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Forms and availability of sediment phosphorus in carbonate sand of Bermuda seagrass beds

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Abstract
Primary production by seagrasses in tropical and subtropical carbonate sediments often appears to be phosphorus (P) limited, and several studies have sought to identify the possible sources of P for long-term growth. Here, we quantify concentrations of particulate and dissolved P and fluoride (F⁻) in carbonate sediments, sediment-water P exchange, and leaf-tissue P concentrations in three seagrass beds in Bermuda. We also present data on the sequential extraction of P and F⁻ from the sediments at each site. Total sediment P (TP₏ₐ) in the upper 20 cm ranged from 650 to 1,250 mmol P m⁻² and was some 500-fold larger than the pool of P dissolved in pore waters. Loosely adsorbed inorganic P comprised 2% of TPₚₚ while a surface-bound inorganic P pool extracted by dithionite buffer constituted 15–20%. Most of the remaining P and nearly all of the Ca and F⁻ present in the sediment was recovered when the remaining sediment was dissolved in an acetic acid buffer solution. This pool includes calcium-fluoroapatite (CFA), which is considered the primary diagenetic sink for P in carbonate sands. Dissolved inorganic P and F⁻ were both elevated in the rhizosphere pore waters from the three seagrass beds. In combination with our analysis of sediments by sequential extraction, this result indicates that the carbonate matrix of the sediment is being dissolved in the rhizosphere, with a resulting release of P to the pore water and hence to the seagrass roots. We suggest that this is important in the P economy of these subtropical seagrass (Thalassia testudinum) beds and note that the carbonate-bound P pool is large enough to sustain seagrass P requirements for decades. Nonetheless, primary production in such seagrass systems can remain P limited if the rate of P release from sediment dissolution is too slow to support maximum seagrass growth rates. Analysis of seagrass leaf tissues revealed that P availability was highest at the site with the highest anthropogenic influences. This site was also characterized by the highest sediment P release, indicating that high P availability may also be partly due to higher release of P as sediments are dissolved. Phosphorus was released from the sediment mainly as dissolved organic P, causing a net efflux of dissolved P at all sites in April and at two sites in August.

Carbonate sediments of tropical and subtropical coastal waters are thought to trap phosphorus (P) efficiently by strong adsorption of dissolved inorganic P (DIP) (i.e. phosphate) onto CaCO₃ particles. This mechanism of P immobilization is inferred from adsorption experiments where excess DIP disappears rapidly from solution when added to sediment slurries (deKane and Morse 1978; Morse et al. 1987; Short et al. 1990; McGlathery et al. 1994), and from stoichiometric nutrient regeneration models that indicate a depletion of DIP relative to ammonium in sediment pore waters (Gaudette and Lyons 1980; Hines and Lyons 1982). Berner (1974) found that concentrations of DIP in the pore water of shallow carbonate sediments were approximately in equilibrium with carbonate-fluoroapatite (CFA). This feature is unique to carbonate-rich sediments and is probably caused by CFA formation on carbonate surfaces. Kitano et al. (1978) observed that DIP uptake by calcite occurred in two steps, with a rapid initial adsorption onto the surface of particles and a subsequent slower incorporation of P with F⁻ in CFA. This authigenic mineral probably represents the primary sink for P in carbonate sediments.

The retention of P in carbonate sediments is considered to be the main reason that primary production often appears to be P limited in tropical and subtropical coastal waters (e.g. Short et al. 1990; Fourqurean et al. 1992a; Lapointe et al. 1992; Howarth et al. 1995). Nutrient enrichment experiments with seagrasses (Short et al. 1990) and spatial patterns of tissue C:N:P contents with respect to nutrient loading (Short et al. 1985; Fourqurean et al. 1992a) have shown that seagrasses are generally P limited in carbonate sediments. However, some exceptions have been reported that suggest either nitrogen (N) or iron (Fe) limitation of seagrass growth.

Acknowledgments
We thank Emily Ehrenfeld for technical assistance with laboratory work and Robbie Smith for assistance during fieldwork. Kaj Sand-Jensen, J. W. Fourqurean, B. Boudreau, and one anonymous reviewer are thanked for comments on the manuscript. The study was supported by grant 11-0355-1 from the Danish National Science Foundation to H.S.J., by grant DEB93-07337 from the U.S. National Science Foundation to R.W.H., and by a grant-in-aid from Bermuda Biological Station for Research. This is publication 1477 from the Bermuda Biological Station for Research.

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in carbonate environments (Powell et al. 1989; Erftemeijer and Middelburg 1993; Duarte et al. 1995). Despite the nutrient-poor conditions of most tropical and subtropical coastal waters, seagrass productivity is quite high. For the seagrass *Thalassia testudinum*, growth rates are often >2.5 g C m\(^{-2}\) d\(^{-1}\) (McRoy and McMillan 1977). In the case of P-limited growth, reallocation of P from decaying leaves to younger leaves and to roots and rhizomes may partly support the P demand for growth (e.g. Perez et al. 1991), but an external source of P is still required to balance losses and to sustain the high rates of production.

