Solid-phase Phosphorus Pools in Highly Organic Carbonate Sediments of North-eastern Florida Bay

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Currently, few studies have investigated sediment phosphorus (P) pools or identified the chemical processes important in the P cycle of fine-grained carbonate sediments, particularly in coastal estuaries with high organic matter. To determine the role of fine-grain calcium carbonate and high organic matter on sedimentary P, we investigated the solid-phase P pools in seagrass sediments of north-eastern (NE) Florida Bay at the bay–mangrove ecotone. Sediments were fractionated by sequential extractions into seven chemically-defined groups: exchangeable inorganic and organic P, reducible inorganic and organic P (Fe-bound), acid extractable inorganic and organic P (Ca-bound), and residual organic P. Calcium-bound P accounted for approximately 56% of total P and 96% of inorganic P. Our total calcium-bound P was in the range ($34–151\ \mu g\ P\ g^{-1}$) reported for coarse-grained low organic sediments, while the organic P associated with this fraction was slightly ($\sim 10\%$) higher than those reported for other carbonate systems. The second dominant P fraction was residual organic P ($30–71\ \mu g\ P\ g^{-1}$) accounting for 42% of TP. This high residual pool suggests the importance of fringing mangrove and seagrass detritus in long-term P storage. In contrast to temperate estuaries, the iron-bound P fraction in NE Florida Bay sediments was low ($<70\ \mu g\ g^{-1}$) at the surface and undetectable ($<1\ \mu g\ g^{-1}$) below 10 cm. Based on our findings, we hypothesize that carbonate chemisorption reactions, along with potential reactive organic surfaces, and the sequestering of P into recalcitrant organic pools, maintain low exchangeable and pore-water P concentrations across the NE Florida Bay estuary, and account for the reported autotrophic P-limitation.

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Introduction

Sediments of aquatic ecosystems play a key role in phosphorus (P) cycling between dissolved and solid-phase pools, and control long-term P diagenesis (Mortimer, 1941; Stumm & Leckie, 1970; Petterson, 1986; Golterman, 1988; Sundby *et al.*, 1992). The major biogeochemical processes that transform inorganic P from a dissolved to solid state include anion adsorption onto iron- and aluminum-oxyhydroxides and carbonate minerals; precipitation/co-precipitation with minerals containing calcium, iron, and aluminum; and uptake by microbes and plants (Mortimer, 1941; Stumm & Leckie, 1970; Otsuki & Wetzel, 1972; , Kitano *et al.*, 1978; Jensen & Thamdrup, 1993). Dominance by a particular biogeochemical process is dependant on sediment type and other physiochemical factors. Because tropical/subtropical estuaries are typically dominated by

calcium carbonate sediments, as opposed to silicate or clay-dominated sediments of coastal temperate regions, carbonate chemical equilibria can be more important than redox reactions in controlling sediment P transformations. The formation of inorganic solid-phase P reservoirs in carbonate sediments is primarily driven by chemisorption of P onto calcite ($CaCO_3$) and/or aragonite ($CaCO_3$, dimorph of calcite) followed by co-precipitation to form apatite (Stumm & Leckie, 1970; De Kanel & Morse, 1978; Kitano *et al.*, 1978). Common marine apatites are hydroxylapatite $[Ca_{10}(PO_4)_6(OH)_2]$, fluoroapatite $[Ca_{10}(PO_4)_6(F,OH)_2]$, and chloroapatite $[Ca_{10}(PO_4)_6Cl]$ (Morel & Hering, 1993; Greenwood & Earnshaw, 1997; Yen, 1999), however, fluoro-apatite (CFA) is considered to be the primary diagenetic sink in tropical marine carbonate sediments (Ruttenberg & Berner, 1993; Jensen *et al.*, 1998).

The ecological importance of P-sorption, precipitation, and release processes in carbonate sediments of tropical estuaries and lagoons is the effect they have

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on the bio-availability of P. Unlike many temperate coastal marine systems, tropical and subtropical estuaries typically have low concentrations (<0·03 to 0·6 µM) of dissolved inorganic P in their pore- and surface-waters (Patriquin, 1972; Rosenfeld, 1979; Morse *et al.*, 1987; Fourqurean *et al.*, 1993; Jensen *et al.*, 1998; Koch and Solomon, in prep.). Because of this extremely low inorganic P, benthic autotrophs (e.g., seagrass and macroalgae) growing in marine carbonate sediments frequently exhibit P-limitation (Short *et al.*, 1985; Lapointe, 1987; Short, 1987; Powell *et al.*, 1989; Fourqurean *et al.*, 1992a, b). Phosphorus limitation in seagrasses and macroalgae growing in fine-grained calcium carbonate mud of Florida Bay has been documented through tissue nutrient stoichiometric analyses and correlative studies (Lapointe, 1987; Fourqurean *et al.*, 1992a, b). Nutrient studies conducted in coarse-grained carbonate sediments have shown more variable results. Erftemeijer *et al.* (1994) reported relatively high concentrations of pore-water inorganic P ($10·9 \pm 3·9$ µM) and an insignificant seagrass growth response to *in situ* P additions in coarse carbonate sediments of Indonesia, while Short *et al.* (1990) found strong evidence for seagrass (*Syringonium filiforme*) P-limitation in coarse-grained sediments of the Bahamas. Physically, however, fine-grained sediments typical of some sites in the Bahamas and South Florida (Florida Bay) would provide greater surface area for P-sorption and thereby enhance the potential for P-limitation in primary producers. P-limitation in these sediments may be related to the mechanisms by which P is sequestered and stored in the sediment and the efficiency of these processes.

Currently, few studies have investigated sediment P pools or identified the chemical processes important in the P cycle of fine-grained carbonate sediments, particularly in coastal estuaries with high organic matter. Although most carbonate-dominated marine ecosystems in the tropics have low dissolved organic matter in the surface waters, DOC has been shown to influence nutrient uptake in carbonate sediments. Surface active organic matter can compete for inorganic phosphate adsorption sites on carbonate particles, create organic coatings on carbonate surfaces that can physically reduce adsorptive sites (Chave, 1965; Suess, 1970; Morse, 1986), as well as modify other biogeochemical factors that influence the formation and release of solid-phase P (e.g. pH and Eh). Organic P compounds (e.g. phospholipids) have also been shown to adsorb to carbonate particles as organo-carbonate associations (Suess, 1973), thus high DOC in surface- and pore-waters of coastal estuaries in the tropics could increase carbonate-

associated organic P. To determine the role of fine-grain calcium carbonate and high organic matter on sedimentary P, we investigated the solid-phase P pools in seagrass sediments of northeastern (NE) Florida Bay at the bay–mangrove ecotone. Sediments were fractionated by sequential extractions into seven chemically-defined groups: exchangeable inorganic and organic P, reducible inorganic and organic P (Fe-bound), acid extractable inorganic and organic P (Ca-bound), and residual organic P. Depth profiles of P fractions were examined to provide information on P diagenesis as a function of the various storage forms. Furthermore, physical characteristics, including grain size analysis and chemical composition of the sediments are related to the solid-phase P pools.

Materials and methods

Site description

Florida Bay is a large (2200 km^2), shallow lagoon at the southern tip of South Florida (Figure 1), with a mean depth of approximately 1 m. We chose the NE Florida Bay estuary as a study area because it has been characterized by low P concentrations (0·03 to 0·10 µM) in pore- and surface waters (Fourqurean *et al.*, 1993; Koch and Solomon, in prep.) compared to the western portion of the Bay, which receives P inputs from the Gulf of Mexico. Our sites were also chosen because detailed pore-water nutrient, salinity, and pH profiles (Koch & Solomon, in prep), and nutrient fluxes (Rudnick *et al.* in prep.) were being examined at these sites.

