

Geochemistry of Phosphorus in a Carbonate Aquifer Affected by Seawater Intrusion

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ABSTRACT

The concentrations of total and dissolved phosphorus in groundwater were found to increase linearly with salinity within the seawater intrusion zone beneath southwestern Florida. Digestion of the limestone resulted in an average total phosphorus (TP) concentrations from 54 $\mu\text{g/g}$ to over 850 $\mu\text{g/g}$. Adsorption experiments confirmed that the limestone aquifer had a high affinity to adsorb phosphate dissolved in fresh water. Phosphate adsorption decreased in the presence of seawater. Geochemical modeling determined that dissolution of calcite and aragonite was responsible for the release of phosphorus in brackish groundwater at low salinities. At higher salinities, desorption of phosphate as a result of bicarbonate sorption was the dominant reaction.

INTRODUCTION

Areas of seawater intrusion are geochemically active, particularly in carbonate aquifers, where carbonate mineral dissolution (Back et al., 1986) and ion exchange (Sivan et al., 2005) are important. These reactions may be responsible for an observed linear increase of phosphorus with salinity in groundwater along the southwestern coast of Florida (Price et al., 2006). Dissolved phosphorus may be transported to surface coastal waters via either submarine groundwater discharge (Moore, 1999) or coastal groundwater discharge (Price et al., 2006) where it can serve as an additional source of this important nutrient.

In carbonate aquifers with little iron, P exists either as phosphorus minerals such as apatite (Jensen et al., 1998) or adsorbed onto calcite and aragonite (DeKanel and Morse, 1978). TP in carbonate sediments throughout south Florida range from 56 – 678 $\mu\text{g/g}$ soil (Chambers and Pederson, 2006; Zhou and Li, 2001). Adsorption and desorption of phosphate to calcium carbonate sediments from Florida Bay under both fresh water and seawater have been investigated with less P adsorption occurring with an increase in salinity (Millero et al., 2001). The capacity of P sorption by carbonate also depends strongly on its surface area with higher adsorption occurring on fine grain sediments (Zhou and Li, 2001). The objectives of this research were to 1) further document the occurrence of elevated total P concentrations in the brackish groundwater underlying south Florida; 2) quantify the amount of P available in the limestone of the Biscayne Aquifer, and 3) to identify which reactions were responsible for the release of P from the bedrock as a result of seawater intrusion.

METHODS

Groundwater sampling was conducted at 11 sites (Fig. 1) from Sept. 9-13, 2007. Groundwater temperature, pH, salinity, and dissolved oxygen were monitored until stable. Water samples were collected for TP and dissolved phosphate (soluble reactive phosphate; SRP) in vials that were first flushed with nitrogen and then evacuated to remove any exposure of the sample to oxygen.

Rock core was collected from five locations in the Biscayne Aquifer (Fig.1). Cores CP and RB were located near the coastline in a zone of known seawater intrusion. Core LMB was collected from Florida Bay. Cores (G3778 and G3784) were far inland in a region of fresh groundwater. A

sub-sample of 0.5 g of rock was taken from the interior of each half of the core at determined intervals. These rock samples were digested for TP determination.

A cube, 0.2m on a side, was extracted from a large block of Key Largo Limestone (Fig 1). The limestone cube was sealed in a Plexiglass permeameter. A constant discharge was maintained at 120 L d⁻¹ using a 20 L carboy filled with a solution of phosphate (PO₄³⁻) varying from 0 to 20μM in either Dionized water (DIW) or seawater. The final part of the experiment consisted of flushing the stone with DIW and then seawater to observe SRP desorption. Water discharging from the block was monitored for pH, salinity, and temperature. A subsample of 40 ml of water for every liter discharged was collected for determinations of SRP, alkalinity, potassium, calcium, sodium, magnesium, chloride and sulfate. The concentrations of the major ions, pH, temperature, and alkalinity were input to the geochemical model PHREEQC version 2.14.2 to determine the saturation states of the water with respect to calcite and aragonite.

