

Final Report

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**Relationship of Sedimentary Sulfur, Iron and Phosphorus Cycling to
Water Quality in Florida Bay: How Seagrass Die-offs Contribute to
Algal Blooms
Research 1997-1999**

**Randolph M. Chambers, PI
Biology Department
Fairfield University
and**

**James W. Fourqurean, Co-PI
Southeast Environmental Research Program
Biology Department
Florida International University**

Executive Summary

This study was completed to examine the coupling of biogeochemical processes between the sediment and water column in Florida Bay, with a specific goal of determining the potential impact of these processes on seagrass and algal production. Sediment samples from Florida Bay and the southwest Florida shelf were collected and analyzed to determine the concentrations of iron-sulfide minerals and selected forms of iron and phosphorus. We found that both iron and sulfur exhibited a general gradient of decreasing concentration from north to south in Florida Bay, but that phosphorus decreased from west to east across the bay. All three elements tended to occur in higher concentrations in the bay relative to sediments on the southwest Florida shelf. The predominant sulfide mineral in bay sediments is pyrite (up to 50 μ moles per gram dry weight of sediment), with concentrations of mackinawite typically an order of magnitude lower. A four-step extraction scheme for forms of iron and phosphorus determined that a significant portion of sediment phosphorus in Florida Bay was associated with the dithionite extraction step, but this phosphorus did not appear to be associated exclusively with reactive iron oxides. A strong positive correlation between total iron and phosphorus was found for unvegetated sediments from the southwest Florida shelf, but not for sediments from Florida Bay. We found no evidence suggesting a phosphorus and/or iron source from a hypothesized Miocene sand channel. Further, it does not appear that reactive iron oxides—because of their low concentration in the sediments—are a major influence on the dynamics of phosphorus cycling throughout much of Florida Bay.

An index of iron availability, used to quantify the capacity of surface sediments to buffer sulfide production and act as a cap to phosphorus release, was smallest in the north-

central portion of Florida Bay. This portion of the bay is where seagrass die-offs were most extensive a decade ago and where water column algal blooms are ongoing. Water column chlorophyll concentrations were negatively correlated with the index of iron availability, showing the strong coupling of sediment-water column processes: where iron availability in the sediments is low, there is more primary production in the water column (algae). Seagrass die-offs could either be a cause or a consequence of this sediment characteristic.

By stimulating authigenic sulfide mineral formation through the experimental addition of reactive iron to sediments, we demonstrated that iron-sulfide mineral formation in bay sediments was limited by the availability of reactive iron. Eight months after adding iron oxides to small plots near Rabbit Key Basin, both mackinawite and pyrite concentrations increased 10-cm into the sediment. Also, the amount of phosphorus sorbed to sediments increased dramatically in surface sediments, representing phosphorus retention in the sediments and/or removal from the water column. Iron oxides buffered sediment sulfide toxicity to seagrasses, and the seagrasses responded by producing more vigorous shoots. Because iron oxides also exacerbate nutrient limitation to seagrasses by sorbing phosphorus, standing crop did not increase. In these experiments we also measured much higher mineral sulfide concentrations in the winter relative to the summer, suggesting a dynamic seasonal component to mineral sulfide formation/dissolution in Florida Bay sediments.

Based on our results, we conclude that sulfide toxicity in sediments may contribute to seagrass die-offs, but that the plants are well-adapted to this carbonate environment where iron concentrations naturally are low and the buffering capacity is scant relative to other estuaries with sediments derived from terrigenous sources. The major influence of sulfide in Florida Bay sediments may be its reduction of reactive iron oxides, making iron unavailable to serve as a sorption site for reactive phosphorus. Phosphorus may be freer to migrate to the water column where this limiting nutrient can stimulate algal growth. Although a large-scale addition of iron oxides to Florida Bay potentially could limit algal growth by sorbing water column phosphorus, both a biological process (the growth of sulfide-adapted seagrasses) and a geochemical process (phosphorus sorption to carbonate minerals) are capable of performing this task naturally. Our hypothesis that seagrass die-offs—whatever their cause—lead to a positive feedback of decreased system resistance to declining water quality is supported by the negative correlation between the sediment index of iron availability and water column chlorophyll concentrations. The observation of continuing recovery from the extensive seagrass die-off occurring more than a decade ago, however, suggests the Florida Bay system is resilient to these sorts of perturbations and that multiple disturbances have been the rule—not the exception—in this sub-tropical ecosystem.

Introduction

Recent catastrophic die-offs of seagrasses in Florida Bay have led to increased sediment decomposition of organic matter and increased production of free sulfide, the by-product of sulfate reduction. In terrigenous sediments, reactive iron is able to "buffer" the toxic effects of sulfide, but this buffering capacity probably is quite low in the carbonate sediments of Florida Bay. Reactive iron also functions to control the release of phosphate from marine sediments. Without the buffering of reactive iron, phosphorus and nitrogen from enhanced decomposition in areas of seagrass die-off may be released to surface sediments and to the water column, thereby stimulating algal blooms in the system. Decomposition of the blooms could stimulate further nutrient release and disrupt the stability of the Florida Bay ecosystem. The combination of large amounts of decomposing organic matter and low amounts of reactive iron may lead to a positive feedback loop of ecosystem disturbance in Florida Bay.

Florida Bay is undergoing dramatic changes in ecosystem structure and function (Fourqurean and Robblee 1999). Since 1987, large expanses of seagrass die-offs have occurred, creating extensive, foul, smelly sections of water in a region historically known for exceptional water quality. Algal blooms now are seasonally common and threaten to alter the food web of Florida Bay. This change could translate into fewer fish, fewer birds, and fewer tourists, the heart of south Florida's economy. On a larger ecological scale, disruption of the Florida Bay ecosystem suggests that nature's apparent "stability" has been thrown out of balance, i.e., the ability of the system to resist change has been overwhelmed.

Environmentalists are quick to identify the influx of people to southern Florida and subsequent land development as the proximal cause of declining water quality in Florida Bay. Although this scenario has been played out countless times in coastal waters of the U.S.--most waterways near population centers suffer significant pollution problems--no current evidence supports the hypothesis that runoff from the land has contributed substantially to declining water quality in most of Florida Bay. Instead, the dramatic disruption of ecosystem stability may be caused by other factors.

We hypothesized that the recent die-off of seagrass in Florida Bay initiated a positive feedback loop of declining water quality, a process driven by the natural biogeochemistry of the sediments and the long residence times of surface waters in Florida Bay. The characteristics of the sediments (mostly carbonate muds) are such that little natural "buffering" is provided to resist environmental disturbance such as seagrass die-offs. Irrespective of the reason for the die-off of seagrasses, the disturbance has set into motion a series of biogeochemical reactions which tend to decrease quality of surface waters. These reactions are perfectly natural and occur in every coastal environment, but the unique characteristics of Florida Bay sediments and the relatively long residence times of surface waters lead to more dramatic impacts.

Florida Bay is a carbonate-rich system receiving little freshwater runoff of terrestrial materials. The amounts of iron in the system probably are low (Berner 1984; Morse et al. 1985). Yarbrow et al. (1997) have shown that surface sediments of Florida Bay contain up to 25 μ moles of acid-extractable iron per gram-dry-weight of sediment, but that amounts

of reactive iron are about 2 orders of magnitude smaller. Without reactive iron, free sulfides--the by-product of sulfate reduction-- accumulate in sediments (Cornwell and Sampou 1995), inhibiting plant growth via phytotoxicity (Carlson et al. 1994) and inhibiting microbial nitrification/denitrification (Joye and Hollibaugh 1995). Whether in terrigenous or carbonate sediments, systems in which free sulfides accumulate exhibit a large ammonium signal in the water column, and phytoplankton production tends to be phosphorus limited. Further, calcium carbonates in the biogenic sediments of Florida Bay may contribute to P limitation (Fourqurean et al. 1992, 1993), as some of the inorganic phosphates are geochemically removed from the water and sorbed onto or incorporated into carbonate minerals. Yarbro et al. (1997), however, have shown a fairly close association between amounts of extractable iron in surface sediments and amounts of extractable phosphorus. To a degree, active phosphorus cycling in the carbonate sediments of Florida Bay appears to be under some geochemical controls mediated by iron availability. Because of the long residence times of surface waters in Florida Bay (Fourqurean et al. 1993), the biogeochemistry of the sediments and the water column should be tightly coupled.

In addition to a local maximum in iron accumulation nearest the mainland of south Florida, iron (Fe) and phosphorus (P) accumulation in sediments exhibits a general pattern of decrease from west to east across Florida Bay (Yarbro et al. 1997). Fourqurean (1992) showed that seagrasses were increasingly phosphorus-limited along the same west-east gradient. Although it has been assumed that higher concentrations of Fe and P in the western region of Florida Bay were due to their proximity to Fe and P sources from the Gulf of Mexico, the presence of a Miocene sand channel oriented north-south through the western region of Florida Bay recently has been suggested as an alternative Fe and P source. Study sites used by Florida DEP do not extend far west of the location of the Miocene sand channel (P.R. Carlson, Jr., pers. comm.) and cannot be used to determine the pattern of sediment Fe and P in far-western Florida Bay. If Fe and P concentrations increase with further distance west of the Miocene sand channel, then the channel bed is probably not the iron and phosphorus source.

Regardless of source, conditions of Florida Bay (low concentrations of reactive iron and organic-rich, biogenic sediments) are such that even small decreases in the amounts of reactive iron could alter dramatically the biogeochemistry of the system. Reactive iron is electroactive and cycles between reduced and oxidized forms. Oxidized forms (reactive iron oxides) occur near the sediment surface and potentially along roots of living seagrasses. Florida Bay is a shallow system, so under most conditions, physical wind-mixing of water and aeration of sediments must maintain an oxidized sediment surface. Iron oxides sorb inorganic phosphate and tend to "buffer" the effects of high sediment sulfide concentrations by either oxidizing the sulfide or removing the sulfide from solution as iron-sulfur minerals (e.g., pyrite). The microenvironments around seagrass roots are to some extent protected from sulfide toxicity by reactive iron. Reactive iron on the sediment surface also acts as a "cap" against the diffusion of free phosphorus into surface waters by sorbing soluble phosphate, contributing to P limitation of surface waters (Froelich 1988; Chambers and Odum 1990). Iron oxide "plaques" around roots could also limit the availability of P to seagrasses, but have not been reported in Florida Bay sediments (P.R. Carlson, Jr., pers. comm.).

With the recent die-offs of seagrasses in Florida Bay, direct mineralization of labile organic matter perhaps has led to increased inputs of phosphorus to the water column, and to increased rates of sulfate reduction in the sediments. With greater amounts of sulfides produced soon after die-off (Carlson et al. 1994), the reactive iron buffer system may be overwhelmed, even at the sediment surface, thus setting into motion a positive feedback loop which contributes to decreasing water quality in Florida Bay: Reactive iron is reduced and phosphates are released from inorganic sources, iron-sulfide minerals and free sulfide concentrations increase, belowground portions of plants die off and phosphates are released from organic sources, high concentrations of phosphate in the surface sediments and water column stimulate algal blooms, increased deposition of labile organic matter to Florida Bay sediments increases the rates of sulfate reduction and toxic sulfide production. Thus, exhaustion of the reactive iron pool as a buffer system could initiate dramatic changes in ecosystem structure and function.

The pattern of reactive iron depletion and subsequent impacts on sulfur and phosphorus dynamics in estuaries has been described for many terrigenous systems (Canfield 1989). Most recently, Chambers et al. (2000) were able to show how historical changes in the availability of reactive iron pools could be used to identify sediment sources and to describe sediment diagenesis, accounting for temporal and spatial shifts in nutrient availability for primary producers.

Aside from ongoing work by P.R. Carlson and associates at Florida DEP, similar assessments of the impacts of iron on the sulfur and phosphorus cycles have not been made for the Florida Bay system dominated by biogenic carbonate sediments. Barber and Carlson (1993) found that amounts of free sulfide in sediment porewater of Florida Bay were disproportionately low relative to the amounts of carbon dioxide, a pattern they suggested (among other scenarios) might be caused by precipitation of sulfide minerals such as pyrite. We proposed to determine sulfur, reactive iron and phosphorus profiles in the carbonate sediments of Florida Bay, to allow us to assess the importance of iron-sulfide mineral accumulation. Further, we hypothesized that recent seagrass die-offs have enhanced free sulfide accumulation in the system, leading to positive feedbacks including decreased surface water quality and increased numbers of algal blooms. We suggested that the Index of Iron Availability developed for systems with terrigenous sediments (Chambers et al. 2000) would also provide a measure of ecosystem resistance to disturbance effects for Florida Bay.

