PHOSPHATE UPTAKE IN COASTAL LIMESTONE AQUIFERS: A FRESH LOOK AT WASTEWATER MANAGEMENT

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INTRODUCTION AND BACKGROUND
Eutrophication (i.e., high productivity caused by abundant nutrients) is pervasive in aquatic ecosystems throughout the world. The usual suspects in this coastal water quality dilemma are surface inputs, such as sewage effluent, storm water runoff, and agriculture. In addition to surface water, submarine ground water discharge may contribute to the transport of nutrients to coastal waters, especially in areas with a high density of sewage disposal and treatment facilities (e.g., Simmons and Lyons 1994).

To understand how ground water enters coastal waters through nearshore sediments, the concept of a “subterranean estuary” (Moore, 1999) provides a nice representation of this freshwater-marine interface. Ground water may enter coastal waters anywhere it flows from an underlying aquifer that intercepts coastal sediments. In turn, nutrients and other dissolved constituents present in these aquifers move with the ground water into coastal zones.

Ground water flow into coastal surface waters may be enhanced by certain geologic features such as permeable limestone. The Earth’s land surface is 15% karst, of which carbonate rocks are the predominant features (White and White 1989). Karst topography is formed by dissolution of limestone, dolomite, or gypsum leading to the formation of sinkholes, caves, springs, and enhanced underground flow. Some areas where ground water flow may be enhanced by karst at the coastal freshwater-marine interface include Florida, the Yucatan Peninsula, East Africa, the Philippines, some Mediterranean coastlines, Australia, southeast Asia, and carbonate islands such as Bermuda, Jamaica, and Barbados.

Subterranean carbonate mixing zones induce various physical and chemical alterations, the nature of which depends on the volume of transport, sources of ground water flow, and differences in ground water and seawater chemistries. In the Florida Keys, subsurface mixing and flow of fresh and marine waters through carbonate rock are driven mainly by tides in the Atlantic Ocean (Figure 1). These Keys make up a 240-km long, low-lying archipelago located off the southern tip of...
PHOSPHORUS REMOVAL MECHANISMS

Phosphate behaves non-conservatively (i.e., it is reactive) during aquifer mixing within KLL, as shown by use of SF$_6$, a conservative (non-reactive) tracer (Corbett et al. 2000). Phosphate uptake in subsurface mixing waters was evaluated by addition of tracers (SF$_6$, $^{32}$P) to injection wells. Bulk radiolabeled and unlabeled phosphate as well as SF$_6$ were released in one large pulse to an injection well during typical effluent disposal operations, and P uptake rates in subterranean waters were monitored relative to SF$_6$. If the subsequent behavior of phosphate was conservative, then the ratio of tracers would remain the same throughout time in the mixing zone where waters are essentially devoid of tracers. Instead, non-conservative behavior of phosphate and radiolabeled phosphate was observed at Long Key (i.e., where data fall below the conservative mixing line for bulk addition of tracers; Figure 2). Non-conservative behavior of phosphate was also demonstrated with respect to salinity in KLL aquifer mixing waters (Elliott 1999). A first-order removal rate constant, $k$, was calculated from several of these uptake experiments using samples collected in time series (Corbett et al. 2000). Use of the first-order equation ($P = P_0 e^{-kt}$) showed that about 95% of injected phosphate was removed from solution in the aquifer within 20 to 50 hours (i.e., within 10 to 15 feet of the injection site). This discovery is significant because it indicates that phosphate remains close to the point of injection.

What other evidence is available to support this discovery? First, these coastal limestone aquifer waters are supersaturated with carbonate fluorapatite [CFA, Ca$_{10}(PO_4)_{6-x}(CO_3)x(F,OH)_{2+x}];$ thus, formation of CFA is at least thermodynamically feasible (Elliott 1999). While thermodynamics favor carbonate fluorapatite, simply calculating saturation indices does not prove the actual occurrence of this potential phosphate removal mechanism. Laboratory microcosm experiments of uptake processes in limestone baths revealed that a cryptocrystalline form of calcium phosphate may be sequestering phosphorus in the aquifer (Elliott 1999). Elliott found in her study of injected wastewater at Key Colony Beach, Florida, that phosphate minerals were too sparse or were amorphous rather than crystalline,
and therefore were not detectable by x-ray diffraction.

Previous researchers have shown that formation of more stable phases of apatite \([\text{Ca}_5(\text{F,Cl,OH})(\text{PO}_4)_3]\) is kinetically slow (e.g., Bentor 1980; Van Cappellen and Berner 1991). In addition, Golubev (1999) demonstrated in the laboratory that metastable mix precipitates of amorphous Ca and Mg phosphates were more likely to form in interstitial fluids than the less soluble crystalline apatite. Corbett et al. (2000) suggested that phosphate is actively removed from solution in aquifer mixing zones of the Keys via rapid adsorption onto active or charged sites with low activation energies. This hypothesis is further supported by the experimental work of Van Cappellen and Berner (1991), who found that secondary marine apatite growth kinetics are controlled by surface processes at low temperatures. Their study showed that rapid nucleation of a precursor non-apatitic calcium phosphate in aqueous solutions, probably as octacalcium phosphate \([\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot x\text{H}_2\text{O}}\) precursor], can occur under the conditions of CFA supersaturation and phosphate concentrations exceeding about 290 \(\mu\text{mol L}^{-1}\). Therefore, the likely phase responsible for removing phosphate is an octacalcium phosphate precursor.

