

pH-Dependent iron oxide precipitation in a subterranean estuary

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Abstract

Iron-oxide-coated sediment particles in subterranean estuaries can act as a geochemical barrier (“iron curtain”) for various chemical species in groundwater (e.g. phosphate), thus limiting their discharge to coastal waters. Little is known about the factors controlling this Fe-oxide precipitation. Here, we implement a simple reaction network in a 1D reactive transport model (RTM), to investigate the effect of O₂ and pH gradients along a flow-line in the subterranean estuary of Waquoit Bay (Cape Cod, Massachusetts) on oxidative precipitation of Fe(II) and subsequent PO₄ sorption. Results show that the observed O₂ gradient is not the main factor controlling precipitation and that it is the pH gradient at the mixing zone of freshwater (pH 5.5) and seawater (pH 7.9) near the beach face that causes a ~7-fold increase in the rate of oxidative precipitation of Fe(II) at ~15 m. Thus, the pH gradient determines the location and magnitude of the observed iron oxide accumulation and the subsequent removal of PO₄ in this subterranean estuary.

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1. Introduction

Submarine groundwater discharge (SGD) provides an important transport pathway for land-derived dissolved nutrients to coastal waters (Charette et al., 2001; Slomp and Van Cappellen, 2004). The chemical composition of SGD is not only determined by the terrestrial freshwater source(s), but also by the biogeochemical processes occurring along the groundwater flow path, particularly in the “subterranean estuary” where freshwater and seawater mix (Moore, 1999).

Removal of dissolved metals and nutrients subterranean estuaries is thought to be mainly controlled by the redox characteristics of the freshwater and seawater (Slomp and Van Cappellen, 2004). For instance, the accumulation of iron oxides observed near the fresh-

water–seawater interface of Waquoit Bay (Cape Cod, Massachusetts; Fig. 1), referred to as the “iron curtain”, has been attributed to the oxidative precipitation of groundwater Fe upon transport through oxygenated coastal sediments (Charette and Sholkovitz, 2002).

Here, we propose an alternative mechanism, where the precipitation of Fe-oxides results from the differences in pH between the freshwater and seawater. To test this hypothesis, we use a 1D RTM to assess the combined effects of O₂ and pH changes on Fe-oxide precipitation and the subsequent phosphate (ΣPO_4) removal along a flow line in the subterranean estuary of Waquoit Bay.

2. Hydrogeology and biogeochemistry of the Waquoit Bay subterranean estuary

Waquoit Bay is a shallow estuary located on the southern shoreline of Cape Cod (Fig. 1). A significant

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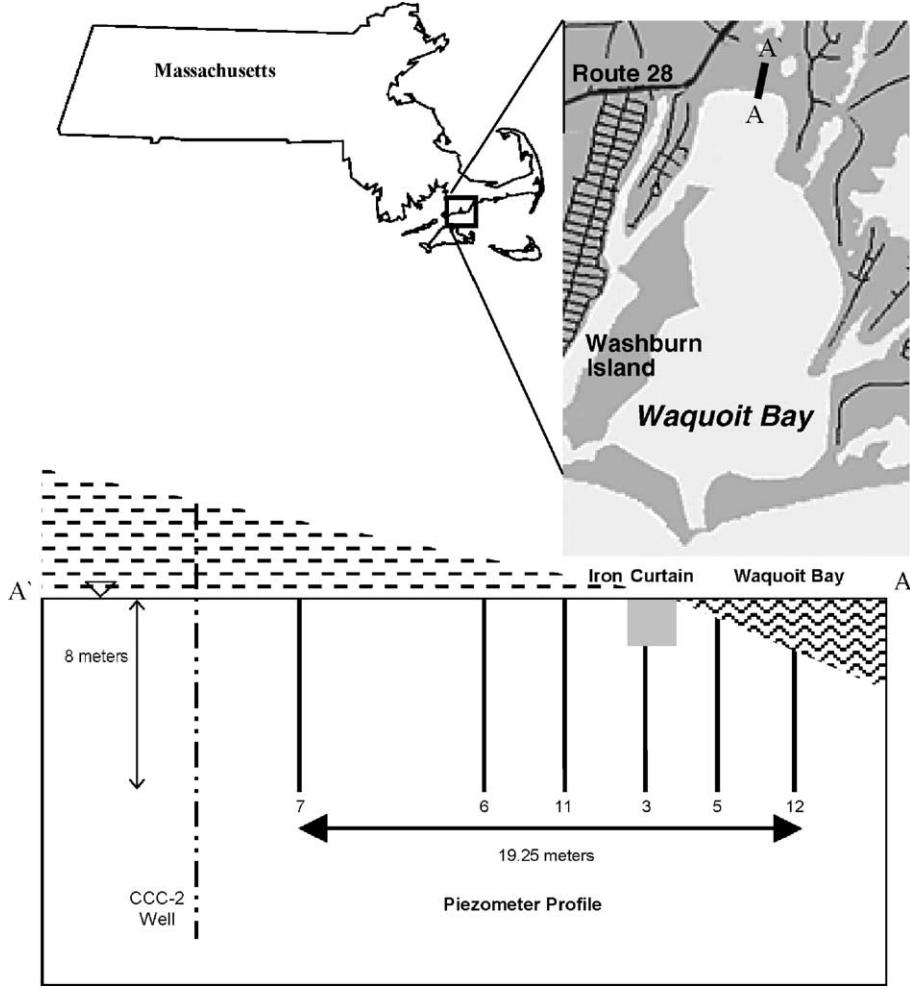


