Potential availability of sedimentary phosphorus to sediment resuspension in Florida Bay

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[1] Several studies have suggested that phosphorus is a limiting nutrient for seagrass and phytoplankton growth in much of Florida Bay. In fact, soluble reactive phosphate concentrations in Florida Bay waters can be as low as a few nM. Sediments represent the largest phosphorus reservoir because Florida Bay sediments are dominated by carbonate, which has a strong capacity to retain phosphorus. The supply of phosphorus to the water column from sediment resuspension is potentially important in providing the nutrients required for phytoplankton production. Applying an improved sequential extraction technique to sediments collected from 40 geographically representative stations in Florida Bay, this study provides the first detailed spatial distribution of total sedimentary phosphorus (TSP) and its partitioning into five chemically distinguishable pools in the surface, fine-grained sediments of the bay. A strong gradient of decreasing TSP concentration was observed from the west (14.6 \( \mu \text{mol g}^{-1} \)) to east (1.2 \( \mu \text{mol g}^{-1} \)) across the central bay. The spatial pattern of TSP is consistent with distribution of both seagrass and phytoplankton that are limited by available phosphorus in Florida Bay. Among the five pools, the authigenic carbonate fluorapatite, biogenic apatite and \( \text{CaCO}_3 \)-bound phosphorus account for the largest fraction (45%) of TSP, of which inorganic phosphorus is the dominant form, and organic phosphorus accounts for about 30% in the western and north central regions and less than 10% in other areas of Florida Bay. The second largest pools are the refractory organic phosphorus (24% of TSP) and reductant-soluble inorganic phosphorus (19% of TSP). Readily exchangeable phosphorus accounts for 8% of TSP, of which organic phosphorus is 60%. Detrital apatite phosphorus of igneous or metamorphic origin represents the smallest fraction, only 5% of TSP. Spatial distribution of phosphorus and iron in sediments indicates that external sources of these two essential plant nutrients to Florida Bay are spatially separated with phosphorus introduced by west coast waters across the western margin of Florida Bay and iron from freshwater flow into the eastern region.

INDEX TERMS: 1030 Geochemistry: Geochemical cycles (0330); 1050 Geochemistry: Marine geochemistry (4835, 4850); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; KEYWORDS: Florida Bay, phosphorus, sediment


1. Introduction

[2] River-borne suspended particulate matter accounts for more than 90% of the total phosphorus transported into estuarine and coastal regions [Burton and Liss, 1976; Meybeck, 1982, 1993]. Once in the estuaries, a significant portion of the particulate phosphorus is released to seawater by a desorption process promoted by increasing ambient salinity. Nonetheless, most particulate phosphorus in this suspended matter is aggregated and settles out into the bottom sediments [Gibbs, 1981; Meade, 1982]. Particulate phosphorus in suspended matter and sediments has been identified as the dominant reservoir of phosphorus in diverse estuarine ecosystems [e.g., Lebo, 1991; Lebo and Sharp, 1992; Conley et al., 1995]. However, the particulate phosphorus in suspended matter and sediment constantly interacts with dissolved phosphate ions in the water through adsorption/desorption and co-precipitation/dissolution processes. It has been proposed, therefore, that sedimentary phosphorus, under varying degrees of kinetic restriction, can function as a buffer system, regulating dissolved phosphate concentration in the overlying water [Mayer and Gloss, 1980; Froelich et al., 1982; Froelich, 1988].

[3] Biogenic calcium carbonates, i.e., calcite and aragonite, are major components of sediments in many tropical
and subtropical estuaries. Phosphate is strongly adsorbed on the surfaces of both calcite and aragonite [Cole et al., 1953; Kitano et al., 1978; de Kanel and Morse, 1978; Millero et al., 2001]. Adsorption has been used to explain why calcium carbonate-rich sediments contain low concentrations of dissolved phosphate in their pore waters. The kinetics of phosphate uptake has been characterized as initially fast chemisorption, followed by slow diffusion of adsorbed phosphate into interior crystal lattice to form crystalline apatite [Kitano et al., 1978]. Various forms of apatite have been identified in marine sediments including, among other things, hydroxyapatite, fluorapatite, and chloroapatite. Among them, fluorapatite is believed to be the primary sink for phosphorus in tropical marine carbonate sediments [Gaudette and Berrylyn, 1980; Ruttenberg and Berner, 1993].

[4] Recent changes in Florida Bay, including mass mortality of turtle grass, increased algal blooms, reduced sponge abundance, and changes in fish species abundances, have brought Florida Bay widespread attention [Fourqurean and Robblee, 1999]. Nutrients over-enrichment and eutrophication are hypothesized to be causally related to some of these changes [Brand, 2002]. Existing water column nutrient data indicate that nitrogen, mainly as ammonia and dissolved organic nitrogen, is relatively abundant in the interior of Florida Bay, while phosphate concentrations are generally low [Boyer et al., 1999; Rudnick et al., 1999]. Accurately quantifying the sedimentary phosphorus pools and their potential availability through resuspension is essential to understanding nutrient cycling in Florida Bay. As in many tropical lagoonal estuaries, the sediments in Florida Bay are dominated by biogenic calcium carbonate, which has a strong capacity to adsorb phosphate. The amount of adsorption is known to be proportional to sediment surface area that increases exponentially with decreasing particle size. Walter and Morse [1984] found that fine particles accounted for only 16% of weight but represented 76% of total surface area in bulk sediments. Equally importantly, fine particles are easier to resuspend into the water column by tidal or wind mixing. Once in the water column, their residence times are much longer than coarser particles given that their settling velocity is proportional to the square of particle diameter [Gibbs, 1974]. Not surprisingly, suspended particulate matter in estuarine and coastal region is dominated by particles with diameters <100 μm [e.g., Kranck, 1981; Teeter, 1993; Mitchell and West, 2002]. In the shallow waters of Florida Bay (average water depth ~1 m), fine sediments are readily suspended into surface water by wind and tidal mixing and supply nutrients to water column [Lawrence et al., 2004]. Wind conditions sufficient to resuspend fine-grained sediments throughout Florida Bay occur at approximately weekly intervals during the dry season and more localized strong convective events are common during the wet season [Wang et al., 1994].

