Florida Bay Watch Report

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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) rotten eggs, 2) a broken septic system, or 3) a natural gas leak?

The closest correct answer is number 3. Florida Bay is leaking natural gases, but not the kind commonly used for cooking and heating our homes. Instead, the gases are sulfur compounds — mostly hydrogen sulfides — that are emitted from bottom sediments in Florida Bay as well as from rotting wrack found along the shoreline.

These gases are produced by the natural decomposition in organic-rich marine muds, where bacteria decompose dead plant and animal matter that settles 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, common occurrence in 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 need some form of energy to live. In oxygen-rich environments, primary producers such as algae and seagrass create organic matter through photosynthesis; consumers such as fish, humans, and bacteria break down organic matter to create energy. All organisms generate energy to live and, like us, most use oxygen and organic matter in a series of biochemical steps to accomplish this. However, in Florida Bay sediments 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 carbon dioxide. Of these, sulfate is the most abundant alternate energy-producing compound in seawater. 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. Because of the chemistry of sediments, the majority of hydrogen sulfide produced remains there in dissolved form.

However, some escapes to the overlying water column where it is chemically transformed back to sulfate. An even smaller amount escapes to the atmosphere as sulfide gas, accounting for the rotten egg smell that sometimes occurs in the Keys and in Florida Bay. In fact, we are quite good at smelling very low concentrations of sulfide gas, which is why it is added to propane (which has no odor) to identify dangerous leaks.

High concentrations of sulfide are toxic to humans and many other organisms. In Florida Bay, where most of the sediment contains large amounts of hydrogen sulfide, organisms that cannot move away, such as rooted plants and animals living in the mud, have developed strategies to cope with high sulfide levels. For example, living seagrass roots leak oxygen to the surrounding sediments, providing 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 aided by organisms such as seagrasses, 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 when exposed to reactive elements such as iron. However, iron cannot contribute much to hydrogen sulfide removal in Florida Bay because its concentration is very low in the chalky sediments. Although iron is the fourth most abundant element in the Earth's crust, compared to other locations, Florida Bay is downright "anemic." Why?

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, giving them a brownish-orange color. When these "rusty" compounds are deposited in marine systems, they cushion the toxic sulfide production. The more iron, the bigger the cushion.

In contrast, the sediments of Florida Bay are biologically generated. They 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. Because there is so little iron in these biologically generated sediments, there is little to cushion the sulfide toxicity. That is why Florida Bay can be considered anemic.

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).

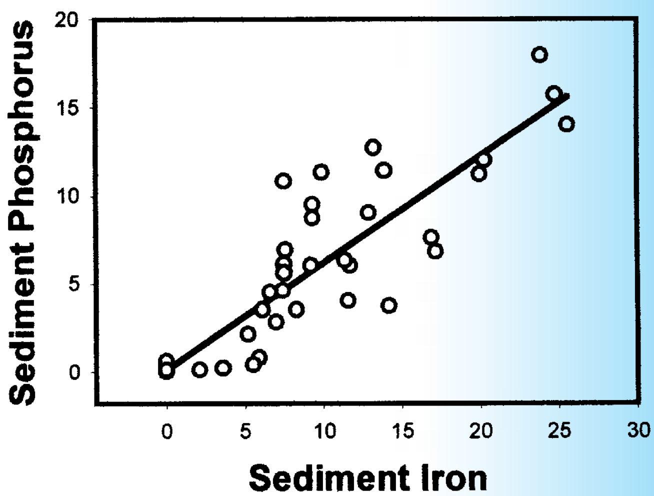

Figure 1. Relationship between sediment iron and phosphorus concentrations in carbonate sediments of south Florida. Where iron is found in high concentrations in the sediments, there is a strong tendency to find high concentrations of phosphorus.

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

In contrast, the “iron curtain” that inhibits phosphorus exchange between the sediment and water column cannot be drawn tightly in Florida Bay where sediments are not rust colored. They are grayish to white because iron concentrations are 10 to 100 times lower than in land-derived sediments. Some iron is found in Florida Bay, but the source of that iron is not obvious. At their highest, concentrations of iron in Florida Bay surface sediments are low when compared to many coastal systems. Iron is found in the northeastern section of the bay, south of Cape Sable, and in smaller pockets along the western margin (Figure 2), suggesting 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 Everglades.