Fig. 1. Map of Waquoit Bay, showing the 20×8 m piezometer transect (A'-A) perpendicular to the shore line at the head of the bay and the location of the “iron curtain”.

portion of the freshwater input and material fluxes to the bay occurs as SGD (Charette et al., 2001). To investigate the chemical constituents of the SGD, 6 piezometers were installed along a transect perpendicular to the coast at the head of the bay where the surface aquifer consists of unconfined, permeable sand (Micheal, 2005). Groundwater samples were collected in June 2004 and analyzed as described elsewhere (Talbot et al., 2003; Charette et al., 2005). Fig. 2 shows depth profiles of total dissolved Fe and ΣPO_4 along the transect. The range of observed pH values and the vertically averaged concentrations are presented in Fig. 3.

Salinity measurements indicate a sharp Ghyben–Herzberg type freshwater–seawater interface (Fig. 2), and surface mixing of seawater and freshwater at the intertidal piezometers PZ-3 and PZ-5 (not shown). A distinct freshwater Fe plume that disappears as the groundwater flows seaward is clearly identified in

Fig. 2. At around PZ-3, the Fe content of the dark red, yellow and orange subsurface sands ranges from 2500 to 4100 ppm, which is 10 to 15 times higher than in “control” sediment (Charette and Sholkovitz, 2002). Although the freshwater ΣPO_4 concentrations are relatively low (maximum $\sim 5 \mu\text{M}$), phosphate removal is observed as the Fe and ΣPO_4 plumes overlap. Measurements of dissolved oxygen (O_2) (not shown) show relatively low values ($40 \mu\text{M}$) in the landward piezometers, increasing up to $\sim 200 \mu\text{M}$ towards PZ-3 and PZ-5. The average pH at the first piezometer in the transect (PZ-7) is 5.5 while at the seaward boundary (PZ-12), the pH is 7.9 (Fig. 3).

3. Model description

The processes included in the Biogeochemical Reaction Network Simulator (BRNS), a flexible 1D RTM