Methods

We completed research designed to address the following structural hypotheses:

1) In Florida Bay, sediment profiles of reactive iron, phosphorus and sulfide minerals will vary with respect to:

- a) Vegetation (zones of live seagrass, dead seagrass, and absent seagrass), and
- b) Location (gradients from western zones to eastern zones)

Per descriptions in our annual report (1998), we modified our sampling regime to include only those areas currently covered by seagrasses. We were careful to include “undisturbed” areas and areas where seagrass die-off and “recovery” had occurred. We

also limited our sampling to include surface sediments, opting to focus on depth profiles at a single station in the bay (Hypothesis 3).

We sampled at a majority of the 29 existing stations of the Florida Bay Monitoring Network for water quality, run by Ron Jones at Florida International University's Southeast Environmental Research Program (SERP). During the first year of the study in 1998, these stations were visited twice. At each sampling station, small-diameter sediment cores were collected in triplicate for separate determinations of sediment concentrations of sulfide minerals and iron and phosphorus species. During that first year of study we also included over 30 additional sampling stations that are part of Southwest Florida Shelf Monitoring Network. These stations are located beyond the western boundary of Everglades National Park, west of the location of the Miocene sand channel, and beyond the sampling stations used by Florida DEP. We determined concentrations of sulfur, iron and phosphorus in surface sediments from these locations, to complement existing data collected farther east in Florida Bay. Almost all sampling sites were selected to coincide with those of existing water quality monitoring programs run by SERP investigators, to provide data on levels of dissolved nutrients, phytoplankton and bacterial activity in the water column, and to correlate with our measure of ecosystem resistance (Index of Iron Availability).

Inorganic sulfur species were extracted and analyzed using methods developed by Chambers et al. (1994). Briefly, a known volume of collected sediment was placed in a reaction vessel purged with nitrogen gas, and a small volume of alcohol was added as a surfactant. The vessel was sealed and 1M HCl was added, thereby liberating free sulfides and sulfides from easily extracted sulfide minerals (mackinawite, FeS). Liberated sulfides passed through the gas train and were trapped in sodium hydroxide, then analyzed for sulfide concentration using a colorimetric technique. Then, concentrated HCl and a chromous chloride solution were added to the reaction vessel which was boiled for one hour. Sulfides liberated from pyrite (FeS₂) were trapped and analyzed as previously described.

Total extractable iron and phosphorus species were determined by ashing and then extracting the sediments in 1N HCl, followed by colorimetric analysis. Different forms of iron and phosphorus in sediments were determined using a sequential extraction scheme developed by Jensen et al. 1998. Briefly, a known volume of collected sediment was placed in a 20-mL vial, and 1M MgCl₂ was added. The vial was capped and shaken for one hour, then sediments were filtered and the filtrate was analyzed colorimetrically for desorbable iron and phosphorus. The filtered sediments were then resuspended in buffered citrate dithionite buffer and shaken for one hour. The sediments were filtered and the filtrate was analyzed for extractable iron and phosphorus, operationally defined as reactive iron and associated phosphorus. The sediments were then resuspended in a buffered acetate solution and shaken for three hours. The sediments were filtered and the filtrate was analyzed for iron and phosphorus as above to determine the amounts associated with the dissolution of calcium carbonate minerals. As a check we also measured the fluoride concentration in these filtrates, to see whether calcium fluoride phosphate minerals such as apatite were extracted during this step. Visually, most of the sediments dissolved during the acetate extraction step, and chemically fluoride was measured in high concentrations in the filtrate. Finally, the filtered sediments were then

resuspended in 1N HCl and shaken for 18 hours. The sediments were filtered and the filtrate was analyzed as above for the determination of "recalcitrant" iron and phosphorus concentrations.

2) Relative to other regions in Florida Bay, seagrass die-off areas will be characterized by:

- a) Lower Indices of Iron Availability in the sediments, and
- b) Lower quality of surface waters, as measured by nutrients, chlorophyll or bacterial activity in the water column

An Index of Iron Availability was developed as a potential measure of ecosystem resistance. The index is a measure of the degree of sulfidization in the sediments; it is a ratio of the amounts of iron incorporated into iron-sulfide minerals (FeS and FeS₂) relative to the total amounts of (reactive + reacted) iron in the sediments. The index is derived directly from the sediment sulfur and iron data collected from surface sediments. The index values for each water quality sampling station in Florida Bay were then plotted against water column chlorophyll concentrations provided by SERP.

3) Addition of Reactive Iron to Florida Bay sediments will:

- a) Alter sulfur and phosphorus cycling, and
- b) Enhance the biogeochemical level of resistance to environmental disturbance created by seagrass die-offs.

During the second year of the study, reactive iron oxides in fine granular form (Peerless[®] iron filings: reactive surface area approximately 1 square meter per gram of material) were added to triplicate, ¼-square meter seagrass plots in Rabbit Key Basin. The application was completed in November 1998. In January and again in July 1999, 30-cm sediment cores were collected from each of the iron-addition plots and from three undisturbed plots that served as controls. Sub-cores at approximate 5-cm intervals down the length of each core were collected for determinations of bulk sediment properties, sulfide mineral extractions, and iron and phosphorus determinations. These analyses were completed as described above, yielding a comparison of sulfur, iron and phosphorus profiles from control and experimental plots.

We hypothesized the addition of iron oxides would buffer sulfide toxicity in the sediments, thereby enhancing conditions for seagrass growth. We measured seagrass shoot production, shoot density and shoot biomass in January and July for both control and experimental plots to determine whether iron additions influenced the growth of seagrasses.

Results

Synoptic Survey of Iron, Phosphorus and Sulfur

Relative to terrigenous sediments, the iron concentrations in Florida Bay were extremely low and exhibited a strong gradient of decreasing concentration away from the Florida mainland (Figure 1). The concentrations in Florida Bay ranged from a high of 26 µmoles per gram dry weight of sediment in the northeast corner of Florida Bay to a low of 4-6

μmoles per gram dry weight in the southern bay boundary near Long Key. Iron concentrations on the southwest Florida shelf, in contrast, were generally lower and exhibited no clear gradient in any direction. Some higher concentrations were measured nearest the western coast of Florida and a distinct region of low concentrations was found west of Cape Sable.

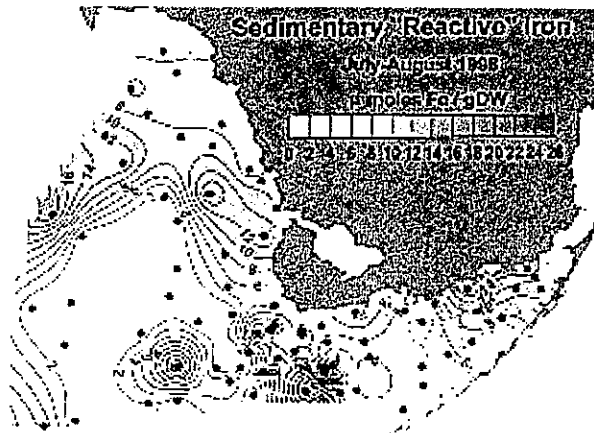


Figure 1. Extracted iron ($\mu\text{mol gDW}^{-1}$) from surface sediment samples, summer 1998, with distribution of sampling stations.

Sediment concentrations of phosphorus from the southwest Florida shelf were distributed in a pattern similar to iron, with low concentrations found west of Cape Sable and higher concentrations nearest the coast (Figure 2). A strong gradient of decreasing sediment phosphorus concentrations was observed from west to east across Florida Bay in a pattern supporting previous measures of decreasing porewater phosphorus concentrations across the same gradient used to infer phosphorus limitation of seagrass production (Fourqurean et al. 1992).

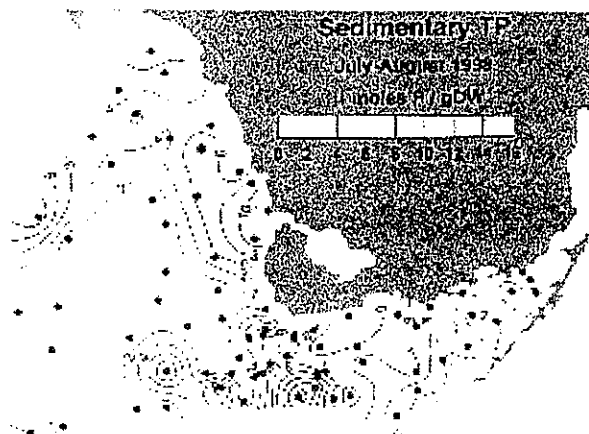


Figure 2. Extracted phosphorus ($\mu\text{mol gDW}^{-1}$) from surface sediment samples, summer 1998.

Most of the reduced sulfur compounds in surface sediments of south Florida were extracted in the chromium-reducible fraction and were assumed to be pyrite. On average less than 10% of the total reduced sulfur pool in surface sediments was AVS. Sulfur

concentrations were higher in Florida Bay than from the southwest Florida shelf and generally higher near the Florida mainland (Figure 3). The close association between concentrations of sedimentary iron and sulfur indicate that the formation of iron-sulfide minerals is iron-limited.



Figure 3. Extracted sulfur ($\mu\text{mol gDW}^{-1}$) from surface sediment samples, summer 1998.

Based on this observation, we calculated an index of iron availability for sites in Florida Bay by calculating the ratio of unreacted, extractable iron to the total pool of reactive and reacted iron, in essence determining the degree of sulfidization (Chambers et al. 2000). The index values were negatively correlated with water column chlorophyll concentrations ($r^2 = 0.54$). Higher indices of reactive iron availability in sediments occurred where water column concentrations of chlorophyll were low.

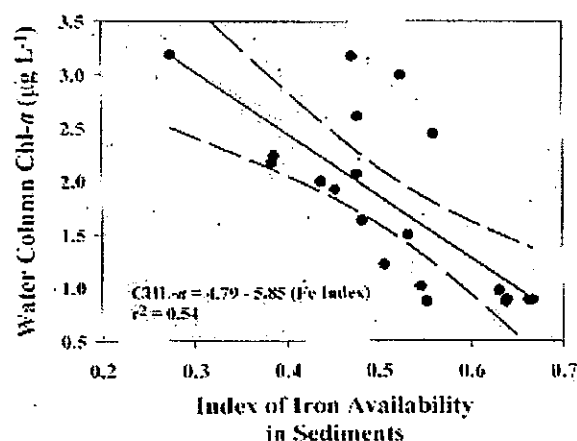


Figure 4. Correlation between index of iron availability in sediments with water column chlorophyll-a concentration, with 95% confidence intervals.

Iron Enrichment Experiment

After two months, the concentrations of iron, phosphorus and sulfide minerals in the upper 2.5 cm of sediment was significantly higher in the iron addition plots relative to

controls (Figure 5). After eight months, the effect had extended down-core to a depth of 10 cm. Interestingly, we also observed differences in the amounts of Fe, P and S below the zone of influence of reactive iron additions. The concentrations of extractable iron were lower in January, whereas the concentrations of extractable sulfide minerals were lower in July.

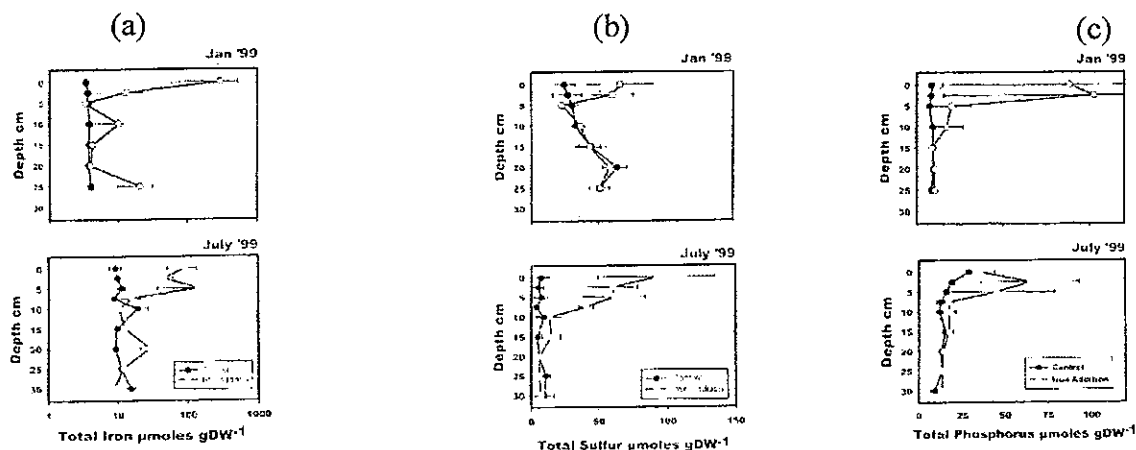


Figure 5. Sediment profiles of (a) iron, (b) sulfur and (c) phosphorus from control and experimental plots, Rabbit Key Basin, two months and eight months after iron additions.

