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Variable rates of phosphate uptake by shallow marine carbonate sediments: Mechanisms and ecological significance

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Abstract. We determined phosphate uptake by calcareous sediments at two locations within a shallow lagoon in Bermuda that varied in trophic status, with one site being mesotrophic and the other being more eutrophic. Phosphate adsorption over a six hour period was significantly faster in sediments from the mesotrophic site. Uptake at both sites was significantly less than that reported for a similar experiment on calcareous sediments in an oligotrophic lagoon in the Bahamas. The difference in phosphorus adsorption between our sites did not appear to be related to sediment characteristics often cited as important, such as differences in surface area (as inferred from grain size distributions), total organic matter content, or iron content. However, the sediment total phosphorus contents were inversely related to phosphorus uptake at our sites in Bermuda, and at the previously studied Bahamas site.

We hypothesize that phosphate uptake in these calcareous sediments is a multi-step process, as previously described for fluvial sediments or pure calcium carbonate solids, with rapid initial surface chemisorption followed by a slower incorporation into the carbonate solid-phase matrix. Accordingly, sediments already richer in solid phase phosphorus take up additional phosphate more slowly since the slower incorporation of surface-adsorbed phosphate into the carbonate matrix limits the rate of renewal of surface-reactive adsorption sites.

Although carbonate sediments are a sink for phosphate, and thereby reduce the availability of phosphorus for benthic macrophytes and phytoplankton in the shallow overlying water, phosphate uptake by these sediments appears to decrease along a gradient from oligotrophic to eutrophic sites. If our result is general, it implies a positive feedback in phosphorus availability, with a proportionately greater percentage of phosphorus loading being biologically available longer as phosphorus loading increases. This pattern is supported by the significantly higher tissue phosphorus content of the seagrass, *Thalassia testudinum*, collected from the eutrophic inner bay site. Over time, this effect may tend to cause a shift from phosphorus to nitrogen limitation in some calcareous marine environments.

Introduction

Many tropical and semitropical lagoons and seagrass beds are considered to be phosphorus limited (Smith 1984; Smith & Atkinson 1984; Short et al. 1985, 1990; Howarth 1988; Fourqurean et al. 1992a). Evidence comes from comparative budgets for nitrogen and phosphorus at the scale of the ecosystem (Smith 1984; Smith & Atkinson 1984) and from nutrient addition experiments with seagrasses (Short et al. 1985, 1990) and with macroalgae (Littler et al. 1988; Lapointe & O'Connell 1989). A common explanation for phosphorus limitation in tropical coastal systems is the high affinity for phosphorus on the calcium carbonate sediments which often dominate these systems, resulting in low phosphate concentrations compared to ammonium in sediment pore waters (Berner 1974; Morse et al. 1985, 1987; Short et al. 1985, 1990).

Ratios of dissolved inorganic nitrogen to phosphorus in tropical and subtropical carbonate sediments do tend to be high, with average values for a variety of sediments in the Bahamas and Bermuda reported in the range of 40 to 50 (Gaudette & Lyons 1980; Short et al. 1985; Morse et al. 1987) and for different sediments in Florida Bay as high as 90 to 900 (Fourqurean et al. 1992a). However, considerably lower ratios are found in some carbonate sediments, with values reported as low as 3.5 (Gaudette & Lyons 1980) to 5 (Morse et al. 1987). And while dissolved phosphate concentrations are typically low in many tropical and subtropical carbonate sediments, often 0.1 μM or less (Morse et al. 1987; Fourqurean et al. 1992a), concentrations can also be quite high compared to temperate clastic sediments. Depth-averaged values for pore water phosphate reported in carbonate sediments underlying seagrass beds in Bermuda, the Bahamas, and Florida Bay are in the range of 2 to 3 μM (Berner 1974; Gaudette & Lyons 1980; Short et al. 1985; Fourqurean et al. 1992a), and as high as 15 μM in seagrass-vegetated carbonate sediments in Indonesia (Erftemeijer & Middleburg 1993) and 25 μM in some unvegetated carbonate sediments near mangroves in Bermuda (Gaudette & Lyons 1980).

While many experiments with tropical seagrasses and macroalgae have found growth limited by phosphorus, some experiments have found nitrogen-limited growth of macroalgae in tropical and subtropical carbonate systems (Lapointe et al. 1987; McGlathery 1992a; McGlathery et al. 1992). McGlathery et al. (1992) suggested that such nitrogen limitation may result in part from a lower capacity of some carbonate sediments to adsorb phosphate. Previous experiments on rates of phosphate uptake by carbonate sediments found from 86% (Short et al. 1990) to 100% (Morse et al. 1987) of added phosphate taken up from solution within 6 hours. However, phosphate interactions with carbonate mineral surfaces potentially can be affected by a variety of sediment chemical parameters, including abundance of organic matter (Suess 1973; Krom & Berner 1980; Morse 1986), abundance of iron (Sherwood et al. 1987), and sediment surface area (Morse 1986). We hypothesized that these or other factors related to the solid-phase chemistry of the sediments may lead to a lower uptake of phosphate by some carbonate sediments, and an increase in the availability of phosphate for benthic macrophytes.

To test this hypothesis, we measured the uptake of phosphate over time by sediments at two sites in Bailey's Bay, Bermuda, one underlying mesotrophic waters and one underlying eutrophic waters. The mesotrophic site is the location where we earlier found nitrogen limitation of macroalgal growth (McGlathery et al. 1992). We followed the approach of Morse et al. (1987) in their study of phosphate uptake by sediments from an oligotrophic site in the Bahamas. We also characterized chemical and physical aspects of our sediments to determine if parameters such as phosphorus content, organic matter, iron, or grain size were related to differences in rates of phosphate uptake. Finally, we measured the phosphorus content of the dominant seagrass at the sites, *Thalassia testudinum*, to determine if differences in sediment phosphate adsorption were associated with differences in the availability of phosphate to benthic macrophytes.