To verify the precursor mechanism, scanning electron microscopy (SEM) analysis was conducted on Key Largo limestone cuttings (samples from a borehole). Polished petrographic sections of the limestone used in Elliott’s (1999) microcosm baths were carbon coated to facilitate elemental mapping analysis by use of the energy dispersive x-ray spectrometer (EDS) mode of the SEM. These analyses demonstrate the presence of phosphorus-bearing streaks along a fracture and along void space edges, as well as an authigenic (i.e., produced in situ) apatite mineral grain (Figure 3). The energy dispersive spectrum for one bright streak in the SEM scan (Fig. 3a, top arrow) shows the dominance of calcium in the limestone matrix and a phosphorus signal for the same streak (Fig. 3b). Given that the precipitation of the more thermodynamically stable carbonate fluorapatite is controlled in part by slow kinetics, these SEM results make a convincing argument that a cryptocrystalline calcium phosphate is removing phosphate from solution and precipitating within the aquifer mixing waters of the upper Florida Keys.

In the presence of organic- and phosphate-rich waters of a coastal subsurface limestone aquifer such as those of the Florida Keys, the stage is set for precipitation of an apatite precursor mineral within the limestone’s interconnected void spaces. For a carbonate aquifer system having a high degree of communication with marine waters, phosphate uptake begins with subsurface waste discharge (i.e., septic systems, injection wells). Thus, two water masses are mixing in a highly porous limestone:

\[
\text{Low Salinity Wastewater} \rightarrow \text{Tidal Marine Waters}\]

\[
\begin{align*}
\text{PO}_4^{3-}, \text{NO}_3^-, \text{NO}_2^- \rightarrow \text{Cl}^-; \text{Na}^+; \text{Ca}^{2+}; \text{Mg}^{2+}; \text{F}^-; \text{HCO}_3^-; \text{etc.}
\end{align*}
\]

Most recent phosphatic mineral deposits are thought to have formed under reducing conditions in organic-rich
sediments (e.g., Burnett 1977; Froelich et al. 1988). These same reducing conditions are present in waters of KLL saline aquifers. As organic- and phosphate-rich wastewater mixes with seawater supersaturated with CFA, phosphate adsorption and precipitation appear to occur in these limestone pore spaces, perhaps as:

\[ 4Ca^{2+} + 3HPO_4^{2-} + xH_2O \rightarrow Ca_4H(PO_4)_3 \cdot xH_2O \text{ (precursor)} + 2H^+ \]

Given sufficient time (i.e., years) for solutions to react with limestone, the precursor mineral will be diagenetically altered so that a carbonate fluorapatite can form:

\[ Ca_4H(PO_4)_3 \cdot xH_2O \text{ (precursor)} \rightarrow Ca_{24}^4(PO_4)_{10}^{2-}(CO_3)^{6-}(FOH)_{24}x^2 \text{ (fluorapatite).} \]

**COASTAL MANAGEMENT IMPLICATIONS**

The environmental effect of phosphate wastewater pollution on coastal waters is significantly decreased if much of the phosphate is removed from the ground water prior to its discharge to surface waters. In a subsurface mixing zone, this phosphorus sink has significant implications for coastal eutrophication and the health of present-day coastal ecosystems. Nevertheless, additional research on the magnitude of phosphate precipitation processes and the long-term stability of a cryptocrystalline precipitate in the aquifer is still needed. For example, will the calcium phosphate precursor remain as deposited on void space edges, or will it periodically be desorbed by changing geochemical conditions in these saline ground waters? Is the input of wastewater phosphate now of less concern in these carbonate aquifers? Even if it is, other wastewater constituents, particularly dissolved nitrogen compounds, are transported through the mixing zones in much greater concentrations (~1000 \( \mu \text{mol L}^{-1} \), N) than phosphorus (~250 \( \mu \text{mol L}^{-1} \)). Although carbonate sediments may not be abiotic sinks for nitrogen, microbiological activity within the sediments may alter nitrogen concentrations (e.g., by denitrification) and should be investigated.

Managing surface water inputs to the coastal zone is a daunting task, but ground water discharge along coastlines may be a particular management challenge since scientists are still trying to understand the magnitude and distribution of the phenomenon itself. Many coastal water bodies have a direct connection with inland aquifers, so any management strategy must consider inland aquifers as integral parts of the plan. In this respect, alterations to the inland aquifer system will ultimately impact the amount and quality of the ground water being discharged into coastal waters. In the past 25 years, submarine ground water discharge research has demonstrated time and again that dissolved constituents are being carried with ground water to coastal waters (e.g., Lapointe et al. 1990; Simmons and Lyons 1994; Moore 1999).

Protecting our coastal resources requires an understanding of nutrient delivery to coastal waters and the chemical changes that occur during transport. It is not always clear how other wastewater constituents (e.g., metals, organics) are processed within the subterranean estuary. Current research demonstrates the importance of understanding subsurface geochemical cycles in predicting the ultimate fate of nutrients in ground water systems. The results presented here show that reactions occurring during transport in the Florida Keys may remove phosphorus effectively before it reaches the sensitive surface waters of Florida Bay and the Atlantic Ocean. Can we expect this process to continue, or will the next major management plan alter the sequestration process?

**ACKNOWLEDGMENTS**

Authors thank W.C. Burnett and J.P. Chanton for their help through previous work on ground water chemistry and movement in the Florida Keys. EPA grants X994871-96-0, X994870-96-0, and X98292-97-0 to JPC, WCB, and L.R. Kump funded the phosphate uptake and geochemical modeling research. Xiaogang Xie of the LSU Geology and Geophysics Microscopy Laboratory performed the SEM scan analyses.

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