

Saltwater intrusion as potential driver of phosphorus release from limestone bedrock in a coastal aquifer



Hilary Flower^{a,*}, Mark Rains^a, David Lewis^b, Jia-Zhong Zhang^c, René Price^d

^a School of Geosciences, University of South Florida, 4202 E. Fowler Ave, Tampa, FL, 33620, United States

^b Department of Integrative Biology, University of South Florida, 4202 E. Fowler Ave, SCA 110, Tampa, FL, 33620, United States

^c Ocean Chemistry and Ecosystems Division, Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, Miami, FL 33149, United States

^d Department of Earth Sciences and Southeast Environmental Research Center, Florida International University, Miami, FL 33199, United States

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ABSTRACT

An important but often overlooked consequence of saltwater intrusion is the potential increase of groundwater soluble reactive phosphorus concentrations. The phosphorus sorption dynamics of two limestone rocks of different composition were investigated by simulating seawater intrusion over a wide range of mixing ratios between freshwater and saltwater. Both rocks exhibited a logarithmic loss of sorption efficiency in mixtures containing more than approximately 3 mM Cl⁻ concentration (100 mg Cl⁻/L; about <1% saltwater). We infer that aquifer solids immersed in freshwater would undergo phosphorus desorption in response to the introduction of this minor amount of seawater. This Cl⁻ concentration is within the range designated as fresh water. Thus we conclude that increased soluble reactive phosphorus availability from saltwater-induced desorption may occur at the ion exchange front, which is actually landward of the saltwater intrusion front as it is commonly defined. Sorption efficiency in our experiments continued to decline as salinity increased, until Cl⁻ concentration reached a second threshold of 50 or 200 mM (1700 or 7700 mg Cl⁻/L), depending on the rock composition, particularly iron content. Further increase in salinity would produce little increase in groundwater soluble reactive phosphorus concentration. Our results have implications for soluble reactive phosphorus availability in estuaries that receive mixing zone groundwater discharge.

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1. Introduction

Geochemical studies of coastal aquifers worldwide have established that intensive water-rock interactions are a globally important consequence of saltwater intrusion (Sivan et al., 2005). Where fresh water and saltwater meet in the aquifer, saltwater typically forms a wedge beneath the more buoyant fresh water, with a flat base at an impermeable layer. Due to the hydraulic gradient between the freshwater and marine waters, fresh and brackish water from the aquifer mix and flow seaward and upward along the saltwater wedge to discharge near the coastline in a process known as submarine groundwater discharge (Moore, 1999). In this way, the products of mixing zone reactions affect water quality in coastal

estuaries.

Phosphorus (P) commonly adsorbs to the surfaces of suspended riverine particles, soils, sediments and aquifer solids. An influx of saltwater can induce mineral solids to desorb P, raising the ambient water P concentration. These reactions are important because the species of P that participates in adsorption/desorption reactions is the bioavailable form, dissolved inorganic P (H₂PO₄⁻ and HPO₄²⁻, measured as soluble reactive P, SRP). As a result of these reactions, saltwater intrusion causes coastal groundwater to be many orders of magnitude higher in SRP than the overlying surface waters in many regions (Slomp and Van Cappellen, 2004; Valiela et al., 1990). Phosphorus desorption reactions that occur at depth in the aquifer are considered to be one of the major abiotic controls of coastal water SRP concentration where P-enriched brackish groundwater discharges to overlying ecosystems (Froelich, 1988). In some estuary P-budgets, groundwater discharge exceeds the input from rivers and atmospheric deposition (Slomp and Van Cappellen, 2004). Phosphorus-enriched brackish groundwater increases the

* Corresponding author.

E-mail addresses: hflower@mail.usf.edu (H. Flower), mrains@usf.edu (M. Rains), davidlewis@usf.edu (D. Lewis), jia-zhong.zhang@noaa.gov (J.-Z. Zhang), pricer@fiu.edu (R. Price).

productivity of many *P*-limited coastal ecosystems such as seagrass beds near Perth, Australia (Johannes and Hearn, 1985), many coral reefs worldwide (Paytan et al., 2006), salt marshes in North Carolina, USA (Krest et al., 2000), and the mangrove swamps of the Everglades, in Florida, USA (Price et al., 2006).

In many coastal aquifers, the transition from freshwater to saltwater is gradational, with mixing zones from meters to kilometers wide (Slomp and Van Cappellen, 2004). Increments of increasing salinity within the transition zone are commonly represented by sets of contours delineating equal Cl^- concentration (isochlors) (Fig. 1). The locations and possible movements of these isochlors are determined by salinity measurements of groundwater in monitoring wells and remote methods such as geophysical mapping (Dimova et al., 2012; Prinos et al., 2014; Spiteri et al., 2008a; Swarzenski et al., 2006). In regions with a broad mixing zone, incremental increases in salinity may be accompanied by incremental or abrupt changes in a variety of chemical constituents resulting from non-conservative mixing and chemical reactions triggered by various proportions of freshwater and seawater at the solid-solution interface. The best known example of this is the ion exchange front, located where freshwater first contacts saltwater; here the major changes in concentration of Ca^{2+} , Na^+ , HCO_3^- , Li^+ , K^+ , B^{3+} , SO_4^{2-} and Mg^{2+} occur due to ion exchange (Prinos et al., 2014). The reason that low salinity groundwater mixtures can have such a large effect is the high ionic strength of seawater compared to the density of limited exchange sites on solid surfaces. Once exchange sites on the mineral surfaces are filled by competing ions, further increase in saltwater content may have little effect.