The partitioning among different forms of sulfur, iron and phosphorus at different depths two months after iron additions is shown in Figures 6-8, respectively.

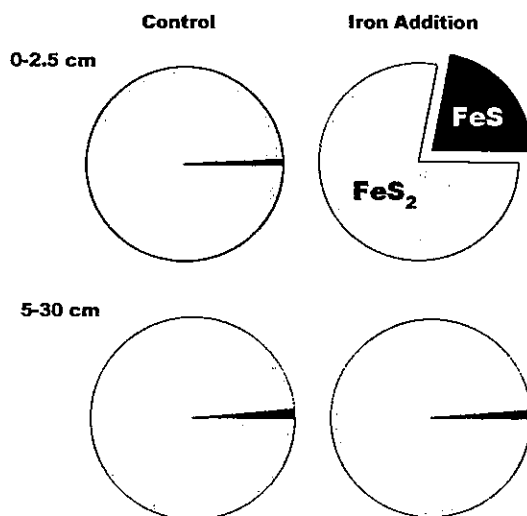


Figure 6. Partitioning of sulfur between mackinawite (FeS) and pyrite (FeS₂) in surficial and deeper sediments from control and iron addition plots, two months after iron addition.

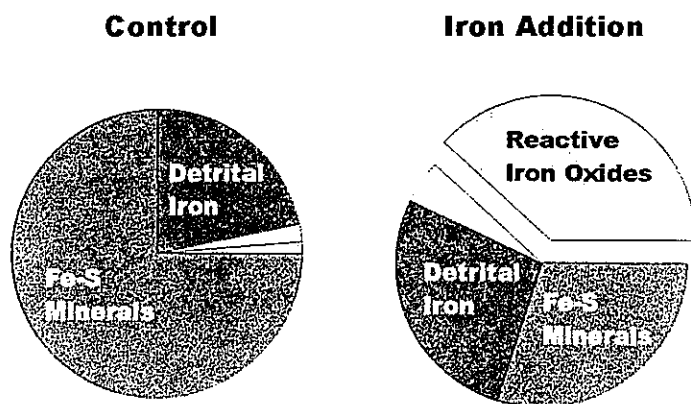


Figure 7. Partitioning of iron into extracted forms in sediments from control and iron addition plots, two months after iron addition.

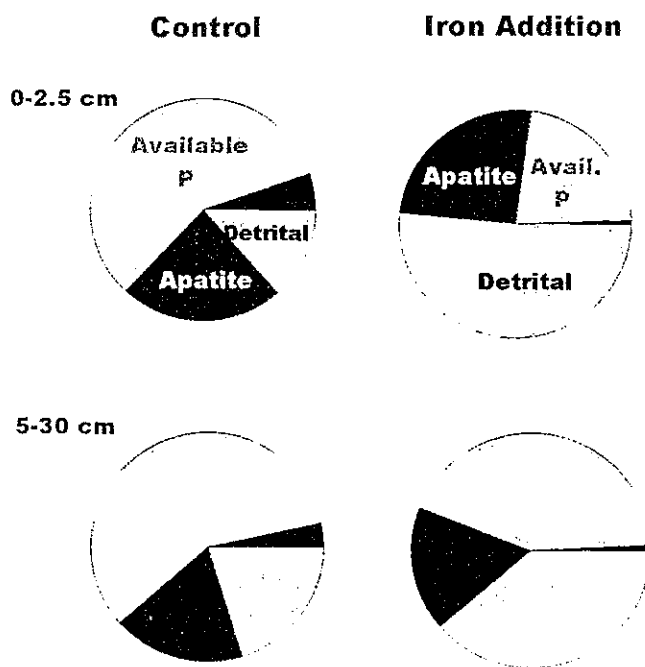


Figure 8. Partitioning of extracted forms of phosphorus from surficial and deep sediments from control and iron addition plots, two months after iron additions.

The response of the plants to iron enrichment, however, was variable (Figure 9). Although shoot growth was significantly higher after 8 months, seagrass standing crop was not significantly different between experimental and control plots.

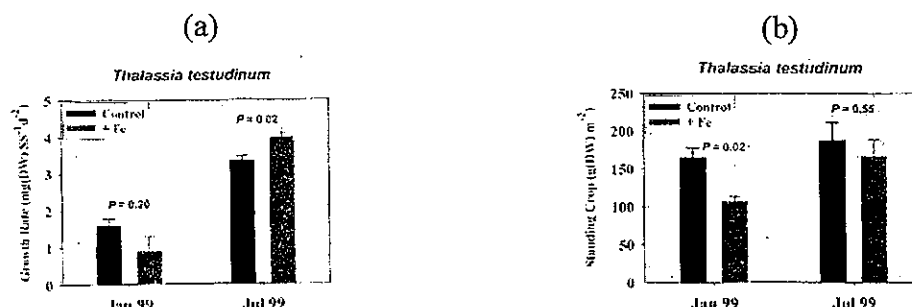


Figure 9. *Thalassia* shoot growth (a) and standing crop (b) two months and eight months after reactive iron additions.

The observed distributions of iron and phosphorus from the current study can be compared to those obtained by Yarbro et al. (1997) who saw similar a pattern of decreasing abundance of P west-east, concomitant with a pattern of decreasing Fe west-east throughout Florida Bay. In contrast, we measured high concentrations on the western boundary of Florida Bay but also high concentrations in the northeastern corner. The mechanisms for depositing iron and generating its observed distributions in south Florida hydroscape are not well known. A terrigenous source from clastic sediments is indicated (Gene Shinn, pers. comm.), but the occurrence of spatially variable amounts of iron may be the result of deposition of sediments derived from outside the system and redistributed via water and/or wind currents. Aeolian deposits of dust from the African continent have been documented by others; the importance of this process to the observed distribution of iron and phosphorus has not yet been determined.

Barber and Carlson (1993) found that free porewater sulfide concentrations were far below what would be predicted from sulfate reduction stoichiometry relative to measured concentrations of CO_2 , suggesting a significant sulfide sink in the sediments. With porewater sulfide concentrations up to 5 mM, however, 5 umoles of free sulfide per mL of sediment is small relative to the concentrations of sulfide precipitated as pyrite, measured as high as 50 umol g^{-1} in the present study (Figure 3). Although low relative to terrigenous sediments, reactive iron concentrations Florida Bay are sufficiently high to be a significant sink for sulfides produced in carbonate sediments.

In a series of papers (Walter and Burton 1990; Walter et al. 1993; Ku et al. 1999), Walter has argued that both sulfate reduction and sulfide oxidation are capable of generating sufficient acidity to dissolve carbonates and increase sediment CO_2 concentrations. The mechanism for sulfide oxidation below the zone of active bioirrigation is thought to be driven by oxygen transport down or through root channels of seagrasses in vegetated sediments (Blackburn et al. 1994). This process would produce the elevated sediment ratio of $\text{CO}_2:\text{H}_2\text{S}$ observed by Barber and Carlson (1993), but their measurements were made in sediments with both living and dead seagrasses to a depth of 20 cm. Given this,

either oxygen is transported down both live and dead root channels or other physical process may contribute to sediment oxidation as discussed by Grant (1983).

Sulfide oxidation in vegetated sediments would provide obvious benefits to seagrasses sensitive to high sulfide concentrations. Presumably both free sulfide and pyrite sulfide would be oxidized, generating acidity. Subsequent dissolution of carbonates could release a portion of the sediment phosphorus pool (Rude and Aller 1991), making P available to the plants (McGlathery et al. 1994; Jensen et al. 1998). Nutrient stimulation of plant growth would provide a potential positive feedback (*sensu* Howes et al. 1986) by increasing oxygen transport to the roots, buffering sediment sulfide toxicity and increasing P availability. Pyrite oxidation might also make iron available for uptake by seagrasses that may experience iron deficiency growing in carbonate sediments (Duarte et al. 1995).

Our depth profiles of iron, sulfur and phosphorus provide some insights to these processes. In January, extracted iron was lower and total sulfur was higher, relative to July (Figure 5). This pattern is consistent with winter precipitation of sulfides and removal of iron from the extractable sediment pool (net sulfide removal from the porewater to the sediment as pyrite). Lower rates of primary production occur during winter, with less oxygen transport to the sediment, low amounts of extracted P (the P is tied up in living seagrass tissue). During summer, higher rates of primary production occur, causing more sediment oxidation and pyrite oxidation. The results include lower concentrations of sulfide minerals, addition of iron to the extractable sediment pool, carbonate dissolution and increased P availability to seagrasses. Although we expected to find higher sediment P in winter and lower in summer, but we measured a slightly reversed pattern (Figure 5), suggesting that seasonal P enrichment in sediment via contributions from organic matter mineralization must contribute to the pool of P generated by carbonate dissolution (extractable P generated in sediments during summer; removed during winter).

In our experiments adding reactive iron to vegetated carbonate sediments, the plant response is suggestive of the dual nature of iron (Figure 9). First, the overall shoot growth increased after eight months, a phenomenon consistent with the buffering from toxic sulfides provided by additions of reactive iron. The general absence of additional shoot growth and overall lack of an increase in areal productivity, however, is consistent with the notion that the plants in the iron-enriched plots were strongly phosphorus limited. Thus, although sulfide stress may have been relieved by iron-sulfide mineral formation, phosphorus limitation may have been exacerbated by phosphate sorption to reactive iron, this in addition to the carbonate mineral sink for P (Morse et al. 1985).

Powell et al. (1989) showed that exogenous addition of nutrients reduced P-limitation in Florida Bay sediments and stimulated seagrass growth. Further, common sense indicates that seagrasses must have a high tolerance to sediment sulfide toxicity, otherwise they would not occur to such proliferation in shallow marine carbonate environments. Terrados et al. (1999) reviewed the literature on sediment redox and concluded species of seagrasses have different sensitivities to sulfides and reducing conditions in sediments. Different sulfide tolerances have not yet been measured for seagrass species in Florida Bay.

Although Duarte et al. (1995) have suggested that production by seagrasses in some instances is iron-limited, our sense is that the influence of iron on benthic production in carbonate sediments may be less dramatic than its influence on water column production. In addition to benthic algae (an organic sink), the presence of reactive iron in surface sediments (an inorganic trap) may contribute to “capping” the release of large amounts of P that otherwise would diffuse into the water column and stimulate algal blooms there. The negative correlation between the index of iron availability and water column chlorophyll concentrations in Florida Bay demonstrates the close coupling of sediment chemistry and surface water quality in this shallow subtropical system.

Conclusions

We collected surface sediments from over 50 locations throughout Florida Bay and the adjacent western shelf to determine the spatial distribution of sulfur, iron and phosphorus compounds and their relationship to primary production in Florida Bay. A measured decreasing gradient in total P in surface sediments from west-east across Florida Bay supported the observed P-limitation of seagrass production along the same gradient. Further, sediment P correlated positively with total P in the water column, demonstrating strong benthic-pelagic coupling in the bay.

Total sediment P also correlated positively with 1N extractable iron, with a Fe:P ratio of 2:1. Although iron concentrations are low in these carbonate surface sediments relative to terrigenous sediments, iron oxides can influence P mobility. This relationship was stronger in unvegetated shelf sediments relative to seagrass vegetated sediments of Florida Bay. In the absence of iron oxides in surface sediments, released P may stimulate phytoplankton production in the water column. A sediment index of iron availability correlated negatively with water column chlorophyll concentrations that were highest near regions of seagrass die-off.

The observed distributions of Fe and P in surface sediments to the north and west of Florida Bay suggest multiple sources including local dissolution and transport, discharge from Shark River Slough, and transport from the Gulf of Mexico. Water currents appear to redistribute the iron and phosphorus, leading to zones of relative abundance and depletion. We saw no evidence for the occurrence of a Miocene sand channel. The contribution of aeolian transport and deposition to the observed distribution of iron and phosphorus in south Florida marine sediments has been hypothesized but not yet quantified.

Confirming the work of other researchers in Florida Bay, the deposition of iron-sulfide minerals in Florida Bay is Fe-limited. In areas north and west of Florida Bay where Fe concentrations were high but seagrass was absent, Fe-S mineral deposition is limited by organic matter as an energy source for sulfate reduction. Pyrite is the most abundant Fe-S mineral in Florida Bay sediments, found in concentrations up to $50 \mu\text{mol gdw}^{-1}$.

