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



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ABSTRACT

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 ²²²Rn 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, $\epsilon_{Nd}(0)$, 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 $\epsilon_{Nd}(0)$ 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,

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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 $\sim 1 \times 10^8$ 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 ²²⁶Ra and ²²⁸Ra 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 HNO₃ (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 (Ca²⁺, Mg²⁺, Na⁺, K⁺) and for major anion (Cl⁻, SO₄²⁻) analysis. Major cation samples were acidified with a drop of ultra-pure HNO₃ (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 (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻) 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 H₂SO₄. Measurements for dissolved Fe (II), total Fe, and ΣS(-II) (= H₂S + HS⁻ + S²⁻ + ...) 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

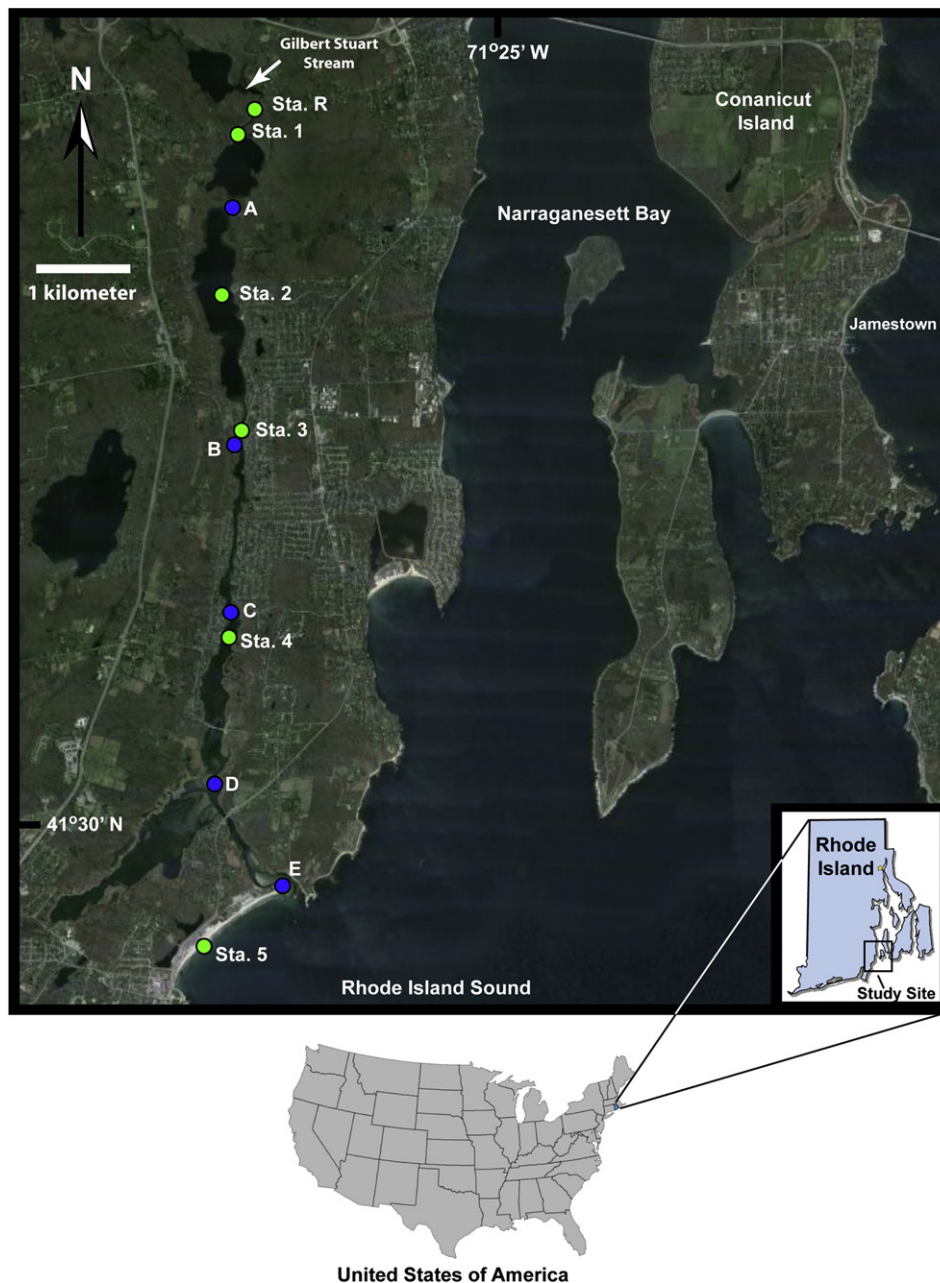


Fig. 1. Map of the Pettaquamscutt Estuary with sampling sites marked. The groundwater samples are the blue dots labeled A–E. The estuary surface water sites are labeled Sta. 1–5. Sta. R is the sample of the Gilbert Stuart Stream.

organic carbon concentrations were quantified at Old Dominion University by high temperature combustion using a Shimadzu TOC-V total carbon analyzer.