Methods

Site description

Bailey's Bay is a shallow (1–3 m depth) lagoon of some 2×10^4 m^2 on Bermuda's north shore. Within the bay there is a nutrient gradient extending from the shore seaward, presumably resulting from groundwater inputs (Fig. 1; McGlathery 1992a). At the time of our experiment in August, 1990, extensive monospecific seagrass beds (*T. testudinum*, *Syringodium filiforme*, *Halodule wrightii*) and mixed stands of seagrass and green rhizophytic macroalgae (*Penicillus* spp., *Halimeda* spp.) occurred throughout the bay, except for the deeper, dredged center. The filamentous red macroalga, *Spyridea hypnoides*, dominated the high-nutrient inner bay, but was absent from the outer bay (McGlathery 1992b).

Phosphate adsorption experiment

We collected triplicate 30 cm cores from vegetated sediments of mixed seagrass and macroalgae in the inner (eutrophic) and outer (mesotrophic) parts of Bailey's Bay. The cores were transported to the laboratory and extruded, and the section from 2.5–7.5 cm depth was homogenized. This depth represented the zone where both macroalgal rhizoid filaments and seagrass roots access sediment pore water nutrients. All sediment cores were anoxic at this depth interval and smelled strongly of hydrogen sulfide.

We followed the general procedure of Morse et al. (1987) to assess the affinity of the carbonate sediments to adsorb phosphate. Time-series replicates were set up by placing approximately 4.5 g wet weight (3 cc) of the homogenized sediment from each core into 125 ml filtered (0.45 μm) seawater in Erlenmeyer flasks. To start the adsorption experiments, we spiked each flask with a KH_2PO_4 standard to achieve a starting concentration of 50 μM. Phosphorus adsorption was calculated from the disappearance of phosphate from the incubation water over time; triplicate flasks were sampled destruc-

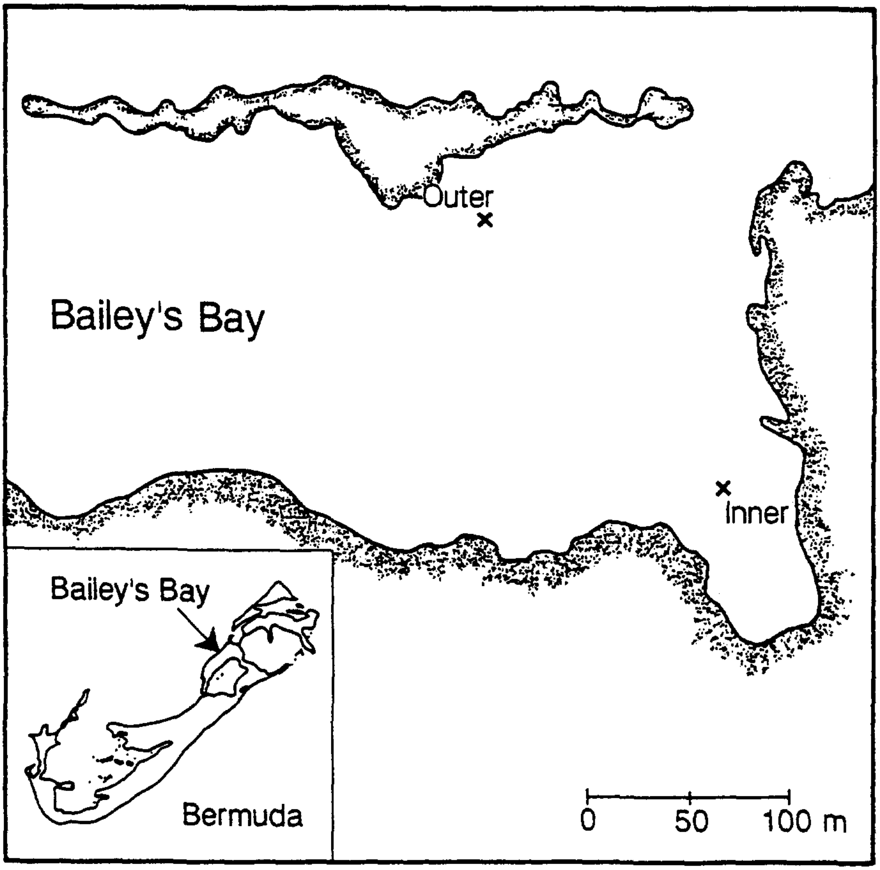

Fig. 1. Map of Bailey's Bay, Bermuda. Sediment cores were collected in vegetated sediments in the eutrophic inner bay and the mesotrophic outer bay adjacent to the island. Sites are marked by 'x's'.

tively at each of 5 time intervals (1, 5, 10, 30, and 360 min). During the incubation periods, samples were mixed vigorously every 2.5 min to keep the sediment in suspension; the 6 hr samples were shaken at 2.5 min intervals for the first 30 min, and then every 15 min thereafter. At the end of the incubation period for each flask, a 10 ml water sample was withdrawn and immediately pressure filtered through a GF/F (nominal pore size of 0.7 μm) glass fiber filter; a 1 ml subsample was diluted to 10 ml with deionized water. The phosphate concentration was determined as soluble reactive phosphorus (SRP) within 2 hr, following the antimony-molybdate method of Stainton et al. (1974). Adsorption at each time interval was calculated as the difference between the initial and final phosphate concentrations normalized to sediment dry mass (μmol P g^{-1} dw). In a separate experiment, we found no significant differences in phosphate adsorption between replicate sediment samples incubated in anoxic versus oxic conditions (McGlathery et al., *unpublished* *data*). This is to be expected if phosphate uptake is by adsorption to carbonate minerals since these would not be affected by the oxidation-reduction potential. However, we do recognize that changes in redox conditions can have marked effects on the adsorption capacity of clastic, coastal marine sediments where phosphate uptake is principally onto iron (III) phases (Krom & Berner 1980; Howarth et al., in press).