Because of the dual influence of iron oxide as a contributor to P limitation and a buffer to sulfide toxicity, we compared the depth distribution of sulfur, iron and phosphorus

compounds in sediment cores collected from control sites and experimental sites amended with a surface application of reactive iron aggregates. Eight months after amendment, deposition of iron monosulfides (FeS) and pyrite (FeS₂) in the upper 10 cm of sediments was significantly greater in iron-enriched plots relative to controls. Sediment phosphorus concentrations were higher in surface sediments and elevated in iron-enriched plots relative to controls, concomitant with elevated concentrations of dithionite-extractable iron oxides. Seagrasses growing in iron-enrichment plots clearly responded to the dual geochemical nature of iron, with individual shoots growing more vigorously in the presence of a buffer from sulfide toxicity. Total seagrass standing crop on an areal basis, however, did not increase owing to exacerbation of phosphorus limitation.

Nuisance algal blooms in Florida Bay are stimulated by water column phosphorus, so phosphorus sorption to iron-enriched sediments could enhance bay water quality. Given that reactive iron operates to 1) "cushion" toxic sulfide production and 2) keep phosphorus out of the water column, one might argue that ecosystem resistance to perturbations could be enhanced with more iron in the sediments. If the growth of seagrasses is negatively affected by sulfide toxicity and low iron availability, then more iron should stimulate growth of the plants and stabilize sediments. With more capacity for phosphorus retention in the sediment, less phosphorus in the water column should decrease microalgal activity. The overall result should be fewer algal blooms in the long term.

Because the Florida Bay ecosystem operates against a historical backdrop of substantial variation over spatial and temporal scales, however, gin-clear water probably should not be the goal of bay management (see "Florida Bay's Murky Past", BayWatch Report #4). Florida Bay experiences occasional and dramatic changes in ecosystem structure with the passage of large hurricanes, yielding increased sulfide production in some regions of the bay and decreased sulfide production in other areas. Also, seasonal winter storms regularly resuspend inorganic sediments and increase turbidity of the water. And dramatic events like seagrass die-offs have occurred in the past and will certainly occur again in the future. Thus, there is no need to promote artificial system stability by adding iron. Even without human tinkering, the Florida Bay ecosystem is going through changes (Fourqurean and Robblee 1999), and change is a natural property of this shallow, sub-tropical system where the sediment, water column, and atmosphere are so closely linked.

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d. Names of Scientific Collaborators Connected to this Project:

PI: Randolph M. Chambers, Associate Professor of Biology, Fairfield University

Co-PI: James W. Fourqurean, Associate Professor of Biology, Florida International University

Students: Regis Hoppenot, Lisa Millman (Fairfield University), Kevin Cuniff (Florida International University)

Poster and Oral Presentations Resulting from this Project:

R.M. Chambers and J.W. Fourqurean. 1998. Reactive iron availability as an ecological indicator of ecosystem resistance: a case study of Florida Bay. Oral Presentation, ASLO Meeting, St. Louis, MO, 5-9 June 1998.

Chambers, R.M, and J.W. Fourqurean. 1999. Sulfur, iron and phosphorus diagenesis in Florida Bay: Indicators of ecosystem resistance. Poster presentation, May 1999 All-Scientists meeting, Key West, FL.

R.M. Chambers, J.W. Fourqurean and R. Hoppenot. 1999. The effects of iron enrichment on sulfur, iron and phosphorus distributions in carbonate wetland sediments. Presentation, Wetlands Biogeochemistry Symposium, Ft Lauderdale, FL, 11-14 July 1999.

Chambers, R.M., J.W. Fourqurean and R.G. Hoppenot. Iron-sulfur chemistry in the carbonate sediments of Florida Bay. Estuarine Research Federation Biennial Meeting, New Orleans, LA, 25-30 September 1999.

Chambers, R.M., J.W. Fourqurean and L. Millman. 1999. Relationship of Sedimentary Sulfur, Iron and Phosphorus Cycling to Water Quality in Florida Bay: How Seagrass Die-Offs Contribute to Algal Blooms. 1999 All-Scientists Meeting, Key Largo, FL, November 1999.

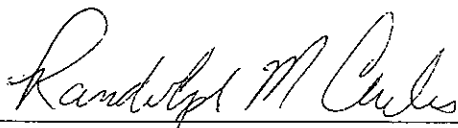
Papers Resulting from this Project:

Florida Bay Watch Report. June 2000. Rust and Rotten Eggs: Iron and Sulfur in Florida Bay. The Nature Conservancy and Florida Sea Grant Program.

Chambers, R.M. and J.W. Fourqurean. In Prep. Biogeochemical ramifications of iron-limited pyrite formation in carbonate sediments. Paper to be submitted to Biogeochemistry.

Copies of papers and presentation abstracts are included as Appendix A.

e. Signature of Principal Investigator:



Randolph M. Chambers

6-20-00

Date

f. Copy of Data Summaries

Data Summaries are included as Appendix B.

g. Diskette of Data with metadata file.

Diskette attached. Metadata file included as Appendix C.

APPENDIX A

R.M. Chambers and J.W. Fourqurean. 1998. Reactive iron availability as an ecological indicator of ecosystem resistance: a case study of Florida Bay. Oral Presentation, ASLO Meeting, St. Louis, MO, 5-9 June 1998.

Declining water quality in Florida Bay may be due to natural perturbations of ecosystem structure and function caused by seagrass die-offs. We are using sequential extraction schemes to determine the spatial distribution of reactive iron, sulfur and phosphorus species in sediments from vegetated and die-off regions throughout Florida Bay. The transformations of these chemical species are interrelated in most shallow-water systems, and reactive iron may be used as an indicator to assess ecosystem resistance to disturbance. Iron is of particular importance in Florida Bay owing to the biogenic carbonate sediments and very low total iron concentrations. As available iron is titrated by reduced sulfides during seagrass die-off and decomposition, the ability of the sediments to retain phosphorus is diminished. When reactive iron becomes unavailable, a positive feedback of sulfide accumulation in sediments and phosphorus release to the water column occurs, leading to nuisance algal blooms and ongoing seagrass decline. As an ecological indicator, reactive iron is important as a buffer to sulfide toxicity and as a contributor to phosphorus limitation of primary production in Florida Bay.

Chambers, R.M, and J.W. Fourqurean. 1999. Sulfur, iron and phosphorus diagenesis in Florida Bay: Indicators of ecosystem resistance. Poster presentation, May 1999 All-Scientists meeting, Key West, FL.

We are analyzing our sulfur data within the context of research from 25 years ago on Florida Bay sediments that argued the amounts of pyrite (up to 50 $\mu\text{moles/gdw}$) were "not appreciable" (Berner 1972). Although small relative to terrigenous sediments, the pyrite pool is an important measure of sulfide removal from the carbonate sediments of Florida Bay. Given the large, bay-wide variation in iron available for sulfur mineral formation, the concentrations of toxic sulfides in sediments should vary in relation to rates of sulfide production and sulfide removal via iron-sulfur mineral formation (Figure 2b). To make this assessment, we are considering bay-wide gradients in both reactive iron availability (Figure 4a) and organic matter production/decomposition (Figure 4b). We expect to show how some sections of Florida Bay may be resistant to sulfide toxicity owing to the reactive iron buffer mechanism.

Concomitant with reactive iron-sulfide mineral formation in sediments is the release of phosphorus sorbed to the iron. If this phosphorus is exchanged with the overlying water, it could contribute to the general decline in water quality observed over the past decade at some stations in Florida Bay. For example, in the eastern half of Florida Bay, we compared the calculated Index of Iron Availability in the sediments with a measure of surface water quality, as Chl-a concentration. Iron availability in the sediments correlated with bay water quality ($r^2 = 0.83$); decreases in iron availability (due to sulfide mineral accumulation) correspond with stronger algal blooms. In the western half of the bay with high concentrations of organic matter, however, this relationship is not found. High chlorophyll in the presence of a high iron index could be a consequence of additional P sources to the western half of the bay via surface water flow from the Gulf of Mexico; P release associated with seagrass die-off might also contribute. Also, these

samples were collected during winter; high iron availability in surface sediments measured at these stations during winter may decrease during the summer.

Mineral sulfide formation in surface sediments of Florida Bay appears to be iron-limited, as both iron and sulfur concentrations decrease with distance from the southern Florida mainland and from the western boundary of the bay. Sediment phosphorus concentrations decrease from west-east across the bay. In sediments with low organic content (the eastern half of Florida Bay), iron availability in surface sediments is closely correlated with algal production in the water column.

R.M. Chambers, J.W. Fourqurean and R. Hoppenot. 1999. The effects of iron enrichment on sulfur, iron and phosphorus distributions in carbonate wetland sediments. Presentation, Wetlands Biogeochemistry Symposium, Ft Lauderdale, FL, 11-14 July 1999.

Florida Bay is a shallow, seagrass-dominated wetland system formed atop iron-poor carbonate sediments. We compared the depth distribution of sulfur, iron and phosphorus compounds in sediment cores collected from control sites and experimental sites amended with a surface application of reactive iron aggregates. After two months, deposition of iron monosulfides (FeS) and pyrite (FeS₂) in the upper 2.5 cm of sediments was significantly greater in iron-enriched plots ($63.3 \pm 13.1 \mu\text{mol S/gdw}$) relative to controls ($25.6 \pm 6.0 \mu\text{mol S/gdw}$). Elevated concentrations of extractable iron, however, were detectable to 20 cm, suggesting that sediment mixing had occurred and that rates of sulfide formation were higher in surface sediments. Our hypothesis that decreases in sediment sulfide toxicity would be apparent in measurements of plant vigor has not been supported to date. Sediment phosphorus concentrations were higher in surface sediments and elevated in iron-enriched plots ($51.9 \pm 26.5 \mu\text{mol P/gdw}$) relative to controls ($7.7 \pm 0.8 \mu\text{mol P/gdw}$), concomitant with elevated concentrations of dithionite-extractable iron oxides ($41.7 \pm 14.3 \mu\text{mol Fe/gdw}$ in experimental plots versus not detected in controls). Nuisance algal blooms in Florida Bay are stimulated by water column phosphorus, so phosphorus sorption to iron-enriched sediments could enhance bay water quality.

Chambers, R.M., J.W. Fourqurean and R.G. Hoppenot. Iron-sulfur chemistry in the carbonate sediments of Florida Bay. Estuarine Research Federation Biennial Meeting, New Orleans, LA, 25-30 September 1999.

We are using chemical extractions to determine the spatial distribution of particulate sulfur, iron and phosphorus in surface sediments throughout Florida Bay. Particulate sulfur decreases away from the south Florida mainland ($< 50 \mu\text{mol S per gram dry weight of sediment}$). Iron availability controls the deposition of iron-sulfide minerals (primarily pyrite), but iron occurs in carbonate sediments at concentrations much lower than in temperate estuaries. Experimental addition of reactive iron to seagrass plots in Florida Bay effectively doubles the precipitation of iron sulfides in surface sediments. Because iron may serve as a buffer to sediment sulfide toxicity, we are also measuring seagrass growth and tissue C:N:P ratios in plots with and without iron additions. Extractable iron and phosphorus in Florida Bay sediments are positively correlated, suggesting that iron may influence the availability of phosphorus to seagrasses that are known to be P-limited. When sediment iron is titrated by reduced sulfides, phosphorus release to the water column can occur, contributing to nuisance algal blooms in the system.

Chambers, R.M., J.W. Fourqurean and L. Millman. 1999. Relationship of Sedimentary Sulfur, Iron and Phosphorus Cycling to Water Quality in Florida Bay: How Seagrass Die-Offs Contribute to Algal Blooms. 1999 All-Scientists Meeting, Key Largo, FL, November 1999.

We collected surface sediments from some 70 locations throughout Florida Bay and the adjacent northwestern shelf to determine the spatial distribution of sulfur, iron and phosphorus compounds and their relationship to primary production in Florida Bay. A measured decreasing gradient in total P in surface sediments from west-east across Florida Bay supported the observed P-limitation of seagrass production along the same gradient. Further, sediment P correlated positively with total P in the water column, demonstrating strong benthic-pelagic coupling in the bay.

Total sediment P also correlated positively with 1N extractable iron, with a Fe:P ratio of 2:1. Although iron concentrations are low in these carbonate surface sediments relative to terrigenous sediments, iron oxides can influence P mobility. In the absence of iron oxides in surface sediments, released P may stimulate phytoplankton production in the water column. A sediment index of iron availability correlated negatively with water column chlorophyll concentrations that were highest near regions of seagrass die-off.

The observed distributions of Fe and P in surface sediments to the north and west of Florida Bay suggest multiple sources including local dissolution and transport, discharge from Shark River Slough, and transport from the Gulf of Mexico. Water currents appear to redistribute the iron and phosphorus, leading to zones of relative abundance and depletion. We saw no evidence for the occurrence of a Miocene sand channel.