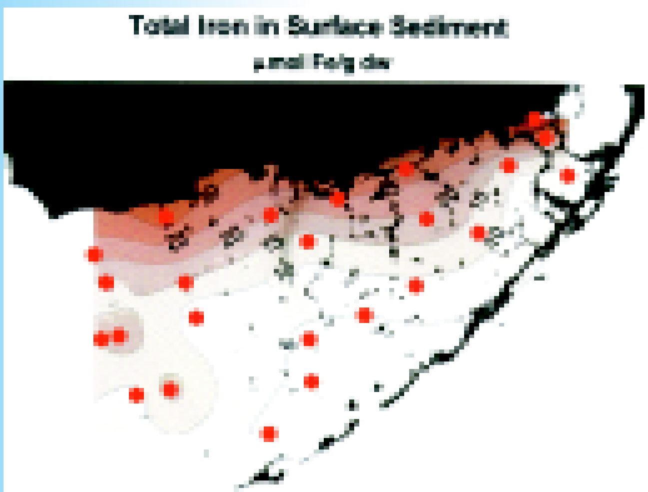

Figure 2. Concentration of iron in surface sediments of Florida Bay. The spatially variable pattern suggests multiple sources of small amounts of iron.

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 with depth in the sediment, starting at about 10 centimeters (cm; equivalent to four inches) below the sediment surface (Figure 3).

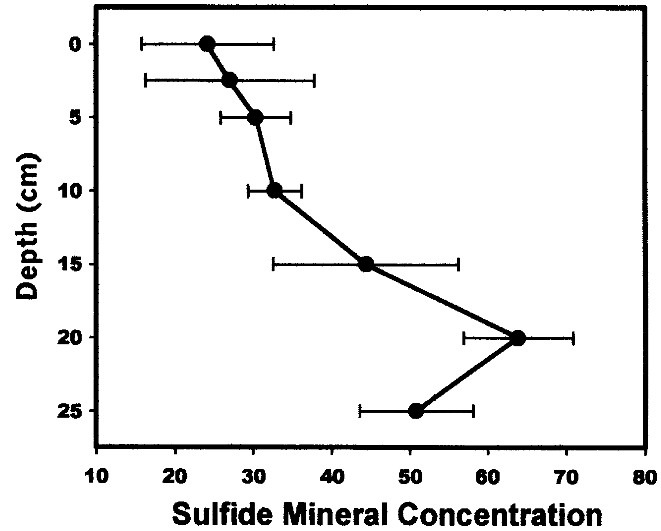

Figure 3. Depth profile of sediment sulfide minerals from Rabbit Key Basin. Note the increase in sulfide minerals deeper than 10 cm.

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.

In addition to the observed spatial variability in iron and sulfide distribution, sulfide production and iron availability also vary seasonally. For example, rates of organic matter production and sulfide production are higher during the warm summer months than during cooler winter months. Because high rates of sulfide production occur in surface sediments during the summer, an organism’s capacity to retain a chemical cushion from sulfide toxicity may diminish rapidly and may even be overwhelmed entirely. Under these circumstances, all iron is chemically associated with sulfide, further complicating the phosphorus dynamics.

The Phosphorus Problem

When organic matter decomposes in the absence of oxygen, phosphorus is released. If 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. When rates of sulfide production are so great that all chemically reactive iron in surface sediments is exhausted, as in the summer, phosphorus concentrations increase in surface waters, where phosphorus-limited microalgal growth may be stimulated.

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 into the water column 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 bay's resistance to further ecosystem-level changes.

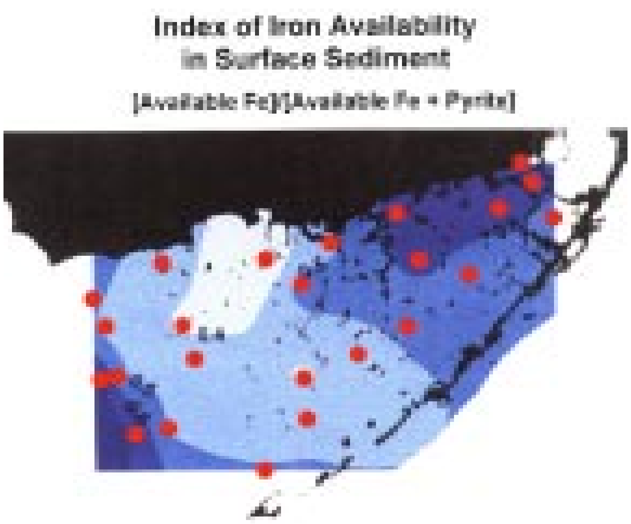

Figure 4. Low indices of iron availability are observed in north-central Florida Bay; the index is higher on the western margin and in the northeastern Bay.