Sediment analysis

At the time of the adsorption experiments, the remaining sediment slurry was frozen for later analyses of grain size distributions and solid-phase chemistry. We determined the total P, inorganic P, and (by difference) organic P content of triplicate sediment samples from each of three cores collected at both sites. Total P was measured on dried, ground 0.25 g samples using a modification of the persulfate oxidation method of Koroleff (1983), with 200 mg $K_2S_2O_8$ added per sample. Carbonates were first dissolved with 5 ml of 1 N HCl (Instra-Analyzed grade) and the sample brought to 25 ml total volume before oxidation in an autoclave at 120 °C for 30 minutes. This method was tested on replicate sediment samples against a dry oxidation procedure where samples were ashed (550 °C) after a pre-treatment with 1 N HCl to remove carbonates and 50% (w/v) $MgNO_3$ as an oxidant to avoid P volatilization during combustion (Krom & Berner 1981; Morse et al. 1985). Phosphate was then determined as SRP by spectrophotometric analysis after hot acid extraction by the method of Stainton et al. (1974). There were no significant differences in the total phosphorus measured by both methods, so we chose the persulfate method since it required less reagent additions and manipulation of the sample, and hence less potential for contamination. Inorganic P was also determined by spectrophotometric analysis after extracting the sediment in 1 N HCl for 16 hr on a shaker table. This extraction represents the total inorganic P fraction as described by Ruttenberg (1992), and includes loosely sorbed P, ferric iron-bound P, and calcium phosphate mineral P (apatites). Organic P was calculated by difference using the total and inorganic P measurements. Fe concentrations were also measured in a subsample of the 1 N HCl extraction using a Varian 1475 atomic absorption spectrophotometer.

Organic carbon was determined using a persulfate oxidation of an ampulated sample after acidification and sonication with phosphoric acid to drive off all inorganic carbon, as in Mills & Quinn (1979). We removed seagrass root components and other large, visible pieces of detritus by hand with forceps before proceeding with the organic carbon analysis (Morse et al. 1987). 400 mg of persulfate was used as an oxidant for a 50 mg (dried, ground) sample, and ampoules were sealed using a propane torch and observing the cautions outlined in McDowell et al. (1987). Sealed ampoules were autoclaved at 120 °C for 2 hours. CO_2 was measured after oxidation was complete using a 5010 CO_2 Coulometer (Coulometrics Inc.). All glassware used for the analysis was pre-combusted at 550 °C to remove organic carbon contamination. Both reagent and pure calcium carbonate blanks were run to determine that all traces of inorganic carbon were being removed by the procedure prior to ampoule sealing and oxidation. A standard curve was generated using glucose; recovery of glucose standard additions to samples was also checked to assess whether there was enough persulfate added to oxidize the sample organic carbon with some excess present. Recovery of standards in the sample matrix was 100% ± 3.3%.

The grain size distribution for each core was determined by dry sieving the homogenized sediment into 5 size fractions using polypropylene macro filter meshes (Spectrum): > 710 μm, 210–710 μm, 105–210 μm, 52–105 μm and < 52 μm. The sum of the individual size fractions for each core indicated that in all cases we had > 99% recovery in the sieving procedure. We calculated the % dry weight represented by each size class, and then measured the inorganic P content of each fraction as described above. It was necessary to pool the 2 smallest size classes to obtain enough mass for the P analyses.

Seagrass tissue analysis

The carbon, nitrogen, and phosphorus contents of the dominant seagrass, *T. testudinum*, were determined on shoots collected from our two sites. At both sites, 8 shoots were harvested from each of 4 plots (0.25 m^2) and transported in seawater to the laboratory, where the tissue was scraped clean of epiphytes and rinsed with deionized water before drying to a constant weight at 60 °C. These individual shoots were pooled for each plot and the site averages were determined from the four pooled samples. The dried samples were ground to a fine powder with a SPEX 8000 Mixer/Mill and duplicate subsamples were analyzed for tissue carbon and nitrogen using a Carlo-Erba NA-1500 CNS analyzer. Tissue phosphorus content was determined using a modification of the procedure of Stainton et al. (1974), as follows: triplicate 5 mg subsamples were analyzed first by dry-ashing at 550 °C for 6 hr, followed by hot acid extraction (2 ml 1 N HCl plus 10 ml deionized water) for 2 hr, and subsequent colorimetric measurement of PO_4^{3-}. The recovery of tissue phosphorus in a reference plant material (NBS no. 1572, citrus leaves) with a P content of 0.13% dry weight was 102% ± 6% using this method.

Results

Phosphate uptake

Sediments from both sites exhibited a similar pattern of phosphate uptake, with an initial rapid phase followed by decreasing uptake with increasing exposure time (Fig. 2). This is essentially the same pattern observed by Morse et al. (1987) for sediments underlying a seagrass bed in the Bahamas, except