Confirming the work of other researchers in Florida Bay, the deposition of iron-sulfide minerals in Florida Bay is Fe-limited. In areas north and west of Florida Bay where Fe concentrations were high but seagrass was absent, Fe-S mineral deposition is limited by organic matter as an energy source for sulfate reduction. Pyrite is the most abundant Fe-S mineral in Florida Bay sediments, found in concentrations up to $50 \mu\text{mol gdw}^{-1}$.

Because of the dual influence of iron oxide as a contributor to P limitation and a buffer to sulfide toxicity, we compared the depth distribution of sulfur, iron and phosphorus compounds in sediment cores collected from control sites and experimental sites amended with a surface application of reactive iron aggregates. After two months, deposition of iron monosulfides (FeS) and pyrite (FeS₂) in the upper 2.5 cm of sediments was significantly greater in iron-enriched plots ($63.3 \pm 13.1 \mu\text{mol S gdw}^{-1}$) relative to controls ($25.6 \pm 6.0 \mu\text{mol S gdw}^{-1}$). Sediment phosphorus concentrations were higher in surface sediments and elevated in iron-enriched plots ($51.9 \pm 26.5 \mu\text{mol P gdw}^{-1}$) relative to controls ($7.7 \pm 0.8 \mu\text{mol P gdw}^{-1}$), concomitant with elevated concentrations of dithionite-extractable iron oxides. Nuisance algal blooms in Florida Bay are stimulated by water column phosphorus, so phosphorus sorption to iron-enriched sediments could enhance bay water quality. Our hypothesis that decreases in sediment sulfide toxicity would be apparent in measurements of plant vigor is being tested during summer 1999.

Rust and Rotten Eggs: Iron and Sulfur in Florida Bay

You wake up on a warm, clear morning in the Keys, luxuriating in the sights and sounds of yet another glorious day on Florida Bay. But as you take a deep breath of salty air, your nose tells you something unhealthy is wafting on the breeze. Is it: 1) a skunk, 2) a broken septic system, or 3) a natural gas leak?

The closest correct answer is 3. Florida Bay is leaking natural gases, but virtually none are the gases commonly used to cook with and heat our homes. Instead, the gases are sulfur compounds — mostly hydrogen sulfides — that are emitted from the bottom sediments of Florida Bay as well as from rotting wrack along the shoreline. These gases are produced as part of the natural decomposition in organic-rich marine muds, where bacteria decompose the dead plant and animal matter that settle to the bottom. To some, the “rotten eggs” smell of hydrogen sulfide indicates something wrong, but the chemistry and biology of Florida Bay combine to make sulfide a normal and, in some areas, prominent part of this shallow-water ecosystem. Interestingly, the shortage of iron minerals in Florida Bay contributes to this smelly sulfide story.

The Sulfide Source

All living organisms must use some form of energy to live. In oxygen-rich environments, primary producers such as algae and seagrass make organic matter through photosynthesis; consumers such as fish, humans, and bacteria break organic matter down to create energy to live. In fact, all organisms generate energy to live, and most (like us!) use oxygen and organic matter in a series of biochemical reactions to accomplish this. However, in the sediments of Florida Bay the rates of oxygen use,

mostly by sediment-dwelling bacteria, typically exceed the rates of supply from oxygen-rich surface waters. Under these oxygen-starved conditions, a variety of bacteria (unlike us!) are capable of using chemical compounds other than oxygen to produce energy. These compounds include sulfate, nitrate, reactive metals, and even carbon dioxide. In seawater, sulfate is the most abundant of these alternate compounds. Although the sediment-dwelling bacteria do not get much energy from these reactions, the use of sulfate and organic matter is the dominant form of energy generation in oxygen-free marine sediments.

Just as water is the by-product of oxygen-based energy production, the by-product of sulfate-based production is hydrogen sulfide. The large amounts of organic matter available in Florida Bay sediments, combined with low oxygen concentrations, cause high rates of hydrogen sulfide generation in the sediments. Because of the chemistry of the sediments, a majority of the hydrogen sulfide produced remains in the sediments in dissolved form, but some escapes to the overlying water column where it may be chemically transformed back to sulfate. An even smaller amount escapes to the atmosphere as sulfide gas, and it is this small amount that your nose sometimes detects in the air surrounding the Keys and out in Florida Bay.

The human nose is quite good at detecting very low concentrations of sulfide gas, which is why it is added to propane (which has no odor) to identify dangerous leaks. At high concentrations sulfide is toxic to many organisms — including humans — so they tend to avoid areas full of sulfides. In Florida Bay, where most of the sediment contains large amounts of

hydrogen sulfide, organisms such as rooted plants and animals living in the mud must have strategies to cope with the sulfide levels that in some areas can exceed 170 milligrams per liter of water — thousands of times more concentrated than what your nose can detect. For example, living seagrass roots leak oxygen to the surrounding sediments and thus provide a sulfide-free environment along each root channel. Like many other aquatic plants, seagrasses also have biochemical methods for lessening the effects of sulfide toxicity.

“Anemia” in Florida Bay

In addition to the biochemical neutralization of sulfide facilitated by organisms such as seagrasses, a number of geochemical processes can also help protect organisms from the toxic effects of high sediment sulfide concentrations. At the sediment surface where oxygen concentrations are high, hydrogen sulfide may be oxidized and converted to elemental sulfur or sulfate, both of which are non-toxic to marine organisms. Sulfides may also form solid, non-toxic minerals in the sediments upon exposure to reactive elements such as iron. However, in Florida Bay iron cannot contribute all that much to hydrogen sulfide removal because its concentration is very low in the white, chalky sediments of the Bay. Although iron is the fourth most abundant element in the Earth’s crust, compared to other locations Florida Bay is downright anemic. Why?

Biologically generated sediments, like those of Florida Bay, are composed mostly of calcium/magnesium carbonates, in essence the skeletal remnants of certain kinds of algae, microscopic organisms called foraminifera, and other plants and animals. There are few sources of iron and thus little “cushion” to sulfide toxicity. That is why Florida Bay is anemic.

Throughout much of the world, coastal marine sediments originate from the

erosion of rocks and soils and are washed into the sea by rivers. Sediments formed in this way are often rich in iron oxides that give them a brownish-orange color. When these “rusty” compounds are deposited in marine systems, they serve as a “cushion” to toxic sulfide production. The more iron, the bigger the “cushion.”

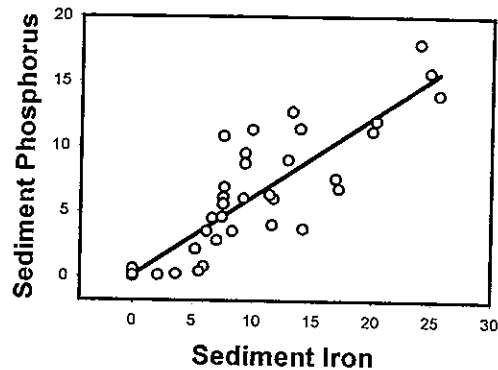


Figure 1. Relationship between sediment iron and phosphorus concentrations in carbonate sediments of south Florida. Where iron is found in high concentrations in the sediments, there is a strong tendency to find high concentrations of phosphorus.

Iron oxides are also important as sites that hold inorganic phosphorus in the carbonate sediments, as demonstrated by the relationship between iron and phosphorus in surface sediments from Florida Bay and the Southwest Florida Shelf (Figure 1). Dissolved phosphate occurs in very low amounts in the surface waters of Florida Bay because it is quickly bound to the abundant biologically generated calcium carbonate minerals. Recent studies suggest that this is a dynamic sedimentary source of phosphorus, but phosphorus is also associated with both the organic matter and the iron oxide minerals in the sediments. Living seagrass and algae require phosphorus as a nutrient and they concentrate phosphorus extracted from the Florida Bay environment. When seagrass and algae die and decompose in the sediment, some of that phosphorus may be

released into the water column. In most coastal systems, iron oxides may act as a “cap” on phosphorus release by chemically retaining it in the sediments and thus inhibiting its movement out of the sediments and into the overlying water.

In contrast, the “iron curtain” inhibiting phosphorus exchange between the sediment and water column cannot be drawn that tightly in Florida Bay where sediments are not “rusty” in color. They are grayish to white, and iron concentrations are ten to one hundred times lower than in land-derived sediments. Some iron is found in Florida Bay, but the source of that iron is not obvious. The “highest” concentrations of iron in Florida Bay surface sediments are still low compared to many coastal systems, and are found in the northeastern section of the Bay, south of Cape Sable, and in smaller pockets along the western margin (Figure 2). This spatially variable distribution suggests multiple land sources of small amounts of iron. Some iron may come from distant sources along the Gulf of Mexico and some may slowly make its way into Florida Bay from the “River of Grass.”

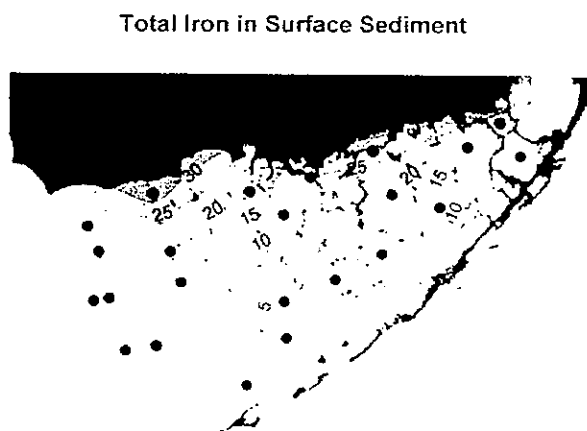


Figure 2. Concentration of iron in surface sediments of Florida Bay. The spatially variable pattern suggests multiple sources of small amounts of iron.

Whither Iron, So Goes Sulfide?

Given the observed variable distribution of iron in surface sediments, the formation and burial of iron-sulfide minerals

in Florida Bay sediments provides a history of iron availability and net sulfide formation (the difference between sulfate used by bacteria and hydrogen sulfide removed by the processes described above). In Rabbit Key Basin, for example, iron-sulfide mineral accumulation increases going deeper into the sediments, starting about 10 centimeters (4 inches) below the sediment surface (Figure 3). Even though the rates of sulfate use and sulfide production are highest in surface sediments, free sulfide does not always accumulate there. This suggests that some of the sulfides produced within the upper 10 cm of sediment either escape to the water column or are re-oxidized in place. Below 10 cm, however, sulfides are retained in the sediments, primarily as free sulfide and pyrite, an iron-sulfide mineral.

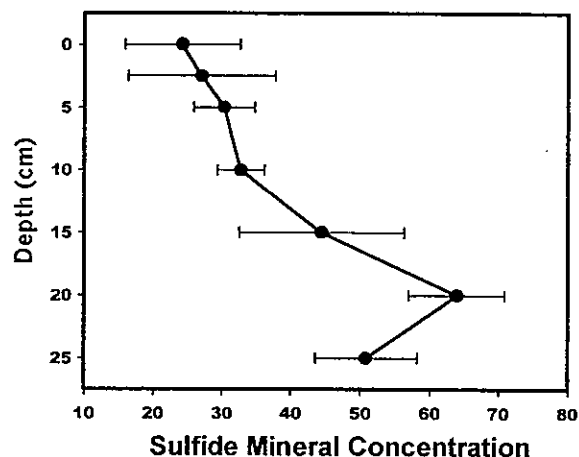


Figure 3. Depth profile of sediment sulfide minerals from Rabbit Key Basin. Note the increase in sulfide minerals deeper than 10 cm down into the sediments.

In addition to the observed spatial variability in iron and sulfide distribution — “rust and rotten eggs” — throughout Florida Bay and within sediments, sulfide production and iron availability probably vary over seasonal time scales as well. For example, rates of organic matter production and sulfide production are higher during the warm summer months than during cooler

winter months. With high rates of sulfide production in surface sediments during the summer, the capacity for organisms to retain a chemical “cushion” from sulfide toxicity may be diminished quite rapidly and perhaps even overwhelmed entirely. Under these circumstances, all iron would be chemically associated with sulfide, leading to a doubly sticky problem with respect to phosphorus dynamics.

The Phosphorus Problem

When organic matter decomposes in the absence of oxygen, phosphorus is released from the organic matter. If the iron is chemically associated with hydrogen sulfide, it is no longer able to chemically bind to phosphorus, which then gets released from the sediments into the water column. Thus, when rates of sulfide production are so great that all chemically reactive iron in surface sediments is exhausted (such as in the summer), phosphorus concentrations increase in surface waters, where phosphorus-limited microalgal growth may be stimulated. A positive feedback of increased decomposition of sedimentary organic matter and declining water quality is set into motion as the release of phosphorus stimulates microalgal blooms in the water column and organic matter (dead microalgal cells) stimulates anaerobic respiration in the sediments.

