Dissolved Iron Cycling in the Subterranean Estuary of a Coastal Bay: Waquoit Bay, Massachusetts

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Iron oxides have a strong affinity for dissolved phosphates and certain trace metals (1). Charette and Sholkovitz (2) observed iron oxide-coated sands in sediment cores extracted from the intertidal zone of Waquoit Bay, Massachusetts, and determined that the iron oxides were intercepting phosphates entering the bay in groundwater. They subsequently hypothesized the formation of an "iron curtain," following the oxidation of dissolved ferrous iron to various iron oxides when iron-rich groundwater mixes with intruding saltwater in the subterranean estuary (3). Although the iron oxide-rich sands proved the formation of iron precipitates, more information was needed about the aqueous phase of iron and the conditions surrounding its oxidation. In this study, we have mapped the distribution and concentration of dissolved iron in the subterranean estuary of Waquoit Bay.

Water samples were collected from two transects on the north shore of Waquoit Bay. A map of Waquoit Bay is included in Charette *et al.* (4). One transect spanned 178 m and was orientated parallel to the beach; the second transect, which we examine in this paper, was placed perpendicular to the beach. This 17-m transect extended from the berm of the beach to the intertidal zone. Water samples were collected at 0.5-m intervals to depths of up to 8 m using retract-a-tip, well-point piezometers and a peristaltic pump. At each depth, water was pumped from the ground and immediately filtered to remove particulates, using 10% HCl-cleaned 0.22-μm filters. We measured dissolved ferrous iron, total dissolved iron, salinity, dissolved oxygen, phosphate, nitrate, ammonium, and silicate in each sample. Ferrous iron and total dissolved iron concentrations were determined using the ferrozine method (5). An automated Winkler titration system was used to determine dissolved oxygen concentrations, and a salinometer was used to measure salinity (6). Concentrations of phosphate, nitrate, ammonium, and silicate were measured colorimetrically, using a Lachat nutrient auto-analyzer (Zellweger Analytics, Quickchem© 8000 Series).

Using a 2D-cross-sectional view, we identified three distinct regions of high ferrous iron in groundwater and pore water profiles (Fig. 1). Region 1 was located in upland groundwater between 2.5 and 4.5 m below sea level, and from 15 to 6 m from the shoreline. Region 2 was found below 4.5 m in the high-salinity subterranean estuary, and region 3 was located between depths of 0.15 to 1 m in the bay sediments.

Region 1 contained the highest measured concentrations of ferrous iron (21.9 μM) and was located in completely freshwater (Fig. 1B). Dissolved ferrous iron concentrations in this plume decreased close to the shoreline (Fig. 1A). Dissolved oxygen did not exceed 1 mg/l in this region. We identify this region to be a

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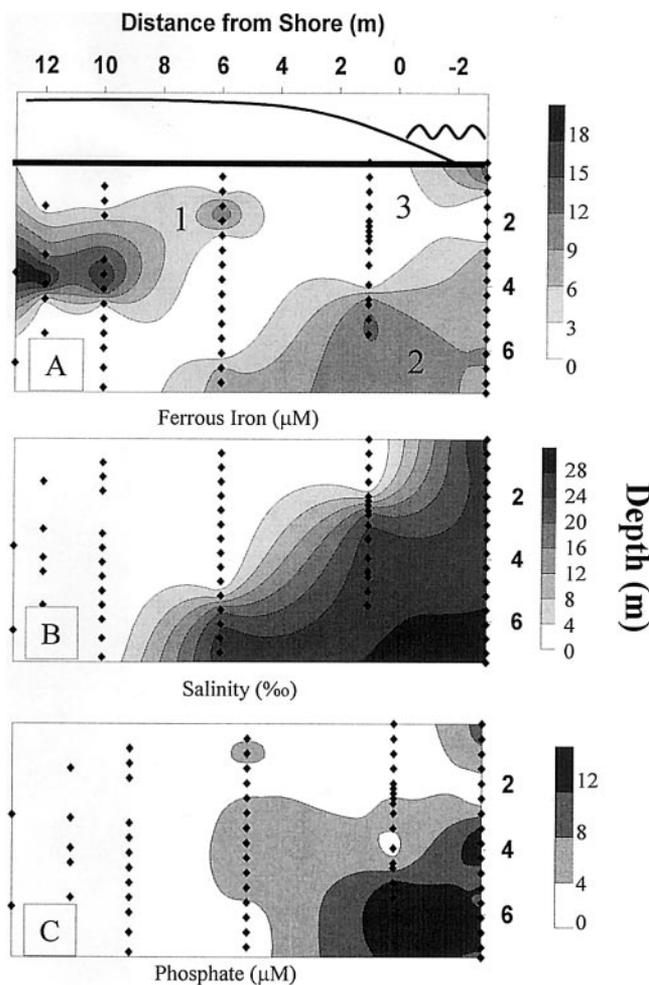
Figure 1. *Contour plots showing a 2D cross-sectional view of dissolved ferrous iron (A, contour line interval 3 μM), salinity (B, contour line interval 4‰), and dissolved phosphate (C, contour-line interval 4 μM) in water samples from the perpendicular transect. Diamonds (♦) represent where individual samples were extracted. Contours were generated using kriging in SURFER software (version 6.01), which statistically estimates the values of unknown data, based on actual data.*