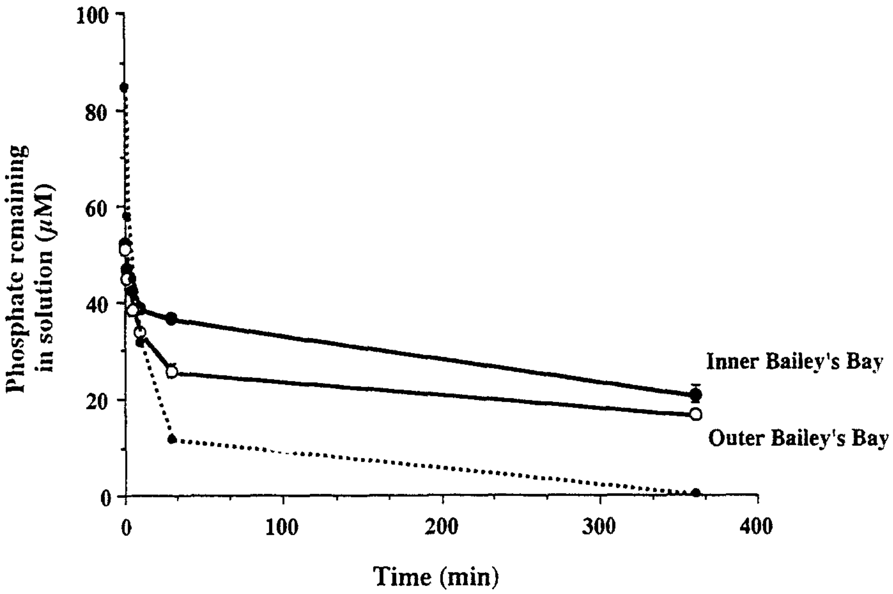

Fig. 2. Phosphate uptake by homogenized sediments from the 2.5–7.5 depth interval of cores (n = 3) collected from the mesotrophic outer bay and the eutrophic inner bay. Error bars represent ± 1 standard error. Dashed line shows the data of Morse et al. (1987) for comparison.

they observed more rapid uptake, both initially and at the end of the 6 hour incubation period. Throughout the duration of the experiment, the sediments from the mesotrophic outer bay had a greater phosphate uptake than those from the eutrophic inner bay. A two-way analysis of variance (ANOVA) of phosphate concentration remaining in solution (time and site as classes) demonstrated this effect to be highly significant (for site, F = 80, $p < 0.0001$; for time, F = 327, $p < 0.0001$ for the interaction of time and site, F = 7.1, $p < 0.0003$). At the end of the first 10 min, a mean of approximately 34% of the available phosphate in solution had been adsorbed by the outer bay sediments verses 24% adsorbed by sediments in the inner bay. During the 6 hour incubation, a total of 67% of the dissolved phosphate in solution was removed by the outer bay sediments (corresponding to 1.30 μmol P g^{-1} dw sediment), while only 56% (1.13 μmol P g^{-1} dw) was taken up by the inner bay sediments.

The phosphate removal by the sediments at both our sites was considerably slower than that determined by Morse et al. (1987) for an oligotrophic site in the Bahamas (Whale Cay, Berry Islands), where they found 100% removal of phosphorus from solution after 6 hours (see Fig. 2). Our data are comparable to Morse et al. (1987) since our experiments used very similar ratios of wet weight sediment to seawater in the slurry (36 g $liter^{-1}$ for us vs. 33 g $liter^{-1}$ for Morse et al. 1987) and similar initial phosphate concentrations (50 μM for us vs. 85 μM for Morse et al. 1987). In another similar uptake experiment, Short et al. (1990) used several different initial phosphate concentrations (1.5, 6, and 60 μM) and found the same percentage uptake after 6 hours in all cases. This apparent insensitivity of P adsorption to starting concentration in these short-term experiments adds to our confidence in comparing our data with those of Morse et al. (1987), even though we used slightly different initial phosphate concentrations.

Sediment grain size distribution and chemistry

Figure 3 shows the average sediment grain size distributions for triplicate cores from the vegetated sediments collected in the outer (mesotrophic) and inner (eutrophic) parts of the bay. The sediments from both sites were dominated by the large, coarse-grained size fractions. Approximately 75% of the outer bay sediment was in the > 210 size fraction and 66% of the inner bay sediments was in these two largest size classes. The finest fraction (< 52 μm) accounted for < 2% of the sediments in both sites.

The total P and inorganic P concentrations of the bulk sediments were significantly higher in the eutrophic inner bay than in the mesotrophic outer bay (Table 1; $p < 0.001$, t-test). The difference in total P is due largely to

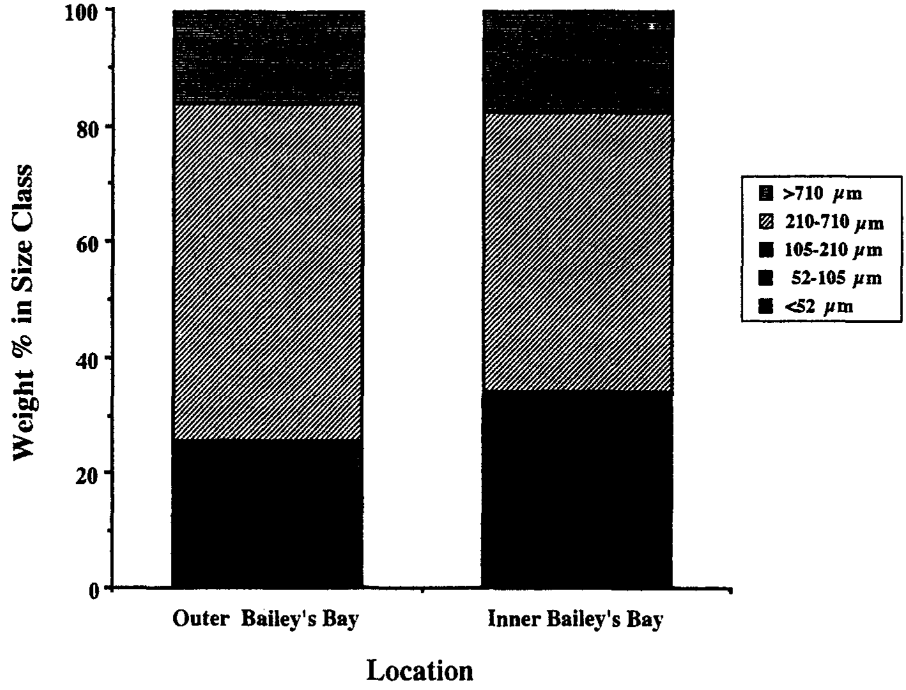

Fig. 3. Sediment grain size distribution determined by dry sieving triplicate cores at each site. The sum of the individual size fractions indicated that in all cases there was < 1% loss in the sieving procedure.

inorganic P; inorganic P is the dominant phosphorus pool at both sites, making up 70 to 74% of total sediment P (Table 1). There was a pattern of declining inorganic P concentration with increasing grain size for both the inner bay (Fig. 4; $p < 0.0001$, ANOVA) and outer bay sediments (Fig. 4; $p < 0.001$, ANOVA).