For the REE analyses, approximately 60 mL of each sample was passed through Bio-Rad® Poly-Prep columns packed with ~2 mL of Bio-Rad® AG 50 W-X8 (100–200 mesh, hydrogen form) cation-exchange resin to separate the REEs from the major dissolved solutes (Greaves et al., 1989; Johannesson et al., 2005, 2011). Two 3 mL acid rinses of 1.75 M ultra-pure HCl and 2 M ultra-pure HNO₃ were performed to elute Fe and Ba, respectively, from the columns. The REEs were then eluted from each column with 10 mL of 8 M ultra-pure HNO₃, and the eluted solutions collected in Teflon® beakers. The sample was evaporated to dryness and subsequently taken up in 10 mL of a 1% v/v ultra-pure HNO₃ solution. Because of high total REE concentrations, groundwater samples B, C, and D were rerun using ferric iron coprecipitation (Wiesel et al., 1984; Welch et al.,

1990). Here, 200 µL of an ~1 M ferric nitrate solution was added to 50 mL of sample. Approximately 3 mL of ultra-pure ammonium hydroxide (30% v/v) was added to induce the precipitation of the dissolved iron. The samples were briefly shaken and left for an hour to allow the precipitate to form. The samples were then centrifuged and the supernatant was removed. The precipitate was rinsed with Milli-Q water and then centrifuged again and the supernatant was removed. The ferric hydroxide precipitate was then dissolved in 2 M HCl, and the resulting solution was then passed Bio-Rad® Poly-Prep columns packed with ~2 mL of Bio-Rad® AG 50 W-X8 (100–200 mesh, hydrogen form) cation-exchange resin to separate the REEs from the major dissolved solutes following the procedure described above. The only difference was that the 1.75 M HCl rinse was omitted due to the fact that the sample matrix was 2 M HCl and, therefore, should prevent the Fe in solution from binding to the cation exchange resin.

Each water sample was spiked with ^{115}In at $1 \mu\text{g kg}^{-1}$ for use as an internal standard and run for the REEs by HR-ICP-MS (Thermo Fisher Element II) at Tulane University. We monitored ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{145}Nd , ^{146}Nd , ^{147}Sm , ^{149}Sm , ^{151}Eu , ^{153}Eu , ^{155}Gd , ^{157}Gd , ^{158}Gd , ^{159}Tb , ^{161}Dy , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{167}Er , ^{169}Tm , ^{172}Yb , ^{173}Yb , and ^{175}Lu in low and high-resolution modes. In addition, we also monitored ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , and ^{145}Nd in low and medium-resolution modes during the analyses. Although many of these isotopes are free of isobaric interferences, monitoring them in medium or high-resolution in addition to low-resolution helps to resolve mass interferences such as those caused by BaO^+ on the Eu isotopes, and LREEO^+ on isotopes of the HREEs. The HR-ICP-MS was calibrated with a series of REE calibration standards (i.e., 5, 20, 100, 500, 1000 ng kg^{-1}) that were prepared from NIST traceable High Purity Standards (Charleston, SC). Check standards for the REEs were also prepared using Perkin-Elmer multi-element solutions. The Canadian Research Council Standard Reference Material (SRM) for estuarine waters (SLEW-3) was analyzed as an additional check for accuracy by comparison to the measured REE values for SLEW-3 reported by Lawrence and Kamber (2006). Analytical precision of REE analyses was always better than 5% relative standard deviation (RSD), and generally better than 2% RSD.

3.3. Geochemical modeling

Rare earth element solution complexation modeling was carried out for the broad range of ionic strength found in Pettaquamscutt waters ($0.06 \text{ M} < I < 0.63 \text{ M}$; Table 1) by employing a combined specific ion interaction and ion-pairing model initially developed for the REEs by Millero (1992). The model links the specific ion interaction approach (Pitzer, 1979) with an ion pairing model (Garrels and Thompson, 1962; Millero and Schreiber, 1982), thus allowing for the evaluation of REE complexation with inorganic ligands in dilute to highly saline natural waters (Johannesson and Lyons, 1994; Johannesson et al., 1996a,b). The model was updated by adding the most recently determined stability constants for REE complexation with inorganic ligands (Lee and Byrne, 1992; Schijf and Byrne, 1999, 2004; Klungness and Byrne, 2000; Luo and Byrne, 2001, 2004). Free concentrations of inorganic ligands (e.g. $[\text{CO}_3^{2-}]_f$, $[\text{SO}_4^{2-}]_f$) used in solution complexation modeling were computed from the major solute composition of Pettaquamscutt waters via the SpecE8 program of the Geochemist's Workbench® (release 7.0; Bethke, 2008) using the thermodynamic database from PHRQPITZ (*thermo_phrqpitz.dat*; Plummer et al., 1989), and following the approach outlined by Millero and Schreiber (1982). We did not model REE complexation with naturally occurring organic ligands because previous laboratory investigations (e.g. Sonke and Salters, 2006; Pourret et al., 2007; Marsac et al., 2010; Tang and Johannesson, 2010) were conducted using background electrolyte solutions with ionic strengths less than 0.1 M. It is not clear how to correct for ionic strength

effects on the activity coefficients of natural organic matter in simulations for the higher salinity waters of the Pettaquamscutt Estuary (Remi Marsac, 2014, pers. comm.; Stephen Lofts, 2014, pers. comm.)

