

Geochemistry of redox-sensitive trace elements in a shallow subterranean estuary



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ABSTRACT

Submarine groundwater discharge (SGD) is an important component of chemical fluxes in the coastal ocean. The composition of SGD is influenced by biogeochemical reactions that take place within the subterranean estuary (STE), the subsurface mixing zone of fresh and saline groundwaters. The STE is characterized by redox gradients that affect the speciation and mobility of redox-sensitive elements (RSEs). We examined the distributions and behavior of the RSEs Mo, U, V, and Cr within the larger redox framework of a shallow STE and evaluated the source-sink function of the STE for these elements. We found that the advection of water through the STE and the apparent respiration of organic matter drives the formation of a “classic” redox sequence typically observed in diffusion-dominated fine-grained sediments. High concentrations of dissolved organic matter (up to 2.9 mM) lead to extensive sulfide production (up to 1.8 mM) within 3 m of the surface. Both Mo and U are quantitatively removed as oxalic surface waters mix into ferruginous and sulfidic zones. Molybdenum removal appears to occur where sulfide concentrations exceed $\sim 11 \mu\text{M}$, a previously reported threshold for quantitative formation of highly particle-reactive thiomolybdate species. Uranium removal apparently occurs via reduction and formation of insoluble phases or sorption to sediments. It is not clear how readily sequestered metals may be returned to solution, but SGD may be an important sink in the marine budget for both Mo and U. In contrast, both V and Cr show non-conservative addition across the salinity mixing gradient. Increases in pH appear to promote dissolution of V from minerals within the shallow aquifer, and mobilization may also be associated with dissolved organic matter. Chromium enrichment is associated with higher dissolved organic matter and is likely due to the formation of soluble Cr-organic complexes. Fluxes of these elements were constrained using SGD volume fluxes, determined using radium isotopes as well as direct discharge measurements by Lee-type seepage meters, and concentrations in directly-sampled seepage (Mo: -0.21 to $-7.7 \mu\text{mol m}^{-2} \text{day}^{-1}$; U: -0.02 to $-0.6 \mu\text{mol m}^{-2} \text{day}^{-1}$; V: 0.05 to $2.0 \mu\text{mol m}^{-2} \text{day}^{-1}$; Cr: 0.12 to $4.4 \mu\text{mol m}^{-2} \text{day}^{-1}$).

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1. Introduction

Submarine groundwater discharge (SGD) is any flow of water along continental margins from the seabed into the coastal ocean (Burnett et al., 2003), and represents an important chemical flux in the coastal ocean. For example, SGD has been shown to be a source of nutrients (D'Elia et al., 1981; Slomp and Van Cappellen, 2004) and metals (Windom et al., 2006; Bone et al., 2007) to coastal waters. Submarine groundwater discharge also plays an important role in the global budget of elements such as Nd (Johannesson and Burdige, 2007), Ba (Shaw et al., 1998), and $^{87}\text{Sr}/^{86}\text{Sr}$ (Beck et al., 2013), potentially affecting their use as paleoproxies.

The chemical composition of SGD is strongly influenced by biogeochemical reactions that take place within the subterranean estuary

(STE), the subsurface mixing zone of fresh and saline groundwaters (Moore, 1999; Charette and Sholkovitz, 2006; Beck et al., 2007). Subterranean estuaries are characterized by steep redox gradients known to affect the speciation and mobility of redox sensitive elements (RSEs) in fine-grained sediments (Brumsack and Gieskes, 1983; Goldberg and Forster, 1998; Morford and Emerson, 1999; Morford et al., 2005; Scholz et al., 2011). Subterranean estuaries are therefore also likely sites of intense RSE cycling. For example, previous studies have shown extensive formation of iron and manganese oxides along the freshwater/saltwater interface (Charette and Sholkovitz, 2002; Windom et al., 2006), and DOC can fuel Fe and Mn reduction as well as sulfide production in the STE (Snyder et al., 2004; Roy et al., 2010).