The Fe content of the sediment was significantly higher at the inner bay site than the outer bay site (Table 1; $p < 0.05$, t-test). However, at both the inner and outer bay sites the concentrations were extremely low for marine sediments, representing < 0.02% of the sediment dry weight (< 3.6 μmol Fe g^{-1}). Sediment organic carbon concentrations were also quite low, comprising approximately 0.5% of the dry weight (0.4 to 0.5 mmol C g^{-1}; Table 1). The two sites did not differ significantly in organic carbon content ($p > 0.05$, t-test).

Seagrass tissues

There was no difference in the carbon content of *T. testudinum* leaves collected from the inner and outer bay sites (Table 2; $p < 0.05$, t-test). Both the N and P contents were significantly higher in the inner bay seagrasses ($p < 0.05$ and $p < 0.0001$, respectively, t-test). However, there was a greater increase in P content relative to N (Table 2). This difference is reflected in both the lower N:P ratio of the inner bay leaf tissue and the larger difference in C:P than C:N ratios between *T. testudinum* collected at the two sites.

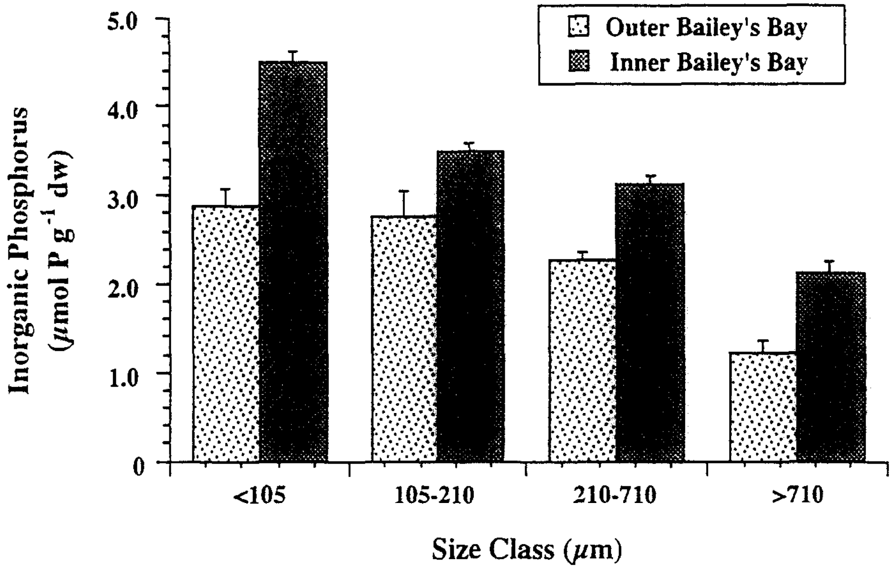

Fig. 4. Solid-phase inorganic phosphorus concentrations of the Bailey's Bay sediments as a function of sediment grain size ($n = 3$ for each site). Vertical bars are ± 1 standard error.

Table 1. Chemical composition of Bailey's Bay sediments. Values represent means of 3 cores ± 1 SE.

	P (μmol g^{-1} dw)			Acid-extractable Fe	Organic C
Location	Total	Inorganic	Organic	(μmol g^{-1} dw)	(mmol g^{-1}dw)
Outer Bailey's Bay (mesotrophic)	3.37 ± 0.20	2.16 ± 0.09	1.21 ± 0.22	1.97 ± 0.36	0.47 ± 0.03
Inner Bailey's Bay (eutrophic)	4.77 ± 0.03	3.37 ± 0.10	1.40 ± 0.11	3.23 ± 0.18	0.39 ± 0.02

Table 2. Elemental composition of *Thalassia testudinum* leaf tissue from Bailey's Bay. Values are means (n = 4) ± 1 SE.

	dry wt %			mol : mol		
Location	C	N	P	C:N	C:P	N:P
Outer Bailey's Bay (mesotrophic)	34.1 ± 0.24	1.89 ± 0.05	0.132 ± 0.005	21.0 ±0.52	670 ± 21.5	31.8 ± 0.40
Inner Bailey's Bay (eutrophic)	33.4 ± 0.27	2.11 ± 0.05	0.187 ± 0.005	18.6 ± 0.34	464 ± 14.8	25.0 ± 0.67
t-test	$p > 0.05$	$p < 0.05$	$p < 0.0001$	$p < 0.01$	$p < 0.0001$	$p < 0.001$

Discussion

The interaction of phosphate with carbonate sediments is an important control of phosphorus availability in shallow tropical and subtropical marine environments (Short et al. 1985, 1990; Morse et al. 1987; Howarth 1988). Our results show that phosphate uptake onto carbonate sands can vary, with significantly lower uptake at our more eutrophic site, and with uptake at both our sites significantly lower than at the Whale Cay site in the Bahamas studied by Morse et al. (1987). Our results also suggest lower phosphate adsorption than that observed by Short et al. (1990) at another site in the Bahamas (San Salvador Island). These workers found somewhat slower uptake than observed by Morse et al. (1987) but faster than we observed, with 86% P removal from solution after 6 hours. However, the results of Short et al. (1990) are somewhat less comparable since they used a higher ratio of sediment to water in their slurry, 50 g wet weight liter^{-1}, which could have resulted in a higher percentage removal.

We considered several sediment characteristics in the context of models of dissolved P-solid phase interactions put forward by both aquatic and soil scientists (Stumm & Leckie 1970; Berner & Morse 1974; Barrow 1983; Froelich 1988) to gain insight into the mechanism leading to the observed, variable rates of phosphate uptake in the different sediments. Specifically, we considered grain size and concentrations of iron, phosphorus, and organic carbon.