Geochemist's Workbench® (release 7.0; Bethke, 2008) was used to construct a geochemical mixing model to examine the influence of SGD on the shale-normalized REE fractionation patterns of the Pettaquamscutt surface estuary waters. The Lawrence Livermore National Laboratory data base provided with the software (i.e., *thermo.dat*; Delany and Lundeen, 1989) was modified by adding the 14 naturally occurring REEs and important solution complexation reaction with inorganic ligands (bicarbonate, carbonate, chloride, sulfate, hydroxide, phosphate, and fluoride) using the most up-to-date stability constants (Lee and Byrne, 1992; Schijf and Byrne, 1999, 2004; Klungness and Byrne, 2000; Luo and Byrne, 2001, 2004). To account for solubility limits on REEs we also added the solubility products for the REE-phosphate phases (i.e., $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$) determined by Liu and Byrne (1997) to *thermo.dat*. We assumed that groundwater with a composition identical to groundwater from site A best represents the SGD composition to the surface estuary (Table 4). The composition of Rhode Island Sound waters was modeled using the major solute and REE concentrations of the Station 5 surface water sample, and the Gilbert Stuart Stream endmember was modeled using the measured REE concentrations of this stream and assuming a major ion concentration similar to the Connecticut River (Table 4). This substitution of Connecticut River major ion concentrations is reasonable to a first approximation because broadly similar rock types characterize both drainage basins (Douglas et al., 2002). Previously published phosphate data for groundwater, Gilbert Stuart Stream, and Rhode Island Sound were also employed in the model (Kelly and Moran, 2002; Gaines and Pilson, 1972; Pilson, 1985; Table 4).

4. Results

4.1. REE concentrations

Rare earth element concentrations for surface and groundwaters from the Pettaquamscutt Estuary are presented in Table 2. Rare earth element concentrations in the groundwaters of the Pettaquamscutt Estuary are generally higher than those of the local surface waters. The only exception is groundwater sample E, which has similar REE concentrations to the mean surface waters of the estuary. Unlike the surface waters of the Pettaquamscutt Estuary, all of which have similar REE concentrations, the groundwaters from the subterranean estuary exhibit a large range in their REE concentrations (Table 2). For example, Nd concentrations of the groundwaters range from $0.43 \text{ nmol kg}^{-1}$ up to 198 nmol kg^{-1} (mean \pm SD = $42.1 \pm 87.2 \text{ nmol kg}^{-1}$; Table 2). By comparison, the Nd concentrations of the surface waters of the estuary range from 259 pmol kg^{-1} to 649 pmol kg^{-1} (mean \pm SD = $421 \pm$

Table 1

Ancillary data for the surface and groundwaters of the Pettaquamscutt Estuary. Major ions, alkalinity, and DOC are in mmol kg^{-1} . Fe^{2+} , total Fe, and S(-II) are in $\mu\text{mol kg}^{-1}$.

	Na	K	Mg	Ca	Cl	SO_4^{2-}	pH	Alkalinity	Fe^{2+}	Total Fe	S(-II)	DOC
<i>Groundwaters</i>												
A	149	3.32	20.8	2.22	179	5.47	6.49	8.41	BD	BD	9.61	0.80
B	38.3	1.14	7.12	1.36	40.2	2.95	4.78	0.08	3.58	6.45	0.125	0.38
C	154	3.13	25.9	2.44	175	5.90	8.13	12.2	0.895	2.15	25.1	7.28
D	422	8.18	59.5	6.10	448	24.6	6.57	10.9	0.895	1.07	27.5	6.36
E	455	9.20	58.9	7.27	449	24.4	7.47	2.84	BD	3.58	0.717	0.44
<i>Surface waters</i>												
Sta. 1	225	4.60	30.4	3.49	251	15.0	8.04	0.56				0.001
Sta. 2	333	6.94	48.3	9.96	333	17.4	7.98	1.67				0.08
Sta. 3	332	6.49	47.2	8.84	346	17.5	7.95	1.82				0.31
Sta. 4	428	8.57	56.9	9.82	453	25.0	?	1.13				0.15
Sta. 5	437	9.01	55.1	5.46	460	26.9	8.04	2.28				0.18
Mean ^a	333 ± 74	6.84 ± 1.46	46.8 ± 9.9	8.66 ± 2.88	344 ± 75	18.6 ± 4.0	7.99 ± 0.03	1.35 ± 0.51				

BD indicates below detection.

^a Weighted mean of the surface waters within the Pettaquamscutt Estuary (18.7% Sta. 1, 54.5% Sta. 2, 5.1% Sta. 3, and 21.7% Sta. 4).