[5] The amount of phosphorus that can be supplied to the water by sediment resuspension depends upon the abundance of exchangeable phosphorus in near surface fine-grained sediments. In order to understand the contribution of sediment resuspension to the water column phosphorus cycle in Florida Bay, it is essential therefore to quantify total phosphorus in surficial fine-grained sediments and to distinguish between the different forms of sedimentary phosphorus.

[6] Sequential extraction techniques are commonly used to separate and quantify different forms of phosphorus in sediment samples. These methods were originally developed by soil chemists to fractionate soil phosphorus [Chang and Jackson, 1957] and subsequently adapted for lake sediments [Williams et al., 1967, 1976]. Recently, these extraction procedures have been applied to marine sediments [Ruttenberg, 1992; Eijsink et al., 1997]. The extraction procedure used in this study is based upon the scheme developed by Ruttenberg [1992] for marine sediments but substantively modified to facilitate phosphate determination and extended to quantify the organic phosphorus content in the MgCl₂ and acetate buffer extracts. In this study, total sedimentary phosphorus was fractionated into five distinct pools: (1) adsorbed inorganic and exchangeable organic phosphorus, (2) reductant-soluble inorganic phosphorus, (3) authigenic carbonate fluorapatite, biogenic apatite, and calcium carbonate-bound inorganic and organic phosphorus, (4) detrital apatite phosphorus, and (5) refractory organic phosphorus.

2. Methodology

2.1. Site Description

[7] Florida Bay is a large (2200 km² area), shallow lagoon located at the southern end of the Florida peninsula. It is triangularly shaped, with its northern boundary formed by the mainland of Florida, and its eastern and southern boundaries by a chain of islands known as Florida Keys which extends from Biscayne Bay to Key West. Its western margin is open to the Gulf of Mexico, although highly restricted by extensive shallow mudbanks running approximately northwest to southeast along this western margin. Dotted mangrove islands and a complex network of carbonate mudbanks, many of which are awash at low tide, effectively divide Florida Bay into numerous isolated sub-basins with maximal water depths of 2–3 m. Water exchange between them is restricted to narrow cuts and overbank wash. Florida Bay experiences tropical savanna climate with strong wet-dry seasonality. Annual precipitation is about 120 cm, with 70% of the rainfall occurring from June to October. Historically fresh water flowed into Florida Bay from sheet flow across the marl prairies of southern Everglades through the Buttonwood embankment into the north central bay and from numerous creeks fed by Taylor Slough. More recently, with implementation of extensive upstream water management, the C-111 canal discharging into the northeastern Bay has become the major freshwater input and flow across the embankment has become rare. Water from Shark River Slough flows to the west into Whitewater Bay and can subsequently exchange with Florida Bay when this water flows around Cape Sable and enters the western region of the bay. Prevailing wind direction from southeast inhibits this connection, but strong and sustained winds from the north or west during winter months can facilitate west coast waters entering Florida Bay.
Surface sediment samples were collected during an underway survey of Florida Bay on 13–14 November 2000 at 40 regular monthly water sampling stations (Figure 1) using a Petite Ponar Grab sediment sampler (Woldco, Buffalo, New York). This sampler obtains surface sediment over an area of 230 cm² to a depth of <5 cm. The sediment samples were stored on ice in a portable cooler and returned to the laboratory at days end. They were then freeze-dried to constant weight using a Labconco model 75050 (Kansas City, Missouri) freeze-dryer. The freeze-dried samples were then sieved with a motor-driven sieve shaker (Tyler Industrial products) to separate fine particles from bulk sediment. Comparative analysis of phosphorus composition in freeze-dried and “wet” sample has detected no significant differences [De Lange, 1992; Andrieux-Loyer and Aminot, 2001]. Freeze-drying is advantageous in comparison with oven drying (typically at 60°C or above), which consolidates sediment samples, requiring further grinding before sample analysis or treatment.

Because fine-grained sediment dominates the benthic flux of phosphorus through resuspension, the <124-μm fraction [Ruttenberg, 1992] was used for determination of total sedimentary phosphorus, and CaCO₃ content, and then for sequential extraction of different forms of sedimentary phosphorus.

### 2.2. Sequential Extraction

Sequential extraction techniques utilize a series of solutions of increasing chemical reactivity, each of which is tailored to dissolve a particular form of phosphorus. The five-step sequential extraction scheme (Figure 2) allows us to make an operational separation between five different phosphorus pools and within each pool into organic and inorganic forms. Procedures used in this study are similar to those used by Ruttenberg [1992] with specific improvements highlighted below.

One-half gram of dry sediment (<124 μm size) was placed into 50 mL of the extractant solution in a 60-mL high-density polypropylene bottle. The mixture was agitated by a bench-top shaking incubator (VMR) at 200 rotations per minute for designed periods at 25 ± 0.1°C. Samples were then filtered through a glass filter (Whatman GF/F) with the aid of a vacuum pump. The filtrate was collected for analysis of dissolved phosphate and total dissolved phosphorus from which dissolved organic phosphorus was calculated by difference. The filter containing the sediment residue was used for the subsequent extraction.

In previous studies, dithionite-citrate reagent was found to be ineffective in separating iron-bound from CaCO₃-bound phosphorus, presumably because citrate is a strong complexing agent for both Fe and Ca (pK of 4.7) [Hieltjes and Lijldema, 1980]. Furthermore, citrate has also been found to interfere with spectrophotometric determination of phosphate. Solvent extraction has been used to circumvent this interference, but the resulting analytical precision was poor [Ruttenberg, 1992]. For these reasons, citrate was not used as the extraction reagent for reductant-soluble phosphorus in this study.