Redox gradients play an important role in controlling the geochemical behavior of RSEs such as V, Cr, Mo, and U, though little is known about their behavior in the STE. These RSEs tend to form soluble oxyanions under oxidizing conditions but become more insoluble or particle-reactive (i.e., more likely to sorb to sediments) under reducing

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conditions (Bruland and Lohan, 2006). Due to this behavior, these RSEs are widely used as paleoproxies to examine past oceanic oxygen levels, productivity, and circulation (e.g., Adelson et al., 2001; Lyons et al., 2003; Nameroff et al., 2004; Riboulleau et al., 2003; Rimmer et al., 2004; Rimmer, 2004; Morford et al., 2005; Tribovillard et al., 2006; Algeo et al., 2012; Arnold et al., 2012). The use of elements like Mo and U as paleoindicators is influenced by material budgets controlling their oceanic concentrations and isotopic composition (Klinkhammer and Palmer, 1991; Siebert et al., 2003; Archer and Vance, 2008). Submarine groundwater discharge is a poorly-characterized but likely important component of RSE budgets in the coastal and global ocean.

Previous work shows that reactions within the STE are important for determining the SGD-driven fluxes of RSEs. Molybdenum shows nonconservative removal from porewater in some STEs (Windom and Niencheski, 2003), but is mobilized in the salinity transition zone in others (Beck et al., 2010). Dissolved U tends to exhibit non-conservative removal in the STE (Windom and Niencheski, 2003; Duncan and Shaw, 2003; Charette et al., 2005; Santos et al., 2011), apparently due to reduction and partitioning into the sediment phase (Charette et al., 2005). At one site (Great South Bay, NY), dissolved V showed lowest concentrations in the salinity transition zone, indicating removal (Beck et al., 2010). To our knowledge, no data have been reported for dissolved Cr in the STE.

In fresh groundwater systems and low-oxygen fine-grained sediments along continental margins, the distribution of RSEs is influenced by reduction potential, sorption to Fe and Mn oxides, presence of sulfide, and complexation with organic matter (Brumsack and Gieskes, 1983; Goldberg and Forster, 1998; Morford and Emerson, 1999; Morford et al., 2005; Dotro et al., 2011; Wright and Belitz, 2010; Scholz et al., 2011; Pourret et al., 2012). Metal oxides, sulfides, and organic matter are all cycled intensively in the STE, and are likely important to the geochemical behavior of RSEs in coastal groundwater.

Detailed information about the mechanisms that control the behavior of these RSEs in the STE is lacking. Based on the redox geochemistry of these elements and previous observations in other STEs, we initially hypothesized that Mo, U, V, and Cr would be removed in the reducing portions of the STE. Therefore, the current study examined the behavior of the RSEs Mo, U, V, and Cr within the larger redox framework of a shallow STE, and evaluated the source-sink function of the STE for these elements.

2. Methods

2.1. Study site

The study site is located in Gloucester Point, VA, USA (37.248884 N, 76.505324 W) on the York River estuary (a sub-estuary of the Chesapeake Bay; Fig. 1a). The York River estuary is microtidal, with a range of ~0.8 m at the study site. The site is a small (20–30 m wide) beach comprising fine to coarse sands, with a slope of approximately 0.2. The beach is flanked to the east by a maritime forest and upland marsh, and to the north by beachfront residences. An intermittent series of granite rock breakwaters lines the beach ~40 m from the dune line (Fig. 1b). Surface water salinity at the site varies seasonally between 15 and 25, with higher salinity in summer and lower salinity in winter (Luek and Beck, 2014).