Four seagrass sites: Pond 1 (P1; 25°11.75′, 80°38.27′), Little Madeira Bay (LMB; 25°11.35′, 80°38.47′), Terrapin Bay (TB; 25°09.49′, 80°43.90′), and Crocodile Point (CP; 25°08.56′, 80°43.44′) were selected along the mangrove–bay interface in NE Florida Bay (Figure 1). P1 and TB sites are shallow (<2 m), semi-enclosed bays receiving freshwater from the north through mangrove creeks and estuarine influences from south-west Florida Bay. P1 receives greater freshwater flow than TB because of its association with Taylor Slough. However, both interior bays can become hyper-saline due to high evaporation rates in the summer months and during drought conditions. Bayward of these two sites, CP and LMB receive more influence from Florida Bay, thus maintain meso-haline conditions. LMB becomes more oligo-haline than CP because of its association with Taylor Slough. Circulation at all four sites is primarily limited by wind events and/or extreme freshwater flow during the rainy season, as tidal fluxes are minimal
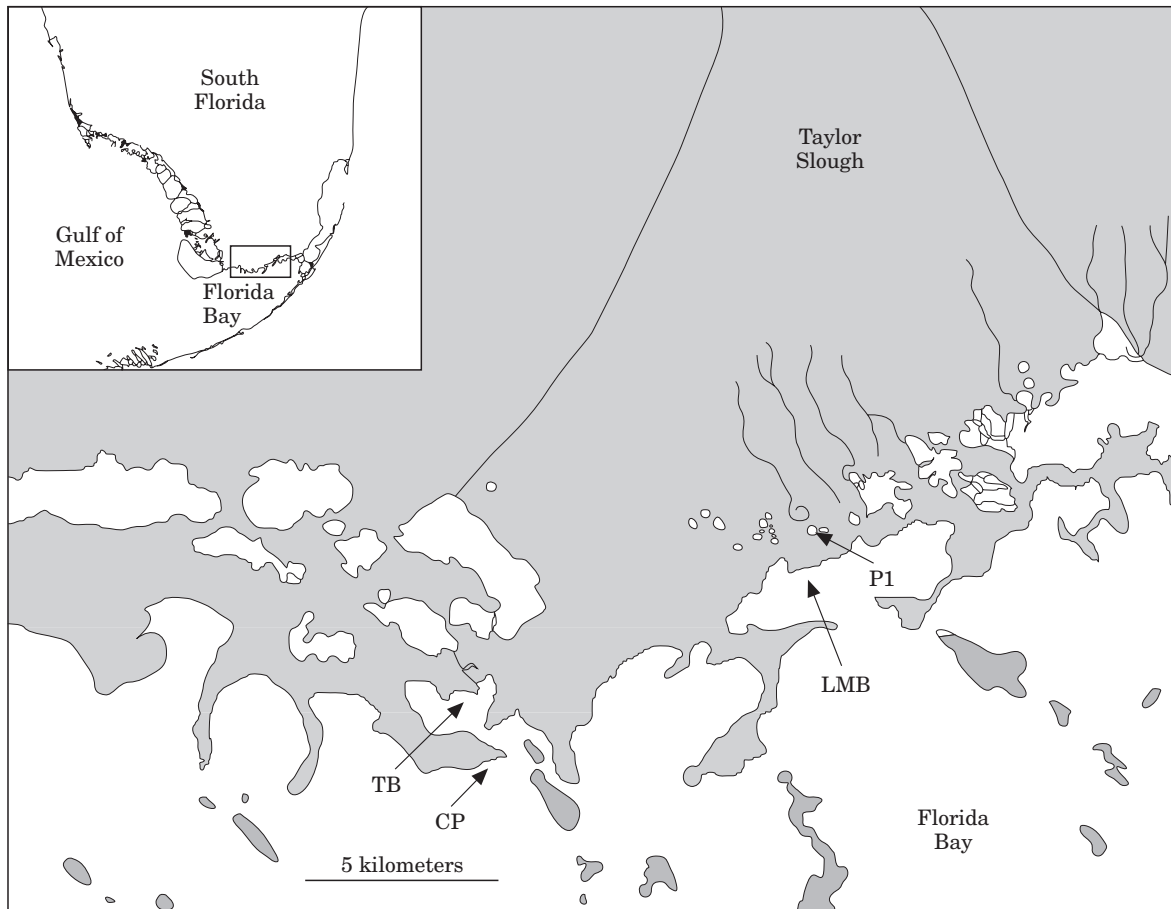
FIGURE 1. Location of study sites: Pond 1 (P1), Little Madeira Bay (LMB), Terrapin Bay (TB), and Crocodile Point (CP) in north-eastern Florida Bay (South Florida) along the Bay-mangrove ecotone.

(<0·5 m). All four sites are in close (<100 m) proximity to the fringing mangrove forest.

Sediment cores

At each site, four replicate sediment cores (PVC, 5 cm diameter × 40 cm length) were collected on 25 July 1997. Cores were carefully removed from the sediment, capped at both ends to limit contamination, mixing, and oxidation, and placed upright in 5 gallon buckets with ice for transport to the laboratory. Each core was sectioned into 5 cm depth increments: 0–5, 5–10, 10–15, 15–20, and 20–25 cm, weighed and homogenized by mixing the sample thoroughly in a sealed bag. Large seagrass leaves and roots (>5 mm) were removed prior to homogenization. A 1 g sub-sample was taken from each bag for sequential P extraction. Additional sub-samples were taken for analysis of bulk density, percent organic matter (loss on ignition), total calcium, iron, aluminum,

magnesium, manganese, carbon, phosphorus, and nitrogen, and pore-water salinity.