In previous studies, the filtrate was acidified to decompose the excess dithionite to SO₂, which was then stripped with nitrogen gas. Unfortunately, acidifying sam-

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Figure 1. Locations of 40 sediment and water sampling stations in Florida Bay. RK denotes the Rabbit Key basin.
samples and bubbling with N₂ has been found to induce elemental sulfur precipitation, presumably facilitated by the O₂-depleted condition, which interferes with subsequent phosphate and Fe analyses by spectrophotometry. To avoid this interference, two aliquots of filtrate were separately collected in this study for phosphate and total iron analyses, respectively, and these samples were not acidified. Samples for total iron analyses were performed immediately after collection; therefore no preservation by acidification was necessary. Samples for phosphate analyses were left open to the air for 72 hours to allow a complete decomposition of excess dithionite to SO₂ that was slowly released and oxidized by dissolved oxygen in the solution. This procedure prevents the formation of elemental sulfur and allows direct spectrophotometric determination of phosphate in the BD extract, eliminating the tedious organic solvent extraction procedure.

2.3. Analysis of Phosphorus

Dissolved phosphate was determined by the phosphomolybdenum blue method [Zhang et al., 1999]. At first, an auto-analyzer was employed to determine phosphate concentrations in the sequential extraction samples. However, we soon noticed that in some samples the matrix varied significantly from the reagent blank, presumably due to the dissolution of unintended sediment constituents into the extract solution. Although there was no visible turbidity in such samples, the baseline was elevated up to 0.03 absorbance unit. Conventional auto-analyzers are usually equipped with single wavelength detectors and are unable to make specific baseline correction for individual samples. Using a scanning spectrophotometer, however, a spectra can be recorded over a range of wavelengths, and any baseline shift due to a matrix effect can be readily corrected by subtracting the absorbance from that at reference wavelengths, selected to be outside the absorbance range of the analyte of interest. We used a Hewlett Packard 8453 spectrophotometer to quantify dissolved phosphate concentration in the sequential sediment extraction samples and a three-point drop technique to correct any baseline shift.

In standard phosphate methods used in natural water analysis, the amount of acid in the molybdate reagent is designed to handle samples that contain about 2 mM buffer capacity (mainly bicarbonate ion) and can effectively lower the pH of mixture (sample plus reagents) to about 1 for optimal color development. This standard method, however, cannot be directly applied to the analysis of phosphate in samples obtained from the sequential extraction, since they contain much higher concentrations of ions. Although there is little or no salt effect on the sensitivity of phosphate analysis using the molybdenum blue method, we found that ionic strength does affect the linear dynamic range of the method. The linear dynamic range in 1 M NaCl solution is about one half of that in water. Therefore the linear dynamic range of phosphate determination in a given matrix needs to be carefully examined for each extract.

In addition to ionic strength, the buffer capacities of extracts are often several orders of magnitude higher than natural water samples. It is essential to neutralize all bases with acid before the pH of mixture can be effectively lowered to 1. In previous studies, individual samples were usually adjusted with addition of acid or base to a desired pH prior to analysis of phosphate. This is labor intensive and time consuming. The strategy we used was to modify

![Figure 2. Procedure used for sequential extraction of different forms of sedimentary phosphorus in surficial sediment of Florida Bay. Extractions were conducted at 25°C with 50 mL of extractant for all steps. Extracts were determined for dissolved inorganic phosphorus (DIP) and total dissolved phosphorus (TDP), from which dissolved organic phosphorus can thus be calculated by difference.](image-url)
the reagent recipe to accommodate the required acidity in a given extract for optimal color development. This is an efficient procedure for a large number of samples of similar composition because no individual sample adjustment is required. To improve the stability of phosphomolybdic blue complex in MgCl₂ solution [Ruttenberg, 1992], our molybdate reagent was prepared by dissolving 0.71 g ammonium molybdate in 10 mL concentrated sulfuric acid and 50 mL antimony potassium tartrate solution (3 g L⁻¹) and diluting the final volume to 1 L with distilled water. In step 2 the above molybdate solution was modified by using 15.38 g ammonium molybdate and 174 mL concentrated sulfuric acid. The high concentration of molybdate used in the latter reagent is designed to match H⁺ concentration, maintaining a ratio of H⁺/molybdate at about 70 for optimal color development [Zhang et al., 1999]. In step 3, an addition of HCl to individual samples is required to titrate acetate in buffer solution and carbonate dissolved from sediments. Sulfuric acid was found not suitable for pH adjustment due to the formation of CaSO₄ precipitate. In step 4 and 5, an addition of NaOH is required to neutralize 1 M HCl and raise the pH to neutral.

2.4. Determination of Total Dissolved Phosphorus

[17] Total dissolved phosphorus in the extract was determined by autoclave-assisted boiling temperature persulfate oxidation of the organic phosphorus, followed by the standard colorimetric determination of liberated orthophosphate. The oxidizing reagent was prepared by dissolving 5.0 g K₂S₂O₈ in 100 mL of 0.45N H₂SO₄ solution. An aliquot of 10.0 mL of the sample was mixed with 1.0 mL of oxidizing reagent in a 100-mL capped glass tube. Samples were autoclaved for 60 min at a pressure of 2 atm and temperature of 120°C. Calibration standards were autoclaved and processed like the samples.

[18] In digesting the acetate buffer extracts (step 3), sulfuric acid was replaced by nitric acid to avoid precipitation of gypsum that interfered with subsequent phosphate analysis. Although using HCl can avoid gypsum precipita-

tion, it results in the formation of chlorine. The use of nitric acid yielded a 95% recovery (for model organic phosphorus compound adenosine tri-phosphate, ATP), which is similar to that obtained from using sulfuric acid reagent.

2.5. Determination of Total Sedimentary Phosphorus

[19] Total sedimentary phosphorus in each sample was determined by wetting sediment samples with Mg(NO₃)₂ solution and combustion at 550°C for 2 hours followed by 1 M HCl extraction for 16 hours at 25°C [Cembella et al., 1986; Solorzano and Sharp, 1980]. Liberated orthophosphate in the extracts was determined by the aforementioned spectrophotometric method.

2.6. Surface Reactive Iron

[20] Reactive iron oxides were determined as part of sequential extraction procedure (step 2). Iron oxides were reduced by BD reagent to dissolved iron. Total dissolved iron, Fe(III) + Fe(II), in the extract solution was reduced to Fe(II) with ascorbic acid. Fe(II) was then spectrophotometrically determined with ferrozine reagent in a pH 5.5 buffer solution at a maximum absorption wavelength of 562 nm [Stookey, 1970; Zhang et al., 2001].