Table 2
REE concentrations and loading ratios for surface and groundwaters of the Pettaquamscutt Estuary. REE ground water concentrations are in nmol kg⁻¹, REE surface water concentrations are pmol kg⁻¹.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
<i>Groundwater</i>															
A	1.4	2.06	0.31	1.37	0.25	0.035	0.24	0.04	0.25	0.047	0.14	0.02	0.13	0.019	3
B	364	475	58	198	36.4	3.75	46.4	8.74	50.4	9.76	26.1	3.19	16.7	2.4	512
C	4.44	11.6	1.38	5.67	1.33	0.202	1.26	0.231	1.3	0.224	0.593	0.074	0.429	0.058	7.13
D	4.13	14.8	1.3	5.12	1.11	0.16	0.956	0.191	1.08	0.222	0.659	0.092	0.581	0.078	8.04
E	0.31	0.07	0.081	0.43	0.059	0.01	0.039	0.0072	0.048	0.0056	0.016	0.0024	0.015	0.0027	0.39
E Dup.	0.31	0.071	0.081	0.43	0.058	0.01	0.039	0.0072	0.049	0.0055	0.016	0.0027	0.014	0.0027	0.39
<i>Surface water</i>															
Sta. R ^a	453	350	95.3	367	73.9	12.2	91.4	16.5	94.6	22.3	64.5	10.6	64.8	24.8	827
Sta. 1	378	522	64.1	385	45.2	6.38	39.3	7.24	62.5	9.2	31.6	5.09	38.1	7.08	1094
Sta. 2	776	584	103	552	103	8.94	76.7	13	105	19.1	60.9	9.11	54.6	9.26	1883
Sta. 3	927	707	128	649	87.8	11.5	104	16.8	133	25	80	11.2	70.1	11.8	2332
Sta. 4	258	460	53.1	312	38.9	5.74	39.2	6.31	48.4	7.16	23	3.48	21.7	2.99	611
Sta. 5	211	398	43.9	259	32	4.4	31.5	4.87	37.4	5.13	16.7	2.58	16.5	2.21	493
Mean ^b	597 ± 44.3	552 ± 150	86.3 ± 48.7	473 ± 22.2	57.5 ± 3.36	7.90 ± 0.40	63.0 ± 4.98	10.6 ± 0.79	86.2 ± 4.41	15.0 ± 1.39	48.2 ± 4.41	7.25 ± 0.60	45.2 ± 3.62	7.62 ± 0.66	1482 ± 68.7

^a Gilbert Stuart Stream sample.

^b Weighted mean of the surface waters within the Pettaquamscutt Estuary (18.7% Sta. 1, 54.5% Sta. 2, 5.1% Sta. 3, and 21.7% Sta. 4).

149 pmol kg⁻¹). Therefore, the Nd concentrations of Pettaquamscutt Estuary groundwaters are a factor of 100 greater, on average, than the Nd concentrations of the surface waters.

Surface and groundwater samples from the Pettaquamscutt Estuary have negative Eu anomalies (Table 3) that most likely reflect water–rock interactions with the local bedrock and glacial deposits, all of which are also characterized by negative Eu anomalies (e.g., Buma et al., 1971; Taylor and McLennan, 1985; Maria and Hermes, 2001; Dorias, 2003; Schulz et al., 2008; Dorias et al., 2012). Furthermore, it is unlikely that redox conditions are sufficiently reducing in the Pettaquamscutt subterranean estuary to reduce Eu³⁺ to Eu²⁺ (Sverjensky, 1984; Middelburg et al., 1988; Leybourne et al., 2006; Leybourne and Johannesson, 2008). In addition, geochemical modeling of E_h using the SpecE8 and Act1 program of Geochemist's Workbench® (release 7.0; Bethke, 2008) further suggests that the redox conditions are not sufficiently reducing to form Eu²⁺.

Groundwaters from the Pettaquamscutt subterranean estuary display middle REE (MREE) enriched shale-normalized patterns, with most of the samples having Gd/Yb_{PAAS} and Gd/Nd_{PAAS} ratios greater than 1 (Fig. 2a; Table 3). In contrast, the surface waters generally exhibit flat to slightly HREE enriched, shale-normalized fractionation patterns (Fig. 2b; Table 3). The shale-normalized REE pattern of groundwater sample E near the outflow of the Pettaquamscutt Estuary to Rhode Island Sound exhibits an “M-shaped” pattern with depleted HREEs and LREEs, positive Nd and Dy “anomalies”, and a concave upwards pattern between Nd and Dy (Fig. 2c). Duplicate analyses of groundwater E produced identical, shale-normalized REE patterns, indicating that the unusual REE fractionation pattern of groundwater E is indeed characteristic of groundwater from this location. The shale-normalized REE pattern of groundwater sample E is similar to Narragansett Bay water collected from the surf zone at Station 5 (Sta. 5), approximately 0.2 km to the southeast (Figs. 1 and 2). Specifically, the shale-normalized REE pattern of Sta. 5 water also exhibits HREE and LREE depletions and positive Nd and Dy “anomalies”. Furthermore, the “M-shaped” shale-normalized REE patterns of the Sta. 5 water and groundwater E differ from the HREE enriched coastal seawater of Buzzard's Bay and Long Island Sound (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Fig. 2).

4.2. REE solution complexation

The results for the REE solution complexation modeling for the surface and groundwaters of the Pettaquamscutt Estuary are presented

Table 3

Shale-normalized fractionation factors, Ce-(Ce/Ce*), and Eu-anomalies (Eu/Eu*) for surface and groundwaters of the Pettaquamscutt Estuary.