Extraction method

Sequential chemical extractions provide a method for separating sediment solid-phase P pools. Each step of the extraction is specific to the reactivity and dissolution rates of a particular P pool (Chang & Jackson, 1957). Recently, extraction methods have been specifically adapted for marine sediments (Ruttenberg, 1992; Jensen & Thamdrup, 1993; Jensen *et al.*, 1998). The extraction procedure used in this study (Figure 2) was a modified version of Ruttenberg (1992) and Jensen and Thamdrup (1993) and is similar to the scheme specifically designed for carbonate sediments by Jensen *et al.* (1998). Our extraction procedure was selected based on its selectivity for the P fractions of interest in this study and for its adaptability to carbonate sediments. For example, the acid
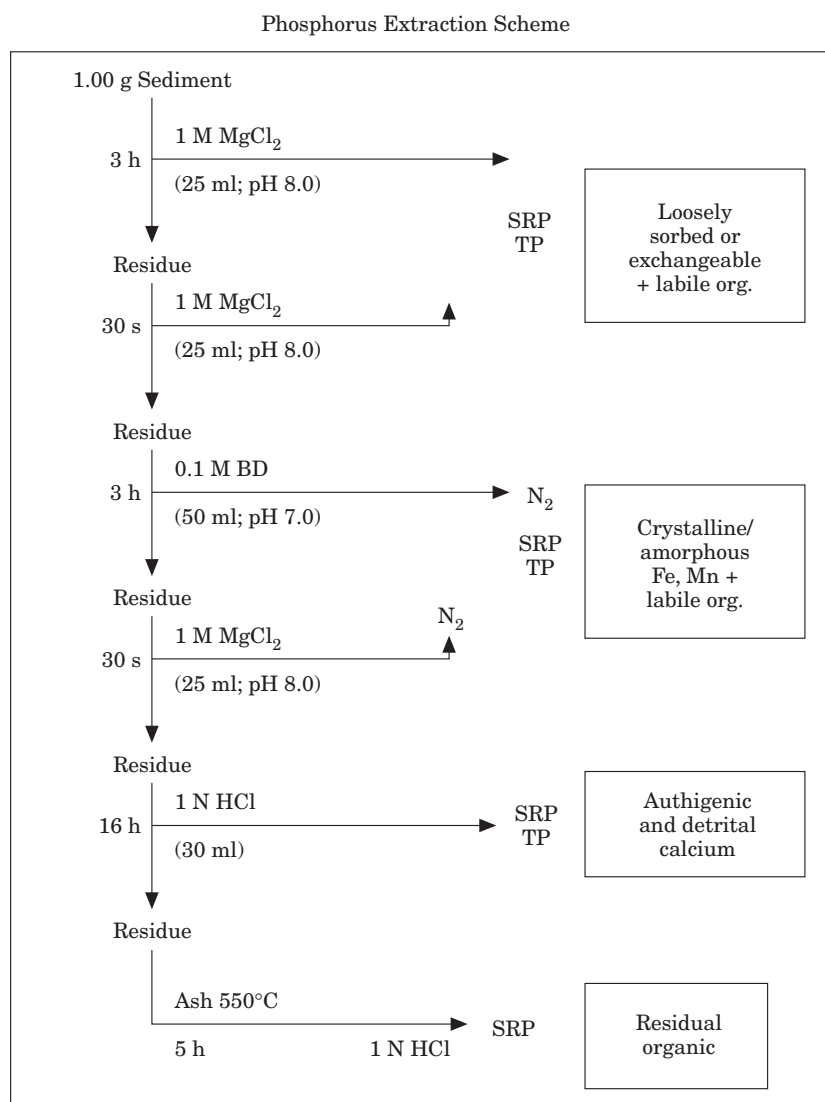
Phosphorus Extraction Scheme

FIGURE 2. Phosphorus fractionation scheme illustrating the sequential chemical extractions used for this study: magnesium chloride (MgCl$_2$), bicarbonate-dithionite (BD), hydrochloric acid (HCl), and ashing followed by acidification.

extractable fraction required a higher normality of acid than that used by Jensen and Thamdrup (1993) or Ruttenberg (1992) based upon the buffering capacity of Florida Bay's carbonate sediments. The procedure also addressed secondary adsorption to solid particles by adding a magnesium chloride (MgCl$_2$) rinse between the first two extraction steps (Ruttenberg, 1992). All extracts were refrigerated until analysis and analysed for both soluble reactive phosphorus (SRP) and TP. TP was determined by oxidation with persulfate under acidic conditions (EPA Method 365·1). Organic P was calculated as the difference between TP and SRP.

Loosely sorbed or exchangeable P, along with some labile organic P, was extracted by placing 1·00 g wet weight of sediment into 25 ml of 1 M MgCl$_2$ at pH 8·0, agitating the mixture for 3 h by mechanical shaker, centrifuging for 5 min at 4000 rpm, and decanting the supernate (Figure 2). This procedure was repeated using 24 ml of 1 M MgCl$_2$ with the exception that it was shaken for 30 s. Sulfuric acid (1·0 ml, 1 N) was added to the supernate (pH <2) for sample storage.

The sediment residues from the MgCl$_2$ extraction were subsequently extracted with bicarbonate dithio-niote (BD, 0·11 M NaHCO$_3$ and 0·11 M Na$_2$S$_2$O$_4$), a strong reducing agent, to liberate P adsorbed by crystalline and amorphous iron and manganese compounds (Jensen & Thamdrup, 1993). The residue was placed in 50 ml of BD solution at pH 7·0,

mechanically agitated for 3 h, centrifuged for 5 min at 4000 rpm, and the liquid layer decanted. The residue was then placed in 25 ml of 1 M $MgCl_2$ at pH 8·0 and shaken for 30 s, centrifuged for 5 min at 4000 rpm, and decanted. Prior to preservation, the supernate was bubbled with nitrogen gas (N_2) for 20 min to drive off sulfides. The supernate was then preserved by the addition of 4 ml of 1 N sulfuric acid (pH <2) and brought to volume with the addition of 21 ml of deionized water. Upon preservation, elemental sulfur precipitated from solution. The precipitation of sulfur was necessary to limit interference during analysis.

Sediment residues from the BD extraction were extracted with 30 ml of 1N HCl to liberate authigenic and detrital calcium-bound P as well as nonreducible metal oxides and hydroxides. The sediments were shaken several times in HCl and purged to release pressure before extraction. This was repeated until the carbon dioxide evolution ceased. The samples were mechanically agitated for 16 h, centrifuged for 5 min at 4000 rpm and decanted. The samples were brought to volume by adding 20 ml of deionized water.

Residual organic P was determined by transferring the remaining sediment residues to borosilicate culture tubes and combusting at 550 °C in a muffle furnace. The culture tubes were cooled and 10 ml of 1 N HCl was added to the combusted material. The tubes were placed in an autoclave for 50 min at 121 °C and 21 psi for 50 min. The contents of the tubes were transferred to centrifuge tubes and brought to 50 ml.

TP was determined by weighing out 1·00 g of sediment into a borosilicate culture tube and combusting the sediment at 550 °C in a muffle furnace. The culture tubes were cooled and 15 ml of 5N HCl was added. The tubes were autoclaved at 121 °C and 21 psi for 50 min. The liquid contents of each tube were filtered and brought to a final volume of 100 ml. For method verification, additional samples were digested by both acid-persulfate/autoclave and combustion as described above. The agreement between methods for spikes and samples was 98%.

Analyses

P was analysed with ammonium molybdate and antimony potassium tartrate (catalyst) under acidic conditions following standard procedures (EPA methods 365·1) on a spectrophotometer (Spectronics 301; 880 nm, 50 mm cell path). Blanks, spiked blanks, matrix spikes, and calibration standards were all prepared using the same chemical matrix as the extracted samples. Matrix spikes were prepared and extracted as samples, however each matrix spike was only used for one extraction step. Acceptable limits for spike recov-

eries were set at 80–120%. The $MgCl_2$ extracts were analysed at a 1:2 dilution to overcome difficulties with colour development. The BD extracts were bubbled with N_2 for 20 min and left overnight in order to drive off any excess hydrogen sulfide and allow further precipitation of elemental sulfur. The extract was then diluted 1:5 with deionized water before analysis to limit interference with antimony and hydrogen sulfide reactions. Antimony and hydrogen sulfide react to form a yellow-green complex, causing high blank readings and poor recovery of low-level spikes. Due to this interference, the detection limit of this extraction was raised to $1·0 \, \mu g \, g^{-1}$ dry weight to ensure accuracy. The extracts for acid extractable P, residual organic P, and TP were neutralized to a pH of 6·5–7·0 with sodium hydroxide to ensure consistency in colour development with the mixed reagent, and diluted 1:4 before analysis.

Aluminum, calcium, iron, magnesium, and manganese were analysed on a Thermal Jerol Ash Model 61 E ICP-AES. The samples were prepared for analysis by closed vessel microwave digestion in an aqua regia solution (EPA method 3052). Carbon (C) and nitrogen (N) were analysed on a CNS elemental analyser. Salinity was measured by centrifuging 20 g of wet sediment, withdrawing the pore-water, and reading the salinity on a refractometer (VISTA A366ATC). Sediment grain size was determined by wet sieving using 1000, 500, 250, 125, and 63 μm sieves (Fisher Scientific). Due to the high organic content of the calcium carbonate sediments, organic matter (% loss on ignition) was determined by combustion at both 450 and 550 °C for 12 h.