2.7. Calcium Carbonate Content

[21] The percentage of calcium carbonate was determined from a separate set of <124-μm-size sediment samples by dissolution in 1 M HCl solution, separation of particulate residuals by filtration, and drying to a constant weight at 105°C. The amount of CaCO₃ in the sediment was operationally defined as the weight loss, due to the dissolution, from the original sediment sample weight.

3. Results and Discussion

3.1. CaCO₃ Content

[22] CaCO₃ is the dominant constituent of Florida Bay’s fine-grained sediments, ranging from 81.2% to 95.6% by weight with an average of 89.2 ± 4.3% (Figure 3). The lowest contents (81.2%) were found at northwest coastal stations 9 and 12. The second to the lowest (82.4–82.8%) were found at stations 30 and 31 in Rabbit Key basin. Eastern bay sediments contained the highest percentage (>92%) of calcium carbonate. Variations in sedimentary CaCO₃ content are mainly caused by dilution of CaCO₃ with buried organic matter. Therefore the spatial distribution of CaCO₃ should inversely reflect the accumulation pattern in sediment organic matter. Indeed it is well documented that the eastern bay is the least productive subregion in regard to average water column chlorophyll, seagrass coverage, and benthic biomass [Ziemann et al., 1989; Boyer et al., 1999]. On the other hand, northwest coast and north central regions are known to have frequent phytoplankton and cyanobacterium blooms [Phlips and Badylak, 1996; Phlips et al., 1999].

3.2. Total Sedimentary Phosphorus

[23] Total sedimentary phosphorus in Florida Bay ranges from 1.22 to 14.63 μmol g⁻¹ and shows a strong east-west gradient (Figure 4). The highest concentrations of total

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Figure 3. Spatial distribution of percentage of calcium carbonate in surface fine-grained sediments of Florida Bay.
sedimentary phosphorus (>9 \textmu mol g\textsuperscript{-1}) are found in the northwest corner of Florida Bay, along the coast from Flamingo to Cape Sable. The lowest concentrations (<3 \textmu mol g\textsuperscript{-1}) are found in the eastern region of Florida Bay. A sharp decreasing gradient in sedimentary phosphorus concentration was observed from the west to east across central Florida Bay, essentially separating the two very different western and eastern regimes.

[24] The abundance of total sedimentary phosphorus in Florida Bay covers a wide range in comparison to other shallow water carbonate sediments. The eastern region of Florida Bay has a low total sedimentary phosphorus concentration similar to Sharp Bay, Western Australia (<1 \textmu mol g\textsuperscript{-1} [Atkinson, 1987]). Higher total sedimentary phosphorus (~9–14 \textmu mol g\textsuperscript{-1}) in western region of Florida Bay are within the range of reports for other relatively pristine environments like Davis Reef, Australia [Entsch et al., 1983], Bahamas [Patriquin, 1972], and Barbados [Erftemeijer and Middelburg, 1993] but at the low end of the range reported along the western Florida coast (8–20 \textmu mol g\textsuperscript{-1} [Weng et al., 1994]). Much higher total sedimentary phosphorus (31–38 \textmu mol g\textsuperscript{-1}) has been reported at a couple of stations in Tampa Bay along the west coast of central Florida, but those locations are almost certainly influenced by nearby phosphorus mining and processing operations and the nearby urban population [Weng et al., 1994].

### 3.3. Adsorbed Inorganic and Exchangeable Organic Phosphorus

[25] A considerable fraction of exchangeable phosphorus is potentially bioavailable in that it can be easily released into the water column through desorption processes. The extent of such release depends on the ambient phosphate concentration as well as other environmental conditions, such as temperature and salinity. Macroalgal-available phosphorus has been assessed by incubating algae in direct contact with sediments and monitoring the decrease in sediment phosphorus by chemical extraction [Dorich et al., 1980, 1985]. Total exchangeable phosphorus extracted by MgCl\textsubscript{2} solution in Florida Bay sediments ranges from 0.10 to 1.30 \textmu mol g\textsuperscript{-1}. On average, exchangeable phosphorus accounted for 8.2 ± 2.2% of total sedimentary phosphorus. Further fractionation of total exchangeable phosphorus into organic and inorganic phosphorus forms indicates that the organic phosphorus concentration is generally higher than the inorganic. The percentages of organic phosphorus are fairly uniform across Florida Bay, with an average of 61.4 ± 9.0%, even though the concentration of total exchangeable phosphorus varied more than an order of magnitude. Total exchangeable phosphorus shows an east-
west spatial gradient like total sedimentary phosphorus (Figure 5a), but their distributions are not identical. The highest concentration (>1 μmol g⁻¹) was found in the northwest region of the bay, near Cape Sable. The next highest (>0.8 μmol g⁻¹) were found at stations 30 and 31 in Rabbit Key basin. Low concentrations were observed in the eastern bay (<0.3 μmol g⁻¹), with the lowest concentration of 0.1 μmol g⁻¹ at coastal station 3. Our values for central coastal stations (stations 3–5) are similar to values of 0.1 μmol g⁻¹ of exchangeable phosphorus reported for a nearby location by Koch et al. [2001]. Given their fairly constant ratios, the inorganic and organic fractions of exchangeable phosphorus show similar spatial distributions as total exchangeable phosphorus (see Figures 5b and 5c, respectively). In addition to organic phosphorus adsorbed to sediment particle surfaces, it has been hypothesized that organic phosphorus in benthic microalgae cells attached to the sediment surface might be released, when cells are broken by mechanical shaking, and contribute, in part, to the high percentage of organic phosphorus measured in the exchangeable pool. However, the constant ratios observed argue against the significance of this source, since benthic microalgae are not uniformly distributed in Florida Bay.