2.2. Conductivity transects and seepage meters

The location and structure of the STE were characterized using a bulk conductivity probe (Stieglitz et al., 2000, 2008). Assuming reasonably homogenous sediment composition, observed variations in bulk conductivity reflect changes in porewater salinity. Sediment bulk conductivity was calibrated in the laboratory against water of known conductivity, and checked against surface water conductivity at the field site before deployment. A subsurface conductivity transect was

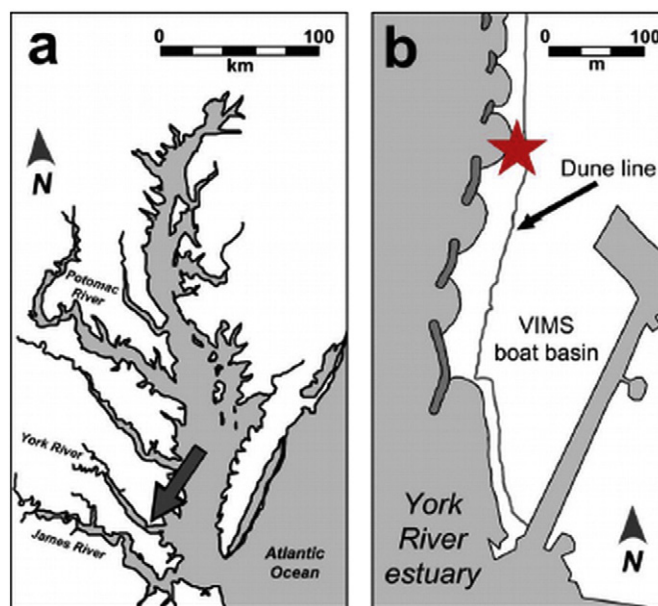


Fig. 1. (a) The Gloucester Point site on the York River estuary (which drains to the Chesapeake Bay). (b) The study site is on VIMS beach, down-gradient of a marsh. Samples were taken at the mid-tide line in the location indicated by the star.

measured in August 2013. The transect began at the mid-tide line and extended 50 m offshore, with depth profiles taken every 5 m. The depth of each profile was determined by the depth of probe refusal.

Seepage measurements and samples were obtained using Lee-type seepage meters (Lee, 1977) made from steel or polypropylene drums. Seepage meters were emplaced at least 3 days prior to sampling to allow for equilibration and headspace flushing. Seepage was collected in acid-washed soft polyethylene bags, and salinity was measured using a refractometer. Seepage rates and seepage metal concentrations were measured in the summer of 2012, and the seepage rate measurements repeated in summer of 2013, using four seepage meters deployed along a shore-normal transect starting immediately below the low tide line (Fig. 2).

2.3. Groundwater collection and analysis

Groundwater samples were collected monthly between July 2012 and September 2013 from a depth profile at the mid-tide line. Sampling occurred during the week of the spring tide during the ebb phase of the tidal cycle. From July 2012 to January 2013, samples were collected from 4 to 6 depths ranging from 25 to 200 cm using a retract-a-tip stainless steel sampler (Charette and Allen, 2006). From February to June 2013, samples were collected from 1 cm-long well-points (installed at 65 cm, 90 cm, 125 cm, 170 cm, 215 cm, and 325 cm depths) screened with stainless steel mesh (AMS, Inc.; e.g. Gonnee et al., 2013) and attached to 3 mm diameter No-Ox® PTFE tubing (Supelco/Sigma-Aldrich). From July to September 2013, additional shallow porewater samples were collected from an all-plastic multi-level sampler with 10 cm depth increments to 70 cm (Beck, 2007). Groundwater was pumped from depth using a portable peristaltic pump and filtered through a 0.45 μm Millipore polypropylene capsule filter into sampling containers. Due to progressive changes in the sampling plan over the course of the project, not all geochemical parameters were measured at all time points. Specific periods during which different constituents were measured are noted below. Ancillary water quality parameters (salinity, pH, oxidation–reduction potential) were measured at the time of collection with a hand-held YSI556 multi-probe. Oxidation–reduction potential was converted to Eh by adding 200 mV (YSI Environmental, 2005).

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