plume of terrestrially derived ferrous iron, given the absence of saltwater and the fact that the pocket of high iron appeared to shoal as it neared the shoreline (Fig. 1A). Basic hydrology suggests that groundwater will discharge into coastal waters after travelling upward at the seepage face, in order to pass over heavier, saline waters that are encroaching into the aquifer. This path permits the mixing of ferrous iron-rich groundwater with shallower aquifer

waters that contain higher concentrations of dissolved oxygen. In fact, we recorded a plume of oxygen-rich groundwater ($\sim$5 mg/l) at 1.5–2 m in all profiles in our transect parallel with the beach. Ferrous iron appears to oxidize when interacting with this plume. It should be noted that iron-oxidizing bacteria have been recognized to potentially occur in neutral pH groundwater at the oxic/anoxic boundary and could be contributing to iron oxidation (7).

Region 2 was associated with salinity values of 16 to 28‰ and also contained high concentrations of ferrous iron (Fig. 1A, B). This region is located where saltwater is encroaching into the aquifer. Given the hypoxic nature of the groundwater in this region (0.5–1 mg/l), iron-reducing bacteria may be active, utilizing iron oxides as an alternative electron acceptor to oxidize organic material (8). Hypoxia may prevail in the stagnant waters of this region, where fresh groundwater is passing over the saline waters. Encroaching saltwater may also deliver organic substrates from bay sediments that contribute to bacterial activity.

Region 3 contains high levels of ferrous iron in the first meter of sediment, where a black precipitate of iron sulfide exists just beneath the sediment surface. Organic matter deposition in this region results in the utilization of oxygen in decay processes that contribute to reducing conditions. In addition, peak temperatures in summer months increase respiration in benthic communities occupying these sediments, which reduce oxygen concentrations (9).

If we assume that a given concentration of iron oxides will scavenge a proportional amount of dissolved phosphate, then proportional concentrations of dissolved ferrous iron and dissolved phosphate should be released in regions where iron oxide deposits are dissolved. We did not, however, find a strong linear relationship between dissolved ferrous iron and dissolved phosphate in region 1 ($r^2 = 0.32$) (see Fig. 1A, C). This supports the idea that the ferrous iron is not released from previously oxidized iron, but is being transported to Waquoit Bay *via* groundwater. The correlation between ferrous iron and phosphate in region 2 is positive, but not strong ($r^2 = 0.24$). We did, however, find a strong linear correlation between ferrous iron and dissolved phosphate in region 3 ($r^2 = 0.89$), suggesting the reduction of iron oxides (see Fig.

1A, C) and the release of dissolved phosphate. In region 2, processes aside from iron oxide dissolution must be controlling the concentration of phosphate (see Fig. 1A, C), and these factors are probably present in region 3 as well. Likely processes are the mineralization of organic matter to release phosphate and the formation of iron-phosphorus minerals.

Charette and Sholkovitz (2) suggested that dissolved ferrous iron in the subterranean estuary was removed from solution *via* precipitation to iron oxides following mixing with oxygen-rich seawater. It appears the mechanisms responsible for groundwater iron oxidation are more complex. In fact, this study shows that the conversion of ferrous iron to various iron oxides occurred in almost completely salt-free water and that the oxidation and dissolution of iron is also a dynamic process.

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Nutrient and Freshwater Inputs From Sewage Effluent Discharge Alter Benthic Algal and Infaunal Communities in a Tidal Salt Marsh Creek

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Nutrient loading of coastal aquatic ecosystems is becoming a globally important issue. Elevated nitrogen, such as near sewage discharge pipes, has been found to be responsible for algal blooms in coastal areas (1). Raising nitrogen and phosphorus concentrations results in increased algal productivity and standing stock and has been shown to favor filamentous algae and diatom communi-

ties (2). Other studies demonstrated a decline in algal species diversity with nutrient inputs, although species richness was unaffected (3). Although a number of studies have linked nutrient loading with algal growth, the response of animal communities to nutrient inputs has been less well studied, especially in salt marsh estuaries (4).

Greenwood Creek, a tidal salt marsh creek in the Plum Island Sound estuarine system of northern Massachusetts, has been the site of sewage effluent input from the secondary wastewater treatment facility for the town of Ipswich, Massachusetts, for over 40

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