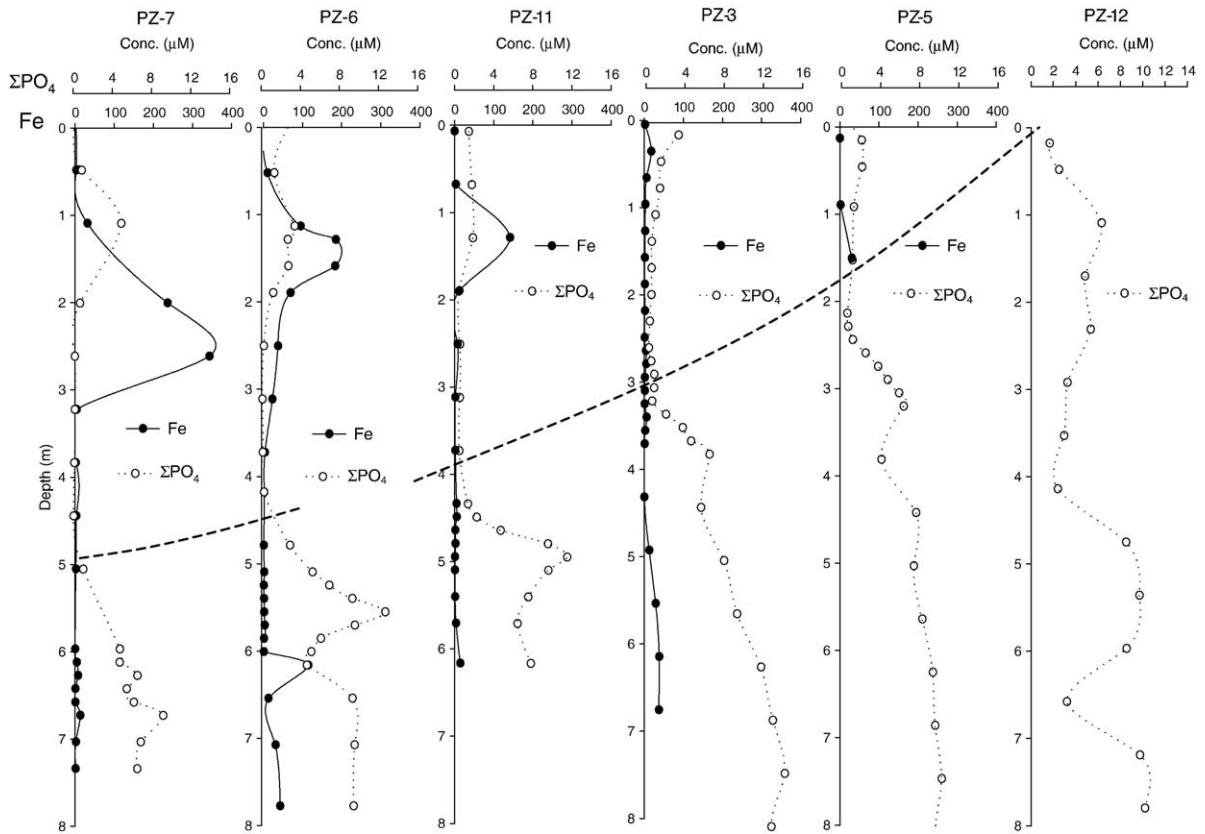


Fig. 2. Concentration profiles of total dissolved Fe and ΣPO_4 in the X - Z plane. The dotted line indicates the position of the salt-wedge, based on salinity measurements.

(Regnier et al., 2003; Aguilera et al., 2005), are pH-dependent oxidative precipitation of Fe(II), ΣPO_4 adsorption onto Fe-oxides and advective plus dispersive groundwater transport (Table 1). At the upstream boundary ($x=0$ m), a Dirichlet boundary condition is applied, which fixes the concentration of Fe(II), O_2 , ΣPO_4 and pH at the freshwater side of the domain (Table 2). The Fe(II) concentration is set equal to the measured dissolved Fe, based on field measurements (Charette et al., 2005). At the outflow ($x=20$ m), a zero concentration gradient boundary condition is specified for all dissolved chemical species. Although it would be possible to incorporate pH and O_2 as master variables in the RTM (e.g. Aguilera et al., 2005), the current data set for Waquoit Bay does not allow the reaction network required to model these variables to be fully constrained. Instead, both O_2 and pH are implemented as forcing functions, either as constant values or as a longitudinal gradient along the flow line (Table 2). The solid species, i.e. Fe-oxides (Fe(OH)_3) and Fe-bound phosphate (Fe-P) are considered immobile and hence are only affected by local biogeochemical transformations.