This scenario has been played out countless times in estuaries throughout the U.S., but only recently have we seen the pattern demonstrated graphically in Florida Bay. With the die-off of seagrasses in the 1980s, massive amounts of plant organic matter decomposed in the oxygen-free environment of surface sediments, releasing phosphorus to the water column of the Bay and stimulating microalgal blooms. The evidence of the die-offs remains in north-central Florida Bay sediments, where the available iron is lowest and where die-offs were most extensive (Figure 4). The low

capacity of these sediments to “cushion” toxic sulfide production is likely a consequence — not a cause — of seagrass die-off, but this sort of historical event has decreased the resistance of Florida Bay to further dramatic ecosystem-level changes.

Index of Iron Availability
in Surface Sediment



Figure 4. Low indices of iron availability are observed in north-central Florida Bay; the index is higher on the western margin and in the northeastern Bay.

Florida Bay is unique relative to most other estuaries in the U.S. because it has not been altered dramatically by anthropogenic additions of nitrogen and phosphorus via atmospheric input or runoff through the Everglades. These nutrients stimulate microalgal blooms in the water column and sulfide production in the sediments of other estuaries, but their concentrations are low in the small volume of freshwater that actually enters Florida Bay. But will it always be this way? Will the restoration of the Everglades and proposed increase of water delivery to Florida Bay dramatically affect the sedimentary sulfur cycle?

The short answer is “probably not.” Even with more freshwater runoff into Florida Bay, increased localized discharge of low-nutrient water should not stimulate microalgal blooms throughout the Bay. Although additional reactive iron may be eroded and transported into the bay, the impact of enhancing the capacity of sediments to “cushion” toxic sulfide

production should be localized to the Everglades/Bay margin where iron concentrations are relatively high already (Figure 2).

The Big Picture

The die-off of seagrasses in the 1980s set into motion a chain of events ultimately leading to decreases in water clarity because of microalgal blooms and increased sediment resuspension. Florida Bay has demonstrated some resilience to that disturbance — seagrasses are growing back, and the size and extent of some seasonal microalgal blooms has diminished. But how will the Florida Bay ecosystem respond to future perturbations to the cycle of iron, sulfur and phosphorus in the sediments and water column? Given that reactive iron operates to 1) “cushion” toxic sulfide production and 2) keep phosphorus out of the water column, one might argue that ecosystem resistance to perturbations could be enhanced with more iron in the sediments. To make a good thing even better, why don’t we dump iron into Florida Bay?

Adding iron oxides to sediments does pretty much what scientists expect: more phosphorus is retained by the iron (phosphorus release to the water column is impeded) and more sulfide is removed via the formation of non-toxic iron-sulfide minerals (more “cushioning”) (Figure 5). If the growth of seagrasses is negatively affected by sulfide toxicity and low iron availability, then more iron should stimulate growth of the plants and stabilize sediments. With more capacity for phosphorus retention in the sediment, less phosphorus in the water column should decrease microalgal activity. The overall result should be fewer algal blooms in the long term.

Because the Florida Bay ecosystem operates against a historical backdrop of substantial variation over spatial and temporal scales, however, gin-clear water

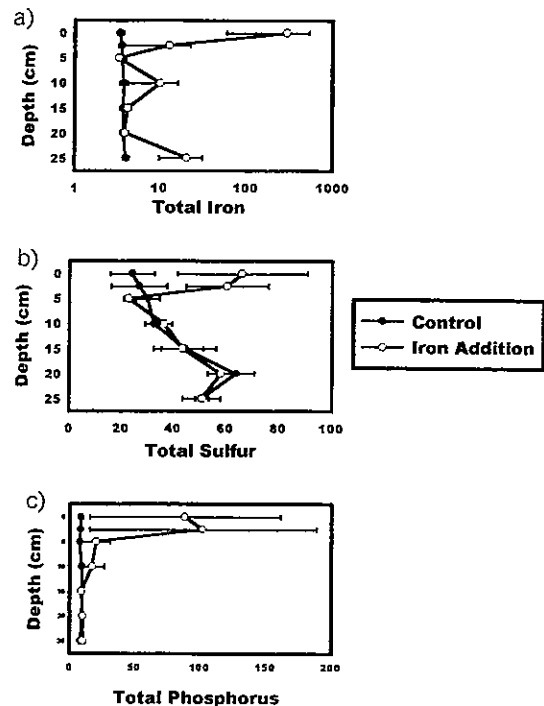


Figure 5. Addition of iron to surface sediments of Florida Bay (a) stimulates sulfide mineral formation (b) and increases phosphorus retention (c).

should not be the goal of Bay management (see “Florida Bay’s Murky Past”, BayWatch Report #4). Florida Bay experiences occasional and dramatic changes in ecosystem structure with the passage of large hurricanes, yielding increased sulfide production in some regions of the bay and decreased sulfide production in other areas. Also, seasonal winter storms regularly resuspend inorganic sediments and increase turbidity of the water. And dramatic events like seagrass die-offs have occurred in the past and will certainly occur again in the future. Thus, there is no need to promote artificial system stability by adding iron. Even without human tinkering, the Florida Bay ecosystem is going through changes, and change is a natural property of this shallow, sub-tropical system where the sediment, water column, and atmosphere are so closely linked.

One whiff ought to tell you that.

Additional Reading

- Barber, T.R., and P.R. Carlson, Jr. 1993. Effects of seagrass die-off on benthic fluxes and porewater concentrations of ΣCO_2 , $\Sigma\text{H}_2\text{S}$, and CH_4 in Florida Bay sediments. In: R.S. Oremland (ed.), *Biogeochemistry of global change: radiatively active trace gases*. Chapman and Hall, NY, pp. 530-550.
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APPENDIX B

Copies of Data Summaries

Attached on the following pages.

MAPDATA

Sta	lat	long	TP	SRP	APA	CHL A	TOC	TURB	TSCV	BSCV
1	2516.413	8022.475	0.33	0.05	0.42	0.97	538	1.69	0.13	0.13
2	2517.102	8023.702	0.32	0.05	0.46	0.89	666	8.26	0.20	0.18
3	2515.062	8024.91	0.30	0.06	0.64	0.80	711	1.43	0.19	0.19
4	2513.30	8023.30	0.30	0.05	0.69	0.91	611	0.87	0.18	0.15
5	2510.44	8025.39	0.30	0.05	0.52	0.87	631	1.79	0.20	0.19
6	2512.40	8026.42	0.35	0.08	0.80	0.88	766	9.10	0.37	0.33
7	2513.64	8027.70	0.44	0.07	0.89	0.88	838	9.99	0.50	0.44
8	2510.62	8029.49	0.28	0.05	0.33	0.89	659	12.46	0.23	0.20
9	2510.51	8037.62	0.31	0.06	0.50	0.87	916	24.34	0.36	0.30
10	2508.422	8042.967	0.68	0.09	2.86	3.17	1513	10.36	0.23	0.21
11	2505.49	8045.29	0.74	0.09	2.86	2.45	1307	12.47	0.20	0.17
12	2507.28	8048.17	0.99	0.08	2.48	3.19	1261	14.16	0.21	0.19
13	2507.096	8056.379	1.06	0.06	0.31	2.61	411	33.92	0.11	0.11
14	2502.55	8054.89	0.65	0.04	0.98	2.18	532	24.34	0.11	0.11
15	2500.15	8054.01	0.54	0.05	1.30	1.92	611	5.93	0.10	0.09
16	2458.66	8045.21	0.46	0.04	1.77	2.24	854	6.38	0.13	0.11
17	2455.77	8045.03	0.34	0.04	1.33	1.63	622	4.28	0.08	0.08
18	2500.40	8040.88	0.39	0.05	2.53	2.00	1139	5.91	0.14	0.13
19	2502.405	8036.843	0.31	0.04	1.17	1.49	906	13.92	0.18	0.17
20	2507.08	8035.98	0.31	0.04	0.44	0.97	777	17.88	0.27	0.23
21	2506.105	8031.884	0.30	0.04	0.34	1.01	750	22.11	0.23	0.22
22	2458.84	8100.10	0.78	0.03	0.61	3.00	339	37.52	0.06	0.05
23	2455.12	8056.09	0.64	0.03	0.87	2.07	328	22.45	0.06	0.06
24	2452.03	8048.43	0.26	0.02	0.51	1.22	243	3.88	0.06	0.05

MAPPING!

July 1998 Analysis of surface sediments from selected stations in Florida Bay

lat	long	AVG S	AVG P	AVG Fe
2506.105	8031.884	9.5	1.7	7.5 Butternut Key
2507.078	8035.983	17.2	1.9	10.1 Park Key
2510.51	8037.615	22.3	2.3	16.1 L. Madeira Bay
2508.422	8042.967	29.1	2.9	6.2 Terrapin Bay
2505.485	8045.287	34.7	5.5	4.2 Whipray Basin
2507.283	8048.173	19.0	7.1	5.2 Rankin Lake
2507.096	8056.379	21.5	10.0	11.2 Murray Key
		15.0	5.3	6.8 Middle Ground. South green Marker
		7.6	3.5	6.5 Western Park. Marker South
		9.2	5.4	7.9 15' W of boundary marker
		29.1	11.1	5.2 Carl Ross Key
2502.548	8054.889	23.7	8.3	6.0 Johnson Key Basin
2502.405	8036.843	21.0	2.5	7.5 Captain's Key
2510.443	8025.385	57.3	5.2	11.0 Blackwater Sound
2512.401	8026.424	18.2	1.6	12.3 L. Blackwater Snd
2513.642	8027.7	27.3	2.4	16.4 Long Sound
2510.624	8029.494	45.3	5.3	10.9 Duck Key
2500.396	8040.876	13.9	1.7	5.5 Porpoise Lake
2455.77	8045.028	7.2	2.2	4.6 Peterson Key
2458.66	8045.211	16.3	7.0	5.5 Twin Key Basin
2500.145	8054.006	13.9	4.6	4.0 Rabbit Key Basin
2458.844	8100.098	13.7	5.0	4.8 Oxfoot Bank
		6.8	5.6	7.0 Two miles West of Red 8
2455.116	8056.092	10.3	9.7	4.1 Sprigger Bank
		10.3	6.2	5.2 two miles West of Sprigger Bank
2452.032	8048.429	4.3	2.4	4.7 Old Dan Bank

