Annual Progress Report

Project title: The Role of Sediments Resuspension in Phosphorus Cycle in Florida Bay

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1. Work accomplishments

During this project period, we have developed trace level phosphate analytical technique utilizing a liquid wavequide technology (Zhang et al, 2002). Using an autoanalyzer equipped with a liquid wavequide long flow cell (2 m) we were able to accurately determine the nM concentrations of dissolved phosphate in water samples and to obtain a high resolution of spatial distribution of dissolved phosphate in Florida Bay waters (Figure 1). Our results have demonstrated that Florida Bay water contains very low phosphate concentrations (2 - 64 nM) and sedimentary phosphorus is a dominant reservoir of phosphorus in Florida Bay ecosystem. Because a mean water depth in the bay is only about 2 m, sediment resuspension becomes even more important in shallow water like Florida Bay. The release of phosphate from the suspended sediment can be the source of this limiting nutrient for the onset and sustainment of the algae bloom.

Our most recent study provided the first dataset on the distribution, abundance and reactivity of sedimentary phosphorus over entire Florida Bay. The sediment samples were collected from 40 stations that cover every sub-basins of Florida Bay (station locations indicated as "+" in Figure 1). Total sedimentary phosphorus has been determined in sediment samples and fractioned into five different pools using a sequential extraction technique. Our results have shown a strong spatial gradient in sedimentary phosphorus in Florida Bay. The highest concentration of total sedimentary phosphorus (11-14 μmol/g) was found at the northwest bay, near Cape Sable. The lowest concentration (1-2 μmol/g) was found in eastern bay where low chlorophyll concentrations are usually found. A strong gradient of decreasing sedimentary phosphorus concentration was observed from the west to east across the central Florida Bay.

Calcium carbonate accounts for an average of 90.1 ± 4.3% in Florida Bay sediments, with a spatial variation from 83.7 to 97.5%. The areas of relatively low percentage of calcium carbonate were found in northwest and north central bay, corresponding to areas of high productivity. Calcium carbonate contents in these sediments are apparently been diluted by organic matters generated from plankton production.

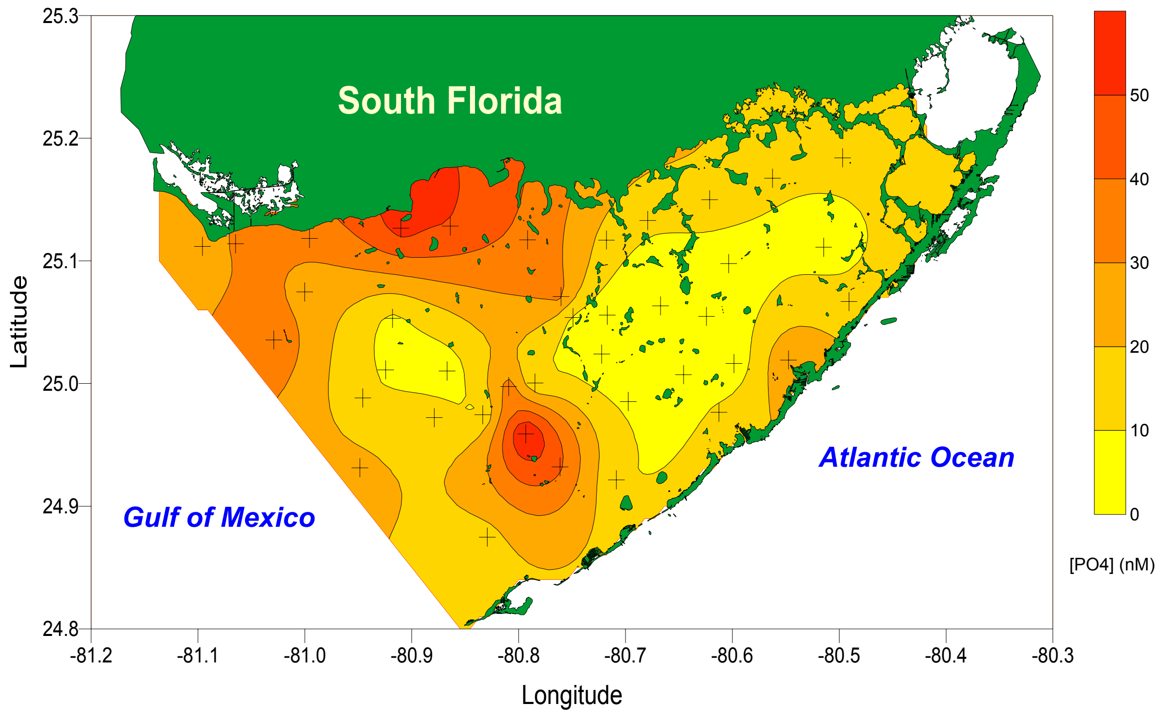

Figure 1. Spatial distribution of dissolved phosphate in Florida Bay water. Total of 40 stations (station locations indicated as +) were occupied for sampling water and sediment during the survey.

The reactive phosphorus concentrations extracted by $MgCl_2$ solution show a similar pattern as total sedimentary phosphorus. The highest concentration (1 µmol/g) was found at the northwesten bay, near Cape Sable. The lowest concentration was found in eastern bay. This fraction of sedimentary phosphorus is exchangeable with water column and is generally considered as bioavailable. The spatial pattern of dissolved phosphate in water as shown in Figure 1 is in good agreement with the exchangeable inorganic phosphorus in sediment obtained from sequential extraction method. It is hypothesized that sedimentary phosphorus behaves as a buffer system and regulates the concentrations of dissolved phosphate in the water column of Florida Bay. In other words, the dissolved phosphate concentrations in the shallow waters of Florida Bay is controlled by the exchange of phosphate between water and sediment and its concentration is determined by the concentration of exchangeable phosphate in sediment and the amount of suspended sediment in the water column.