When the DIP concentration in the water is low, rooted macrophytes take up most P through their roots (e.g. Carignan and Kalf 1980). Accordingly, Fourqurean et al. (1992b) found positive correlations between porewater DIP and leaf P content and between leaf P content and areal biomass in 18 *T. testudinum* stands in Florida Bay. Porewater P, however, is a transient pool and will be exhausted rapidly by root uptake to meet the metabolic demands for growth. We calculated a turnover time of 54 h for porewater P at the Florida Bay sites based on a DIP concentration of 0.5 μM (Fourqurean et al. 1992b), a porosity of 0.8 (Rude and Aller 1991), a root-zone depth of 40 cm, and a P demand for growth of 70 μmol P m\(^{-2}\) d\(^{-1}\) (Fourqurean et al. 1992b). Similarly, Patrichin (1972) estimated the turnover time of porewater DIP in two Caribbean *T. testudinum* stands to be 13–45 h. Several authors have suggested that porewater DIP can be renewed from the pool of inorganic P (IP) that is adsorbed loosely onto the sediment particles (Patrichin 1972; Short 1987; Delgado and Vidal 1989). Patrichin (1972) estimated that this pool would be large enough to sustain growth for 300 d. In addition, Erftemeijer and Middelburg (1993) suggested that porewater DIP could be renewed by the remineralization of organic matter in a *T. hemprichii* seagrass bed in Indonesia. Even though these views differ on how porewater DIP can be renewed, it has generally been assumed that the solid CaCO\(_3\)-bound P fraction of sediments does not constitute an available source of P for seagrass growth (e.g. Patrichin 1972; Erftemeijer and Middelburg 1993).

In the study reported here, we show that most of the solid sediment P fraction (including CFA and other CaCO\(_3\)-bound P components) is a potentially significant source of P for tropical seagrasses. This argument is based primarily on the observation that CFA is being dissolved in the rhizosphere in three Bermuda *T. testudinum* stands. Through quantification of various P pools in the sediment we show that the available pools are large enough to sustain seagrass growth for decades, provided that they are mobilized fast enough. We further suggest that the sediment also may be a source of P for growth of micro- and macroalgae in the overlying water. This is inferred from measurements of diffusive fluxes of dissolved P across the sediment–water interface in undisturbed sediment cores.

Methods

**Site description**—Sampling sites were selected to represent a gradient in terrestrial and anthropogenic nutrient load-

![Fig. 1. Three sampling sites representing a gradient in anthropogenic and terrestrial influence at Bermuda (32°N, 64°W): Bailey’s Bay inner station (BBI), Baileys Bay outer station (BBO), and the offshore north channel station (NC). BBI and BBO are identical with stations used by McGlathery (1995) and McGlathery et al. (1992, 1994).](image)

ing. Two stations, influenced by nutrient loading from domestic septic systems, are located in Bailey’s Bay on the north coast of Bermuda (32°N, 64°W; Fig. 1); these sites are identical to those sampled by McGlathery et al. (1994) and McGlathery (1995). The inner bay site (BBI) is eutrophic, and the outer bay site (BBO), located 200 m from shore, is mesotrophic (McGlathery 1995). The third station (NC) is located offshore in the north channel of the Bermuda crater platform, 10 km NW of Bailey’s Bay (Fig. 1). The NC station represents the more typical oligotrophic conditions of these subtropical waters. Sampling at all three sites was in 2–5-m water depth in dense seagrass beds, dominated by *T. testudinum*, which was mixed with *Syringodium filiforme* at the outer bay site. Sediment cores and seagrass leaves were sampled by scuba diving in late April and late August 1993, and pore waters were sampled in August.

**Sediment and water chemistry**—Porewater profiles in the seagrass stands were obtained using sippers, drawing pore water through a ceramic filter (1 μM pore size) at depths of 5, 10, 20, 30 and 40 cm. Water samples were withdrawn from a luer-lock sampling port using a syringe. The first 10 ml was discarded, then 25 ml was sampled and immediately filtered (Whatman GF/F with Swinnex filtering system) into a polypropylene vial containing 50 μl of 2 M H\(_2\)SO\(_4\). The pore water was analyzed for DIP and TDP (detection limit 0.03 μM) using the colorimetric methods of Koroleff (1983). Porewater concentrations of F\(^-\) were measured using an Orion 96–09 combination F\(^-\) electrode with 1:1 addition of low-level TISAB (Orion standard procedures). The resolution at ambient seawater F\(^-\) concentrations (46 μM) was ±1.8 μM.

Several shoots of *T. testudinum* were collected at each site and pooled for analysis of tissue nutrient content. The leaves were scraped to remove epiphytes, dried at 65°C, and homogenized before analysis of total P (by combustion fol-
owed by hot 1 M HCl extraction and colorimetric assay of DIP, C and N (using a Europa Scientific CHN analyzer), and Fe (using the Ferrozine colorimetric method [Gibbs 1979] on the HCl extract of combusted tissue).

Sediment cores were sectioned in depth intervals of 1, 2, or 5 cm, and the specific depth intervals from three different cores were pooled for analysis of solid-fraction P after removing visible roots and rhizomes. Three portions of the sediment from each depth were dried (105°C, 24 h), homogenized, and ground in a mortar with a pestle before analysis of total P. Total sediment P (TPsed) was measured by first dissolving the CaCO3 sediment in 1 M HCl and then applying a wet oxidation technique with persulfate (Koroleff 1983), followed by measurement of DIP in the solution (as described by McGlathery et al. 1994).