	(Gd/Nd) _{PAAS}	(Gd/Yb) _{PAAS}	Ce/Ce*	Eu/Eu*
<i>Groundwater</i>				
A	1.46	1.17	0.72	0.61
B	1.95	1.69	0.74	0.38
C	1.85	1.78	1.06	0.67
D	1.55	1.00	1.45	0.68
E	0.74	1.60	1.01	0.94
E Dup.	0.74	1.62	1.01	0.92
<i>Surface water</i>				
Sta. R ^a	2.07	0.85	0.39	0.62
Sta. 1	0.85	0.62	0.76	0.66
Sta. 2	1.16	0.85	0.46	0.53
Sta. 3	1.33	0.90	0.46	0.51
Sta. 4	1.04	1.10	0.90	0.63
Sta. 5	1.01	1.16	0.95	0.60
Mean ^b	1.08	0.86	0.61	0.58

Ce/Ce* = Ce_{PAAS}/(0.5 × La_{PAAS} + 0.5 × Pr_{PAAS}).

Eu/Eu* = Eu_{PAAS}/(0.5 × Sm_{PAAS} + 0.5 × Tb_{PAAS}).

PAAS = Post-Archean Australian Shale composite.

^a Gilbert Stuart Stream.

^b Weighted mean of the surface waters within the Pettaquamscutt Estuary (18.7% Sta. 1, 54.5% Sta. 2, 5.1% Sta. 3, and 21.7% Sta. 4).

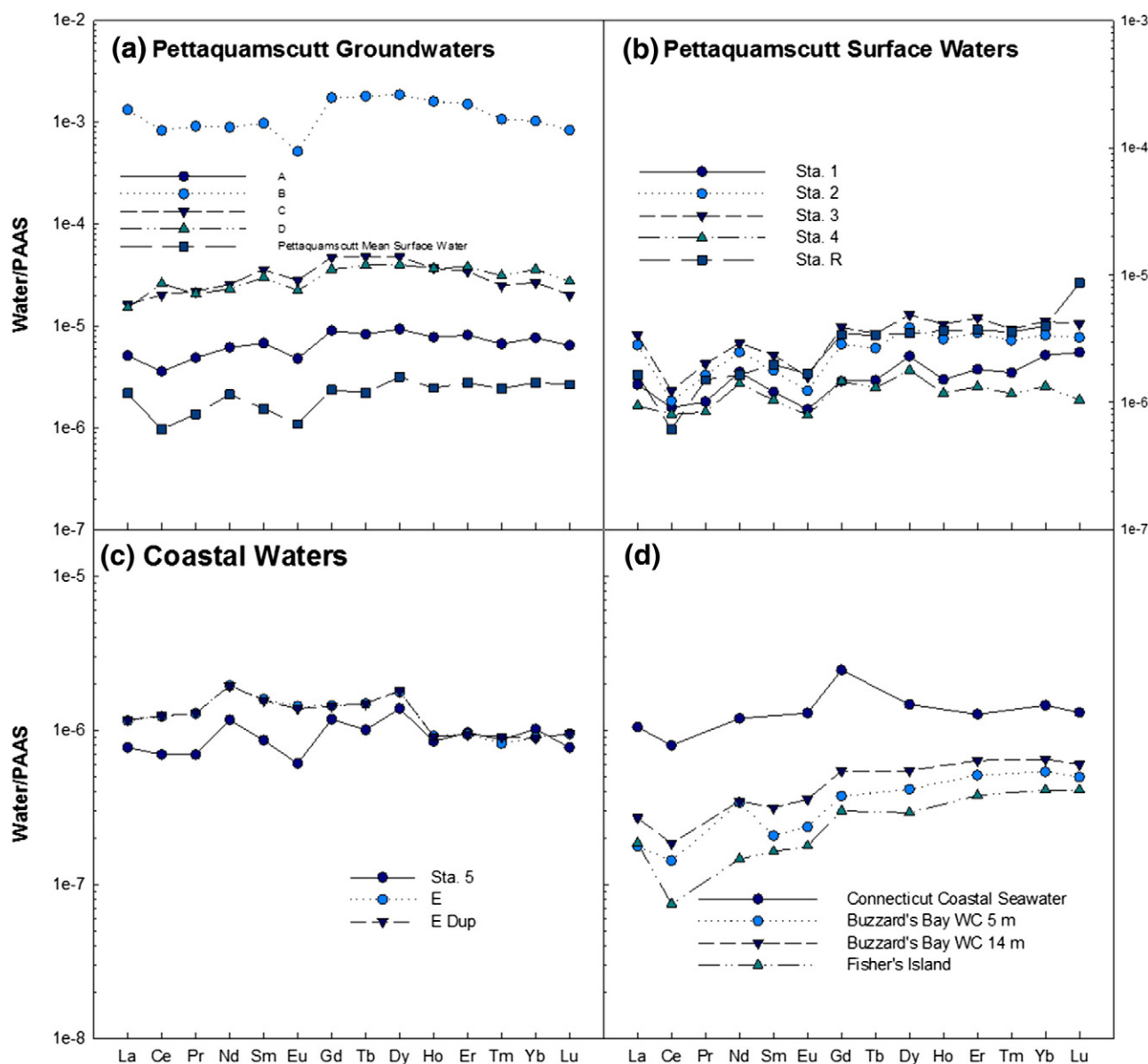


Fig. 2. REE patterns normalized to Post-Archean Australian Shale (PAAS; Nance and Taylor, 1976) for all surface and groundwaters presented in this study. (a) groundwaters A–D and weighted mean of Pettaquamscutt Estuary surface water (18.7% Sta. 1, 54.5% Sta. 2, 5.1% Sta. 3, 21.7% Sta. 4, see text for details), (b) Pettaquamscutt Estuary surface waters, (c) coastal groundwater discharging to (E and E Dup) and surface water (Sta. 5) of Rhode Island, and (d) Connecticut coastal seawater (Elderfield et al., 1990), Buzzard's Bay, MA water column (Sholkovitz et al., 1989), and Fisher's Island (Long Island Sound; Elderfield and Sholkovitz, 1987).

