Submarine groundwater discharge of rare earth elements to a tidally-mixed estuary in Southern Rhode Island

Darren A. Chevis [a,*], Karen H. Johannesson [a], David J. Burdige [b], Jianwu Tang [a], S. Bradley Moran [c], Roger P. Kelly [c]

[a] Department of Earth and Environmental Sciences, Tulane University, New Orleans, LA 70118, United States
[b] Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529, United States
[c] Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, United States

A B S T R A C T

Rare earth element (REE) concentrations were analyzed in surface water and submarine groundwater within the Pettaquamscutt Estuary, located on the western edge of Narragansett Bay in Rhode Island. These water samples were collected along the salinity gradient of the estuary. Rare earth element concentrations in the majority of the groundwater samples are substantially higher than their concentrations in the surface waters. In particular, Nd concentrations in groundwater range from 0.43 nmol kg^{-1} up to 198 nmol kg^{-1} (mean ± SD = 42.1 ± 87.2 nmol kg^{-1}), whereas Nd concentrations range between 259 pmol kg^{-1} and 649 pmol kg^{-1} (mean ± SD = 421 ± 149 pmol kg^{-1}) in surface waters from the estuary, which is, on average, 100 fold lower than Nd in the groundwaters. Groundwater samples all exhibit broadly similar middle REE (MREE) enriched shale-normalized REE patterns, despite the wide variation in pH of these natural waters (4.87 ≤ pH ≤ 8.13). The similarity of the shale-normalized REE patterns across the observed pH range suggests that weathering of accessory minerals, such as apatite, and/or precipitation of LREE enriched secondary phosphate minerals controls groundwater REE concentrations and fractionation patterns. More specifically, geochemical mixing models suggest that the REE fractionation patterns of the surface waters may be controlled by REE phosphate mineral precipitation during the mixing of groundwater and stream water with incoming water from the Rhode Island Sound. The estimated SGD (Submarine Groundwater Discharge) of Nd to the Pettaquamscutt Estuary is 26 ± 11 mmol Nd day^{-1}, which is in reasonable agreement with the Nd flux of the primary surface water source to the estuary, the Gilbert Stuart Stream (i.e., 36 mmol day^{-1}), and of the same order of magnitude for a site in Florida.

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1. Introduction

Submarine groundwater discharge (SGD) is most commonly defined as water that flows from the seafloor to the overlying marine water column on the continental margin, without regard to the origin or composition of the fluid (Burnett et al., 2003). Thus, SGD can be driven by several mechanisms, including terrestrial hydraulic gradients, tidal and wave action, temperature and density differences, and bioirrigation (Li et al., 1999; Kelly and Moran, 2002; Michael et al., 2005; Moore and Wilson, 2005; Martin et al., 2007; Smith et al., 2008a,b). Through the use of geochemical tracers such as ^{222}Rn and radium isotopes, a number of studies have shown that SGD can contribute a substantial amount of water to the coastal ocean, which can be of similar magnitude as river input (Cable et al., 1996; Moore, 1996, 2010; Moore et al., 2008). Specifically, Moore (2010) reported that the annual average SGD flux to the South Atlantic Bight on the southeastern coast of the U.S.A. is three times greater than riverine supply in this region. Furthermore, SGD has also been reported to be an important source of nutrients and trace elements to the coastal

ocean (Kelly and Moran, 2002; Duncan and Shaw, 2003; Charette and Sholkovitz, 2006; Johannesson et al., 2011).

Recently, Johannesson and Burdige (2007) examined the contribution of SGD to the flux of rare earth elements (REEs) to the coastal ocean and suggested that SGD may be a source of the missing Nd required to resolve the "Nd Paradox". Resolving the "Nd Paradox", which refers to the apparent decoupling of the Nd concentration profiles and present-day Nd isotopic measurements, $\varepsilon_{Nd}(0)$, in the ocean (Bertram and Elderfield, 1993; Jeandel et al., 1995; Goldstein and Hemming, 2003), is important because Nd isotopes are widely used to investigate past changes in ocean circulation over glacial–interglacial periods (Frank, 2002; Goldstein and Hemming, 2003; Via and Thomas, 2006; Muinos et al., 2008). Johannesson and Burdige (2007) computed a mean Nd concentration and $\varepsilon_{Nd}(0)$ value by employing data from previous studies of terrestrial groundwater, together with an estimate of the terrestrial SGD volumetric flow rate, to compute an SGD Nd flux. The computed SGD Nd flux by Johannesson and Burdige (2007) is similar to the "missing Nd" flux that Tachikawa et al. (2003) and Arsouze et al. (2009) proposed was needed to balance the ocean Nd budget. Despite the relatively good agreement between the "missing Nd flux" and the estimated terrestrial SGD Nd flux,