Grain size

The grain size distributions at our two sites in Bermuda, and at the locality reported by Morse et al. (1987) in the Bahamas, were similar in that they were all dominated by the largest (> 250 µm) size classes. A slightly greater proportion (80% by weight) of the sediment was over 250 µm in size in the vegetated sites studied by Morse et al. (1987) than in the sediment collected from the mesotrophic outer and eutrophic inner parts of Bailey's Bay (Fig. 3; 75% and 66%, respectively). These differences in grain size distribution are not likely to be the cause for the observed variation in phosphate uptake potentials because they are in opposite direction as would be necessary to explain the lower adsorption of the Bermuda sediments relative to the Bahamas. That is, the sediments with the slightly smaller grain size overall showed lower phosphate uptake.

It is possible that the surface area per sediment weight is not directly related to grain size. Because of their microporous texture, biogenic carbonates vary in the degree to which the surface area of the inner pores is in contact with the outside medium (Suess 1973; Walter & Morse 1984; Morse 1986). As a result, the relationship between surface area and particle size does not follow a simple solid-surface geometric model, and the measured surface area can be 5–500× greater than that predicted by this model (Walter & Morse 1984).

Further, it is difficult to estimate the proportion of measured surface area available for reaction because the surface roughness (or relative reactivity for a given grain size as calculated from measured dissolution rates) varies for different biogenic carbonates (Walter & Morse 1984). However, the sediments at our two sites in Bermuda are presumably derived from the same source material of calcareous algae since they are in close proximity.

We did not make surface area measurements and, given the complications with assessing the reactive surface area as a function of grain size for these carbonate sediments, we did not attempt to calculate the surface area and the potential availability of reaction sites for phosphate adsorption. However, we note that at both our sites there was a direct relationship of increasing sediment inorganic phosphorus content with decreasing grain size (Fig. 4). This is consistent with a general pattern of decreasing surface area with larger particle sizes and with a surface-related mechanism for phosphate uptake, as was observed by Suess (1973) for biogenic carbonates from Fanning Island Lagoon in the Pacific Ocean. Erftemeijer & Middleburg (1993) also recently showed experimental evidence for decreasing adsorption capacity with increasing particle size for coarse-grained biogenic carbonates in South Sulawesi, Indonesia.

Organic carbon concentrations

We had hypothesized that differences in phosphate uptake might be related to sediment organic matter content. Chemisorption of organic acids onto calcite and competition for sorption sites with phosphate anions have been documented in laboratory studies (Suess 1968, 1970; Carter 1978; Carter & Mitterer 1978; Lahann & Campbell 1980). Krom & Berner (1980) also found very low phosphate adsorption in the anoxic portion of sediments in Long Island Sound despite the presence of carbonate grains; they suggested the low adsorption may have resulted from organic coatings on the grains. However, the sediments of our two sites did not differ significantly in organic carbon content of the sediments (Table 1), and both were quite low relative to temperate sediments or some calcareous sediments, such as those in mangrove swamps and algal mats (Morse et al. 1985). Morse et al. (1987) did not report organic carbon concentrations at their site in the Bahamas, but data from an earlier study at similar locations showed that these sites were also characterized by a low organic carbon content (0.24–0.34 weight percent; Morse et al. 1985).

Overall, our data suggest that variable rates of phosphate uptake in carbonate sediments are not principally a result of differences in organic carbon content. However, organic matter-carbonate interactions are complex in natural systems because the organic matter can be present as a surface adsorbate, as a precipitate or coprecipitate, or as biogenic coating or occluded tissue (Morse 1986). We therefore cannot exclude the possibility that a small percentage of the total carbon, such as bacterial slimes on particles or specific organic anions which compete for sorption sites, might vary among the sites and have some effect on phosphate uptake (Morse 1986).

Iron concentrations

The affinity of pure carbonate minerals for phosphate adsorption is actually much lower than that for many other minerals (Krom & Berner 1980). Both in soils (Hamad et al. 1992) and in deep-sea sediments derived from foraminifera (Sherwood et al. 1987), phosphate adsorption onto carbonates has been found to be greatly facilitated by iron coatings on the carbonates. Our data suggest that iron is not responsible for differences in phosphate uptake between our two sites. Acid-extractable iron concentrations were significantly higher in the more eutrophic inner site (Table 1). This is the site where phosphate uptake rates were slower, not faster as would be expected if differences in iron coatings associated with the carbonate sediments were an important control on phosphate adsorption at these sites. Overall, iron concentrations at both our sites were extremely low (< 0.02% by weight), as is typical for carbonate sediments (Berner 1982). These low iron concentrations make it unlikely that differences in iron coatings had a strong effect on phosphate uptake in the experiments reported here. Morse et al. (1985) also showed low iron concentrations (approximately 40 ppm, or 0.004% by weight) for sites in the Bahamas similar to those where Morse et al. (1987) measured phosphate uptake.

Phosphorus concentrations

For our two sites in Bermuda, both the inorganic phosphorus concentrations and the total phosphorus concentrations were inversely related to the phosphate uptake observed. That is, the eutrophic inner bay sediments had higher total and inorganic phosphorus contents and a lower uptake than the outer bay sediments (Table 1; Fig. 2). Morse et al. (1987) did not report total sediment phosphorus or inorganic sediment phosphorus concentrations for the site where they conducted their phosphate uptake experiment in the Bahamas, but for a nearby site where pore water phosphate concentrations were some 3 to 4-fold higher, they found a total sediment phosphorus concentration of approximately 0.006 μmole g^{-1} (Morse et al. 1987). This concentration is some 3 orders of magnitude lower than those we found at our Bermuda sites. We suggest that these differences in sediment phosphorus content may be important factors related to the observed differences in phosphate uptake rates, with greater uptake in more phosphorus-poor sediments. Possible mechanisms for phosphate uptake, and reasons for why phosphate uptake onto carbonate mineral surfaces may be related to solid-phase phosphorus concentrations, are discussed in the next section.