Results

Site characteristics

During the time of our sampling, the four NE Florida Bay sites encompassed a broad range of pore-water salinity (Table 1). Pond 1 (P1) and Little Madeira Bay (LMB) were characteristically oligo- to meso-haline, because of their location within the Taylor River slough system (Figure 1), while the other two sites ranged from meso-haline to full-strength seawater at depth. Terrapin Bay (TB) was hyper-saline at 20 cm depth, but had a salinity of 20 in the upper sediment profile. Crocodile Point (CP) exhibited the most stable salinity, probably influenced by direct hydrologic exchange with the open Bay (Figure 1).

North-eastern Florida Bay sediments were found to be predominantly fine-grained, with 59% of the sediment passing through a 63 μm sieve (Figure 3). The second to largest size fraction was sediment greater

TABLE 1. Sediment pore-water salinity, bulk density, organic matter (OM) as percent loss on ignition at 450 and 550 °C, total carbon (TC), total nitrogen (TN), total phosphorus (TP), and TN:TP molar ratios in four sites of north-eastern Florida Bay: Pond 1 (P1), Little Madeira Bay (LMB), Terrapin Bay (TB), and Crocodile Point (CP). Means presented with ± standard error (*N*=4)

Site	Depth (cm)	Salinity (PSU)	Density (g cm^{-3})	OM$_{450°}$ (%)	OM$_{550°}$ (%)	TC (mg g^{-1})	TN (mg g^{-1})	TP (µg g^{-1})	TN:TP
P1	0–5	5·3 ± 0·3	0·27 ± 0·03	11·0 ± 0·3	18·3 ± 0·8	146 ± 1·7	6·08 ± 0·31	369 ± 87	38 ± 3
P1	5–10	8·3 ± 0·4	0·48 ± 0·03	8·2 ± 0·4	14·3 ± 1·1	135 ± 1·8	3·61 ± 0·36	172 ± 45	48 ± 7
P1	10–15	11·5 ± 0·6	0·58 ± 0·02	7·0 ± 0·3	14·3 ± 0·6	130 ± 0·5	2·95 ± 0·33	114 ± 26	58 ± 4
P1	15–20	14·8 ± 0·6	0·55 ± 0·02	7·7 ± 0·2	13·3 ± 0·3	128 ± 1·0	2·76 ± 0·17	106 ± 21	60 ± 7
P1	20–25	16·0 ± 0·4	0·59 ± 0·05	6·6 ± 0·4	13·3 ± 2·0	126 ± 2·0	2·67 ± 0·31	89 ± 16	67 ± 5
LMB	0–5	8·8 ± 0·5	0·58 ± 0·04	6·2 ± 0·7	9·8 ± 0·8	123 ± 0·5	2·35 ± 0·03	106 ± 6	50 ± 3
LMB	5–10	10·3 ± 0·3	0·75 ± 0·08	5·8 ± 0·9	8·5 ± 0·8	121 ± 0·4	1·58 ± 0·17	83 ± 8	44 ± 7
LMB	10–15	16·5 ± 1·3	0·91 ± 0·06	5·3 ± 1·1	8·6 ± 1·1	119 ± 0·6	0·85 ± 0·13	65 ± 11	30 ± 4
LMB	15–20	22·3 ± 1·7	0·99 ± 0·05	4·6 ± 0·7	8·5 ± 0·7	118 ± 1·2	0·80 ± 0·23	50 ± 4	35 ± 9
LMB	20–25	27·5 ± 1·2	1·01 ± 0·03	4·5 ± 0·9	7·2 ± 0·2	116 ± 0·3	1·08 ± 0·09	56 ± 5	43 ± 5
TB	0–5	19·8 ± 1·2	0·48 ± 0·06	7·6 ± 0·8	11·6 ± 1·2	125 ± 0·5	2·89 ± 0·19	124 ± 9	52 ± 2
TB	5–10	19·8 ± 1·9	0·71 ± 0·08	6·8 ± 0·9	10·0 ± 1·5	119 ± 0·9	3·00 ± 0·67	87 ± 17	77 ± 12
TB	10–15	28·3 ± 1·5	0·82 ± 0·04	6·1 ± 0·9	8·7 ± 1·2	117 ± 0·3	1·70 ± 0·19	67 ± 10	58 ± 6
TB	15–20	34·8 ± 1·4	0·91 ± 0·01	5·9 ± 0·8	9·0 ± 0·7	117 ± 1·3	1·30 ± 0·17	65 ± 5	45 ± 7
TB	20–25	37·3 ± 1·0	0·96 ± 0·05	5·9 ± 1·3	9·1 ± 0·4	115 ± 0·3	1·08 ± 0·12	57 ± 7	43 ± 4
CP	0–5	21·0 ± 0·4	0·44 ± 0·05	9·0 ± 0·9	15·2 ± 2·8	123 ± 2·3	4·65 ± 0·50	143 ± 8	74 ± 12
CP	5–10	21·8 ± 0·5	0·58 ± 0·05	8·6 ± 1·1	14·6 ± 1·3	124 ± 1·0	3·86 ± 0·27	164 ± 16	52 ± 2
CP	10–15	23·3 ± 0·8	0·65 ± 0·02	8·5 ± 0·3	14·2 ± 1·2	121 ± 1·3	2·98 ± 0·23	119 ± 8	56 ± 5
CP	15–20	26·0 ± 0·4	0·74 ± 0·02	8·0 ± 1·0	13·1 ± 2·2	119 ± 0·6	2·72 ± 0·15	120 ± 6	51 ± 5
CP	20–25	28·0 ± 1·2	0·76 ± 0·04	7·1 ± 0·6	12·1 ± 1·1	117 ± 0·6	2·48 ± 0·14	117 ± 12	47 ± 2

than 1000 µm, consisting mostly of shell fragments and organic debris. Sediment size fractions were similar among sites and no significant relationship was
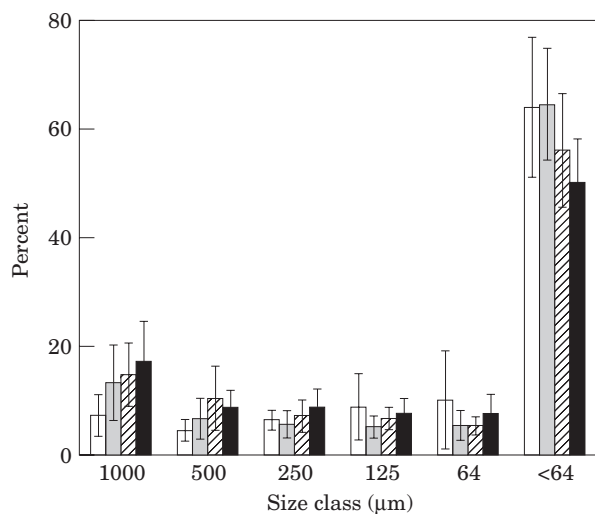

FIGURE 3. Sediment grain size distribution for the four north-eastern Florida Bay sites: Pond1 (P1), Little Madeira Bay (LMB), Terrapin Bay (TB), and Crocodile Point (CP). Means averaged across depth are shown with ± standard deviations (*N*=4). □ P1; ▨ LMB; ▨ TB; ■ CP.

found between size fractions and depth. The fine-grained, highly compacted nature of these marine sediments is also evident in the relatively high bulk densities found at all four sites in NE Florida Bay (Table 1). Bulk densities ranged from 0·27 ± 0·03 g cm^{-3} in the upper layers to 1·01 ± 0·03 g cm^{-3} at 20–25 cm in depth. Patterns of bulk density followed a reverse trend to percent organic matter (Table 1).