A portion of wet sediment was processed immediately after sampling through a sequential extraction procedure in order to identify major binding sites for P in the sediment. We modified the extraction scheme originally developed for silicilastic sediments (Psenner and Pucsko 1988; Jensen and Thamdrup 1993) to a six-step scheme (Fig. 2) that allowed us to make an operational discrimination between seven different P pools and to quantify the sequential leaching of Ca, Fe, Mn, and F- in each of the steps. The major modifications of the Jensen and Thamdrup (1993) method were the use of 1 M MgCl2 instead of 0.35 M NaCl for extraction of loosely adsorbed P in the first step and the inclusion of an additional acetate buffer extraction (pH 4.0) after extraction with NaOH and before the HCl extraction (Fig. 2). Both modifications were adapted from Ruttenberg (1992). With this modified extraction procedure (Fig. 2), we intended to first extract loosely adsorbed IP, along with some organic P (OP), in step 1. In step 2, dithionite reduces oxidized Fe and Mn species and dissolves both the metals and the associated OP. After extraction, excess dithionite is removed by aeration, and sulfuric acid is added to maintain the extracted metals in solution. The NaOH extraction in step 3 is intended to remove IP adsorbed onto surfaces other than those of reducible metal oxides (e.g. clay minerals, Al2O3). IP associated with humic acids also is extracted in this step and may precipitate upon acidification (Paludan and Jensen 1995). Finally, a large proportion of OP is extracted during the 18-h NaOH treatment (Psenner and Pucsko 1988; Jensen and Thamdrup 1993). In steps 4 and 5, gradually stronger acids are used for dissolving Ca-P compounds. The use of both the acetate buffer and HCl allows for discrimination between authigenic and detritalapatite because the acetate buffer dissolves the biogenic carbonates and associated CFA, while detrital apatite is only weakly attacked (Ruttenberg 1992). Detrital apatite will dissolve in 0.5 M HCl. In step 6, combustion followed by hot HCl extraction dissolves and hydrolyzes the residual OP compounds.

DIP and TDP were measured in the leachates by standard colorimetric methods (Koroleff 1983). Fe, Mn, and Ca were measured by AAS (Perkin Elmer), also using standard procedures, and F- was analyzed as described previously for porewater samples. For each type of analysis, standard curves were prepared in the specific solutions used for extraction and at the final sample dilution. For porosities (0.62, 0.72, 0.76) and densities (1.87, 1.77, 1.73) for the inner bay, outer bay, and offshore sediments were used to calculate the size of various P pools on an areal basis.

Concentration of TDP in the ambient seawater was measured as described for pore water, with a detection limit of 30 nM and an observed standard deviation of ±12 nM at 170 nM (n = 5). Seawater DIP was measured using the MAGIC method (Karl and Tien 1992), where DIP was concentrated by coprecipitation with Mg(OH)2. After a subsequent centrifugation, the Mg(OH)2 pellet was dissolved in HCl, and DIP was measured colorimetrically. The resulting magnification factor for DIP was ~7x. The NaOH and HCl addition gave a slightly higher background absorption in the MAGIC samples than when measuring in unaltered artificial seawater, but an effective detection limit of 7–9 nM was reached with a standard deviation of ±3 nM at 45 nM (n = 5). The precision of the TDP and DIP measurements, and in particular the application of MAGIC, allowed for accurate measurements of dissolved P fluxes between the sediment and water at in situ concentrations.

Sediment water fluxes—Undisturbed sediment cores (5.2 cm i.d.) for flux measurements (5–9 from each station) were sampled in the seagrass beds in April and August. The cores were mounted with a magnetic stirring bar placed 6 cm above the sediment surface, and the cores were placed around a rotating magnet in order to create the same stirring in all cores. The sediment height was 20–30 cm, and the height of the overlying water column was 10–15 cm. After conditioning the cores overnight, the overlying water was changed with fresh station water of 100% O2 saturation. The cores were stoppered, and O2 uptake was measured in the dark as the decline in O2 concentration during 5–7 h in April and 4 h in August using an YSI oxygen electrode. O2 concentrations decreased by up to 30% over the incubation period. After the oxygen measurements, the incubation was continued without stoppers to allow the water to equilibrate to air saturation during the P flux measurements. Samples for DIP and TDP were taken after 48 h in April and 24 h in August.

Results

Solid-fraction P, Ca, Fe, and F in the sediments—In general, the sum of the seven P pools agreed well with the parallel total P measurement (TPsed). For the inner bay sediment, the sum was 4.6% lower than the average TPsed (n = 8), and the absolute deviations were ±9.7%. For the outer bay sediment, the sum was 4% higher than the TPsed (with absolute deviations of ±12.5%) and for the offshore site, the sum was 2.4% lower (with absolute deviations of ±6.6%). Given a standard deviation on TPsed measurements (n = 3) of ±5% as an average for all samples (Fig. 3), the level of uncertainty on P-pool analyses is acceptable. However, because the TPsed measurement probably has less overall error than the measurement and summing of the seven different pools, the pools are always adjusted so that the sum of seven pools becomes equivalent with the parallel value for TPsed.

TPsed was higher at the inner bay site (BBI) than at the outer bay (BBO) and offshore (NC) sites primarily due to a higher content of acetate-extractable IP (Fig. 3). Although
Fig. 2. Procedure used for extraction of solid-fraction P from wet carbonate sand. The method is modified after Jensen and Thamdrup (1993) by adapting the current step 4 from Ruttenberg (1992) and by the use of 1 M MgCl₂ in step 1. BD is an abbreviation of bicarbonate-dithionite, a buffered (pH 7.2) reductant solution. The scheme provides an operational discrimination between various P reservoirs. The interpretation of results as indicated by the name on the P pools (bold, italics) are discussed in the text.

smaller sediment grains have higher P content than do larger grains (McGlathery et al. 1994), the higher TP at the inner bay site as compared with the outer bay site cannot be attributed to the difference in sediment grain size (McGlathery et al. 1994), but must be explained by either a different origin of the sediments or by accumulation of additional P from anthropogenic loading.