In the model, we represent the pH-dependent Fe(II) oxidation by O_2 as:

$$\begin{aligned}
 & - \left(\frac{d[\text{Fe(II)}]}{dt} \right) \\
 & = \left(k_0[\text{Fe(II)}] + k_1\beta_1 \frac{[\text{Fe(II)}]}{[\text{H}^+]} + k_2\beta_2 \frac{[\text{Fe(II)}]}{[\text{H}^+]^2} \right) [\text{O}_2]
 \end{aligned} \quad (1)$$

where $k_0=252 \text{ M}^{-1} \text{ year}^{-1}$, $k_1=.9 \times 10^8 \text{ M}^{-1} \text{ year}^{-1}$, $k_2=252 \times 10^{14} \text{ M}^{-1} \text{ year}^{-1}$ are rate constants corrected for a temperature of 10 °C. The apparent equilibrium constants β_1 and β_2 are equal to $3.2 \times 10^{-10} \text{ M}$ and $2.5 \times 10^{-21} \text{ M}^2$, respectively (Martin, 2003). Our formulation ignores the heterogeneous catalysis of the metal oxide surfaces that enhances the oxidation process at pH values above 7 (Martin, 2003). Eq. (1) leads to a progressive increase in the rate of oxidation with O_2 as the dominant hydrolysis species shifts from $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ to $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^+$ and further to $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^0$ with increasing pH. In the pH range considered here, a unit increase in pH will cause a 100-fold increase in the overall reaction rate.