All of the sites are heavily influenced by either *in situ* and/or allochthonous organic matter deposition, because both bayward (CP) and landward (P1) sites exhibit similarly high organic content. Both LMB and TB are characterized by small stature seagrasses, *Thalassia* intermixed with *Halodule*, perhaps accounting for slightly lower organic matter at these two sites. High organics in P1 may be influenced by rapid seasonal turnover of SAVs (*Chara*-dominated shifts to *Ruppia*-dominated) at this site, driven by dynamic seasonal salinity shifts from 2 to 30 PSU (Koch & Solomon, in prep.).

Chemical composition

Metals. Calcium composed 20 to 30% of the sediment by mass, and was similar among all of the NE Florida

TABLE 2. Total sediment calcium (Ca), aluminum (Al), iron (Fe), and magnesium (Mg) concentrations and the TP to iron+aluminum ratio from four sites in north-eastern Florida Bay ($N=4 \pm$ SE)

Site	Depth (cm)	Ca (mg g^{-1})	Al (mg g^{-1})	Fe (mg g^{-1})	Mg (mg g^{-1})	P:(Fe+Al)
P1	0–5	230 ± 22	8·8 ± 0·4	10·5 ± 0·7	8·1 ± 0·6	23·2
P1	5–10	201 ± 5	8·9 ± 0·1	8·4 ± 0·3	8·4 ± 0·2	11·6
P1	10–15	214 ± 15	9·7 ± 0·1	8·6 ± 0·5	8·5 ± 0·6	7·2
P1	15–20	261 ± 18	10·0 ± 0·5	11·8 ± 0·6	7·4 ± 0·8	5·9
P1	20–25	301 ± 19	8·6 ± 1·3	11·0 ± 1·1	7·1 ± 1·1	5·6
LMB	0–5	227 ± 4	6·6 ± 0·3	5·2 ± 0·2	10·1 ± 0·4	10·1
LMB	5–10	246 ± 14	6·3 ± 0·4	5·3 ± 0·3	10·2 ± 1·0	8·2
LMB	10–15	299 ± 11	6·1 ± 0·2	5·8 ± 0·1	10·6 ± 0·4	6·4
LMB	15–20	257 ± 30	5·7 ± 0·8	5·0 ± 0·6	8·9 ± 0·8	5·4
LMB	20–25	288 ± 19	5·7 ± 0·7	5·6 ± 0·4	11·0 ± 0·5	5·8
TB	0–5	242 ± 20	4·9 ± 0·2	3·6 ± 0·3	10·1 ± 0·2	16·3
TB	5–10	253 ± 28	5·3 ± 0·8	3·9 ± 0·5	10·3 ± 0·6	10·5
TB	10–15	230 ± 24	3·3 ± 0·3	2·7 ± 0·3	8·7 ± 0·9	12·7
TB	15–20	248 ± 21	4·9 ± 0·6	3·8 ± 0·3	13·0 ± 3·3	8·4
TB	20–25	247 ± 21	5·6 ± 0·3	3·9 ± 0·3	12·2 ± 0·3	6·6
CP	0–5	218 ± 21	5·8 ± 0·6	3·3 ± 0·4	9·8 ± 0·3	16·8
CP	5–10	217 ± 29	5·1 ± 0·6	3·2 ± 0·3	9·7 ± 0·5	21·5
CP	10–15	214 ± 4	5·8 ± 0·2	3·4 ± 0·1	9·3 ± 0·9	13·9
CP	15–20	234 ± 12	9·0 ± 0·5	5·3 ± 0·4	9·9 ± 0·2	9·0
CP	20–25	231 ± 16	8·2 ± 0·8	4·6 ± 0·4	9·2 ± 0·8	9·8

Bay sites. Aluminum, iron, and magnesium concentrations were one- to two-orders of magnitude lower than calcium (Table 2). P1 had the highest mean concentration of aluminum and iron, while LMB, the receiving basin for P1 (Figure 1), had the second highest concentrations of trace metals. Iron concentrations did not show any significant trend with depth at any of our sites (Table 2). However, the P:(Fe+Al) ratios were highest in the surface sediments, and decreased with depth at each site. Sediment magnesium concentrations were higher than iron or aluminum with the exception of P1, where all trace metals exhibited similar ranges. Manganese concentrations in the sediment were below detectable limits ($<0·20$ g kg^{-1}) at all sites (data not shown).

Total phosphorus and nitrogen. In general, TP concentrations in the sediment were low in NE Florida Bay (Table 1), and on a volume basis ranged between 50 and 100 µg cm^{-3}. The surface sediments (0–5 cm) in P1 had the highest TP concentration among sites, while below the surface P1 and CP had similar TP levels, approximately 2-fold higher than those found in LMB and TB (Table 1). Patterns of TN and TP were similar among sites; the highest values found in P1 and CP compared to LMB and TB (Table 1).

These same patterns, however, were not evident in the TN:TP elemental ratios, where P1, TB, and CP had similar ranges, while LMB ratios were consistently lower.

Phosphorus fractions. Calcium-bound P (HCl-extractable P) represented the largest fraction of the solid-phase pool, including both inorganic and organic P (Figure 4). On average, approximately 70% of the HCl extractable P was in the inorganic form, while organic P accounted for the other 30% (Table 3). HCl-extractable P decreased significantly from 152 to 75 µg g^{-1} from 0–5 to 5–10 cm depth in P1, but in general HCl-extractable P showed relatively stable concentrations below 15 cm at all sites (Figure 4).

Residual organic P composed the second largest fraction of extracted P and, similar to the HCl-extractable pool, remained relatively stable with depth (Figure 4, Table 3). Total organic P, derived by adding the residual pool with the organic fractions from the other extractions, averaged 60% of the TP with the residual organic fraction alone making up 42%.