in Fig. 3. As mentioned above, major element data used in the model calculations are given in Table 1. Model predictions for the majority of the Pettaquamscutt waters suggest that REEs are predominately complexed with carbonate ions. For example, for groundwaters A and D, which have pH values of 6.49 and 6.57, respectively, the model predicts that carbonate complexes (i.e., LnCO_3^+ , where Ln indicates any of the 14 naturally occurring lanthanides) predominate, accounting for 38% to 58% and 46% to 64%, respectively, of each REE in solution (Fig. 3). The free metal ion, Ln^{3+} , is also predicted to be important in these groundwaters, especially in the case of La, accounting for as much as 40% of La in solution. For groundwaters C and E, Pettaquamscutt surface waters, and Sta. 5 surface waters, the model predicts that REEs occur as both the carbonate and dicarbonate complexes [i.e., $\text{Ln}(\text{CO}_3)_2^-$] in solution (Fig. 3). Generally, dicarbonate complexes are predicted to increase in importance with increasing pH of the subterranean and surface estuary waters (Fig. 3). For example, groundwater C has the highest measured pH of the Pettaquamscutt Estuary waters sampled (pH 8.13; Table 1), and the model predicts that the REEs chiefly occur in this groundwater

as dicarbonate complexes (Fig. 3). As pH decreases, the relative amount of each REE complexed as dicarbonate ions decreases as the relative amount of each REE occurring as carbonate complexes increases (Fig. 3). The primary exception is the acidic groundwater B sample (pH 4.78) where the model predicts that REEs chiefly occur in solution as free metal ion species, followed by sulfate complexes (Fig. 3). We did not attempt to evaluate the possibility that REEs occur in Pettaquamscutt Estuary groundwaters or surface waters complexed to natural organic matter because it is not clear how to correct for ionic strength effects on activity coefficients for natural organic matter in simulations conducted for near seawater salinities.

5. Discussion

5.1. Controls on REE in Pettaquamscutt groundwater

Groundwaters from the Pettaquamscutt subterranean estuary are characterized by MREE-enriched shale-normalized fractionation

patterns [i.e., $0.74 \leq (\text{Gd}/\text{Nd})_{\text{PAAS}} \leq 1.95$; $1.0 \leq (\text{Gd}/\text{Yb})_{\text{PAAS}} \leq 1.78$] negative Eu anomalies [$0.19 \leq \text{Eu}/\text{Eu}^* \leq 0.47$], and both small negative and positive Ce anomalies [$0.72 \leq \text{Ce}/\text{Ce}^* \leq 1.45$] (Fig. 2, Table 3). The MREE-enriched fractionation patterns could reflect a number of processes including geochemical reactions occurring within the Pettaquamscutt subterranean estuary between groundwater and aquifer minerals (e.g., mineral dissolution/precipitation, ion-exchange), salt-induced coagulation and removal of REE-bearing Fe-organic colloids, or aqueous complexation with ligands not included in the REE complexation model (e.g., humic substances). Examining aqueous complexation first, previous studies demonstrate that the predominate ligands complexing REEs are dependent upon solution chemistry, especially pH; therefore, the changes in solution composition that can occur along groundwater flow paths can result in changes in solution complexation of REEs and presumably the REE fractionation patterns (Johannesson et al., 1999, 2005; Dia et al., 2000; Tang and Johannesson, 2006; Tweed et al., 2006; Willis and Johannesson, 2011). A remarkable feature of the Pettaquamscutt subterranean estuary is that the wide pH range ($4.78 \leq \text{pH} \leq 8.13$; Table 1) exhibited by local groundwaters does not appear to correlate with differences in the shapes of the shale-normalized REE patterns, despite the differences in the predicted aqueous complexation of the REEs in these groundwaters (Figs. 2 and 3). For example, shale-normalized $(\text{Gd}/\text{Nd})_{\text{PAAS}}$ and $(\text{Gd}/\text{Yb})_{\text{PAAS}}$ ratios for the acidic (i.e., pH 4.78) groundwater B are similar to those of alkaline (i.e., pH 8.13) groundwater C (1.95 and 1.69 vs. 1.85 and 1.78, respectively; Table 3). The fact that groundwaters from the Pettaquamscutt subterranean estuary all exhibit broadly similar, MREE-enriched shale-normalized fractionation patterns independent of pH, and hence inorganic aqueous complexation, suggests that solution complexation reactions do not directly control the shale-normalized REE patterns of these groundwaters. Nevertheless, solution composition in terms of pH does appear to impart controls on the concentrations of REEs in Pettaquamscutt Estuary groundwaters, as REE concentrations are greatest in the acidic groundwater (pH 4.78) from location B (Table 2). Specifically, the Nd concentration of groundwater B is 198 nmol kg^{-1} compared to a mean \pm SD Nd concentration of $3.15 \pm 2.63 \text{ nmol kg}^{-1}$ for the other Pettaquamscutt groundwaters, which exhibit a mean \pm SD pH of 7.15 ± 0.8 . Many other researchers (Johannesson et al., 1999, 2005; Dia et al., 2000; Tang and Johannesson, 2006; Tweed et al., 2006; Willis and Johannesson, 2011) have noted the importance that pH plays in overall REE concentrations in natural waters although it is recognized that the common inverse relationship between pH and REE concentrations is complicated by the presence of colloidal materials in natural waters (Goldstein and Jacobsen, 1987, 1988a; Elderfield et al., 1990).