Compared to most estuaries in the U.S., Florida Bay is unique because it has not been altered dramatically by anthropogenic additions of nitrogen and phosphorus via the atmosphere or runoff from 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 restoring the Everglades and increasing water flow to Florida Bay 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/ Florida Bay margin where iron concentrations are already relatively high (Figure 2).

The Big Picture

The die-off of seagrasses in the 1980s set into motion a chain of events that ultimately led 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 disturbances to the cycle of iron, sulfur, and phosphorus in the sediments and water column? Because reactive iron cushions toxic sulfide production and keeps phosphorus out of the water column, some might argue that ecosystem resistance to disturbances could be enhanced if there were more iron in the sediments. So, why don't we put more iron into Florida Bay?

Predictably, when you add iron oxides to sediments, the iron retains more phosphorus, impeding phosphorus release to the water column, 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 plant growth 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 clearer water in the long term.

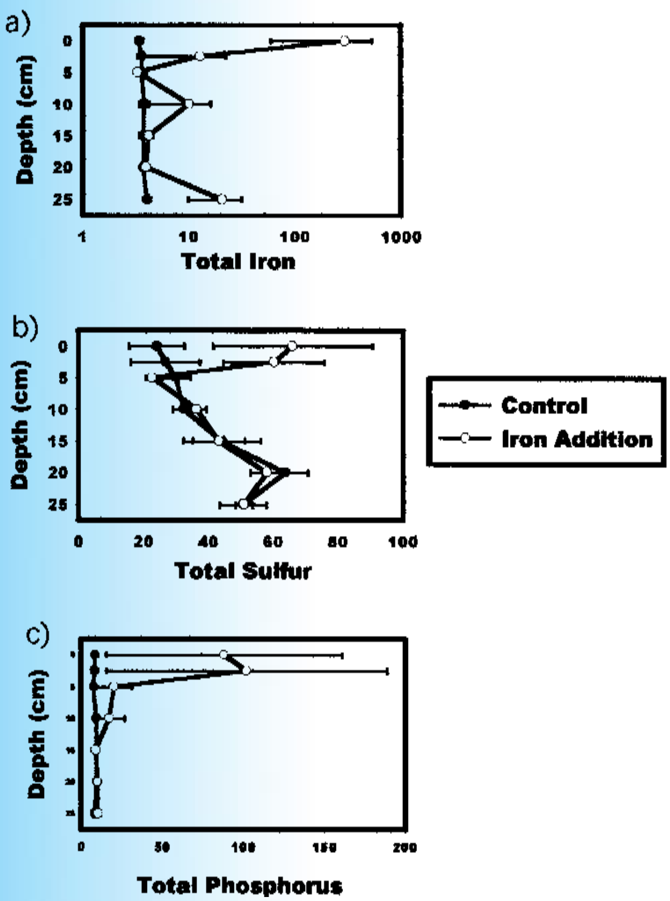

Figure 5. Addition of iron to surface sediments of Florida Bay (panel a) stimulates sulfide mineral accumulation (panel b) and increases phosphorus retention (panel c).

Because the Florida Bay ecosystem operates against a historical backdrop of substantial variation over spatial and temporal scales, gin-clear water probably should not be the goal of bay management (see Florida Bay Watch Report "Florida Bay's Murky Past"). Florida Bay experiences occasional and dramatic changes in ecosystem structure with the passage of large hurricanes, which yield increased sulfide production in some regions and decreased sulfide production in others. Also, seasonal winter storms regularly re-suspend inorganic sediments and increase turbidity of the water. And dramatic events like seagrass die-offs have occurred in the past and will likely occur again. Given this, there is no need to promote artificial system stability by adding iron. Change is a natural property of this shallow, sub-tropical system where the sediment, water column, and atmosphere are so closely linked. Even without human tinkering, the Florida Bay ecosystem will continue to experience change and natural chemical processes. One whiff of rotten eggs ought to tell you that.

Additional Reading

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Acknowledgments

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