Mechanism of phosphate uptake

Although it is well established that shallow tropical and subtropical carbonate sediments take up phosphate, the mechanism or mechanisms of interaction are not well known (Morse 1986). The initial uptake of phosphate onto carbonate mineral surfaces is often described as a chemisorption reaction (Stumm & Leckie 1970; deKanel & Morse 1978; Morse & Mackenzie 1990). Chemisorption is one type of generalized adsorption reaction where some type of chemical bonding between the solid and fluid phases occurs (Morse & Mackenzie 1990). Mechanisms for chemisorption reactions such as that of phosphate on biogenic carbonate surfaces are difficult to analyze because such reactions may not be adequately described by adsorption models developed primarily for gas – solid phase interactions (Froelich 1988), or by models which assume surface homogeneity or equilibrium conditions (Morse & Mackenzie 1990; Stumm 1992). Additionally, it may be difficult to distinguish chemisorption from coprecipitation in systems with carbonate minerals in contact with a solution supersaturated with respect to the solid phase (Morse 1986).

In addition to sorption processes, precipitation of phosphate minerals such as hydroxyapatite or carbonate fluorapatite is thermodynamically favored in many carbonate sediment systems (Kitano et al. 1978; Gaudette & Lyons 1980; Vieillard & Tardy 1984). However, little is known about the kinetics of these reactions in natural systems, especially on biologically relevant time scales. In their study of Bermuda sediments and pore waters, Gaudette & Lyons (1980) described four possible mechanisms for phosphate interaction with carbonate sediments: 1) direct precipitation of apatite onto biogenic silica or inorganic particles, 2) direct precipitation of amorphous calcium phosphate in pore waters, 3) formation of apatite from calcium carbonate by replacement of carbonate with phosphate, and 4) adsorption of phosphate onto calcium carbonate minerals. They inferred phosphate removal onto carbonate mineral grains from their pore water and sediment chemical data, and suggested the last two mechanisms as the ones most likely to be important in these nearshore systems (Gaudette & Lyons 1980). In another study at several sites in Bermuda, Berner (1974) suggested that the sediments were in equilibrium with apatite, based on pore water data and thermodynamic constants for natural marine phosphorites. The mechanism for phosphate interaction with the sediment was postulated to be rapid precipitation of apatite on the fine-grained calcium carbonate particle surfaces (Berner 1974).

Our data show that there is potential for phosphate removal from solution by the calcareous sediments at our two sites in Bermuda, and suggest that the magnitude of the sediment uptake on a time scale of hours (as is biologically significant) is directly related to the total phosphorus content of the sediments. That the higher phosphorus content of the sediment is related to lower phosphate uptake suggests to us a sorption process in which there is some feedback mechanism from the sediment, reducing the active surface sites available for sorption as total phosphorus increases. One way to view such a mechanism is as a two (or more) step process where phosphate is initially rapidly adsorbed to available surface sites and then is more slowly transformed into the near-surface carbonate matrix, possibly as calcium phosphate mineral phases. By this mechanism, the rate at which surface sorption sites become available is related to the rate at which sorbed phosphate is transformed into the mineral phases, which becomes slower as phosphate solid-phases become more abundant.

Such multi-step models for phosphate interactions with solid phases have been described for carbonate in dilute solutions (Stumm & Leckie 1970) and for iron- and aluminum-rich particles in rivers and estuaries (Froelich 1988). Stumm & Leckie (1970) characterized the kinetics of phosphate uptake on calcite surfaces as having three steps: rapid chemisorption of phosphate along with the formation of amorphous calcium phosphate nuclei, followed by the slow transformation of nuclei into crystalline apatite, and then the growth of apatite in the near-surface region. The initial phosphate removal is proportional to the available calcite surface area for sorption. Similarly, Froelich (1988) postulated a two step process of rapid phosphate uptake onto a sediment surface followed by a slower diffusion of this P into the mineral interior. As this process goes on, the surface continues to react with the solution causing the phosphate concentration in the solution to continue to decrease, but more slowly. Both of these multi-step processes are consistent with the kinetic studies of deKanel & Morse (1978), where the reaction curve for phosphate uptake from seawater solutions onto calcite and aragonite surfaces showed two regions, one of very rapid uptake followed by one with a much slower removal of phosphate from solution. DeKanel & Morse (1978) attributed this result to either an exponential decrease in surface reaction sites over time or a linear decrease in activation energy for surface adsorption.

The results of a short-term uptake experiment such as the one presented here or that of Morse et al. (1987) almost certainly reflect the kinetics of the initial sorption phase described by these models. Sorption over this sort of time scale is quite dependent on the immediate time-history of the solid (Froelich 1988), and environmental conditions can play a dominant role in sediment-natural water interactions (Morse 1986). For our Bermuda sediments, high P loading over time, as is consistent with more eutrophic conditions in our inner versus outer bay sites, could result in less calcium carbonate surface area of sediment available to rapidly sorb phosphate from solution as the proportions of calcium phosphate mineral phases increase in the sediment matrix, thereby reducing the renewal rate of reactive surface sites. Similarly, the sediments at the Bahamas site studied by Morse et al. (1987) are probably exposed to much lower phosphate levels, as evidenced by the much lower pore water phosphate and total sediment phosphorus concentrations than at our Bermuda sites. As a result, the Bahamas sediment should have more surface reaction sites available for rapidly removing phosphate from solution.