Values in parentheses are

August FeSP: SOUTHWEST FLORIDA SHELF ANALYSIS, AUGUST 1998

Site	Date	UTMx	UTMy	Depth	Total P umol/cc	Total Fe umol/cc	Total Avg %Org	Total S umol/cc
1005	980812	451758.9394	2852671.9651	4.27	6.0	9.2	2.1	12.9
1007	980812	455541.2116	2846477.6214	4.27	2.8	7.0	1.4	3.8
1008	980813	447566.5020	2834934.6163	6.71	6.9	7.6	2.0	6.9
1011	980813	442863.9051	2841736.7737	4.57	2.1	5.2	1.4	2.1
1013	980813	435559.0984	2828656.7627	8.53	4.0	11.6	1.9	7.5
1014	980813	440723.7682	2820796.2506	9.75	3.7	14.2	3.3	17.0
1017	980812	456966.3750	2828149.6674	4.27	3.5	8.3	1.7	4.6
1020	980814	418859.4350	2746063.7644	16.15	6.1	7.5	5.6	15.0
1021	980814	427744.1059	2747640.2250	14.02	0.1	0.0	4.6	28.2
1023	980814	448130.6950	2752335.4589	9.75	0.1	2.1	4.4	15.9
1025	980814	456456.9998	2752849.1272	6.71	0.1	0.0	3.6	4.0
1030	980810	497168.0417	2758058.2369	3.96	14.0	25.6	9.1	8.3
1032	980810	492465.1752	2755428.5041	4.27	17.9	23.9	10.7	7.7
1033	980810	497732.2616	2761204.5111	4.27	15.7	24.8	9.1	4.5
1036	980811	491443.6484	2771668.5728	3.05	6.0	11.7	5.5	11.7
1039	980811	483635.2926	2780029.9556	4.57	0.2	3.6	6.7	19.1
1041	980811	489353.8315	2766949.4886	3.05	4.5	6.6	5.5	13.7
1043	980811	483626.7414	2774316.5126	4.57	12.7	13.2	7.1	15.6
1044	980817	478915.8331	2772195.2101	5.79	7.6	16.9	4.6	10.8
1045	980811	484649.7244	2764846.5104	3.66	9.0	12.9	5.2	11.3
1048	980811	480460.1078	2761238.5563	4.57	0.8	5.9	3.6	5.1
1049	980816	474224.0086	2762250.9250	4.57	0.1	0.0	4.1	8.5
1050	980817	467444.7604	2762250.5988	7.01	0.2	0.0	2.8	9.2
1051	980812	468460.4688	2831777.2904	3.96	4.6	7.4	2.8	13.0
1053	980812	465855.1310	2825398.0338	5.18	8.7	9.3	2.9	16.9
1056	980815	464836.8375	2811902.3071	6.71	6.8	17.2	3.6	17.6
1058	980812	476326.4050	2818694.4935	3.05	3.5	6.1	2.1	13.9
1059	980812	479869.5542	2815438.7244	2.44	9.5	9.3	4.7	12.4
1062	980812	484151.6743	2807763.0415	3.66	11.3	9.9	5.2	15.4
1064	980811	480468.6307	2799896.8536	4.27	11.4	13.9	7.4	30.5
1067	980816	471577.5407	2777412.6693	5.79	0.1	0.0	3.0	8.9
1069	980816	462170.2602	2775324.3583	7.32	0.0	0.0	4.7	10.5
1070	980815	469531.0900	2794688.8428	5.49	5.6	7.5	4.1	12.9
1072	980815	452266.0001	2810876.2416	8.84	0.3	0.0	3.4	8.0
1073	980815	455948.1809	2804084.9634	8.53	0.4	0.0	3.2	7.7
1074	980815	455952.5202	2790501.9002	7.32	0.0	0.0	4.1	15.8
1075	980815	453849.1179	2782626.7612	8.53	0.2	0.0	4.5	17.9
1076	980814	456471.7867	2762812.5662	9.14	11.2	20.0	4.8	8.4
1078	980817	476327.2568	2766436.2078	5.18	0.2	0.0	3.7	9.2
1079	980816	420942.3789	2806177.4243	14.94	12.0	20.3	4.7	16.1
1080	980816	429283.8717	2799898.3250	13.41	0.6	0.0	1.7	8.7
1084	980815	426159.9496	2781104.6622	13.72	0.0	0.0	3.2	11.7
1086	980815	415177.7242	2779515.0855	17.07	0.0	0.0	3.9	8.7
1087	980814	407361.2382	2749725.9062	17.68	6.3	11.4	5.0	14.3
1088	980815	424565.9939	2769030.4301	15.54	0.0	0.0	4.3	15.3
1091	980815	446032.3215	2772204.4811	9.75	0.1	0.0	4.6	9.9
1092	980816	470551.1567	2785300.4882	5.79	0.4	5.5	4.4	12.6
1095	980817	477799.2888	2754324.2315	5.18	0.1	0.0	3.4	4.2
1096	980817	471177.7954	2758363.1864	6.10	10.8	7.5	5.9	8.1

AVS umol/g	CRS umol/g	Total S umol/g	Total Fe umol/g	Total P umol/g	Fe Reacted	Fe Avail	Index of Fe Avail	Fluoride umol/g
0.2	10.1	10.30	8.46	2.92	5.1	6.2	0.55	7.5
0.6	10.1	10.70	21.26	3.55	5.1	9.9	0.66	5.8
1.1	28.8	29.90	51.96	4.07	14.4	28.8	0.67	3.3
1.3	10.4	11.70	11.87	2.11	5.2	9.2	0.64	6.8
2.5	20.1	22.60	27.44	2.16	10.1	17.7	0.64	6.0
5.2	29.8	35.00	24.96	5.85	14.9	13.3	0.47	9.0
0.9	10.8	11.64	12.23	3.15	5.4	6.9	0.56	12.4
3.8	37.0	40.79	19.95	4.37	18.5	7.0	0.27	10.5
2.3	25.2	27.50	32.88	8.53	12.6	11.5	0.48	
1.7	19.8	21.50	14.47	3.71	9.9	6.2	0.38	
0.2	7	7.20	6.31	1.51	3.5	2.9	0.45	
0.0	4.9	4.98	3.91	3.08	2.5	1.6	0.39	10.3
0.1	4.2	4.27	4.94	4.51	2.1	1.9	0.48	13.7
0.1	7.3	7.45	4.83	3.89	3.7	2.8	0.44	11.6
0.8	8.8	9.58	8.60	2.84	4.4	5.0	0.53	10.9
2.5	14.1	16.60	19.12	3.26	7.1	12.0	0.63	8.9
2.2	16.4	18.60	13.08	3.58	8.2	9.9	0.55	7.8
0.1	13	13.10	18.09	5.97	6.5	7.2	0.52	
2.2	11	13.20	17.56	6.16	5.5	5.0	0.48	
0.0	3.9	3.93	3.28	1.58	1.9	2.0	0.51	10.4
0.0	3.7	3.70	8.07	2.81	1.9	4.3	0.70	
0.0	4.4	4.40	15.13	5.83	2.2	6.7	0.75	
1.5	13	14.50	12.61	4.69	6.5	5.5	0.46	
2.0	16.1	18.10	21.95	5.35	8.1	8.9	0.53	

Year 1 Summary

Sta	Name	wqssta	lat	long	TP	SRP	APA	CHL A	TOC	TURB
5	Blackwater:		2510.44	8025.39	0.30	0.05	0.52	0.87	631	1.79
6	L. Blackw.		2512.40	8026.42	0.35	0.08	0.80	0.88	766	9.10
7	Long Sound		2513.64	8027.70	0.44	0.07	0.89	0.88	838	9.99
8	Duck Key		2510.62	8029.49	0.28	0.05	0.33	0.89	659	12.46
9	L. Madeir.		2510.51	8037.62	0.31	0.06	0.50	0.87	916	24.34
10	Terrapin :		2508.422	8042.967	0.68	0.09	2.86	3.17	1513	10.36
11	Whipray B.		2505.49	8045.29	0.74	0.09	2.86	2.45	1307	12.47
12	Rankin La		2507.28	8048.17	0.99	0.08	2.48	3.19	1261	14.16
13	Murray Ke:		2507.096	8056.379	1.06	0.06	0.31	2.61	411	33.92
14	Johnson K:		2502.55	8054.89	0.65	0.04	0.98	2.18	532	24.34
15	Rabbit Ke:		2500.15	8054.01	0.54	0.05	1.30	1.92	611	5.93
16	Twin Key :		2458.66	8045.21	0.46	0.04	1.77	2.24	854	6.38
17	Peterson :		2455.77	8045.03	0.34	0.04	1.33	1.63	622	4.28
18	Porpoise :		2500.40	8040.88	0.39	0.05	2.53	2.00	1139	5.91
19	Captain's		2502.405	8036.843	0.31	0.04	1.17	1.49	906	13.92
20	Park Key		2507.08	8035.98	0.31	0.04	0.44	0.97	777	17.88
21	Butternut		2506.105	8031.884	0.30	0.04	0.34	1.01	750	22.11
22	Oxfoot Ba:		2458.84	8100.10	0.78	0.03	0.61	3.00	339	37.52
23	Sprigger :		2455.12	8056.09	0.64	0.03	0.87	2.07	328	22.45
24	Old Dan B.		2452.03	8048.43	0.26	0.02	0.51	1.22	243	3.88

Site Summary

Station	Iron Index	chl-a
5	0.55	0.87
6	0.66	0.88
7	0.67	0.88
8	0.64	0.89
9	0.64	0.87
20	0.63	0.97
21	0.55	1.01
19	0.53	1.49
18	0.44	2.00
16	0.39	2.24
17	0.48	1.63
24	0.51	1.22
10	0.47	3.17
11	0.56	2.45
12	0.27	3.19
13	0.48	2.61
14	0.38	2.18
15	0.45	1.92
22	0.52	3.00
23	0.48	2.07

Rabbit Key Basin Pre-Iron Addition, Nov 1998 DATA

Sheet1

Rabbit Key Basin, Pre-Iron Addition November 1998								
	BDens	Porosity		Total P	Total Fe	Total S		
Vial #	g/cc	g/cc	%Org	umol/g	umol/g	umol/g	Depth cm	
101	0.34	0.88	11.8	6.3	10.2	3295	0	Core 1
102	0.24	0.74	13.1	6.0	10.9	7343	2.5	
103	0.21	0.81	15.4	7.3	13.9	11057	5	
104	0.35	0.85	15.5	6.2	13.2	14962	7.5	
105	0.16	0.88	16.5	6.0	19.6	7010	12.5	
106	0.13	0.67	16.4	5.4	19.2	9819	17.5	
107	0.20	0.87	13.7	4.7	14.6	13152	22.5	
108	0.24	0.89	13.9	6.5	12.2	15390	27.5	
109								
110								
111	0.20	0.85	18.8	12.5	8.4	3771	0	Core 2
112	0.15	0.50	15.6	8.6	12.4	4533	2.5	
113	0.27	0.83	14.8	7.8	11.2	6295	5	
114	0.17	0.93	18.4	6.6	13.7	8200	10	
115	0.25	0.87	12.9	4.7	18.2	12771	15	
116	0.29	0.89	12.6	4.1	11.1	12390	20	
117	0.13	0.68	19.4	6.8	12.1	9390	25	
118								
119								
120								
121	0.22	0.84	18.2	9.5	13.3	4105	0	Core 3
122	0.27	1.05	19.3	8.4	9.6	5343	2.5	
123	0.15	0.99	18.4	5.5	9.7	4867	5	
124	0.20	0.71	21.4	7.6	8.7	9581	7.5	
125	0.15	0.93	22.1	7.0	12.1	12295	10	
126	0.22	0.88	22.9	7.5	11.3	13152	12.5	
127	0.21	0.93	21.7	7.3	9.5	9200	15	
128	0.21	0.84	40.2	5.0	8.5	10771	20	
129	0.32	0.85	13.8	5.1	12.4	18486	25	
130	0.22	0.84	16.4	5.6	13.5	7914	30	
131	0.51	0.83	11.8	4.0	10.2	17533	35	
132								
133	0.34	0.76	8.9	5.3	10.9	6390	0	Core 4
134	0.30	0.91	16.2	5.8	9.0	6152	2.5	
135	0.27	0.78	15.6	5.6	9.7	4486	5	
136	0.26	0.74	15.6	6.1	10.5	5771	7.5	
137	0.20	1.10	16.7	5.9	9.7	4962	10	
138	0.28	0.78	16.5	7.6	10.8	11152	12.5	
139	0.24	0.88	16.0	6.3	11.2	9200	15	
140	0.17	0.87	19.3	6.6	13.9	8010	20	
141	0.22	1.02	15.5	6.1	13.2	5867	25	
142	0.21	0.98	20.4	6.6	13.9	8533	30	
143								
144	0.31	0.84	12.4	4.5	16.3	629	35	

RKB SEQUENT

Jan-99

Rabbit Key Basin, Sequential Extractions
Phosphorus Results, 2 Months post iron addition

Vial No.	Depth cm	P MgCl2 nmol/g	P Dithionite nmol/g	P Acetate nmol/g	P HCl nmol/g	P Total P nmol/gDW	
1	0	632	5656	1774	926	8989	Control
2	2.5	321	3454	1192	881	5848	Core
3	5	254	4229	1205	825	6513	
4	7.5	195	5295	1661	1372	8523	
5	12.5	151	4525	1305	1253	7235	
6	17.5	150	3919	1069	1764	6902	
7	22.5	226	4591	1967	2361	9145	
8	27.5	99	2919	1150	876	5043	
11	0	190	4525	1290	1086	7091	Control
12	2.5	205	4183	1255	1255	6898	Core
13	5	162	2702	1013	1266	5143	
14	10	150	4985	1381	1496	8011	
15	15	215	6070	1324	1821	9431	
16	20	168	4791	1278	1118	7355	
17	25	136	5172	1293	1164	7764	
21	0	461	3631	1215	1089	6397	Control
22	2.5	664	5240	4216	1000	11120	Core
23	5	552	3370	1083	1083	6088	
24	7.5	679	5656	1442	679	8456	
25	10	284	2132	888	1386	4691	
26	15	189	2596	1057	1892	5734	
27	20	278	4114	1646	1543	7580	
28	25	381	5485	1646	2674	10185	
29	30	279	4848	2424	2303	9854	
31	0	296	9882	3433	1950	15562	Iron Add.
32	2.5	335	8019	2406	859	11619	Core
33	5	240	5902	1686	1771	9600	
34	10	263	5550	1537	1153	8502	
35	15	150	5193	1224	946	7513	
36	20	198	8347	2043	4481	15069	
37	25	145	7757	1939	1551	11394	
41	0	276	19713	47447	108469	175905	Iron Add.
42	2.5	628	10182	18610	45817	75236	Core
43	5	419	6629	4842	35322	47213	
44	7.5	191	3677	3903	4412	12183	
45	10	245	5704	22645	37418	66012	
46	12.5	100	4371	1388	1890	7749	
47	15	140	5236	1963	1122	8461	
48	20	102	12444	4667	11878	29091	
49	25	134	12291	3687	21704	37816	
50	30	31	12341	2468	4011	18851	