Johannesson and Burdige (2007) did not explicitly account for the recirculated, saline SGD component (marine SGD) of total SGD, which can be important for some trace elements such as Fe (Taniguchi et al., 2002; Roy et al., 2010, 2011), nor did they measure Nd in actual SGD.

Recent investigations of REEs that account for the terrestrial and marine components of SGD indicate that SGD is an important source of REEs to the overlying surface waters (e.g., Duncan and Shaw, 2003; Johannesson et al., 2011; Kim and Kim, 2011, 2014; Chevis et al., in review). Duncan and Shaw (2003) reported, for example, that SGD exiting the North Inlet surficial aquifer, South Carolina, exhibits an increase in REE concentration with salinity. Lower salinity groundwaters of the North Inlet surficial aquifer display shale-normalized HREE-enriched patterns that differ from the primarily LREE-enriched high salinity groundwaters. Submarine groundwater discharge of the REEs to the Indian River Lagoon along Florida's Atlantic coast appears to originate from two distinct sources: a HREE-enriched flux derived from the advection of terrestrial groundwater; and a LREE-enriched flux derived from bioirrigation of marine porewater (Johannesson et al., 2011; Chevis et al., in review). The cycling of REEs in the Indian River Lagoon is closely linked to the Fe cycle in contrast to the North Inlet where REEs are instead released due to degradation of REE-rich, relic terrestrial organic carbon (Duncan and Shaw, 2003). More recently, Kim and Kim (2011, 2014) showed that SGD was a major source of REEs to local coastal waters off Jeju Island, Korea. All of these studies point to the need for further investigation of SGD REE fluxes to ultimately compute a global SGD flux of these important trace elements to the ocean.

In this study, we present REE data in surface water and groundwater of the Pettaquamscutt Estuary, Rhode Island, USA, and evaluate the cycling of REEs in the underlying subterranean estuary. Local aquifers consist of fractured Proterozoic and Paleozoic crystalline bedrock and associated overlying glacial deposits (Hermes et al., 1994), and thus differ lithologically from other sites investigated to date (i.e., North Inlet, South Carolina; Indian River Lagoon, Florida; Jeju Island, South Korea). Hence, the subterranean estuary associated with the Pettaquamscutt Estuary represents a system underlain by old, felsic igneous and related metamorphic rocks and associated glacial sediments, where the REE behavior and SGD fluxes can be compared with our previous work in the Holocene, mixed carbonate-siliciclastic system (i.e., Anastasia Formation) of the Indian River Lagoon, Florida, USA (Johannesson et al., 2011; Chevis et al., in review).

2. Field site

The Pettaquamscutt Estuary is located on the western edge of Narragansett Bay in the State of Rhode Island (Fig. 1). The average depth of the estuary is 2 m; however, there are two deep, stratified anoxic basins, located north of Station 3 (Sta. 3; Fig. 1), with average depths of ~20 m (Kelly and Moran, 2002, and references within). The majority of the associated drainage basin consists of glacial outwash and till deposited on top of Pennsylvanian metasedimentary rocks of the Rhode Island Formation (Hermes et al., 1994; Boothroyd and August, 2008; Nowicki and Gold, 2008). Late Proterozoic (~630–600 Ma) felsic intrusive rocks of the Esmond Igneous Suite characterize the northwestern and western portions of the drainage basin (Hermes and Zartman, 1985; Hermes et al., 1994; Kelly and Moran, 2002). The southern-most portion of the Pettaquamscutt Estuary is underlain by the Permian Narragansett Pier Granite, which intrudes the Rhode Island Formation (Zartman and Hermes, 1987).

