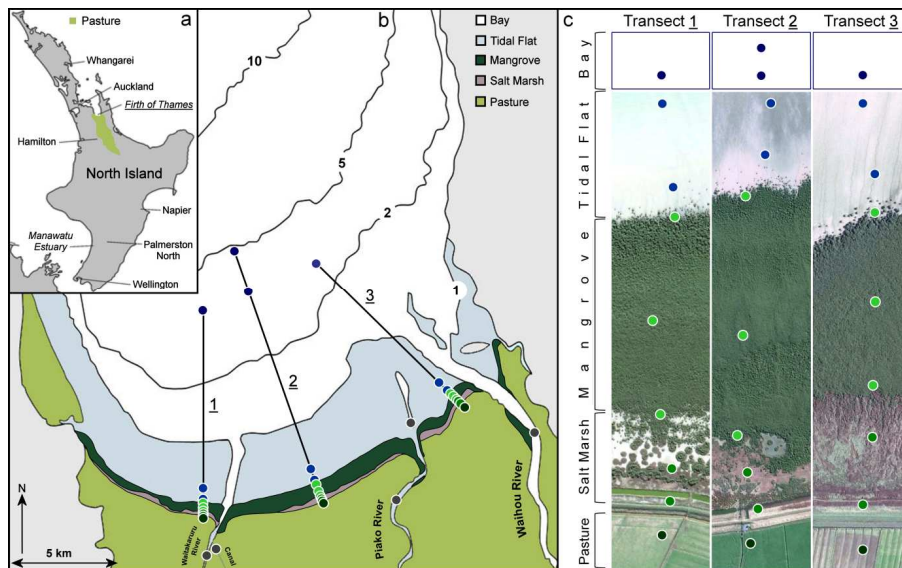


Figure 1. Study area. **(a)** Location of the Firth of Thames, North Island, New Zealand. The area of the catchment area which is predominantly used for pastoral agriculture (1.3 million ha) is shown in green. **(b)** Firth of Thames transects across different ecosystems. **(c)** Plots ($n = 28$) along 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)**.

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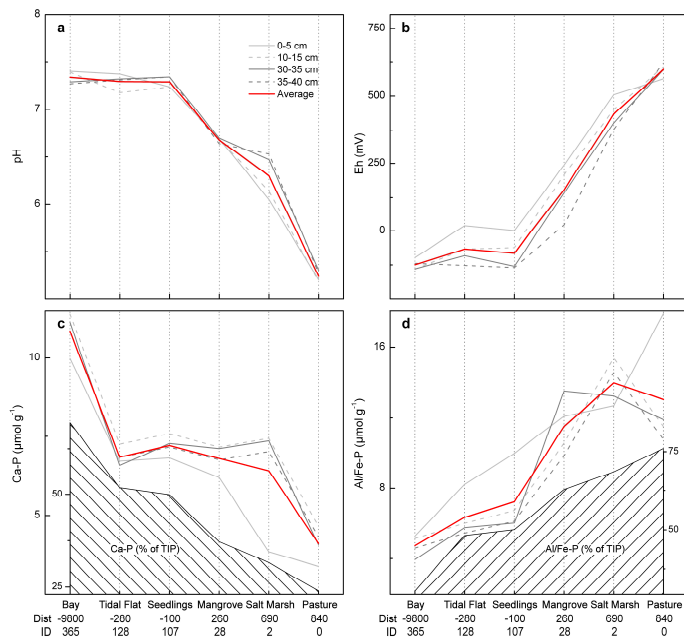


Figure 2. Physical-chemical sediment characteristics (**a**: pH; **b**: Eh) and sediment phosphorus fractions (**c**: Ca-P; **d**: Al/Fe-P) across ecosystems at the Firth of Thames. Each depth interval includes average values of several plots of each ecosystem across the entire site (all transects; see 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, downstream fringing mangroves are set as zero) and mean inundation durations (ID, days yr⁻¹). *r* and *p* values for correlations among these parameters are given in Table 1.

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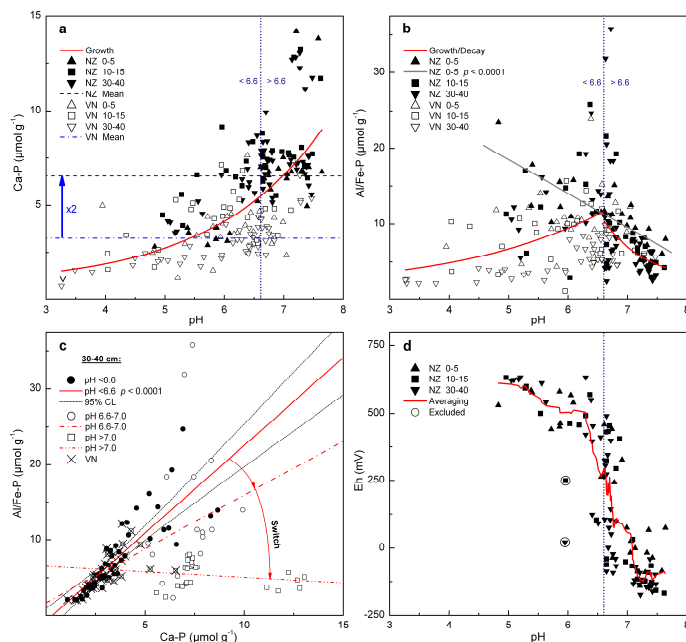