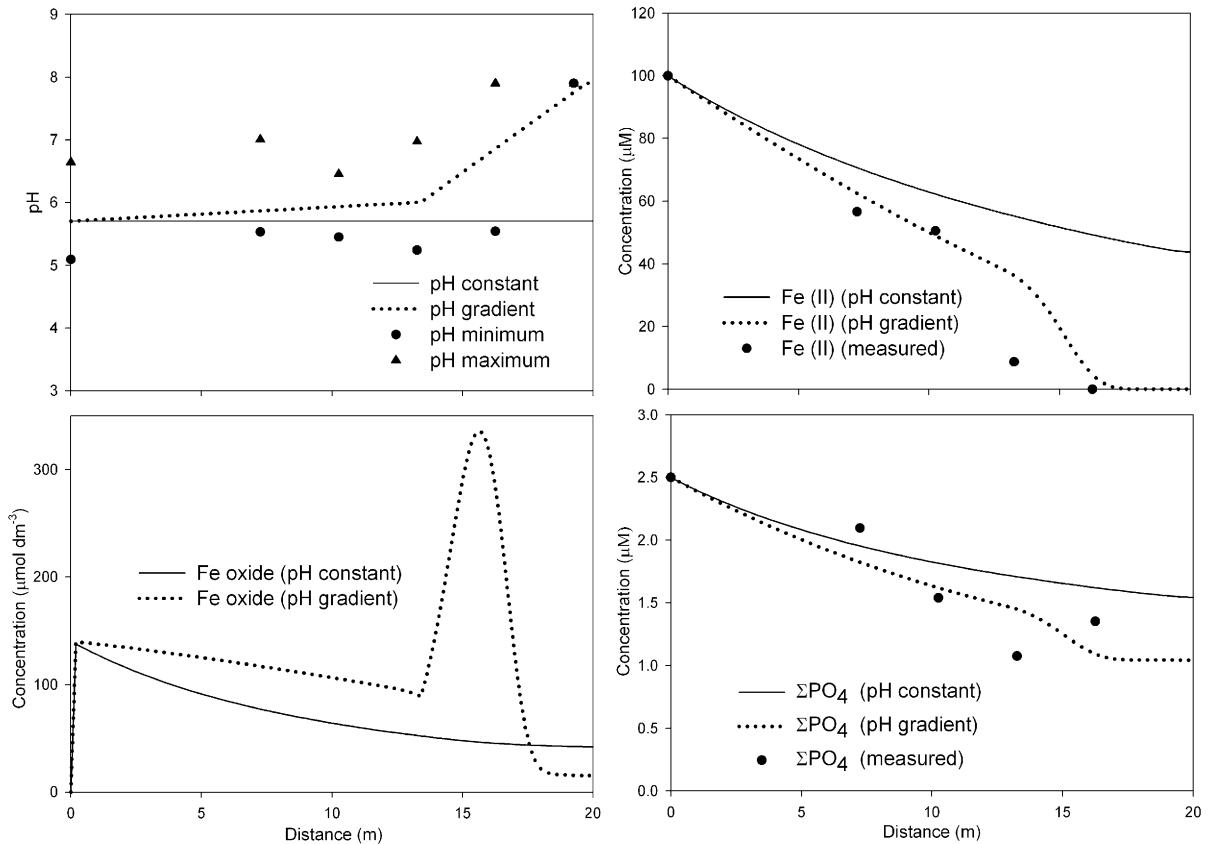


Fig. 3. Model results for scenarios with a constant pH and a pH gradient with distance along the flow line, assuming an O₂ concentration gradient in both. Data points are vertically averaged concentrations of total dissolved Fe and ΣPO₄ in the freshwater plume. The units for solutes are given in μmoles per dm³ pore water (μM) while solid species are in μmoles per dm³ total volume (μmol dm⁻³).

Adsorption of phosphate onto the Fe-oxides is assumed to follow a Langmuir isotherm, in which the extent of sorption is limited by the amount of available surface sites, X_T (mol dm⁻³):

$$[\text{Fe} - \text{P}] = \frac{\alpha X_T [\sum \text{PO}_4]}{1 + \alpha [\sum \text{PO}_4]} \quad (2)$$

with $\alpha = K_d * \phi$ and $X_T = 0.1 * [\text{Fe(OH)}_3]$.

In Eq. (2), K_d is the dimensionless distribution coefficient and X_T defines the amount of Fe-oxides avail-

able for P sorption, assuming a [Fe(OH)₃]:[Fe-P] maximum ratio of 10 (Slomp et al., 1996).

4. Model results and discussion

In a first simulation, the pH is maintained constant over the 1D flow line (pH=5.7). In this case, the model predicts a gradual drop in the Fe(II) and ΣPO₄ in the seaward direction which is significantly smaller than the decline observed in the field. Most Fe oxide pre-

Table 1
Model parameters used in the simulations

Symbol (unit)	Parameter	Value
Δx (m)	Grid spacing	0.2
Δt (year)	Max. time step	1.5×10^{-2}
t_{total} (year)	Total time of simulation	0.4
α_L (m)	Longitudinal dispersivity	0.5*
v (m year ⁻¹)	Advection velocity	182.5**
ϕ (-)	Aquifer porosity	0.35*
K_d (-)	Distribution coefficient	3.0×10^5

* Micheal (2005).

** M. Charette (personal communication).

Table 2
Boundary and initial concentrations for all chemical species

Chemical species	Boundary concentration	Initial concentration
Fe(II) (μM)	100	40
ΣPO ₄ (μM)	2.5	1.0
O ₂ (μM)	40*	40**
pH	5.7*	5.7**
Fe(OH) ₃ (μmol dm ⁻³)	0.0	0.0
Fe-P (μmol dm ⁻³)	0.0	0.0

* Constant.

** Gradient.

cipitation occurs in the freshwater part (Fig. 3). In contrast, in a simulation with an increasing pH (5.7 to 7.9), Fe-oxide precipitation rates increase 7-fold at ~ 15 m and a peak in Fe-oxides is formed. The latter location is consistent with the zone of major Fe-oxide accumulation observed in the field (Charette and Sholkovitz, 2002). The complete disappearance of groundwater Fe(II) observed in the seaward direction (Figs. 2 and 3) is also well captured by the model that includes pH-dependent Fe(II) oxidation. Using either constant O_2 concentrations (40 μM) or a seaward increase in O_2 (from 40 to 200 μM), does not affect the model results significantly, implying that changes in the redox characteristics of the subterranean estuary in Waquoit Bay play a minor role in the removal of Fe(II). Because of the enhanced precipitation of Fe oxides, more groundwater ΣPO_4 is removed when the pH dependency of the precipitation of Fe oxides is considered (Fig. 3).

5. Conclusions

Using a 1D RTM, applied to a groundwater flow line of Waquoit Bay subterranean estuary, we show that the pH gradient in the mixing zone of freshwater and seawater at the beach face is the key factor driving the formation of the “iron curtain”. The pH-dependent Fe-oxide precipitation explains the location and magnitude of the Fe-oxide coated sediments observed in the field and the concomitant removal of groundwater Fe. Results also indicate that the generation of “iron curtains” can significantly attenuate dissolved ΣPO_4 in groundwater prior to discharge to the coastal waters.

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