

The distribution and speciation of dissolved trace metals in a shallow subterranean estuary

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ABSTRACT

Geochemical cycles occurring at the interface between terrestrial and marine groundwaters, in the so-called subterranean estuary (STE), are not well understood for most elements. This is particularly true of the transition metals, many of which have particular ecological relevance as micronutrients or toxicants. To gain a first approximation of trace metal geochemistry in the mixing zone, we examined the distribution of nine dissolved metals (Fe, Mn, Mo, V, Co, Ni, Cu, Pb, and Al) through a shallow STE in Great South Bay, New York, USA. We also performed a simple kinetic and chemical separation of labile and organic-complexed metal species in the STE. Dissolved Mn showed marked subsurface enrichment (up to 755 μM at 15 cm depth) that was suggestive of diagenetic remobilization. Dissolved Fe, however, was higher by more than three orders-of-magnitude in fresh groundwater (90 μM) as compared to marine groundwater (0.02 μM), and pH-mediated removal was evident as slightly acidic fresh groundwater (pH 6.8) mixed with marine groundwater (pH \sim 8.0). Dissolved Mo, Co, and Ni were primarily cycled with Mn, and highly elevated concentrations relative to bay surface waters (up to 300, 75, and 44 nM, respectively) were observed in the STE. High levels of dissolved Pb (up to 4250 pM) observed in the fresh groundwater were nearly quantitatively removed within the salinity mixing zone, in conjunction with marked reduction of dissolved Al. Dissolved Cu exhibited non-conservative removal throughout the STE, and was correlated with the redox potential of the porewaters. Substantial percentages (>15%) of organic-metal species were only observed for Cu and Ni, suggesting that these complexes were not generally very important for metal cycling in the STE. Kinetically labile species were observed for all metals examined except Cu and Pb, and represented an approximately constant proportion (between 10% and 70%) of the total dissolved pool for each metal, indicating equilibrium between labile and non-labile species throughout the mixing zone. The non-conservative behavior observed for all metals examined in this study suggests that reactions occurring in the STE are vastly important to the source/sink function of permeable sediments, and studies seeking to quantify SGD-derived trace metal fluxes must take into account biogeochemical processes occurring in the subterranean estuary.

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1. Introduction

The low organic content (<0.1 wt.%) of permeable sediments led to the early presumption that such sedimentary environments are relatively unreactive, and thus of limited importance for geochemical cycling in the coastal ocean. A number of more recent studies have shown that the low organic content is due to rapid remineralization and flushing (e.g., Shum and Sundby, 1996; Huettel et al., 2003). Consequently, the role of permeable sediments in coastal biogeochemical cycling is being reevaluated, and all indications suggest that these sedimentary environments are vastly important to nearshore

chemical budgets (Shaw et al., 1998; Portnoy et al., 1998; Basu et al., 2001; Kim et al., 2005; Windom et al., 2006; Charette and Sholkovitz, 2006).

At the same time, the importance of porewater advection through such permeable sediments is also now recognized (Moore, 1996). Not only does this submarine groundwater discharge (SGD; Burnett et al., 2003) represent a common and massive flux of water (although, not necessarily fresh) to the coastal ocean, but there is also a very large flux of associated chemical constituents (Moore, 1996, 1997; Shaw et al., 1998; Basu et al., 2001; Charette et al., 2001; Jahnke et al., 2003; Charette and Buesseler, 2004). Although there is substantial literature on nutrient fluxes due to SGD (Zimmermann et al., 1985; Lewis, 1987; Portnoy et al., 1998; Rutkowski et al., 1999; Charette et al., 2001; Jahnke et al., 2003; Ullman et al., 2003; Kim et al., 2005), less is known about the impact of SGD on trace metal fluxes and cycling in the coastal ocean.

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The flux of metals across the sediment–water interface depends largely on their geochemistry, and especially their behavior during early diagenesis (Shaw et al., 1990). Consequently, the subsurface mixing zone of fresh groundwater and saline porewater, termed the “subterranean estuary” (Moore, 1999), is a highly dynamic zone where the composition of the advecting porewater is set before discharging into overlying marine waters (Charette and Sholkovitz, 2006; Bone et al., 2006, 2007). Although some limited data are available for a handful of trace metals (Al, Cu, Co, Ni, Pb, and Ag; Beck et al., 2007), detailed studies of metal cycling in the subterranean estuary have been limited to Mn, Fe, Hg, and Mo (Charette and Sholkovitz, 2002, 2006; Testa et al., 2002; Windom and Niencheski, 2003; Duncan and Shaw, 2003; Snyder et al., 2004; Spiteri et al., 2006;

Windom et al., 2006; Bone et al., 2007). Our limited knowledge of trace metal behavior in this zone severely hinders our ability to understand and quantify the impact of SGD on metal cycling in the coastal ocean.