RKB SEQEXT

551	0	439	13975	5590	3194	23198 Iron Add.
52	2.5	284	7733	1504	1246	10766 Core
43	5					
54	7.5	152	5461	975	2380	8968
55	10	76	5311	765	956	7109
56	12.5	207	10329	1033	1180	12749
57	15	127	7162	830	1660	9780
58	20	127	6903	978	1381	9388
59	25	103	7542	771	1697	10113
60	30	74	11449	1472	2535	15530
70	35	67	6252	759	1206	8284

RKB SED EXT

Rabbit Key Basin, Sequential Extractions
Iron Results

Vial No.	Depth cm	Fe MgCl2 nmol/g	Fe Dithionite nmol/g	Fe Acetate nmol/g	Fe HCl nmol/g	Fe FeS+FeS2 nmol/g	Fe Total Fe nmol/g
1	0	62	0	0	2935	8036	11033
2	2.5	19	0	0	2784	8579	11381
3	5	23	0	0	3834	13396	17252
4	7.5	13	0	0	5981	19807	25801
5	12.5	9	1558	0	4792	16612	22971
6	17.5	10	0	0	7178	20379	27566
7	22.5	0	0	0	9248	38371	47620
8	27.5	0	0	0	4289	28552	32841
11	0	18	0	608	4558	20643	25827
12	2.5	5	0	255	5107	24250	29617
13	5	18	0	227	5329	14872	20446
14	10	10	0	129	4893	19310	24342
15	15	0	0	0	8709	33595	42303
16	20	0	2383	0	6256	26106	34746
17	25	0	0	0	6367	22177	28544
21	0	11	0	1407	2907	8039	12365
22	2.5	38	0	2719	3039	8070	13866
23	5	6	0	808	4041	8194	13050
24	7.5	0	0	950	3229	20149	24327
25	10	0	0	716	5330	13426	19471
26	15	0	0	623	7721	13115	21459
27	20	0	3069	1151	8748	31999	44967
28	25	0	0	1381	11971	29834	43186
29	30	0	1809	2171	14922	44133	63034
31	0	0	40749	5588	6287	10865	63490
32	2.5	0	24361	5577	4808	44454	79201
33	5	0	26424	16043	6983	10736	60187
34	10	0	9556	7454	6594	19609	43212
35	15	0	2491	3238	5355	14676	25760
36	20	0	20652	6638	13129	30259	70677
37	25	0	105633	27349	10419	26599	169998
41	0	0	99286	22565	8575	45332	175758
42	2.5	0	12661	4558	4938	15357	37515
43	5	0	6452	2516	8710	11056	28733
44	7.5	0	3165	1045	3609	11637	19455
45	10	0	0	638	7022	22049	29710
46	12.5	10	6906	173	4403	20319	31811
47	15	15	5860	377	5776	28552	40579
48	20	23	25323	190	12535	33720	71791
49	25	23	38766	375	15944	27660	82768
50	30	21	338406	4834	433539	28463	805263

RKB SECRET

551	0	9	65542	670	20109	63445	149775
52	2.5	12	7693	192	3847	52396	64139
43	5					15618	15618
54	7.5	3	2329	87	3493	9797	15710
55	10	3	1902	143	3638	13157	18842
56	12.5	7	7707	330	7432	17391	32867
57	15	9	2915	0	5028	22473	30425
58	20	21	6009	0	7082	24354	37466
59	25	5	3837	0	6216	23521	33578
60	30	0	17085	183	9885	29030	56184
70	35	4	5998	100	3998	22196	32296

Rabbit Key Post-IRON 2 MONTHS:

Rabbit Key Basin Sediment Analysis, 2 Months Post Iron Addition

No Treatment Cores (Control)

		Sulfur umoles/gDW						
Depth		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Avg	S.E.
0		15.7	41	15.9			24.2	8.4
2.5		16.9	48.3	15.8			27.0	10.7
5		26.5	39.3	29.5	16.2	39.9	30.3	4.4
10		33	38.4	26.7			32.7	3.4
15		40.5	66.8	26			44.4	11.9
20		76.3	51.9	63.6			63.9	7.0
25		56.9	36.3	59.2			50.8	7.3
30								

Treatment Cores (Iron Addition)

		Sulfur umoles/gDW						
Depth		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average	S.E.
0		20.7	72.6	105.1			66.1	24.6
2.5		70.1	29.8	81.4			60.4	15.7
5		20.8	20.9	23.1	30.4	19.3	22.9	2.0
10		38	43.9	40.5	26.2	34.5	36.6	3.0
15		29.1	56.6	44.7			43.5	8.0
20		59.6	66.5	48.5			58.2	5.2
25		52.1	54.7	46.3			51.0	2.5
30								

No Treatment Cores

		Iron umoles/gDW						
Depth		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Avg	S.E.
0		3.6	3.8	2.7			3.4	0.3
2.5		3.7	3.6	3.5			3.6	0.1
5		4.1	4.7	3.6	2.3	3.5	3.6	0.4
10		4.6	3.2	3.7			3.8	0.4
15		3.8	3.2	4.2			3.7	0.3
20		3.9	3.4	3.8			3.7	0.2
25		4.1	3.4	4.6			4.0	0.3
30								

Treatment Cores

		Iron umoles/gDW						
Depth		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5		
0		88.8	763.4	30.5			294.2	235.2
2.5		32.1	3	3.5			12.9	9.6
5		3.1	3.1	3.5	3.5	3.2	3.3	0.1
10		34.5	3.7	4.4	3.9	4	10.1	6.1
15		4.9	3.5	4.3			4.2	0.4
20		4.1	3.3	4.2			3.9	0.3
25		3.8	40.2	17.2			20.4	10.6

30

No Treatment Cores

		Phosphorus umoles/gDW						
Depth		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Avg	S.E.
0		7.7	6.8	11.3			8.6	1.4
2.5		7.1	8.6	9.5			8.4	0.7
5		8	8.2	8.7	4.2	8.6	7.5	0.8
10		8.4	10.1	9.5			9.3	0.5
15		9.8	8.1	9.6			9.2	0.5
20		8.8	8.1	11.5			9.5	1.0
25		8.2	7.3	9.3			8.3	0.6
30								

Treatment Cores

		Phosphorus umoles/gDW						
Depth		Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Avg	S.E.
0		15.8	234.1	15.1			88.3	72.9
2.5		15.5	275.3	15.6			102.1	86.6
5		5.8	64	12.9	10.6	7.1	20.1	11.1
10		9.5	53.8	7.4	6.6	9	17.3	9.2
15		8.6	9.3	8.7			8.9	0.2
20		8.8	11.9	10			10.2	0.9
25		8.9	13.4	8.7			10.3	1.5
30								

RABBIT KEY POST-IRON 8 MONTHS

Rabbit Key Basin 7/15/99:

Iron and Phosphorus

Phosphorus		Experimental			July 1999 Data from RKB		
Depth	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	umol/GDW	S.E.
0.0	32.70	51.70	22.80			35.7	8.5
2.5	16.30	116.30	60.20			64.3	28.9
5.0	9.60	112.70	13.20			45.2	33.8
7.5	14.70	22.90	15.10			17.6	2.7
10.0	12.60	25.20	14.30			17.4	3.9
15.0	16.90	12.70	27.00	13.90	16.00	17.3	2.5
20.0	14.20	14.60	13.70			14.2	0.3
25.0	14.00	12.90	13.50			13.5	0.3
30.0	12.80	14.20	12.60			13.2	0.5
Phosphorus		Controls					
Depth	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	umol/GDW	S.E.
0.0	31.50	29.00	25.50			28.7	1.7
2.5	17.30	17.30	22.00			18.9	1.6
5.0	17.50	16.90	13.00			15.8	1.4
7.5	15.90	13.30	8.60			12.6	2.1
10.0	12.60	10.70	12.70			12.0	0.7
15.0	12.40	20.80	14.40	14.30		15.5	1.8
20.0	10.70	13.60	14.30			12.9	1.1
25.0	12.80	15.50	12.10			13.5	1.0
30.0	7.00	11.50				9.3	2.3

Iron Summary Experimental Group: Iron Addition

Depth	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average	S.E.
0.0	10.5	130.8	128.8			90.0	39.8
2.5	23.5	32.4	78.6			44.8	17.1
5.0	29.7	43.0	344.0			138.9	102.6
7.5	13.2	9.0	25.3			15.8	4.9
10.0	11.9	9.8	9.4			10.4	0.8
15.0	16.2	14.4	11.0	10.1	10.1	12.4	1.2
20.0	14.3	35.9	34.4			28.2	7.0
25.0	11.5	11.6	12.4			11.8	0.3
30.0	9.7	9.1	7.9			8.9	0.5
Iron Control Group							
Depth	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average	S.E.
0.0	7.00	7.70	12.50			9.1	1.7
2.5	8.50	10.30	10.30			9.7	0.6
5.0	9.60	9.90	14.10			11.2	1.5
7.5	8.50	9.60	8.30			8.8	0.4
10.0	9.40	34.40	12.90			18.9	7.8
15.0	9.20	9.40	10.60	9.50		9.7	0.3
20.0	8.80	8.80	10.10			9.2	0.4
25.0	10.10	11.00	12.10			11.1	0.6
30.0	15.20	11.10	19.90			15.4	2.5

Sulfur Extractions: Iron Addition Cores

RABBIT KEY POST-IRON 8 MONTHS

Rabbit Key Basin 7/15/99:

SULFUR

~~Iron and Phosphorus~~ SULFUR

Depth	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average	S.E.
0	71.9	30.7	174.2			92.3	42.7
2.5	27	88.3	64.9			60.1	17.9
5	42.3	34.3	106.9			61.2	23.0
7.5	29.5	47.5	44.1			40.4	5.5
10	3.8	29.5	8.3			13.9	7.9
15	7.1	4.9	41.2	9.5	10.8	14.7	6.7
20	5.3	5.3	7.2			5.9	0.6
25	9	5.5	3.2			5.9	1.7
30	7.2	7.6	7.2			7.3	0.1

Sulfur: Control Group

Depth	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Average	S.E.
0	0.1	1.1	20.3			7.2	6.6
2.5	0.1	1.6	12.8			4.8	4.0
5	18	2.3	1.7			7.3	5.3
7.5	7	1.7	2			3.6	1.7
10	21	2.9	4.1			9.3	5.8
15	5.9	2.5	4.5	5.1		4.5	0.7
20	4.4	5.4	7.4			5.7	0.9
25	4.1	16.7	11.5			10.8	3.7
30	2.4	23.9	2.8			9.7	7.1

APPENDIX C

Metadata Files

File Name and Description:

Mapdata.xls: this file lists station numbers established by Southeast Environmental Research Program personnel and includes lat-long plus surface water quality measurements collected as part of the SERP monitoring program. Many of these stations were used as sediment sampling locations for the current study, to compare sediment characteristics with surface water quality.

Mapping!.xls: this file lists station names and lat/long in Florida Bay, plus total Fe, S, and P from surface sediments, in μmoles per gram dry weight of sediment.

AugustFeSP.xls: this file includes sediment chemistry of locations northwest of Cape Sable, and is a summary of total iron, sulfur and phosphorus from 49 locations (lat-long included). A spatial map of total sulfur in surface sediments northwest of Cape Sable is included.

Year 1 Summary.xls: this file includes summary information from the first year of the study of surface sediments in Florida Bay, from 24 sampling stations. Included are measurements of porosity, bulk density, %organic, sequential P and Fe extractions, sequential S extractions, total Fe, P and S, the index of iron availability, fluoride concentrations from acetate extractions, and information from SERP water quality sampling stations.

Rabbit Key Basin Pre-Iron Addition.xls: this file includes initial depth profiles from 4 cores collected at the site of the iron addition experiment from year 2 of the study (November 1998). Included are measurements of bulk density, porosity, %organic, and total Fe P and S throughout 30 cm core profiles.

RKB Seqext: this file includes results of sequential extractions for both iron and phosphorus from Rabbit Key Basin, site of the iron addition experiment. Comparison between control and experimental (iron addition) cores, 2 months after iron addition.

Rabbit Key Post-Iron 2 Months: this file includes results of total Fe, P and S extractions from Rabbit Key Basin, site of the iron addition experiment. Comparison between control and experimental cores, 2 months after iron addition (January 1999).

Rabbit Key Post-Iron 8 Months: this file includes results of total Fe, P and S extractions from Rabbit Key Basin, site of the iron addition experiment. Comparison between control and experimental cores, 8 months after iron addition (July 1999).