The high percentage of P in the HCl-extractable and residual organic fractions is contrasted by that in the BD-extractable and exchangeable pools.
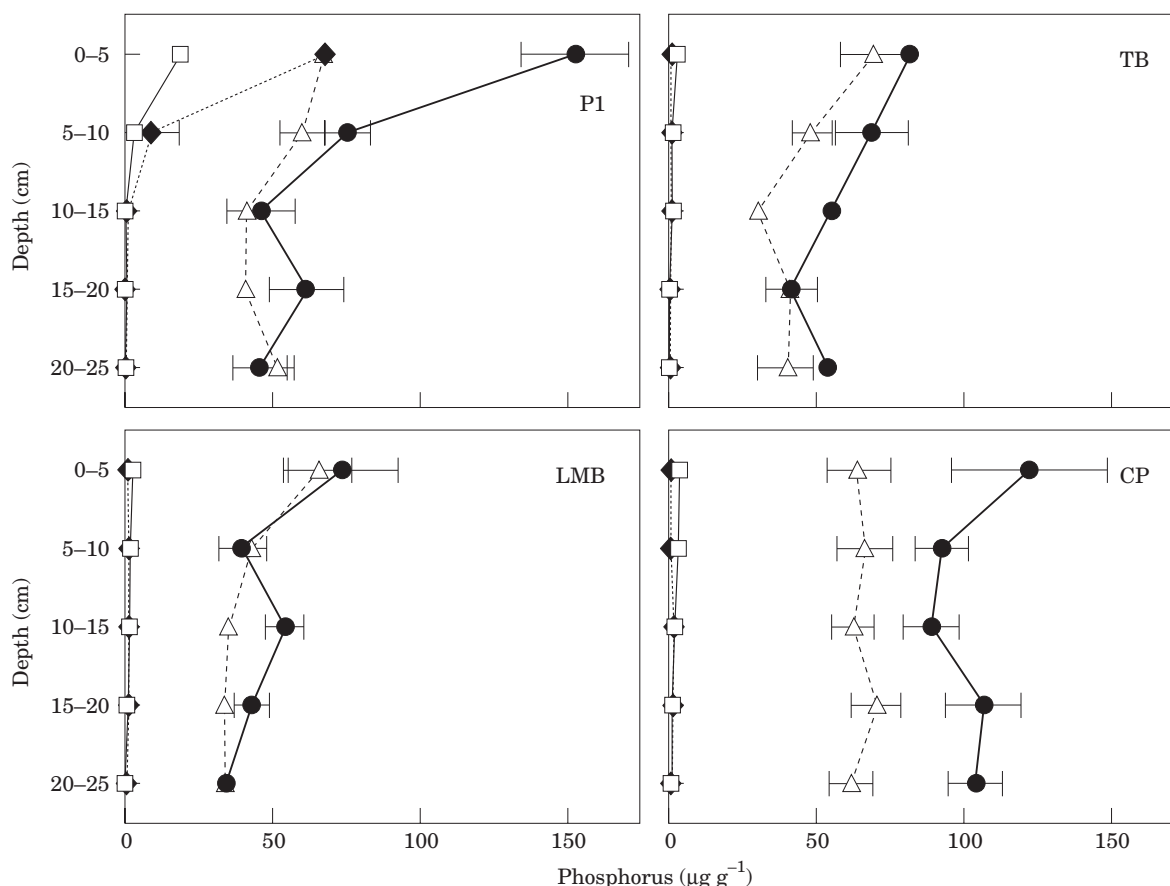
FIGURE 4. Sediment phosphorus (inorganic+organic) fractions: exchangeable (magnesium chloride extractable, MgCl₂), reducible (bicarbonate-dithionite extractable, BD), acid extractable (hydrochloric acid, HCl), and residual organic phosphorus (residual) as a function of depth from north-eastern Florida Bay sites: Pond 1 (P1), Little Madeira Bay (LMB), Terrapin Bay (TB), and Crocodile Point (CP). Means presented with ± standard errors (N=4). –□– MgCl₂; – –◆– – BD; –●– HC; – –△– – Residual.

BD-extractable P was 68 μg g^{-1} at 0–5 cm in P1 and 10 μg g^{-1} at 5–10 cm (Table 3, Figure 4), below which the concentrations were below detectable limits (<1·0 μg g^{-1}). BD-extractable P was below detectable limits at all depths in the other sites. Approximately 60% of the P extracted by BD in P1 was organic. The presence of BD-extractable P in P1 may be linked to several factors, all of which are unique to surface sediments of P1. These sediments had the highest levels of organic material, the highest concentrations of iron and aluminum, and the highest ratio of P:(Fe+Al) (Tables 1, 2).

P1 also had the highest levels of the exchangeable P pool in the 0–5 cm depth interval (19 ± 1·9 μg g^{-1}), five times that of the other sites (Table 3), and continued to be higher at each depth compared to the other sites. Exchangeable P accounted for only 0·1 to 7·0% of the total extractable P. Of this exchangeable P, approximately 10% was labile organic P, with the

exception of P1 at the surface where it accounted for 20%.

Discussion

Calcium-bound P dominates the solid-phase P pools of NE Florida Bay sediment, accounting for 96% of inorganic P and 56% of TP. This acid-extractable pool (34–151 μg P g^{-1}) is within the range reported for carbonate sediments in Bailey's Bay, Bermuda (58–129 μg P g^{-1}, Table 4) with similarly low TP concentrations (100–200 μg P g^{-1}), with the exception of TP in surface sediments at P1 (369 μg P g^{-1}). Interestingly, while the solid-phase calcium-bound P pools are similar between the two sites, the physical characteristics of the sediments differ significantly. For example, 75% of the sediment in Outer Bailey's Bay Bermuda is >210 μm and <2% is <52 μm (McGlathery *et al.*, 1994), while in comparison, 59%

TABLE 3. Sediment phosphorus fractions: exchangeable inorganic ($MgCl_i$) and organic ($MgCl_o$), reducible inorganic (BD_i) and organic (BD_o), acid extractable inorganic (HCl_i) and organic (HCl_o), and residual organic phosphorus (Res_o). Extractions based on the procedure outlined in Figure 2 ($N=4 \pm SE$)

Site	Depth (cm)	$MgCl_i$ ($\mu g\ g^{-1}$)	$MgCl_o$ ($\mu g\ g^{-1}$)	BD_i ($\mu g\ g^{-1}$)	BD_o ($\mu g\ g^{-1}$)	HCl_i ($\mu g\ g^{-1}$)	HCl_o ($\mu g\ g^{-1}$)	Res_o ($\mu g\ g^{-1}$)
P1	0–5	$15·55 \pm 2·24$	$3·36 \pm 1·66$	$28·2 \pm 1·1$	$39·4 \pm 6·6$	$108·4 \pm 14·6$	$43·3 \pm 6·2$	$67·0 \pm 2·7$
P1	5–10	$3·66 \pm 1·21$	$0·16 \pm 0·24$	$1·1 \pm 0·0$	$8·9 \pm 8·6$	$58·7 \pm 5·4$	$16·3 \pm 2·8$	$59·7 \pm 7·7$
P1	10–15	$0·70 \pm 0·16$	$<0·10$	$<1·0$	$<1·0$	$41·6 \pm 5·4$	$7·0 \pm 6·0$	$41·3 \pm 2·7$
P1	15–20	$0·58 \pm 0·11$	$<0·10$	$<1·0$	$<1·0$	$36·9 \pm 4·1$	$24·2 \pm 12·4$	$40·0 \pm 3·1$
P1	20–25	$0·70 \pm 0·19$	$<0·10$	$<1·0$	$<1·0$	$35·6 \pm 3·1$	$9·6 \pm 6·3$	$51·2 \pm 5·8$
LMB	0–5	$2·32 \pm 0·35$	$0·14 \pm 0·04$	$<1·0$	$<1·0$	$37·7 \pm 1·5$	$36·0 \pm 18·8$	$65·2 \pm 11·5$
LMB	5–10	$1·07 \pm 0·44$	$0·16 \pm 0·16$	$<1·0$	$<1·0$	$32·5 \pm 2·9$	$8·1 \pm 5·2$	$42·3 \pm 4·3$
LMB	10–15	$0·64 \pm 0·37$	$0·15 \pm 0·16$	$<1·0$	$<1·0$	$32·9 \pm 4·6$	$20·9 \pm 3·4$	$34·6 \pm 3·3$
LMB	15–20	$0·23 \pm 0·01$	$<0·10$	$<1·0$	$<1·0$	$29·5 \pm 2·7$	$13·0 \pm 3·4$	$33·1 \pm 0·6$
LMB	20–25	$0·11 \pm 0·00$	$<0·10$	$<1·0$	$<1·0$	$27·1 \pm 1·9$	$7·2 \pm 2·0$	$33·1 \pm 1·6$
TB	0–5	$3·40 \pm 0·67$	$0·42 \pm 0·18$	$<1·0$	$<1·0$	$55·4 \pm 3·0$	$26·2 \pm 1·8$	$69·6 \pm 11·7$
TB	5–10	$1·37 \pm 0·52$	$0·11 \pm 0·03$	$<1·0$	$<1·0$	$49·6 \pm 9·4$	$19·3 \pm 3·3$	$48·5 \pm 6·9$
TB	10–15	$0·62 \pm 0·52$	$0·16 \pm 0·20$	$<1·0$	$<1·0$	$35·1 \pm 2·5$	$19·7 \pm 0·8$	$29·8 \pm 3·3$
TB	15–20	$0·44 \pm 0·04$	$<0·10$	$<1·0$	$<1·0$	$34·2 \pm 2·7$	$7·7 \pm 5·3$	$40·9 \pm 3·3$
TB	20–25	$0·11 \pm 0·16$	$<0·10$	$<1·0$	$<1·0$	$32·1 \pm 4·4$	$22·1 \pm 3·8$	$37·8 \pm 9·5$
CP	0–5	$2·22 \pm 0·61$	$0·60 \pm 0·42$	$<1·0$	$<1·0$	$63·1 \pm 4·1$	$59·7 \pm 22·7$	$64·2 \pm 10·8$
CP	5–10	$2·18 \pm 0·25$	$0·39 \pm 0·16$	$<1·0$	$<1·0$	$64·8 \pm 5·4$	$28·2 \pm 9·1$	$66·5 \pm 9·8$
CP	10–15	$1·35 \pm 0·44$	$0·15 \pm 0·07$	$<1·0$	$<1·0$	$62·3 \pm 4·2$	$27·0 \pm 9·5$	$62·3 \pm 7·5$
CP	15–20	$0·48 \pm 0·04$	$<0·10$	$<1·0$	$<1·0$	$73·6 \pm 5·2$	$33·6 \pm 7·6$	$70·5 \pm 8·4$
CP	20–25	$0·32 \pm 0·07$	$<0·10$	$<1·0$	$<1·0$	$73·0 \pm 5·7$	$31·1 \pm 5·0$	$61·7 \pm 7·4$