Depth distributions of the major pools are shown in Fig. 3. For all the pools, there was little change in concentration with depth at the three stations, and the results of the se-
Sequential leaching of P, Ca, Fe, and F\textsuperscript{-} that are presented in Fig. 4 are calculated as average values for all depths. The major P pools identified in the extraction procedure were BD-extractable IP, acetate-extractable IP, and acetate-extractable OP (Fig. 4, upper panels). Loosely adsorbed IP was present in small amounts at all sites, but the largest fraction was observed at the nutrient-rich inner bay station. The largest P pool at all three sites, representing 68–74\% of the TP\textsubscript{sol}, was the acetate-extractable IP. The assumption that CFA is leached preferentially into the acetate buffer (Ruttenberg 1992) is supported by our data, showing that most sediment Ca (Fig. 4, second row of panels) and nearly all sediment F\textsuperscript{-} (Fig. 4, lower panels) was recovered in this step.

Nearly all of the OP was leached in the acetate buffer step (step 4), which is unusual when compared with clastic sediments where leachable OP normally appears only in steps 1 and 3 (Jensen and Thamdrup 1993). It is not likely that the OP in step 4 originated from seagrass debris that had not been removed before analysis. When a similar fractionation scheme was used to analyze P pools in Zostera marina debris, 94\% of the P was recovered in steps 1 and 3 (half of this as DOP), only 1\% of the P was recovered in the acid-extraction step, and 5\% was recovered by the final combustion step (Thomsen 1993). From this observation, and because the sediment pellet in our extraction was almost completely dissolved in the acetate buffer, we assume that the OP leached in step 4 originated mainly from the biogenic CaCO\textsubscript{3} grains. Also, Entschn et al. (1983) found that OP comprised 22\% of TP\textsubscript{sol} in the CaCO\textsubscript{3} particles from carbonate sand of Davis Reef, Australia. This proportion is similar to what we found in the acetate buffer extraction.

A significant fraction of IP was extracted by the BD reagent (step 2) at all three sites (Fig. 4, upper panel). This reagent is considered fairly specific for iron-bound P in clastic sediments (Jensen and Thamdrup 1993; Jensen et al. 1995). However, no Fe was leached in the BD buffer at the outer bay and offshore sites, and for the inner bay sediments, the ratio between Fe and P in the BD leachate is only 2.3, whereas in clastic sediments ratios are normally between 8 and 15 (Jensen and Thamdrup 1993). For all samples (n = 24) the BD-extractable pool correlated positively with the acetate-extractable pool (r\textsuperscript{2} = 0.58, P < 0.001; linear regression with t-test). This observation suggests that the BD reagent extracts some IP bound to the surface of CaCO\textsubscript{3} particles, with only little concurrent dissolution of Ca and F\textsuperscript{-}. Therefore, our results suggest that the BD step is less specific for Fe-bound P with increasing amounts of CaCO\textsubscript{3} present in the sediment. The extraction steps 3, 5, and 6 leached only insignificant amounts of P (Fig. 4). These steps are considered to represent clay- and Al\textsubscript{3}\textsuperscript{+}-bound IP (step 3), detrital apatite (step 5), and refractory organic P (step 6), all of which are P forms that are more likely to be found in sediments influenced by a riverine particle load than in the nearly undiluted marine deposits of Bermuda.

Sediment Fe content decreased dramatically from 474 μg (g DW\textsuperscript{-1} in the inner bay to 140 μg (g DW\textsuperscript{-1} in the outer bay and to only 16 μg (g DW\textsuperscript{-1} in the offshore sediment (Fig. 4, third row of panels), while manganese was below detection limit in all extracts. The sediment Fe content can be considered as an indicator of anthropogenic and(or) ter-

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Fig. 3. Depth distribution of solid sediment total P (TP\textsubscript{sol}) and the four most important P pools (see text) on the three stations in April. Organic P (OP) represents the sum of leachable OP (steps 1, 3, and 4) and refractory OP (step 6). Horizontal bars on the TP\textsubscript{sol} profiles represent standard deviations of three replicate measurements. All samples represent sediment pooled from three cores.
Fig. 4. Simultaneous leaching of P, Ca, Fe, and F⁻ in the three types of sediments sampled in August 1993. The results represent average values for all depth. Iron that leached into the acetate buffer and into 0.5 M HCl was not determined separately. Thus, the broad Fe bars represent the sum of the two fractions. Manganese was below detection limit in all leachates.

Table 1. Element ratio of inorganic P and fluoride (IP:F⁻) and of total P and fluoride (TP:F⁻) in the solid sediment fraction (0–30-cm depth) from the three sampling sites in August (BBI, inner bay site; BBO, outer bay site; NC, north channel station; see Fig. 4).