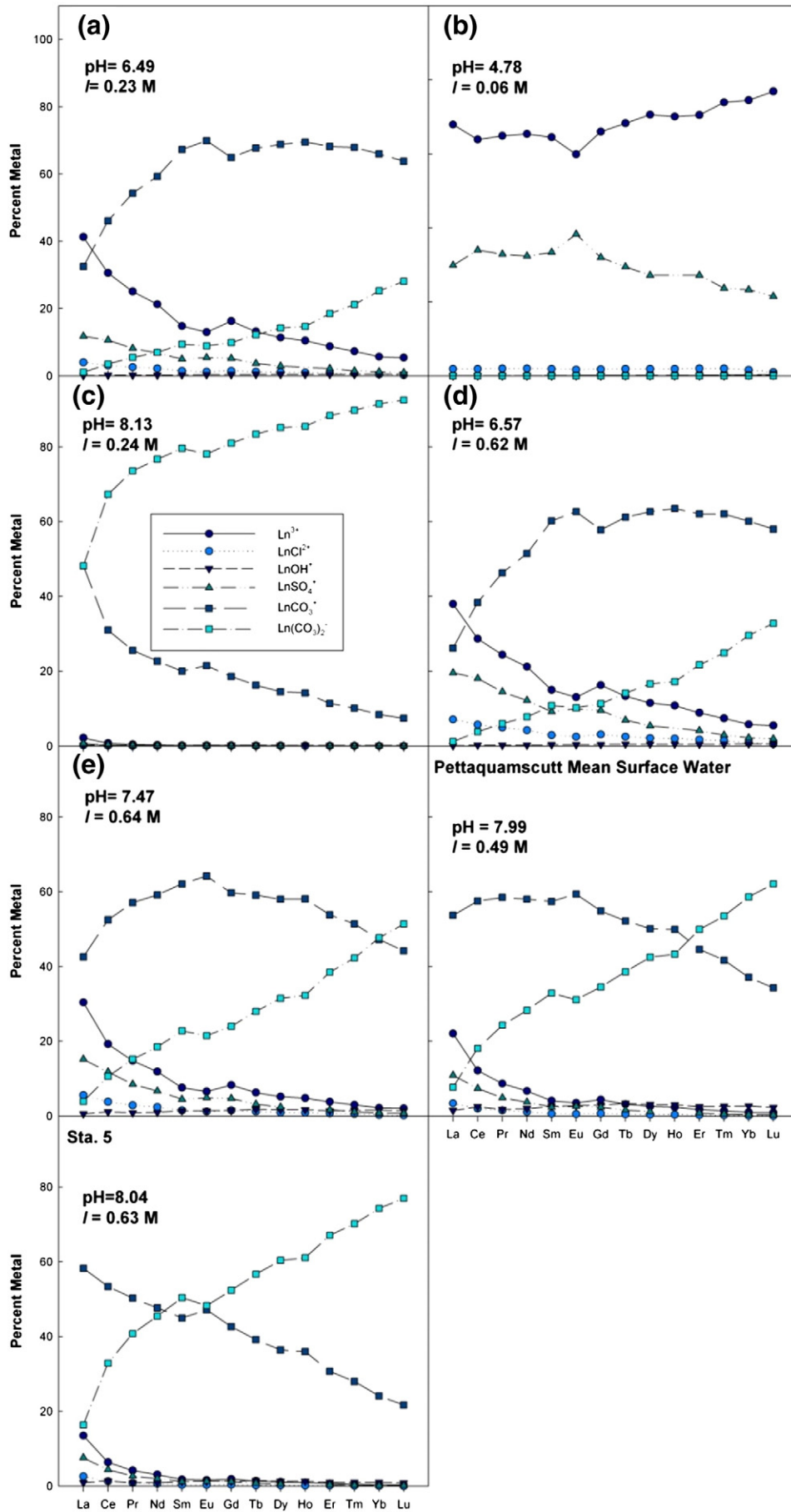
Salt-induced coagulation of Fe-rich, organic colloids is recognized as a major process that removes Fe and other trace elements, including the REEs, as fresh river water mixes with seawater in surface estuaries (e.g., Sholkovitz, 1976, 1978, 1992, 1993, 1995; Boyle et al., 1977; Goldstein and Jacobsen, 1988b). The colloidal pool of REEs in many rivers exhibits MREE-enriched patterns when normalized to shale composites (Elderfield et al., 1990; Åström and Corin, 2003; Stolpe et al., 2013). Because we did not filter Pettaquamscutt Estuary surface or groundwaters through filters with nominal pore sizes less than $0.45 \mu\text{m}$, we cannot explicitly address the possible role that colloids may play in influencing the REE concentrations and fractionation patterns of the Pettaquamscutt Estuary waters. Nevertheless, REE removal via colloid coagulation in surface estuaries fractionates the REEs as the LREEs are preferentially scavenged compared to the HREEs during the process (Elderfield et al., 1990; Sholkovitz, 1992, 1995). Hence, salt-induced colloid coagulation and the resulting REE removal from