of the sediment from NE Florida Bay is <63 μm. The small grain size and potentially high reactive surface area of NE Florida Bay sediments may control the large component of inorganic P stored in the calcium carbonate fraction and contribute to the very low pore-water inorganic P levels observed at these sites (<0·1 μM; Koch & Solomon in prep). However, low inorganic P in the pore waters were also reported at non-eutrophic Bermuda sites (Outer Bailey's Bay and North Channel sites; <0·5 μM) with large grains (McGlathery et al., 1994). Also, in three Bahamas seagrass sites dominated by large grains (80% >210 μm and <13% <52 μm), Morse et al. (1987) reported pore-water inorganic P levels below or close to detection limits (<0·05 to 0·38 μM). Further, based on their adsorption-desorption experiments, the Bahamas sediments were able to sorb 100% of the inorganic P from a 85 μM solution within 6 h.

Although theoretically and experimentally there is a relationship between increasing P adsorptive capacity and decreasing grain size (Chave & Schmalz, 1966; Stumm & Leckie, 1970; Suess, 1970, 1973; Walter & Morse, 1984), assuming greater adsorptive sites, this relationship has shown conflicting evidence in the field. McGlathery et al. (1994) and Erftemeijer and Middelburg (1993) observed decreasing solid-phase inorganic P with increasing grain size in Bailey's Bay,

Bermuda and South Sulawesi, Indonesia, respectively. But McGlathery et al. (1994) were unable to explain, based on grain size, differences in the P adsorption capacity between their two Bermuda sites, as well as lower P adsorptive rates compared to experiments from the Bahamas (Morse et al., 1987; Short et al., 1990). Additionally, Suess (1973) found an exponential increase in P adsorption with decreasing grain size only in the <2–10 μm range, and no correlation between surface area and TP for grains >10 μm in carbonate sediments from Fanning Island, Central Pacific. Although our smallest sieve was 63 μm, sediments from NE Florida Bay are a very fine silt and probably fall within the lower range reported by Suess (1973) which have a high P adsorptive capacity.

One assumption in relating Ca-bound P with grain size is that the size of a particle is related to the reactive surface area, regardless of the fact that these areas can be influenced by physical and chemical factors. Many biogenic carbonates have complex physical structures that would underestimate surface area (Walter & Morse, 1984). This is likely to explain higher adsorption rates for large size particles (McGlathery et al., 1994), but not explain why a larger fraction of P is not stored as Ca-bound in very fine carbonate sediments, such as in NE Florida Bay, compared to larger grain sediments from Bermuda.

TABLE 4. Sediment phosphorus fractions (inorganic+organic) compared among marine carbonate, clastic, and organic sediments; extractants are the same as in this study unless footnoted

Site	Depth (cm)	Exchangeable ($\mu g\ g^{-1}$)	Reducible ($\mu g\ g^{-1}$)	Acid ext. ($\mu g\ g^{-1}$)	Residual org. P. ($\mu g\ g^{-1}$)	TP ($\mu g\ g^{-1}$)	Source
Marine—carbonate							
Pond 1, Florida Bay	0–5	19	68	151	67	369	(2)
Little Madeira, Florida Bay	0–5	2·5	<1·0	74	28	106	(2)
Terrapin Bay, Florida Bay	0–5	3·8	<1·0	82	70	124	(2)
Crocodile Point, Florida Bay	0–5	2·8	<1·0	123	64	143	(2)
Inner Bailey's Bay, Bermuda	0–25	6·2	28	129[a]	4·6	168	(1)
Outer Bailey's Bay, Bermuda	0–25	2·2	14	64[a]	2·2	82	(1)
North Channel, Bermuda	0–25	3·1	19	58[a]	2·2	82	(1)
Pond 1, Florida Bay	20–25	0·7	<1·0	45	51	89	(2)
Little Madeira, Florida Bay	20–25	0·1	<1·0	34	20	56	(2)
Terrapin Bay, Florida Bay	20–25	0·1	<1·0	54	38	57	(2)
Crocodile Point, Florida Bay	20–25	0·3	<1·0	104	62	117	(2)
Marine—clastic							
Gulf of St. Lawrence	0–0·4	34[b]	694[c]	793	105	1625	(3)
Aarhus Bay, Denmark	0–7·5	186[e]	1020	480[f]	155	1874	(5)
Mississippi Delta	0–2	48	182[c]	206[d]	169	605	(4)
Long Island Sound	0–10	35	BDL[c]★	305[d]	96	436	(4)
Mississippi Delta	24–26	23	141[c]	211[d]	117	586	(4)
Marine—organic							
South-east Everglades, Florida	0–10	0·5[e]	15[g]	16	24[h]	54	(6)
Lower Shark River, Florida	0–10	1·7[e]	554[g]	280	504[h]	1340	(6)
South-east Everglades, Florida	10–30	0·6[e]	24[g]	15	28[h]	68	(6)
Lower Shark River, Florida	10–30	1·7[e]	520[g]	354	527[h]	1473	(6)

[a]NaOH+Acetate+HCl, [b]Ammonium Acetate, [c]CBD (Citrate+BD), [d]Acetate+HCl, [e]NaCl, [f]NaOH+HCl, [g]NaHCO$_3$+NaOH, [h]K$_2$S$_2$O$_8$; (1) Jensen *et al.*, 1998; (2) this study; (3) Sundby *et al.*, 1992; (4) Ruttenberg and Berner, 1993; (5) Jensen *et al.*, 1995; (6) Koch, 1997; ★below detectable limits.