<table>
<thead>
<tr>
<th></th>
<th>IP:F⁻</th>
<th>TP:F⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBI</td>
<td>0.12</td>
<td>0.15</td>
</tr>
<tr>
<td>BBO</td>
<td>0.048</td>
<td>0.066</td>
</tr>
<tr>
<td>NC</td>
<td>0.043</td>
<td>0.062</td>
</tr>
</tbody>
</table>

Restrial influence in the three sediments since Fe is likely supplied with groundwater seepage. Iron was primarily leached in the acid-extraction steps (steps 4 and 5), which probably represents Fe-(mono)sulfide, and in the residual pool that includes pyrite (Jensen and Thamdrup 1993). Only in the surface sediment from the eutrophic inner bay site was a significant proportion of Fe extracted by the BD reagent. This fraction represents ferric oxyhydroxides capable of binding reactive P, and therefore some of the BD–IP in the inner bay sediment is likely iron-bound P. The ratios between P, Ca, Fe, and F⁻ differed among the stations (Fig. 4, Table 1). The P:F⁻ ratio at the inner bay site was higher than at the two other sites, and was the result of both a higher P content and a lower F⁻ content at that site.
Table 2. Increments in porewater concentrations (as compared with concentrations in overlying seawater) of dissolved inorganic P (ΔDIP), total dissolved P (ΔTDP), and fluoride (ΔF⁻) as averaged for 0–40-cm depth. Pore water was sampled at two sites (a and b) on each of the three stations in August. The ratios of ΔDIP:ΔF⁻ and ΔTDP:ΔF⁻ also represent average values for 0–40-cm depth.

<table>
<thead>
<tr>
<th></th>
<th>ΔDIP</th>
<th>ΔTDP</th>
<th>ΔF⁻</th>
<th>ΔDIP:ΔF⁻</th>
<th>ΔTDP:ΔF⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBI(a)*</td>
<td>0.40</td>
<td>0.98</td>
<td>1.58</td>
<td>0.25</td>
<td>0.62</td>
</tr>
<tr>
<td>BBI(b)</td>
<td>0.63</td>
<td>0.93</td>
<td>2.35</td>
<td>0.27</td>
<td>0.40</td>
</tr>
<tr>
<td>BBO(a)</td>
<td>0.29</td>
<td>0.67</td>
<td>1.78</td>
<td>0.16</td>
<td>0.38</td>
</tr>
<tr>
<td>BBO(b)</td>
<td>0.16</td>
<td>0.56</td>
<td>1.81</td>
<td>0.088</td>
<td>0.31</td>
</tr>
<tr>
<td>NC(a)</td>
<td>0.25</td>
<td>1.06</td>
<td>5.07</td>
<td>0.049</td>
<td>0.21</td>
</tr>
<tr>
<td>NC(b)</td>
<td>0.36</td>
<td>1.12</td>
<td>6.96</td>
<td>0.052</td>
<td>0.16</td>
</tr>
</tbody>
</table>

and dissolved organic P (DOP) reached concentrations well above those in the overlying water at all three sites. In the pore water from the outer bay and offshore sites, most dissolved P was present as DOP. Because the presence of F⁻ above seawater concentrations indicates dissolution of the carbonate matrix (including CFA; e.g., Rude and Aller 1991), the correspondence between the F⁻, DIP, and TDP maxima suggests that the elevated concentrations of DIP (and perhaps DOP) were partly the result of carbonate dissolution. A comparison of the average increments in DIP, TDP, and F⁻ over the 0–40-cm depth is given in Table 2. The increment in DIP was highest at the inner bay site, while the increment in TDP over the depth profile was high both at the inner bay site and the offshore site. The F⁻ increment was more than twice as high in pore water at the offshore site as in pore water at the bay sites. For the offshore site, the ratio between DIP and F⁻ increments (ΔDIP:ΔF⁻) in the sediment pore water (Table 2) was equivalent to the ratio between IP and F⁻ in the sediment solid fraction (Table 1). The pore water ΔDIP:ΔF⁻ ratios were 2–3 times higher than the solid-fraction ratios at the bay sites. The porewater ratios of ΔTDP:ΔF⁻ (Table 2) were generally 3–5 times higher than the solid-fraction ratios (Table 1) in all three sediments. This was due to the higher ratio between DOP and DIP in pore waters than between OP and IP in the sediment solid fraction.

Fig. 5. Porewater profiles of total dissolved P (TDP), dissolved inorganic P (DIP), and fluoride (F⁻) in vegetated sediment in August. The pore water was sampled from sippers operated by scuba diving. Fully drawn lines and dotted lines, respectively, represents results from the same porewater sample. Concentration of dissolved organic P (DOP) can be calculated as the difference between TDP and DIP.

Porewater profiles—Porewater samples were obtained from sediment depths down to 40 cm during the August sampling. At all three sites, porewater concentrations of DIP, total TDP, and F⁻ increased with depth down to 10 cm, after which a slight decrease was generally observed (Fig. 5). DIP