Thus, the objective of the current study was to examine the distribution and cycling of selected trace metals and their chemical species in a subterranean estuary. A shallow (<1 m) subsurface zone has been chosen as the region of interest, because the near sediment–water interface is the region where biogeochemical processes most strongly affect the composition of the discharging porewater (Santos et al., 2009). For comparison with the profile through the STE mixing zone, we include a profile collected in a nearby fully saline subsurface zone. The mechanisms regulating porewater flow differ between the

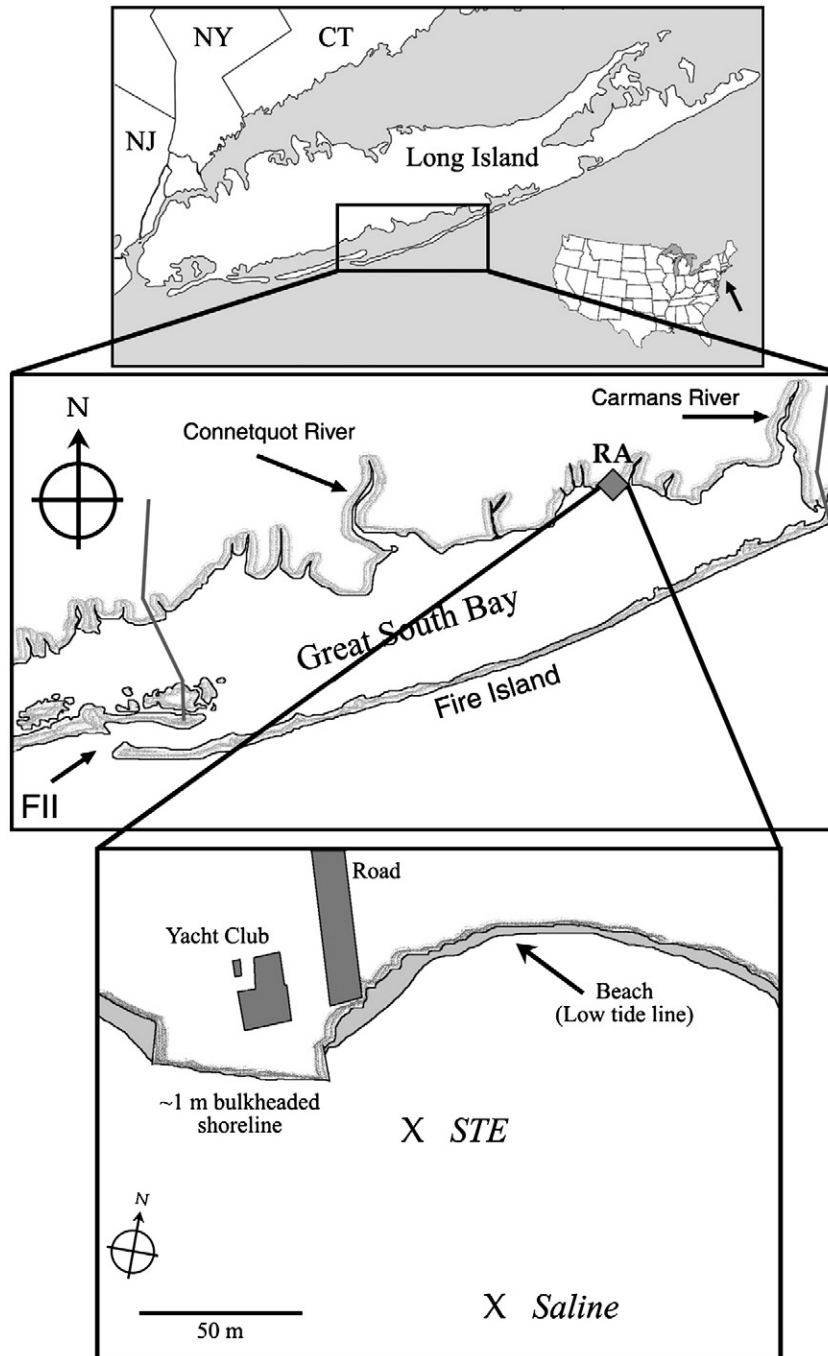


Fig. 1. Study site: Great South Bay, NY. The lowest panel shows an expanded view of the approximate locations of “STE” and “Saline” profiling locations. Both are well below the low tide water level.

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