3.4. Iron Oxides and Reductant-Soluble P

Owing to its low solubility, in aquatic environments, iron is predominantly found in the colloidal and particulate forms. Among the various types of natural particles, iron hydroxide and iron oxides have the strongest adsorption capacity for phosphate [Berner, 1973; Hingston et al., 1974; Khalid et al., 1977]. As a result, the iron hydroxide content in sediments and suspended matter might be an important factor in regulating the phosphorus retention capacity of sediments. In Florida Bay, reductant-soluble phosphorus ranges from 0.23 to 2.22 μmol g⁻¹, and its spatial distribution pattern is similar to that of exchangeable phosphorus, with high concentrations in the northwest region and low concentrations in the eastern bay (Figure 6). The highest concentrations (>2 μmol g⁻¹) occurred at stations 9, 10, 12, and 13 along the northwestern coast of Florida Bay. The next highest concentrations (>1.8 μmol g⁻¹) occurred at stations 30 and 31 in Rabbit Key basin, where exchangeable phosphorus is also high. In Rabbit Key basin, substantial secondary seagrass die-off was observed during 1995 to 1998 [Durako et al., 2002]. Phosphorus from the decay of seagrass tissue might be the source of these surface-reactive phosphorus pools, because in this basin, there is no corresponding high content of phosphorus pools associated with interior matrix, such as CaCO₃-bound phosphorus, as shown in forthcoming discussion.

Surface reactive iron as measured by reduction of ferric oxide ranges from 0.81 to 4.21 μmol g⁻¹. Its concentration decreases away from the Florida mainland (Figure 7a). Along the northern perimeter the maximum concentration was 4.21 μmol g⁻¹ at station 2. Low concentrations were found in the southern regions of Florida Bay where water exchanges with Atlantic Ocean surface water, typically low in iron content, through several channels between the Florida Keys. The distribution of surface reactive iron we observed is similar to that Chambers et al. [2001] observed, although their reactive iron concentrations were about six-fold higher because they included

![Figure 6. Spatial distributions of reductant-soluble phosphorus in surface fine-grained sediments of Florida Bay.](image)

![Figure 7. Spatial distributions of (a) reactive Fe oxides in fine-grained sediments and (b) a typical salinity distribution after a heavy rain event at beginning of the wet season that was preceded by a prolonged dry season in Florida Bay.](image)
iron within the interior of the CaCO₃ matrix. It should be noted that our grab sampling technique did not precisely separate the surficial oxic layer from any underlying anoxic sediments, and our samples could contain both oxic and anoxic sediments, although anoxic layers are usually deeper in sandy sediments. Therefore our surface reactive iron results should be considered as an upper limit. The distribution of reactive iron is spatially correlated with freshwater plume, indicating that freshwater runoff is likely the source of particulate and colloidal iron to Florida Bay. The passage of fresh water runoff into Florida Bay can readily be identified from the salinity distribution after a heavy rain event at the beginning of the wet season that was preceded by a prolonged dry season (Figure 7b). The overlap of freshwater plume with areas of high iron concentrations in north and north central regions of Florida Bay supports the hypothesis that fresh water runoff is a major pathway that transports the terrestrial iron, mainly in particulate and colloidal forms, into Florida Bay.

[28] The Fe/P ratios in this fraction vary from 0.65 to 14.2, with an average of 3.4 ± 3.3 over the entire Florida Bay. Near the coast where reactive Fe concentrations are relatively high (Fe > 3 μmol g⁻¹), the ratio of Fe/P increased to 6.9 ± 4.5, similar to the ratios found in clastic sediments with similar Fe concentrations. Away from the coast, Fe concentrations are lower, and the ratio drops to 2.1 ± 1.0, a value typical of iron-poor oligotrophic marine environments.

[29] There is no clear correlation between reactive Fe and reductant-soluble phosphorus in Florida Bay surface sediments. This apparently results from the spatial separation of the input sources of Fe and P. Most Fe is introduced into Florida Bay from low phosphate freshwater runoff along the northeastern (and very occasionally central) coastline, while waters with high phosphate concentration but low Fe along the southwest Florida coast are introduced into Florida Bay across its western boundary.

3.5. Authigenic Carbonate Fluorapatite, Biogenic Apatite, and CaCO₃-Bound Inorganic and Organic Phosphorus

[30] The concentrations of authigenic carbonate fluorapatite, biogenic apatite, and CaCO₃-bound phosphorus range from 0.63 to 6.94 μmol g⁻¹ and represent the largest pool of sedimentary phosphorus. High CaCO₃-bound phosphorus (>6 μmol g⁻¹) was found in the western regions of Florida Bay, with the highest concentration (6.94 μmol g⁻¹) at station 14 on the far western margin. Low concentrations (<2 μmol g⁻¹) were found in the eastern region of Florida Bay (Figure 8a). Further fractionation into inorganic and organic phosphorus indicates that inorganic phosphorus is the dominant form in this fraction, with its percentage varying from 60 to 98%.

[31] The distribution of inorganic phosphorus in this pool is similar to that of the total pool. High inorganic phosphorus concentrations (>4 μmol g⁻¹) were found in the northwest region, with the highest concentration (5.5 μmol g⁻¹) at station 9 off Flamingo. Lower concentrations of inorganic phosphorus were found in the eastern region of Florida Bay, and its concentration gradually increased from east to west across the central region (Figure 8b). There is a smaller but still significant fraction of organic phosphorus bound by CaCO₃, and its concentration varied with location from less than 0.1 μmol g⁻¹ at stations 1, 2, 3, 4, 5, 26, and 40 to about 2.3 μmol g⁻¹ in stations 13 and 14. Although they both have low values in the east and high values in the west, inorganic and organic forms within this pool differ as to the location of maximum concentration. The percentage of organic phosphorus...
relative to total phosphorus in this pool varies widely from 2% to 40% with an average of 19.4 ± 11%. High percentages of organic phosphorus (>30%) were found in the western and central regions, while low values (2–5%) were found in the far eastern region. While increasing percentages of organic phosphorus seem to be associated with decreasing percentages of CaCO₃, their linear correlation is weak ($r^2 = 0.089, n = 40$). In three coastal stations in the mangrove fringe of north central Florida Bay, Koch et al. [2001] found that organic phosphorus accounted for 32 to 49% of CaCO₃-bound phosphorus, which is similar to what we observed offshore.