C, N, P, and Fe in seagrass leaves—The nutrient (N and P) content of T. testudinum leaves declined gradually from the inner bay site to the offshore site (Table 3). In August, both N and P were lower than in April but with nearly unchanged N:P molar ratios (Table 3). The outer bay site and the offshore site had P concentrations in the lower end of those reported in T. testudinum leaves (Duarte 1990) whereas N concentrations were around the middle of the range reported by Duarte (1990). This indicated that the outer bay site and the offshore site were fairly oligotrophic. Leaf C content was fairly stable, such that C:P ratios reflected the change in leaf P content. Leaf Fe concentration declined gradually from the inner bay site to the offshore site (Table 3), reflecting the gradient in sediment Fe content (Fig. 4) and possibly indicating Fe limitation of seagrass growth (Duarte et al. 1995). Overall, the leaf analyses indicated that the growth of T. testudinum at Bermuda was P and(or) Fe
Table 3. Carbon (C), nitrogen (N), phosphorus (P), and iron (Fe) concentrations in dried Thalassia testudinum leaves from the three Bermuda sites in April and in August.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>P</th>
<th>Fe</th>
<th>C:P Molar ratio</th>
<th>N:P Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% of DW</td>
<td>(ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>April</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBI*</td>
<td>35.3</td>
<td>3.02</td>
<td>0.274</td>
<td>213</td>
<td>322</td>
<td>24.4</td>
</tr>
<tr>
<td>BBO</td>
<td>36.0</td>
<td>2.53</td>
<td>0.162</td>
<td>87</td>
<td>574</td>
<td>34.6</td>
</tr>
<tr>
<td>NC</td>
<td>36.1</td>
<td>2.13</td>
<td>0.141</td>
<td>45</td>
<td>661</td>
<td>33.4</td>
</tr>
<tr>
<td>August</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBI</td>
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<td>1.87</td>
<td>0.171</td>
<td>112</td>
<td>467</td>
<td>24.2</td>
</tr>
<tr>
<td>BBO</td>
<td>34.1</td>
<td>1.80</td>
<td>0.110</td>
<td>65</td>
<td>800</td>
<td>36.2</td>
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<tr>
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<td>1.84</td>
<td>0.116</td>
<td>52</td>
<td>755</td>
<td>35.1</td>
</tr>
</tbody>
</table>

* See Table 1 for definitions of locations.

Table 4. Ambient water temperature and concentrations of total dissolved P (TDP) and dissolved reactive P (DIP) at the three Bermuda stations in April and August 1993.

<table>
<thead>
<tr>
<th></th>
<th>April 1993</th>
<th>August 1993</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>DIP (nM)</td>
</tr>
<tr>
<td>BBI*</td>
<td>22</td>
<td>45</td>
</tr>
<tr>
<td>BBO</td>
<td>22</td>
<td>45</td>
</tr>
<tr>
<td>NC</td>
<td>22</td>
<td>41</td>
</tr>
</tbody>
</table>

* See Table 1 for definitions of locations.

Discussion

Dissolution of CaCO₃-bound P in the rhizosphere—Although F⁻–bearing and P-bearing phases other than CFA are present in carbonate sediments (Rude and Aller 1991; this study), our sequential extraction procedure revealed that no leaching of F⁻ occurred without quantitative leaching of inorganic and organic P. Similarily, Rude and Aller (1991) ob-

![Fig. 6](image-url) Diffusive fluxes of O₂, DIP, and DOP between sediment and water in April and August 1993. Positive bars indicate release from the sediment and negative bars indicate uptake from water to sediment. Vertical lines on top of the bars represent SE values for 5–9 sediment cores. All O₂ fluxes and all DOP fluxes except NC_August are significantly different from zero (two-sided t-test). For DIP fluxes, only BBI_August is significantly different from zero. In April a contamination of the incubation water spoiled the DIP flux measurement at station BBO.
served concomitant leaching of $F^-$ and DIP at a molar ratio similar to that in the bulk material during experimental dissolution of biogenic aragonite (OP was not measured in that study). Thus, the parallel course of elevated porewater concentrations of $F^-$, DIP, and TDP indicate that porewater P originated, at least partly, from dissolution of the carbonate matrix in the *T. testudinum* rhizosphere. If, in the simplest case, we assume a conservative behavior of DIP, DOP, and $F^-$ in the pore water, then a comparison of ratios in concentration increments ($\Delta$DIP : $\Delta$F$, $\Delta$TDP : $\Delta$F$^{-}$) with ratios of IP: F$^-$ and TP$^{sed}$:F$^-$ in the sediment solid fraction suggests that at the offshore station, porewater DIP originated entirely from dissolution of the carbonate matrix since ratios in pore water and solid fraction are similar. At the bay sites, only half of the porewater DIP (inner bay) and one-third of DIP (outer bay) can be attributed to this process. Several factors, however, complicate this simple comparison of porewater and sediment ratios of DIP and F$^-$. First, in situ dissolution of the carbonate grains would probably begin with a preferential leaching of the IP that is bound in the surface of the carbonate particle, similar to what we observe in the stepwise extraction of solid-fraction P with gradually stronger reagents (Figs. 2, 4). This would result in the higher DIP: F$^-$ ratio in the pore water than in the solid fraction that we observed in the bay sediments. Second, the "standing stock" porewater concentration of both DIP and F$^-$ is a result of the balance between generation and removal processes. Neither DIP nor F$^-$ is likely to behave conservatively; instead, both react with the carbonate matrix (e.g. Rude and Aller 1991). DIP also is subject to biological uptake by seagrass roots and by other living organisms (e.g. bacteria) in the sediment. Finally, both DIP and F$^-$ is lost from the rhizosphere by upward and downward transport processes. The removal processes would most likely result in lower DIP: F$^-$ ratios in the pore water than in the leachate. These same considerations can be made for TDP: F$^-$ ratios. In the pore water the larger proportion of TDP consists of DOP that probably has a low affinity for the carbonate matrix, low diffusion constants (being large molecules), and low biological reactivity. If the F$^-$ removal processes exceed those for DOP, this would result in a higher TDP: F$^-$ ratio in the pore water than in the leachate as we observe at all sites. Another possible explanation for the high $\Delta$TDP: F$^-$ is that there is an additional source of DOP (e.g. fresh organic matter) in the sediment.