Figure 3. Changes of sediment phosphorus fractions (Al/Fe-P; Ca-P) as a function of pH and Eh variations at transects at the Firth of Thames (NZ) and Saigon River Delta (VN) site. **(a)** Ca-P increase with pH (exponential; both sites, all samples). Mean Ca-P concentration of Firth of Thames samples ca. twice that of Saigon River Delta samples. **(b)** Al/Fe-P peak at \sim 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 (downstream 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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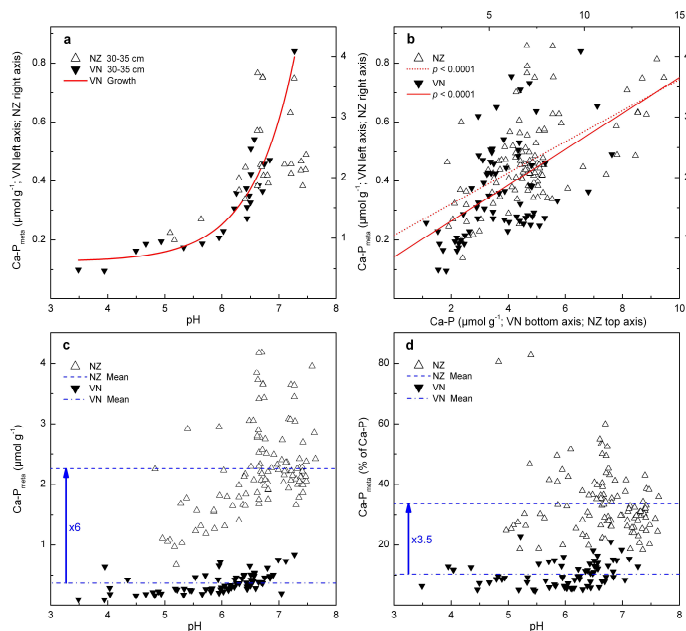


Figure 4. Accumulation and pH dependence of metastable Ca-P ($\text{Ca-P}_{\text{meta}}$) along transects at the Firth of Thames (NZ) site compared to the Saigon River Delta (VN) site. **(a)** Increase of $\text{Ca-P}_{\text{meta}}$ with pH (exponential; 30–35 cm). **(b)** Linear regressions of $\text{Ca-P}_{\text{meta}}$ 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)** $\text{Ca-P}_{\text{meta}}$ 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)**.

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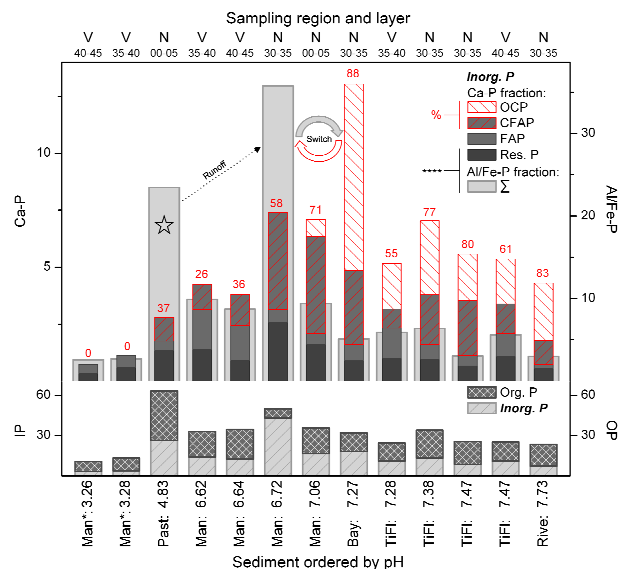


Figure 5. Phosphorus species distributions in sediments across different ecosystems at the Firth of Thames (NZ) and Saigon River Delta (VN) site ordered by pH (all concentrations in $\mu\text{mol P g}^{-1}$). The sampling site (N: NZ, New Zealand; V: VN, Vietnam) and depth interval (cm) is given at the top axis. The portion of more soluble $\text{Ca-P}_{\text{OCP}+\text{CFAP}}$ (hatched area) is given as a percentage of total Ca-P above columns. 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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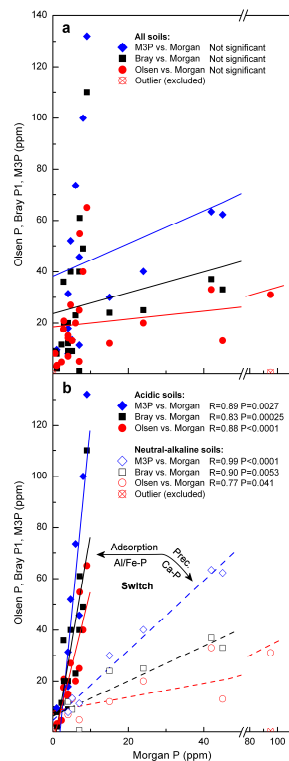


Figure 6. Influence of soil pH on Al/Fe-(hydr)oxide-bound P (Al/Fe-P) and calcium-bound P (Ca-P) as derived from correlations between Morgan P and other available P tests (Olsen P, Bray P and Mehlich M3P). All correlations were non-significant ($p > 0.05$) for the entire pH range (**a**) due to extraction 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 unfertilized forest; different horizons; varying pH.

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