The Gilbert Stuart Stream is the predominant surface source of freshwater to the Pettaquamscutt Estuary, and is estimated to discharge ~1×10^8 L day^{-1} of water to the estuary (Siffling, 1997). Estuarine circulation within the Pettaquamscutt Estuary is tidally controlled and the tidal prism volume is estimated at 1×10^9 L (Siffling, 1997; Kelly and Moran, 2002). Early estimates of groundwater discharge to the Pettaquamscutt, based on tidal exchange (Siffling, 1997) and hydrologic modeling (De Meneses, 1990) suggest that groundwater could account

for 50%–60% of the freshwater input to the estuary. Kelly and Moran (2002) employed ^{226}Ra and ^{228}Ra to estimate the magnitude of the SGD flux to the estuary and showed that it varies seasonally with the highest input of SGD occurring in the summer months (1.2×10^7–3.78×10^7 L day^{-1}) and the lowest SGD input occurring during the winter (0.4×10^7–1.3×10^7 L day^{-1}). Using water residence times in the Pettaquamscutt Estuary ranging between 7 and 20 days (based on Ra isotope analysis and tidal prism calculations), Kelly and Moran (2002) estimated that the average yearly volume of SGD entering the estuary is computed to range from 3.2×10^9 to 9.4×10^9 L. These SGD estimates to the estuary are broadly similar to an independent estimate of the aquifer recharge balance in the drainage basin (10×10^9 L; Kelly and Moran, 2002) suggesting that the system is in balance.

3. Methods

3.1. Sample collection

Groundwater and surface water samples were collected in October 2010 from the same locations previously sampled by Kelly and Moran (2002) (Fig. 1). Groundwater samples were collected from depths of less than 2 m below the surface using a drive-point piezometer. A peristaltic pump was employed to extract groundwater through previously cleaned, acid-washed Teflon® tubing attached to the tip of the drive-point. For groundwaters and surface waters, 1 L of water was filtered through 0.45 μm (pore-size) in-line filter cartridges (Gelman Science, polyether sulfone membrane) attached to the output end of the Teflon® tube, and collected into acid-cleaned HDPE bottles in the field after first rinsing the bottle three times with the filtered water to condition the bottle (Johannesson et al., 2004). All water samples for REE analysis were sealed in two Ziplock®-style polyethylene bags for transport back to the clean laboratory of the Graduate School of Oceanography (GRO) of the University of Rhode Island acidified to pH <2 with ultra-pure HNO$_3$ (Seastar Chemicals, Inc., Baseline) using ultra-clean procedures (Johannesson et al., 2004) within 5 h of collection. Along with the REE samples, ~125 mL of water at each sampling site was similarly collected for major cation (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$) and for major anion (Cl$^-$, SO$_4^{2-}$) analysis. Major cation samples were acidified with a drop of ultra-pure HNO$_3$ (Seastar Chemicals, Inc., Baseline), but the anion samples were not acidified. For DOC analysis, a small aliquot of each filtered sample was taken with a 50 mL polypropylene syringe and stored in a cooler for transport to the laboratory at the GRO of the University of Rhode Island. Once at the laboratory, 5 mL of each sample was placed in individual 10 mL glass ampules (cleaned and precombusted in a muffle furnace prior to use) and acidified with 50 μL of 6 M HCl. The ampules were then torched sealed and stored refrigerated until the time of analysis.

3.2. Sample analysis

Major solutes (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$, Cl$^-$, SO$_4^{2-}$) were measured in pore and surface waters by ion chromatography (Dionex DX300) at The Ohio State University following the procedure of Welch et al. (1996). Alkalinity was titrated in the field on filtered water samples using a "digital" titrator (Hach, Model 16900) and either 0.8 M or 0.08 M H$_2$SO$_4$. Measurements for dissolved Fe (II), total Fe, and ΣS(-II) ($=H_2S + HS^- + S^{2-} + \dots$) in the groundwater samples were quantified in the field using a Hach© 2800 portable spectrophotometer (Haque et al., 2008; Willis and Johannesson, 2011). Dissolved Fe (II) was determined using the 1, 10-Phenanthroline method, and total dissolved Fe was determined by the FerroVerr method (Eaton et al., 1995a). The method detection limits for the Fe (II) and total Fe methods are 0.36 μmol kg^{-1} and 0.16 μmol kg^{-1}, respectively (Eaton et al., 1995a). Dissolved S (-II) was measured by the methylene blue method (Eaton et al., 1995b). The detection limit for the methylene blue method is 0.29 μmol kg^{-1} of S (-II) (Cline, 1969; Eaton et al., 1995b). Dissolved