High organic matter in NE Florida Bay sediments may contribute to the fact that only 38% of the TP was in the inorganic Ca-bound P fraction. Without residual organic P, the HCl fraction accounts for 92% of the TP. In addition to this straight-forward dilution effect by residual organic P, inorganic P may have also been in competition with reactive organic surfaces on the carbonate particles (Suess, 1970; Krom & Berner, 1980; Morse, 1986).

Organic P accounted for 31% of the acid-extractable P in NE Florida Bay sediments, a slightly higher percentage than observed in Bermuda, 20% (Jensen *et al.*, 1998), and Davies reef, Australia, 22% (Entsch *et al.*, 1983). Jensen *et al.* (1998) presumed that the organic P extracted in their calcium-bound fraction and those of Entsch *et al.* (1983) originated primarily from biogenic CaCO$_3$ grains. The higher fraction of organic P in our acid-extractable fraction may also be attributable to biogenic sources. Alternatively, this organic P originated from non-biogenic organic surface coatings on the carbonate particles themselves, because of the high DOC concentrations in the surface waters of NE Florida Bay (900 to 1400 μM; Sutula, 1999, Davis *et al.* in review). Dissolved organic P levels in surface waters, albiet low, are also 10 times greater (0·25–0·50 μM) than inorganic P (0·01–0·1 μM) in this region of the Bay (Sutula, 1999; Davis *et al.* in review). In support of this idea, Suess (1970) identified a 3–4% increase in DOC sorption onto carbonates in organic-rich seawater (1542 *vs.* 225 μM DOC), along with greater organic P (phospholipid) adsorption. Organics associated with carbonates also increased as a function of grain size, greater sorption on fine (0·90 mg C g^{-1}) *vs.* coarse (0·21 mg C g^{-1}) grain particles, although the percentages of removal based on initial concentrations remained relatively constant. Although our bay–mangrove ecotone sites have relatively higher organic matter and smaller grain size that those studied by Jensen *et al.* (1998), the acid-extractable organic P pool is remarkably consistent between the two sites (20–30%). By comparison, the residual organic pool was found to be significantly different (Table 4).

In fact, the concentrations of residual organic P in our NE Florida Bay sites are more comparable to the

residual organic P content of clastic sediments with strong terrigenous influences, such as Long Island Sound and the Mississippi Delta (Table 4). The residual organic P of NE Florida Bay accounted for 42% of the TP compared to <2% in Bermuda carbonate sediments (Jensen *et al.*, 1998). Low residual P to TP ratios were also observed in highly eutrophic clastic sediments (<15%, Table 4), probably a function of the labile nature of the organic C being deposited. The ratio of residual organic P fractions to TP are comparable, however, to mangrove sites in the south-eastern Everglades dwarf mangrove forest (41–44%), just landward of our NE Florida Bay sites, and mangrove forests along the South Florida west coast (36–38%, Table 4; Koch, 1997). Thus, mangrove detritus along with seagrasses may play a key role in this recalcitrant P fraction. Further, the consistency of this large organic pool with depth, with the exception of the top 0–5 cm, provides evidence that these organics are not being remineralized through diagenetic processes, perhaps because they were already in a refractive state upon deposition, and/or decomposition is limited. These results suggest the importance of recalcitrant organic matter in sequestering P for long-term storage in highly organic tropical estuaries.

While calcium-bound and residual organic P are important long-term P reservoirs in NE Florida Bay, the reducible P fraction is close to or below detectable levels. Pond 1 was the only site where we found detectable levels of BD extractable P. The limited role of iron-bound P in NE Florida Bay can be explained by several factors. (1) Although total Fe concentrations in NE Florida Bay are high (2·7 to 12 mg g^{-1}), relative to carbonate sediments in the Bahamas (0·03 to 0·07 mg g^{-1}; Morse *et al.*, 1985), much of the iron may be complexed with organics, and not available for sequestering inorganic P. Low reactive iron levels have been found in Florida Bay sediments with little to no Eh-dependent control on P release (Randolph Chambers, pers. comm.). (2) The second factor that may contribute to low Fe-bound P in NE Florida Bay sediments is sulfide. Under anaerobic conditions, high sulfate availability reduce the P binding capacity of aquatic sediments (Caraco *et al.*, 1989). Caraco *et al.* (1989) suggest that sulfides from sulfate reduction bind iron and subsequently limit the formation of iron oxides at the surface and ferrous phosphates at depth. Because NE Florida Bay sediments are relatively low in reactive iron (Randolph Chambers, pers. comm.), and total Fe compared to temperate estuaries (34–92 mg g^{-1}; Sundareshwar & Morris, 1999) the sequestering of iron by sulfide may be important in controlling the Fe-bound solid-phase

P pool. The location of our sites, close to the mangrove fringe with high organic inputs, may accelerate this sequestering process by providing organic substrates for sulfate reducers. (3) Caraco *et al.* (1989) and Sundareshwar and Morris (1999) proposed that pH as well as salinity influence the binding capacity of P onto iron oxides. Alkaline conditions, promoted by sulfate reduction and/or increased salinity, shift the charge of Fe-oxides from positive to negative (Stumm & Morgan, 1981) reducing P-sorption. Annual (January 1997–1998) pH values range from 7·8 to 8·6 in the overlying surface waters (0–10 cm above sediment surface) and 7·0 to 7·8 in the sediment (0–30 cm depth) at all of our NE Florida Bay sites (Koch & Solomon, in prep.), indicating a neutral to basic sedimentary environment for sorption, precipitation, and diagenetic processes.

An increase in Cl^- and SO_4^{2-} ions in seawater can also increase competition for reactive sites on Fe-oxides, thereby decreasing exchangeable sites for P (Stumm & Morgan, 1981). We did find our lowest salinity site (P1) corresponded with the highest Fe-bound P and MgCl exchangeable P. However, the P:Fe+Al ratio, a relative indicator of metal sorption sites (Sundareshwar & Morris, 1999), did not follow any trend with BD-extractable P at any of our other sites with the exception of P1, or across depths. Thus, inorganic Fe appears to play a minor role in P storage in NE Florida Bay, as has been observed in other tropical marine carbonate systems. Even in Bermuda where a detectable level of P was extracted from the sediment with BD (Table 4), the extracted P was thought to be Ca-bound in Outer Bay and North Channel sites, because no Fe was found in the leachate (Jensen *et al*, 1998). Jensen *et al.* (1998) also found the majority of Fe to be leached in the acid extractions (Fe-mono-sulfides) and residual fraction (pyrite).

Comparing sediment P-sorption capacity and pore-water dissolved reactive P (DRP) along an estuarine gradient, Sundareshwar and Morris (1999) found that as salinity increased from fresh water to marine sites, sorbed P decreased while pore-water P increased. This paradism for temperate estuaries may not be the case in tropical carbonate estuaries, because marine carbonate sediments, both fine and some coarse grained, maintain adsorptive sites that sequester inorganic P. The highly efficient chemisorption reaction, along with potential organic surfaces, and the sequestering of P into recalcitrant organic pools, maintain extremely low pore-water P levels across the NE Florida Bay estuarine gradient from the Everglades freshwater marsh-mangrove ecotone to the higher salinity coastal ponds and bays (<0·2 μM, Koch, 1997; Koch & Solomon in prep). Thus, the

switch from a P to N-limited system, proposed by Sundareshwar and Morris (1999) to be a function of sediment P-sorption potential in temperate estuaries, is short-circuited, and may account for autotrophic P-limitation in NE Florida Bay.

Acknowledgements

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