A significant fraction of sedimentary phosphorus is tied up with Fe(III) and Mn oxides in Florida Bay sediments. Reduction of ferric and Mn oxide in anoxic environment will release this iron-bound phosphorus to surrounding water. The iron-bound phosphorus show a similar pattern as exchangeable phosphorus with high concentration (2 μmol/g) in the northwestern bay and low concentrations in eastern bay. Reactive Fe concentrations from reduction of ferric oxide in sediment show a strong gradient of decreasing concentration away from the Florida mainland. The maximum concentrations were found in the northeastern bay and a second highest concentration at north central coast. Low concentrations were found in southern Bay. The distribution pattern of reactive iron indicates that fresh water runoff is a major pathway that transports the terrestrial iron, mainly as particulate and colloidal iron, into Florida Bay. The passage of fresh water runoff into the bay can easily be identified from the salinity distribution at the beginning of the wet season that was preceded by a prolonged dry season during summer of 2001. The distribution of reactive iron show a good spatial correlation with that of salinity, indicating that freshwater input is the source of iron to the Bay. However, sediments in eastern bay contain high concentrations of iron oxide but have very little phosphate associated with these iron oxides. The eastern bay sediments must have a strong capacity to adsorb phosphate from seawater.

The concentrations of authigenic carbonate fluorapatite and biogenic apatite as well $CaCO_3$ associated phosphorus show a similar pattern as total sedimentary phosphorus. The highest concentration (4.5 μmol/g) was found at the northwest bay, near Cape Sable. The lowest concentration was found in eastern bay. There is a significant fraction of organic phosphorus in associated with this pool. The percentage of organic phosphorus varied from few percent in non-productive area to 30% in regions of high productivity. Detrital apatite phosphorus of igneous or metamorphic origin shows a similar distribution pattern as total sedimentary phosphorus but its maximum concentration is <1 μmol/g. The remaining sedimentary phosphorus was considered to be organic phosphorus residue and its spatial distribution clearly shows its origin from biological production in the western Bay.

Among five pools of sedimentary phosphorus, the authigenic carbonate, fluorapatite and biogenic apatite as well $CaCO_3$ associated phosphorus accounts the largest fraction of phosphorus (46% of total sedimentary P). Organic phosphorus accounts for about 30% in sediments overlying productive water and less than 10% in other areas of the Bay. The second largest pools of sedimentary phosphorus are organic residue and Fe-bound phosphorus, each being 20% of total sedimentary phosphorus. The exchangeable phosphorus accounts 9% of total sedimentary phosphorus, of which organic form accounts 60%. Detrital apatite phosphorus of igneous or metamorphic origin represents the smallest fraction, only 5% of total sedimentary phosphorus. Overall, organic phosphorus is an important fraction that accounts for about 36% of total sedimentary phosphorus.

We have also conducted a series of experiments to study the phosphate adsorption /desorption characteristics of Florida bay sediments. From this study we can quantify the zero equilibrium concentration and the buffer intensity at the zero equilibrium concentration and the distribution coefficients for phosphorus partitioning between sediment/seawater in Florida Bay. The partitioning of phosphorus between water and sediment can be quantified by the distribution coefficient K_d. Distribution coefficient K_d of phosphorus is defined as $K_d = C_s/C_w$, where C_s is the concentration of phosphorus on particle surface and C_w is the concentration of phosphorus in seawater. Our results indicats that K_d is a function of sedimentary phosphorus, temperature and salinity. Since Florida Bay is subdivided by mud banks into partially isolated basins, spatial variation in sediment characteristics is expected due to differences in environmental condition. Further study is underway to verify any spatial variation of K_d in Florida Bay and the effect of salinity and temperature on the K_d.

2. Applications

Results of this study have been presented in 2001 Florida Bay Science Conference at Key Largo, Florida. The spatial distribution of sedimentary phosphorus from this study will be presented at the American Society of Limnology and Oceanography 2002 summer meeting in Canada.

Results of our sequential extraction experiments provide the first and detailed spatial distribution of various pools of sedimentary phosphorus and reactive iron in Florida Bay surficial sediments. It can be used for long term monitoring the impact of change in phosphorus cycle on the health of ecosystem in Florida Bay. Our measurements of distribution coefficients of phosphorus between water/sediment will provide a quantitative relationship between K_d and environmental parameters such as temperature and salinity, which can be used in a water quality model to predict the fate of input phosphorus in Florida Bay.

Followings are some publications resulted from this study:

Zhang, J.-Z., C. Fischer and P. B. Ortner (2001) Continuous flow analysis of phosphate in natural waters using hydrazine as a reductant, *International Journal of Environmental Analytical Chemistry*, 80(1): 61-73.

Zhang, J.-Z., J. Chi (2002) Automated analysis of nanomolar concentrations of phosphate in natural waters with liquid waveguide, *Environmental Science & Technology*, **36**(5): 1048-1053.

Zhang, J.-Z., C. Fischer (2002) Spatial distribution of various forms of phosphorus in calcium carbonate-dominated Florida Bay sediments. In preparation.