Although we are not able to report rates of P mobilization from the carbonate matrix at the Bermuda sites, our results suggest that probably at least one-third to one-half of porewater DIP originated from this dissolution process. Rude and Aller (1991) found model-predicted F$^-$ mobilization rates to range between 170 and 770 $\mu$mol m$^{-2}$ d$^{-1}$ in a carbonate sediment located some distance from a seagrass bed in Florida Bay. Given an IP: F$^-$ ratio of 0.09 in their sediment, the concurrent rate of IP mobilization would be 15.5–70 $\mu$mol m$^{-2}$ d$^{-1}$. Because overall sediment metabolism seems generally higher in seagrass beds than on bare sediment (Morse et al. 1987), we consider it possible that carbonate dissolution could occur with a similar rate in the Bermuda seagrass beds. If so, carbonate dissolution would contribute significantly to the daily P requirement for *T. testudinum* (see below). Because carbonate sands contain the major inorganic P pool available to the seagrasses (see Fig. 7 and discussion below), this finding establishes the potential role of the carbonate sediment as a long-lasting P source for seagrass growth.

Two possible mechanisms can cause CaCO$_3$ dissolution. The first is the lowering of pH due to high metabolic activity and to sulfide oxidation, and the second is the direct action of organic acids released by the seagrass roots on CaCO$_3$. Metabolic activity is often high in the rhizosphere, and the rhizosphere may also be a zone of high sulfide ox-
Table 5. Total sediment P (TP\textsubscript{sed}) concentrations in the Bermuda sediments fall within the range reported for other seagrass beds in carbonate sand.

<table>
<thead>
<tr>
<th>Site</th>
<th>TP\textsubscript{sed} (\textmu mol P (g DW\textsuperscript{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbados</td>
<td>7.7</td>
<td>Patriquin 1972</td>
</tr>
<tr>
<td>Davis Reef, Australia</td>
<td>9.7</td>
<td>Entsch et al. 1983</td>
</tr>
<tr>
<td>Bahamas, offshore</td>
<td>2.5</td>
<td>McGlathery et al. (unpubl.)</td>
</tr>
<tr>
<td>South Sulawesi, Indonesia</td>
<td>8.9</td>
<td>Erftemeier and Middelburg 1993</td>
</tr>
<tr>
<td>Bailey’s Bay, inner station</td>
<td>5.5</td>
<td>This study</td>
</tr>
<tr>
<td>Bailey’s Bay, outer station</td>
<td>3.2</td>
<td>This study</td>
</tr>
<tr>
<td>Bermuda, north channel</td>
<td>3.3</td>
<td>This study</td>
</tr>
</tbody>
</table>

...iation (e.g. Blackburn et al. 1994). High metabolic activity in the rhizosphere may be caused both by decay of belowground biomass and by release of DOC from the roots, which is thought to be significant for seagrasses growing in carbonate sands (Capone et al 1979; Blackburn et al. 1994). No evidence exists that root exudates play a direct role in the mobilization of solid-fraction P for marine angiosperms, but examples from soil science literature are numerous (Lambers and Poorter [1992] and references therein). Organic acids, in particular citric acid (Lipton et al. 1987; Hoffland et al. 1989) and oxalic acid (Lajtha and Harrison 1995), have been identified as root exudates and have been found to enhance mobilization of P from solid fractions, such as phosphyric rocks (Kpomblekou and Tabatabai 1994) and from P precipitated with pure CaCO\textsubscript{3} (Johnson and Miller 1959). Furthermore, because root exudation occurs as a response to P stress (Lipton et al. 1987; Hoffland et al. 1989), P-limited seagrasses growing in carbonate sediments may be expected to have a similar mechanism for extracting P from solid fractions.

**Seagrass P requirement and size of available P pools**—Estimates for the P requirement of T. testudinum derived from net leaf growth and leaf P content range from 30 to 100 \textmu mol P m\textsuperscript{-2} d\textsuperscript{-1} (Patriquin 1972; Fourqueuran et al. 1992b). Similar calculations can be made for the inner and outer sites in Bailey’s Bay using data from McGlathery (1995). Net leaf production rates were 1.18 and 0.666 g DW m\textsuperscript{-2} d\textsuperscript{-1} at the inner and outer bay sites, respectively, with leaf P concentrations being 0.19 and 0.13%. P requirements are then calculated to be 72 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1} for the inner bay site and 28 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1} for the outer bay site in August 1991. These estimates reflect the P needed to maintain the measured leaf P content, which may be higher than the critical level needed to sustain growth. They do not take into account the P requirements of below-ground parts or the P requirements of S. filiforme at the outer bay site.