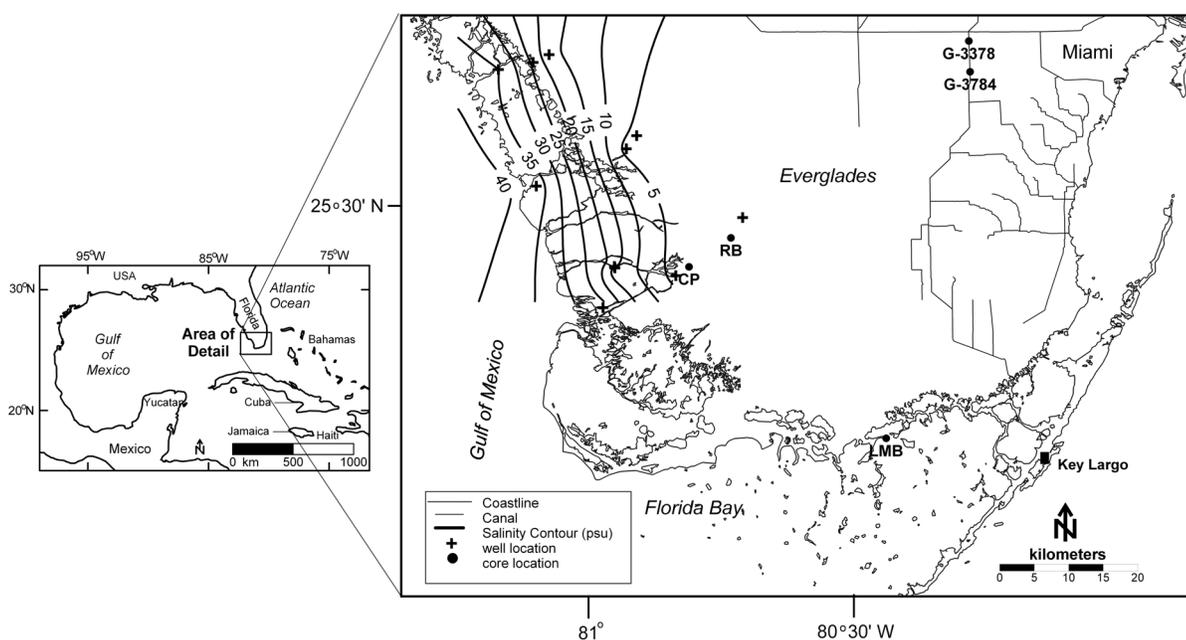


Figure 1. Site location map of groundwater wells (+), rock core (●), and Key Largo limestone (■) used in this study. Contour lines represent salinity of groundwater collected from wells that ranged in depth from 2 to 8 m.

RESULTS

TP in the brackish groundwaters ranged from 0.6 μM to 6.9 μM, and varied linearly with salinity (Fig. 2A). SRP also varied linearly with salinity and ranged from 0.06 to 6.9 μM (Fig. 2B). The concentrations of both TP and SRP in the groundwaters were consistently higher than in either fresh Everglades surface water, or in surface water from the Gulf of Mexico.

The TP concentrations of the limestone core collected from 0 to 10 m depth averaged 54 μg/g of rock (±17 μg/g of rock). Between 10 m and 20 m deep, the concentration of P increased from 200 to 850 μg/g of rock. There was no significant difference in the P concentrations of the limestone core collected from a region of fresh groundwater versus seawater intrusion.

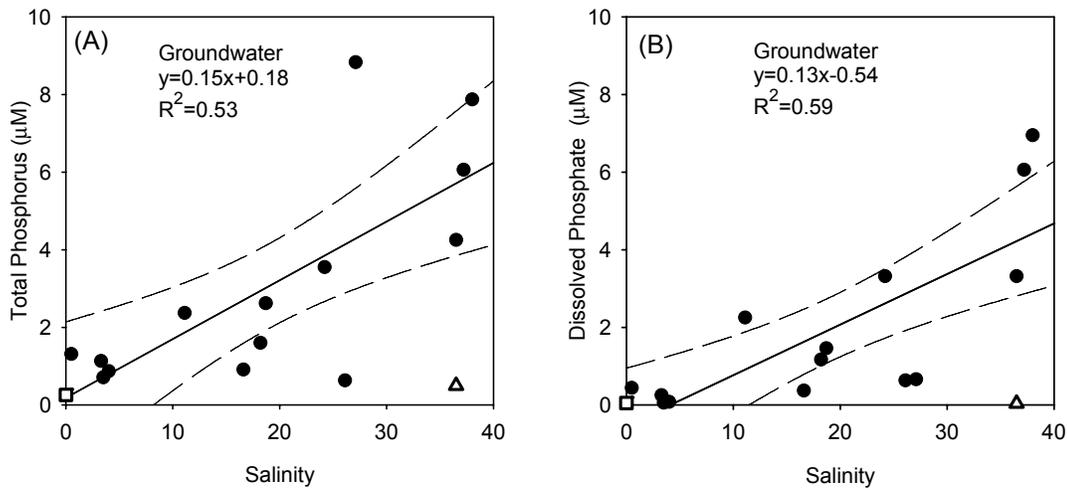


Figure 2. (A) total phosphorus and (B) dissolved phosphate with salinity of groundwater (●), surface water of the Everglades (□), and Gulf of Mexico (△). The linear regression through the groundwater data is the solid black line with a 95% confidence interval.