### 3.6. Detrital Apatite Phosphorus

[32] Concentrations of detrital apatite phosphorus of igneous or metamorphic origin ranged from 0.04 to 1.45 µmol g⁻¹, representing the smallest fraction, only 4.6 ± 2.2% of total sedimentary phosphorus in Florida Bay. However, its spatial distribution showed the strongest east-west gradient, increasing over thirty-fold from the east bay to the northwest corner (Figure 9). High concentrations of detrital apatite (>0.4 µmol g⁻¹) were found in the northwest region, with concentrations rapidly increasing toward the west and reaching a maximum concentration of 1.45 µmol g⁻¹ at station 13 off Cape Sable. Low concentrations (<0.2 µmol g⁻¹) were found throughout the eastern region. The strong spatial gradient toward the northwest suggests that the source of detrital apatite is along the southwest Florida shelf.

### 3.7. Refractory Organic Phosphorus

[33] Any phosphorus in the remaining solid residue (after the HCl extract dissolves all inorganic forms of phosphorus) is considered to be refractory organic phosphorus. Refractory organic phosphorus concentration in Florida Bay sediments ranges from 0.30 to 3.48 µmol g⁻¹. On average, the refractory organic phosphorus fraction constitutes 24.3 ± 4.3% of total sedimentary phosphorus and is the second largest pool of sedimentary phosphorus. Low concentrations (<1 µmol g⁻¹) of refractory organic phosphorus were found in the eastern region, and concentration increases rapidly from <1 to 2 µmol g⁻¹ across the central bay (Figure 10). High concentrations (>2 µmol g⁻¹) of refractory organic phosphorus were found in the western region. The maximum concentrations (>3 µmol g⁻¹) were found in northern coastal stations (8 and 9) and central bay stations 31 and 32. The spatial distribution of refractory organic phosphorus is similar to that of overall organic matter content (see Figure 3).

[34] The percentage of refractory organic phosphorus we measured is about a half of that found by Koch et al. [2001] in sediments from the mangrove fringe of the north central Florida Bay coast. Koch et al. [2001] proposed that mangrove detritus along with seagrass might contribute to the high concentrations of refractory organic phosphorus. The
negative correlation ($r^2 = 0.60, n = 40$) between the concentration of refractory organic phosphorus and the percentage of CaCO$_3$ in Florida Bay sediments as shown in Figure 11 may indicate that much of refractory organic phosphorus in Florida Bay sediment is derived from in situ biological production, dominated by seagrass and benthic algae.

### 3.8. Interregional Variability in Partitioning of Sedimentary Phosphorus

[35] In summary, averaged over the entire Florida Bay, the authigenic carbonate fluorapatite, and biogenic apatite as well as CaCO$_3$-bound phosphorus account for the largest fraction of phosphorus among the five distinguishable sedimentary pools (44.4 ± 5.9% of total sedimentary phosphorus). Organic phosphorus in this fraction varies with location, accounting for about 30% in sediments overlying productive region and less than 10% in other areas of Florida Bay. The second largest pool of sedimentary phosphorus is refractory organic phosphorus, and it constitutes 24.3 ± 4.3% of total sedimentary phosphorus. The third largest pool is reductant-soluble phosphorus, 18.6 ± 5.0% of total sedimentary phosphorus. Exchangeable phosphorus accounts for 8.2 ± 2.2% of total sedimentary phosphorus, of which organic phosphorus and inorganic phosphorus account for 60% and 40%, respectively. Detrital apatite phosphorus of igneous or metamorphic origin represents the smallest fraction, only 4.6 ± 2.2% of total sedimentary phosphorus. Adding all five pools together, organic phosphorus accounts for about 36% of total sedimentary phosphorus. The sum of the five-pool phosphorus obtained by sequential extraction is in good agreement with an independent determination of total sedimentary phosphorus in the same samples by the high-temperature combustion method, with a correlation coefficient of 0.9724 (Figure 12), demonstrating a good recovery of our sequential extraction technique.

[36] Florida Bay can be divided into three regions according to the level of total sedimentary phosphorus. The western region of Florida Bay contains the highest level of total sedimentary phosphorus (9–14 μmol g$^{-1}$), and the eastern region contains the lowest level of sedimentary phosphorus (1–3 μmol g$^{-1}$), with the central region a transition zone (3–9 μmol g$^{-1}$). Although total sedimentary phosphorus levels are as much as an order magnitude lower in the eastern than those in the central region, there is little difference in the partitioning of sedimentary phosphorus into different pools (Table 1). However, the fractionation of sedimentary phosphorus in the western region is noticeably different from both central and eastern regions.

[37] Box-and-whisker plots of the data in three regions also suggest that while the distributions overlap, the differences between regions may in fact be significant (Figure 13). A test of nonparametric of variance (Kruskal-Wallis) analysis of the same data indicates that with respect to the fractions of exchangeable phosphorus, detrital apatite and refractory organic phosphorus, no statistical difference exists between regions. However, reductant-soluble phosphorus, CaCO$_3$-bound phosphorus, and the ratio of total organic phosphorus (TOP) to TSP are all significantly different between regions ($p = 0.0001, 0.0086, \text{ and } 0.0024, \text{ respectively}$). As the pair-wise Mann-Whitney U test in Table 2 indicates, there are in fact two distinct reasons for the interregional differences. The first reason is that in the western region, the partitioning of reductant-soluble phosphorus is significantly lower (from ~20.7% in the eastern and central regions to 14.4% in the western region), and CaCO$_3$-bound phosphorus is significantly higher (from ~42.1% in the eastern and central regions to 48.6% in the western region). The second reason is that

**Figure 12.** Comparison of direct determination of total sedimentary phosphorus by the high-temperature combustion method and the sum of phosphorus pools determined from each sequential extraction step in Florida Bay sediment samples.