Ecological significance

Whatever the specific mechanism of phosphate uptake, the slower adsorption of phosphate onto the sediments we observed in Bailey's Bay has important ramifications for its biological availability, both to seagrasses and to the overlying water column. Phosphate is generated in the sediment from decomposition of organic phosphorus compounds and persists for some discrete period of time as dissolved phosphate in the pore waters before being removed from solution by reaction with carbonate minerals. The slower the adsorption process, the longer the phosphate is present as a readily available, dissolved form which can be assimilated by benthic macrophytes or can move to the overlying water column by diffusion or advective exchange of pore waters (as by wave action). Thus, slower phosphate uptake by carbonate sands can raise the concentration of dissolved phosphate and lower the ratio of dissolved inorganic nitrogen to phosphate in both the sediment and overlying waters.

The difference in phosphorus content of *T. testudinum* leaf tissue in Bailey's Bay suggests that phosphorus availability in the root zone of the sediments is indeed higher in the eutrophic inner bay, as predicted from our phosphate uptake data. We do not know the phosphorus content of seagrass at the Bahamas site studied by Morse et al. (1987) and thus can not compare our tissue nutrient data with his site. However, Short et al. (1990) report values for another seagrass, *S. filiforme*, from a similar oligotrophic site in the Bahamas where they showed rapid phosphate sorption on sediments; these values are three-fold lower (0.06 ± 0.01 %P) than our eutrophic site in Bermuda. The phosphorus content of the leaf tissue doubled (0.12 ± 0.02 %P) after seven months of nutrient enrichment (Short et al. 1990) to a value that is similar to the phosphorus content of the *T. testudinum* from our outer bay site (0.13 ± 0.005 %P), but still considerably less than the *T. testudinum* from the eutrophic inner bay site (0.19 ± 0.005 %P).

The phosphorus content of *T. testudinum* from our eutrophic site is among the highest reported for this tropical species and suggests that P availability is high in this bay relative to other carbonate-dominated systems. For example, Fourqurean et al. (1992b) compared the tissue content of *T. testudinum* from Florida Bay, both on a local scale as a function of distance from a point source of nutrients at a bird colony and regionally within the bay. Along the nutrient enrichment gradient, they found values ranging from 0.16 ± 0.002 %P closest to the colony to 0.08 ± 0.002 %P farthest away from the colony. Regionally, the phosphorus content of *T. testudinum* collected across the bay varied four-fold (0.05–0.2 %P), with an average of 0.10 ± 0.005 %P. The high P content of *T. testudinum* in our eutrophic site is similar to that which has been reported in general for this species following phosphorus enrichment (Duarte 1990).

We have earlier hypothesized that a low phosphate adsorptive capacity may be partly responsible for nitrogen limitation of growth of benthic macroalgae found in Bailey's Bay (McGlathery 1992a; McGlathery et al. 1992). The results we report here support this earlier hypothesis. However, we now believe that the reduced sediment phosphate uptake at this site is more likely to be related to a generally high rate of phosphate loading to Bailey's Bay rather than to more organic rich sediments, as previously suggested (McGlathery et al. 1992). We are unsure whether the slower phosphate uptake rate actually increased phosphate availability in the overlying water column of Bailey's Bay or whether the macroalga we studied, *Penicillus capitatus*, can assimilate phosphate directly from sediment pore waters, as has been shown for another siphonous species (Williams 1984).

Our results suggest the potential for a positive feedback in shallow tropical and subtropical carbonate systems, with phosphorus availability increasing disproportionately as phosphorus loadings increase because the sediment sink becomes less effective. This could cause an increase in primary production in these systems, many of which are probably phosphorus limited (Smith 1984; Smith & Atkinson 1984; Short et al. 1985, 1990; Howarth 1988). The N:P ratios of *T. testudinum* presented here suggest that nutrient loading increases phosphorus availability to a greater extent than nitrogen availability. Our eutrophic site had the lowest ratios (25 verses 32 in the mesotrophic site; Table 2), and these values are considerably lower than those reported for *T. testudinum* from several oligotrophic, carbonate-dominated localities (N:P = 32, 44, 59; Patriquin 1972; Powell et al. 1989; Fourqurean et al. 1992b, respectively).

These results support the hypothesis that increased nutrient loads to shallow carbonate lagoons may cause a switch from phosphorus to nitrogen limitation of net primary production (Howarth et al., in press). Such an effect might in general be expected not only because phosphorus availability in carbonate sediments increases disproportionately to increased inputs, as our data here suggest, but also because nitrogen to phosphorus ratios in nutrient inputs tend to decrease as total nutrient loads increase (Billen et al. 1991; Howarth et al., in press) and because nitrogen availability may decrease disproportionately to its input as the overall productivity of the system increases. Loss of nitrogen from denitrification in sediments increases as organic matter inputs increase (Caffrey & Kemp 1990, 1992). Inputs from nitrogen fixation by heterotrophic bacteria may also be stimulated by higher organic matter inputs in carbonate sands (O'Neil & Capone 1989) as in temperate-zone sediments (Howarth et al. 1988). However, wherever both denitrification and nitrogen fixation have been measured simultaneously in temperate coastal sediments, denitrification rates have exceeded rates of nitrogen fixation, resulting in a net loss of nitrogen from the system (Seitzinger 1988). More limited evidence suggests this is also true for tropical carbonate sediments (Capone et al. 1992). Also, eutrophication increases turbidity from phytoplankton biomass, potentially leading to light-limitation of benthic nitrogen-fixing cyanobacteria (Howarth 1988; Howarth et al., in press).

The population density of Bermuda is high, and groundwater there is rich in phosphate from the use of domestic cesspits for wastewater disposal (Simmons et al. 1985). As in Florida (Zimmerman et al. 1985; Lapointe et al.

1990), groundwater inputs have probably been a significant source of phosphorus loading to these coastal waters. These loadings, combined with surface runoff have resulted in phosphate inputs to Bailey's Bay sufficient to raise sediment phosphorus concentrations by 3-orders of magnitude over those found in more pristine locations in the Bahamas. This P loading has led to eutrophication of the inner bay and may be responsible for the incidence of nitrogen limitation of macroalgal growth in this subtropical lagoon due to decreased effectiveness of the carbonate sediments as a phosphorus sink.

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