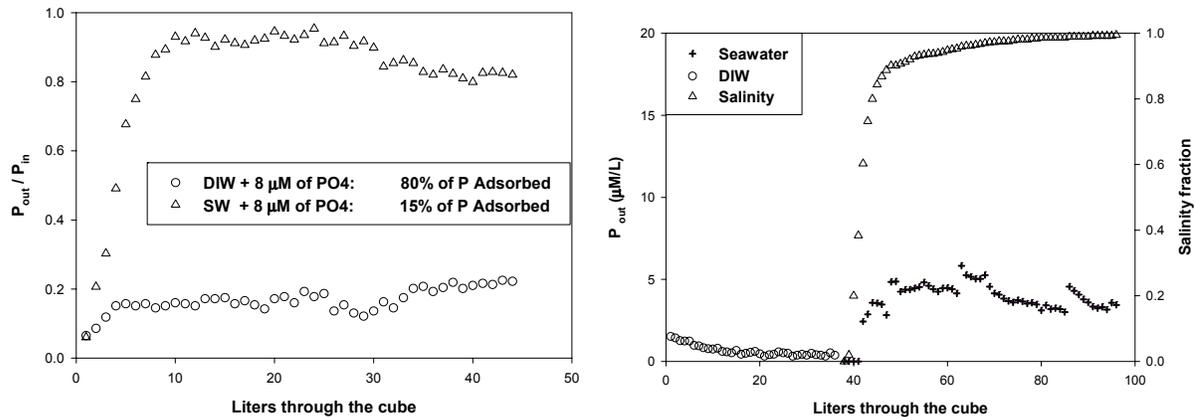


Figure 3. Results of (A) adsorption experiments and (B) desorption of phosphorus from Key Largo limestone in both DIW and seawater.

The adsorption experiments on the Key Largo limestone resulted in more than 80% of the initial phosphate retained on the limestone when the phosphate was dissolved in DIW. Conversely, only 15% of the phosphate was adsorbed in the seawater matrix (Figure 3A). In the desorption experiments, significantly higher concentrations of P were removed from the limestone with seawater than with DIW (Figure 3B). Calcium, magnesium and bicarbonate were found to be in excess in the DIW and in the seawater matrix when salinities were less than 90% seawater. The PHREEQC results predicted undersaturation with respect to both calcite and aragonite in these waters, supporting the geochemical results that these minerals are dissolving in the lower salinity groundwaters, thereby releasing any P either adsorbed or incorporated into the aquifer matrix. At salinities representative of 90% seawater and higher, the PHREEQC results predicted oversaturation with respect to calcite and aragonite. Geochemical analysis of the water at these higher salinities resulted in calcium and magnesium being described by conservative mixing of seawater with DIW, but bicarbonate concentrations were lower than expected for conservative

mixing. These results suggest that at the higher salinities the carbonate minerals are not being dissolved, but instead bicarbonate ions are adsorbed to the aquifer matrix.

SUMMARY AND CONCLUSIONS

Elevated concentrations of P are observed in groundwaters of southwest Florida affected by seawater intrusion. An increase in P with salinity suggests that reactions related to seawater intrusion are responsible for the P in the groundwater. However, conservative mixing of fresh Everglades waters with Gulf of Mexico seawater cannot produce the P, therefore an additional source of P is needed. Water-rock interactions such as carbonate mineral dissolution and adsorption-desorption are most responsible for the P in the brackish groundwaters. Digestion of limestone from the region indicates the presence of available P. Adsorption experiments reveal that the limestone has a high affinity to adsorb P dissolved in fresh groundwater. As the groundwater salinity increases in the presence of seawater intrusion, dissolution of calcite and aragonite minerals in the limestone result in a release of P to the brackish groundwater. At higher salinities equivalent to 90% seawater and higher, bicarbonate ions adsorption forces P to desorb from the limestone to the surrounding groundwater.

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