**Table 1.** Comparison of Averaged Partitioning (as %) of Total Sedimentary Phosphorus into Five Different Forms and Ratio of Total Organic Phosphorus (TOP) to TSP in Florida Bay and Its Eastern, Central, and Western Regions

<table>
<thead>
<tr>
<th></th>
<th>Florida Bay</th>
<th>Eastern Region</th>
<th>Central Region</th>
<th>Western Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable P</td>
<td>8.2 ± 2.2</td>
<td>8.5 ± 2.6</td>
<td>8.4 ± 2.1</td>
<td>7.6 ± 1.9</td>
</tr>
<tr>
<td>Reductant-soluble P</td>
<td>18.6 ± 5.0</td>
<td>21.0 ± 3.6</td>
<td>20.5 ± 5.1</td>
<td>14.4 ± 3.4</td>
</tr>
<tr>
<td>CaCO$_3$-bound P</td>
<td>44.4 ± 5.9</td>
<td>42.3 ± 3.1</td>
<td>42.0 ± 6.3</td>
<td>48.6 ± 5.9</td>
</tr>
<tr>
<td>Detrital apatite</td>
<td>4.6 ± 2.2</td>
<td>4.5 ± 2.0</td>
<td>3.9 ± 1.9</td>
<td>5.4 ± 2.6</td>
</tr>
<tr>
<td>Refractory organic P</td>
<td>24.3 ± 4.3</td>
<td>23.7 ± 4.0</td>
<td>25.2 ± 4.7</td>
<td>24.0 ± 4.7</td>
</tr>
<tr>
<td>TOP/TSP</td>
<td>38.2 ± 5.4</td>
<td>34.3 ± 2.9</td>
<td>38.6 ± 4.5</td>
<td>41.6 ± 5.9</td>
</tr>
</tbody>
</table>
the TOP/TSP ratio is significantly lower in the eastern region.

3.9. Potential Biogeochemical Significance of Sediment Phosphorus

Unlike carbon or nitrogen, phosphorus has no significant atmospheric component in its global biogeochemical cycle. The oxygen-dominated atmosphere sets a high redox potential at the Earth’s surface, which inhibits the reduction of phosphate to gaseous phosphine, except in localized anoxic environments. Transport through the atmosphere in soil dust and seasalt aerosols is several orders of magnitude smaller than the cycling between solid and liquid phases. Most phosphorus on land is derived from the weathering of calcium phosphate minerals, especially apatite. Rivers carry it along with suspended particles to the ocean. Because the major sink for phosphorus is burial in marine sediments, studying the forms of phosphorus in sediments, in combination with pore water chemistry, is critical to understanding the diagenetic recycling and sedimentary burial processes [Ruttenberg and Berner, 1993].

Among different forms of sedimentary phosphorus, exchangeable phosphorus is readily released to ambient water by desorption and thereby becomes available to water column or benthic algae. Reductant-soluble phosphorus can only be released to anoxic bottom water or pore waters in anoxic sediments when iron or manganese oxides undergo reductive dissolution. Even in oxygenated bottom waters, a thin layer of oxic surface sediments is always buried by settling particles, eventually becomes anoxic and thereby releases reductant-soluble phosphorus. Acidity generated by organic matter decomposition and sulfide oxidation in sediments can also dissolve calcium carbonate and thereby release CaCO3-bound phosphorus to pore waters [Ku et al., 1999]. Phosphate dissolved in pore water diffuses, along

![Box-and-whisker plots of fractions of different forms of phosphorus in three regions of Florida Bay. Symbols shown in the plots are median, 25–75%, and the minimum and maximum values of the data, respectively.](image)

**Figure 13.** Box-and-whisker plots of fractions of different forms of phosphorus in three regions of Florida Bay. Symbols shown in the plots are median, 25–75%, and the minimum and maximum values of the data, respectively.

<table>
<thead>
<tr>
<th>Region</th>
<th>Western-Central</th>
<th>Western-Eastern</th>
<th>Eastern-Central</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reductant-soluble P</td>
<td>0.0014</td>
<td>0.00004</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>CaCO3-bound P</td>
<td>0.023</td>
<td>0.003</td>
<td>&gt;0.05</td>
</tr>
<tr>
<td>TOP/TSP</td>
<td>&gt;0.05</td>
<td>0.0011</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Values indicate Mann-Whitney U-test probabilities.

Table 2. Comparisons of Reductant-Soluble and CaCO3-Bound Phosphorus Percent Contribution and TOP/TSP Ratio in Paired Regions Within Florida Bay

[38]
concentration gradients, into overlying water, providing a continuous supply of phosphorus to the water column production. 

[40] In Florida Bay, long-term water quality monitoring studies have documented the concentrations of nutrients and their spatial and temporal patterns. Ammonium is the dominant inorganic nitrogen form, with median concentrations from 1 μM in the western region to 7 μM in the central region of Florida Bay. Nitrate concentrations are usually an order of magnitude lower than that of ammonium, with median concentrations from 0.1 μM in the west to 0.7 μM in the east [Boyer et al., 1999]. Dissolved phosphate concentrations are much lower than dissolved inorganic nitrogen, usually close to or below the detection limit of conventional nutrient auto-analyzers [Fourqurean et al., 1993]. Using a highly sensitive method that enhances the sensitivity of conventional auto-analyzers by 2 orders of magnitude, it has recently been demonstrated that dissolved phosphate in the eastern region of Florida Bay is in fact depleted to a few nM [Zhang and Chi, 2002]. Calculated inorganic nitrogen to inorganic phosphate ratios are higher than the Redfield ratio of 16 [Redfield, 1958] throughout Florida Bay. They also show a strong spatial gradient, from just above 16 in the western margin to 100–300 in the north central region and to over 2000 (using these newly available nM phosphate measurements) in the eastern Florida Bay.

[41] Seagrass studies also provide several lines of evidence, demonstrating that phosphorus is a limiting nutrient and regulates seagrass productivity in much of Florida Bay. Seagrass standing crop shows an east-west spatial gradient, increasing from 0 to 30 g m⁻² (dry weight) in the northeastern region to 60 to 125 g m⁻² in the western margin of the bay [Zieman et al., 1989]. Spatial distribution of C/P and N/P ratios in seagrass tissue also show a strong east-west gradient in Florida Bay [Fourqurean et al., 1992a]. Pore waters in Florida Bay sediment contain low (median value of 0.3 μM) but variable (range from 0.1 to 4 μM) dissolved phosphate concentrations. Pore water phosphate concentrations were found to be correlated not only to seagrass density but also to community structure [Fourqurean et al., 1992b]. For example, bare bottom with no seagrass had the lowest pore water phosphate (0.1 ± 0.1 μM), and seaboards that supported Thalassia testudinum alone had an intermediate concentration (0.5 ± 0.1 μM), while areas that supported Halodule wrightii had the highest concentration (3.1 ± 1.7 μM). Seagrass standing crop and C/P ratios in seagrass tissue are positively correlated with phosphate concentrations in sediment pore water [Fourqurean et al., 1992b]. It has also been observed that bird feces provide a point source of phosphorus and can double local seagrass density in the eastern region of the Florida Bay [Powell et al., 1989]. Large bird colonies roosting on mangrove islands in the eastern region can increase seagrass density in areas as far as 200 m away from the colony islands [Powell et al., 1991]. The above-mentioned seagrass studies not only support the argument that P is a limiting nutrient for seagrass growth in much of Florida Bay but moreover that the spatial distribution of this limitation is consistent with the spatial patterns of sedimentary phosphorus described in this study.