Comparison of the P requirements for T. testudinum at the Bailey’s Bay sites with available P pools (shown in Fig. 7) reveals that the DIP pool in the pore water would be exhausted in 1 d, if not renewed, and that DIP in the overlying water would last for a maximum of 3 d. If DOP is also taken into account, the total dissolved pools would last 2-4 times longer. Thus, neither the porewater pool nor the water-column pool can sustain growth during an active growing season of \textasciitilde200 d without rapid replenishment. In contrast, P pools associated with the solid-sediment fraction are much larger. Although the pool of loosely adsorbed P is small when compared with TP\textsubscript{sed} (Fig. 7, third panel), it is still large enough to potentially sustain growth for 2 years, according to our estimate. The TP\textsubscript{sed} pool in the upper 20 cm of the sediments is 100 times larger than the estimated annual P requirement. The organic fraction of TP\textsubscript{sed} may be less available for the seagrasses, but the total inorganic P pool constitutes 75% of TP\textsubscript{sed} and if made available it can potentially support seagrass growth for decades. The size and distribution of sediment P pools found for the three Bermuda sites are somewhat typical for carbonate sediments, since the P content in the Bermuda sediments were similar to the P content in carbonate sediments elsewhere (Table 5).

Given the observations of P mobilization from a reservoir that is 75–100 times larger than the annual P requirement of T. testudinum, the most likely explanation of the widespread observations of P-limited growth of seagrasses in carbonate sand is that P mobilization from the sediments generally occurs at rates that cannot meet the requirements for maximum growth. The same explanation has been suggested for P-limited growth in terrestrial ecosystems (e.g. Lajtha and Harrison 1995).

**Other possible P sources**—Nutrient inputs from groundwater seepage and from mineralization of organic matter within the sediments may also be potential sources of P for seagrass growth. McGlathery et al. (1994) suggested that both the higher TP\textsubscript{sed} and the higher P content of T. testudinum at the inner bay site reflected greater external P loading closer to the shore. Also mineralization of organic matter in the sediment may provide P for seagrass growth as suggested by Erftemeier and Middelburg (1993). Based on our sediment oxygen uptake measurements (16–34 mmol O\textsubscript{2} m\textsuperscript{-2} d\textsuperscript{-1}) and a C:P ratio of 1,000 in T. testudinum roots and rhizomes (Erftemeier and Herman [1994] for roots of T. hemprichii), we estimate that organic mineralization could contribute 16–34 \textmu mol P m\textsuperscript{-2} d\textsuperscript{-1}. Phosphorus released from mineralization of roots, however, cannot be considered as a P source for net growth of seagrasses, but it may contribute to the observed porewater TDP, as well as the DOP efflux. Alternatively, if we assume that the organic matter had another origin than seagrass production (e.g. microalgae or macroalgae) and a lower C:P ratio, mineralization would release amounts of P to the pore water that could be a significant source for seagrass nutrition. Future studies of P-
sedimentation fluxes to shallow carbonate seagrass beds are needed to elucidate the possible magnitude of this source.

Ecological significance of sediment P mobilization through sediment dissolution—In accordance with the general view of carbonate sands as sinks for P, earlier studies have indicated that Bermuda sediments immobilize IP through CFA formation (Bern 1974; Gaudette and Lyons 1980). Our results of P release through dissolution of sediment in the seagrass rhizosphere do not necessarily contradict this earlier work, which was conducted in sediments without seagrasses (Bern 1974) or at greater depth below the rhizosphere in sediments (Gaudette and Lyons 1980). We observed CFA dissolution to be the dominating process in the upper 40 cm of seagrass-covered sediments.

We found that rhizospheric sediments regularly released significant quantities of DOP to overlying waters, and this usually dominated the net exchange of dissolved P between sediments and overlying water. In one case, the sediment also released DIP, although generally there was neither a clear release or uptake of DIP by sediments in the seagrass beds. Only once did we observe a clear uptake of DIP by the sediment, and this was when we artificially (and accidentally) increased the concentration of DIP in the overlying water in our incubation chamber at the outer bay site in April.

The magnitude of the P efflux from Bailey’s Bay sediments is potentially significant for micro- and macroalgae since water column TDP can be renewed in 16 and 24 d, respectively, by the observed DOP release. At the offshore site, where the DOP efflux was smaller and the water column higher, it would take >400 d to renew water column TDP by this mechanism. The observation that vegetated sediments can also be a source of dissolved P to the overlying water expands our understanding of P cycling in shallow carbonate sediments, and makes a parallel case to lacustrine temperate environments with siliclastic sediments, where sediment P release may be important for primary production in the overlying water.

Within Bailey’s Bay, the inner site receives higher loading of P from terrestrial sources (McGlathery et al. 1994). That Fe concentrations in the sediments are lower at our offshore site than at either of the Bailey’s Bay sites indicates that terrestrial sources of P there are lower yet, as one would expect. In agreement with the gradient of terrestrial (probably anthropogenic) influence, we observed a gradient with the highest O2 uptake and the highest P release rates in the inner bay sediment in August, while the lowest rates were measured at the offshore site. The higher rate of P release from sediments along with the higher external input at the inner bay site provide an explanation for the higher P concentration in seagrass leaves at this site. The P concentrations in leaves at the inner site are high enough to suggest that this site may not be P limited. In accordance with this suggestion, McGlathery et al. (1992) observed N-limited growth of macroalgae in Bailey’s Bay. At the more oligotrophic outer Bailey’s Bay site and at the offshore site, the P concentrations in seagrass leaves were lower and suggest P limitation.

We conclude that even though most of the carbonate-bound P in sediments can become available to the seagrasses as the sediment in the rhizosphere is dissolved, such P release may be too slow to support maximum growth rates at more oligotrophic sites. This may be the explanation for the P limitation that is often observed for seagrasses growing in carbonate sediments. Still, however, the observation that dissolution of carbonate-bound P occurs provides a plausible explanation for how long-term growth can be maintained at the same site by this large pool of P in the sediment.

References


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