Inorganic *P* ions are highly surface-reactive, and SRP is known to change concentration in freshwater-saltwater mixing zones. We hypothesize that, like other highly reactive ions, SRP is actively cycled in the ion exchange front within the aquifer, and thus *P* desorption is triggered at a very low threshold of saltwater content. We chose to test our hypothesis on limestone because carbonate aquifers are extensive in coastal settings, and many have undergone saltwater intrusion. Examples include Florida, USA (Fitterman, 2014), Mallorca, Spain (Price and Herman, 1991), and Apulia, Italy (Cotecchia et al., 1974). With many carbonate coastlines under threat of increased saltwater intrusion due to sea level rise (Barlow and Reichard, 2010; Carter et al., 2014; Loáiciga et al., 2012; Webb and Howard, 2011; Wong et al., 2014), and many coastal estuaries subject to mixing zone groundwater discharge, it is important to

predict how SRP concentrations change as a function of incremental increases in saltwater content. The southern coastal Everglades was chosen as a field location because it has a carbonate aquifer, significant saltwater intrusion, the potential for rapid movement of the freshwater-saltwater interface, a highly gradational transition zone, and SRP-enriched brackish groundwater discharging to a *P*-limited estuary (Price et al., 2006).

To date, most studies of seawater-induced *P* desorption focus on soil, sediment (e.g., suspended river sediment and bottom sediment of lakes, rivers and lagoons), or pure phase minerals (e.g., calcite or goethite) (Clavero et al., 1990; Gao and Mucci, 2001; Gardolinski et al., 2004). In many studies, NaCl or KCl solutions substitute for seawater (Wang et al., 2006), which excludes reactive seawater ions such as Mg^{2+} , Ca^{2+} , SO_4^{2-} , and HCO_3^- (Millero et al., 2001).

Freshwater-seawater mixing is commonly simulated with no more than 4 mixtures (Gao and Mucci, 2003). The few that have considered a wider range of salinity report that sorption behavior changed at the low salinity end of the continuum. Fox et al. (1986) immersed sediments from the Amazon estuary in seawater diluted with deionized water, and observed that the sediments began to desorb *P* at salinities above 4. A laboratory study of calcite and aragonite in seawater diluted with 2 mM NaHCO_3 solution found that the crystal grains gained the most adsorption efficiency (29%) when the salinity was lowered from 5 to 0 (Millero et al., 2001). A sorption study using Florida Bay sediment and seawater diluted with 2 mM NaHCO_3 solution reported that adsorption decreased with increasing salinity, and the effect was much greater for sediment samples with a higher amount of loosely adsorbed *P* (Zhang and Huang, 2011). Suzumura et al. (2000) investigated sand from a coastal aquifer, at Tokyo Bay, Japan; among eight evenly proportioned mixtures of deionized water and artificial seawater, the largest change in *P* sorption behavior of the sand was observed between the lowest two salinity solutions. An important limitation of these previous studies is that mixtures were created by diluting seawater with deionized water or 2 mM NaHCO_3 solution, resulting in mixtures that are not equivalent to mixing seawater with a naturally occurring freshwater, wherein non-conservative mixing reactions may occur due to the reactive ions in the freshwater.

There is no systematic study of the influence of salinity of seawater on *P* sorption by bedrock, but our recent work in the Everglades has highlighted the importance of seawater-induced

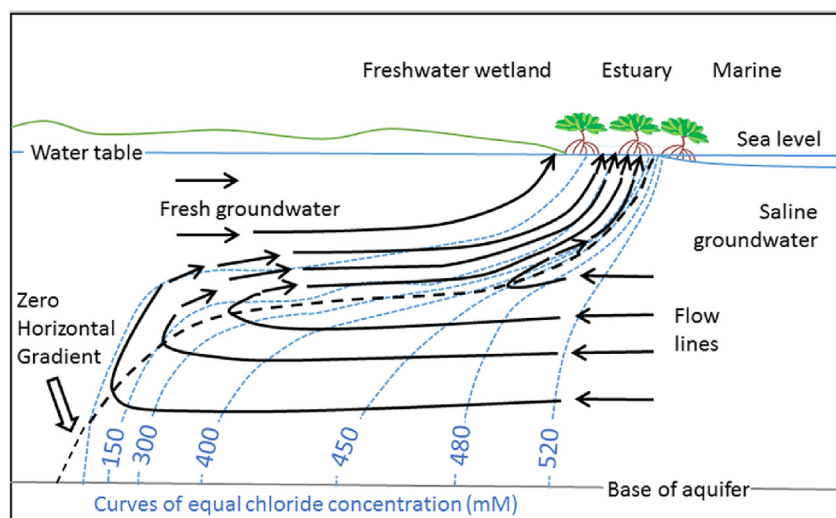


Fig. 1. Schematic cross-section of saltwater intrusion with a broad transition zone, loosely based on Kohout (1964). Where the horizontal hydraulic gradient is zero, the vertical hydraulic gradient dominates and all fluid flow is upward.

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