[42] Phytoplankton biomass in the eastern region of Florida Bay is also generally limited by phosphorus [Fourqurean et al., 1993; Philips and Badylak, 1996; Lavrentyev et al., 1998]. Bacterial growth and biomass production are similarly limited by available phosphorus in the eastern and southern regions of the Florida Bay [Cotner et al., 2000]. Biomass-normalized alkaline phosphatase activity in the northeast and south-central region was 5 to 20 times greater than that in the northwest and north central regions [Cotner et al., 2000], in response to nM level of dissolved phosphate concentrations there [Zhang and Chi, 2002]. The lowest concentrations of chlorophyll a in Florida Bay are always found in the same regions [Boyer et al., 1999]. The north central region of Florida Bay has experienced regular cyanobacteria (synechococcus) blooms [Philips et al., 1999]. In contrast, phytoplanktonic assemblages in the northwestern region of Florida Bay are dominated by diatoms and dinoflagellates, as is the case on the adjacent southwest Florida shelf. It is highly likely that the availability of phosphorus, along with that of silicon and iron, is in part responsible for the observed differences in phytoplankton community in different regions of Florida Bay.

[43] The phosphate concentration of the freshwater input into northeastern Florida Bay is low as a result of retention of source water phosphorus by carbonate soils and vegetation in the upstream Everglades wetlands. The iron in this freshwater inflow is primarily colloidal and in an oxidized form that readily forms coatings on the surfaces of carbonate sediments. Such an iron oxides coating greatly enhances the capacity of sediments to adsorb phosphate ions. The carbonate sediments in the eastern region of Florida Bay must act as an additional strong sink for any external loading of phosphorus, since they are poor in phosphorus but relatively rich in iron. The adsorption of phosphate by the Fe-rich carbonate sediments within Florida Bay in conjunction with the phosphate-depletion of the source waters results in the exceedingly low levels of dissolved phosphate observed in the eastern regions of Florida Bay [Zhang and Chi, 2002].

[44] The origin of higher sedimentary phosphorus in the western corner of Florida Bay presumably derives from the Miocene phosphorite formations in central Florida, where phosphorite deposits close to the surface. In fact, central Florida has been the world’s largest phosphate rock production site for the past half century. Natural erosion of surface phosphorite deposits and phosphate mining transform mineral phosphorus to fine particulate and dissolved phosphate that can be readily transported by the Peace River and other conduits in the area to the coastal waters of west Florida. A concentration of dissolved phosphate as high as 90 μM has been observed in the Peace River [Froelich et al., 1985]. Indeed phosphate concentrations are high all along the southwest coast of the Florida peninsula, especially in Tampa Bay, Charlotte Harbor, and the Ten Thousand Islands areas (our own unpublished data).

[45] While the concentration ratio of biologically available nitrogen to phosphorus is often used as an indicator of nutrient limitation, the relative supply rates of these nutrients also need to be taken into consideration. The exchange of phosphate between water and carbonate sedi-
ments is a rapid process [Millero et al., 2001]. Depending on the relative concentrations of phosphate in sediments and in ambient water, carbonate sediments can act as a sink or a source for dissolved phosphate in water column. Carbonate sediments can adsorb phosphate from ambient water when dissolved phosphate concentration is increased from external loading. On the other hand, sediments can release particle-bound phosphate through desorption processes when dissolved phosphate concentration in ambient water is decreased by processes such as biological utilization. Given its shallow phosphorus-poor water column, sediment is the dominant phosphorus reservoir in Florida Bay. A layer of 5 cm thickness of surface sediment contains potentially $10^2$ to $10^4$ times more phosphorus than the overlying water column. Carbonate sediments in Florida Bay have the capacity to act as a phosphate buffer system, through adsorption/desorption processes, and regulate dissolved phosphate concentrations in the overlying water column [Froelich, 1988]. The strong similarity between the spatial distributions of dissolved phosphate concentrations in the water column [Zhang and Chi, 2002] and exchangeable phosphate in sediments observed in this study supports this working hypothesis.

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References


Lebo, M. E. (1992), Development of a sequential extraction
Redfield, A. C. (1958), The biological control of chemical factors in the
Powell, G. V. N., W. J. Kenworthy, and J. W. Fourqurean (1989), Experi-
Meybeck, M. (1982), Carbon, nitrogen and phosphorus transport by world
Phlips, E. J., S. Badylak, and T. C. Lynch (1999), Blooms of the picoplank-
Phlips, E. J., and S. Badylak (1996), Spatial variability in phytoplankton
Mitchell, S. B., and J. R. West (2002), Particle size distribution in
Patriquin, D. G. (1972), The origin of nitrogen and phosphorus for growth
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Lebo, M. E., and J. H. Sharp (1992), Modeling phosphorus cycling in a
Lebo, M. E. (1991), Particle-bound phosphorus along an urbanized coastal
Luterbacher, K. C. (1992), Analytical methods for different forms of phosphorus in marine sediments,
Ruttenberg, K. C., and R. A. Berner (1993), Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environ-
Solomano, C., and J. Sharp (1980), Determination of total dissolved phosph-
Teeter, A. M. (1993), Suspended transport and sediment-size transport
Phlips, E. J., S. Badylak, and T. C. Lynch (1999), Blooms of the picoplank-
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,
Meybeck, M. (1993), C, N, P and S in rivers: From sources to global inputs,