solution in low- to mid-salinity regions of surface estuaries lead to shale-normalized REE patterns for the waters that are strongly enriched in the HREEs. The fact that we see no fractionation of the REEs with increasing salinity in the Pettaquamscutt subterranean estuary, but do observe a decrease in REE concentrations with increasing salinity and pH (e.g., $r = -0.67$ for Nd vs. Cl^- ; Fig. 4), suggests that salt-induced colloid coagulation is either not important in the subterranean estuary, or if it is occurring, it does not fractionate the REEs. In either case, additional field and laboratory investigations are required to address these issues.

Therefore, we suggest that the MREE-enriched, shale-normalized fractionation patterns that characterize groundwater from the Pettaquamscutt Estuary likely reflect geochemical reactions occurring in the subterranean estuary between the groundwater and aquifer minerals. One possible mineral phase influencing the shale-normalized REE patterns of Pettaquamscutt groundwaters is apatite (Tricca et al., 1999; Aubert et al., 2001; Hannigan and Sholkovitz, 2001). Both biogenic and igneous apatites commonly exhibit enrichments in the MREEs when normalized to shale composites such as PAAS (Hanson, 1980; Gromet and Silver, 1983; Wright et al., 1984, 1987; Grandjean and Albarède, 1989; Grandjean-Lécuyer et al., 1993; Kemp and Trueman, 2003; Leybourne and Johannesson, 2008). Moreover, apatite is a common accessory mineral in both the Esmond Igneous Suite and the Narragansett Pier Granite (Hermes et al., 1994), and is expected to be present as a trace mineral in the local glacial deposits. The solubility of apatite increases with decreasing pH, and becomes substantial at pH less than 7 (Chairat et al., 2007). Consequently, apatite in contact with groundwaters A, B, and D, all of which have $\text{pH} < 7$, is expected to be susceptible to dissolution reactions. Because the pH of groundwaters in the Pettaquamscutt region is generally acidic (Rosenhein et al., 1968; Tim Cranston, 2013, pers. comm.), conditions are expected to be suitable for apatite dissolution within the surficial aquifer, especially where the aquifer is recharged. Specifically, infiltration of acidic meteoric precipitation in conjunction with increased dissolved CO_2 in soil zone waters, owing to microbial respiration, can push the pH of recharge waters to less than 5, which would favor apatite dissolution (Drever, 1997). Apatite dissolution is not favored for groundwaters C and E, which have more alkaline pH values (Table 1); however, the REEs could have been released into the groundwater upgradient of the sampling locations. Instead, for these more alkaline groundwaters, the microbial breakdown of organic material into organic acids may subsequently facilitate apatite weathering (e.g., Taunton et al., 2000a,b; Welch et al., 2002). The relative enrichment of MREEs in Pettaquamscutt groundwaters by apatite weathering may be further enhanced by the precipitation of LREE bearing, secondary phosphate minerals such as rhabdophane and florencite (Banfield and Eggleton, 1987; Braun et al., 1990, 1998). For example, during rhabdophane precipitation, the LREEs between Ce and Eu are preferentially removed from solution relative to heavier REEs (Köhler et al., 2005).

Because many natural waters, including seawater, are saturated with respect to REE-phosphate coprecipitates (i.e., $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$), a number of researchers have argued that dissolved REE concentrations are limited by the solubility of these phases (Jonasson et al., 1985; Byrne and Kim, 1993; Johannesson et al., 1995). Using REE-phosphate solubility product data from Liu and Byrne (1997) and dissolved inorganic phosphorus data for Pettaquamscutt groundwaters (Kelly and Moran, 2002) and surface waters (Gaines and Pilson, 1972), we computed saturation indices for Pettaquamscutt Estuary groundwaters using Geochemist's Workbench® (release 7.0; Bethke, 2008). The model calculations indicate that groundwaters discharging to the Pettaquamscutt Estuary are all supersaturated with respect to the LREE-

Fig. 3. Results for REE complexation modeling for (a) Pettaquamscutt mean surface water. (b) Sta. 5, (c–g) groundwater samples A–E using the combined specific ion interaction and ion-pairing model from Millero (1992) with the most recently determined stability constants for REE complexation with inorganic ligands (Lee and Byrne, 1992; Schijf and Byrne, 1999, 2004; Klungness and Byrne, 2000; Luo and Byrne, 2001, 2004). The major ion and pH data used in the model are listed in Table 1. Plots show relative percent of each REE that occurs in solution as a given aqueous complex.



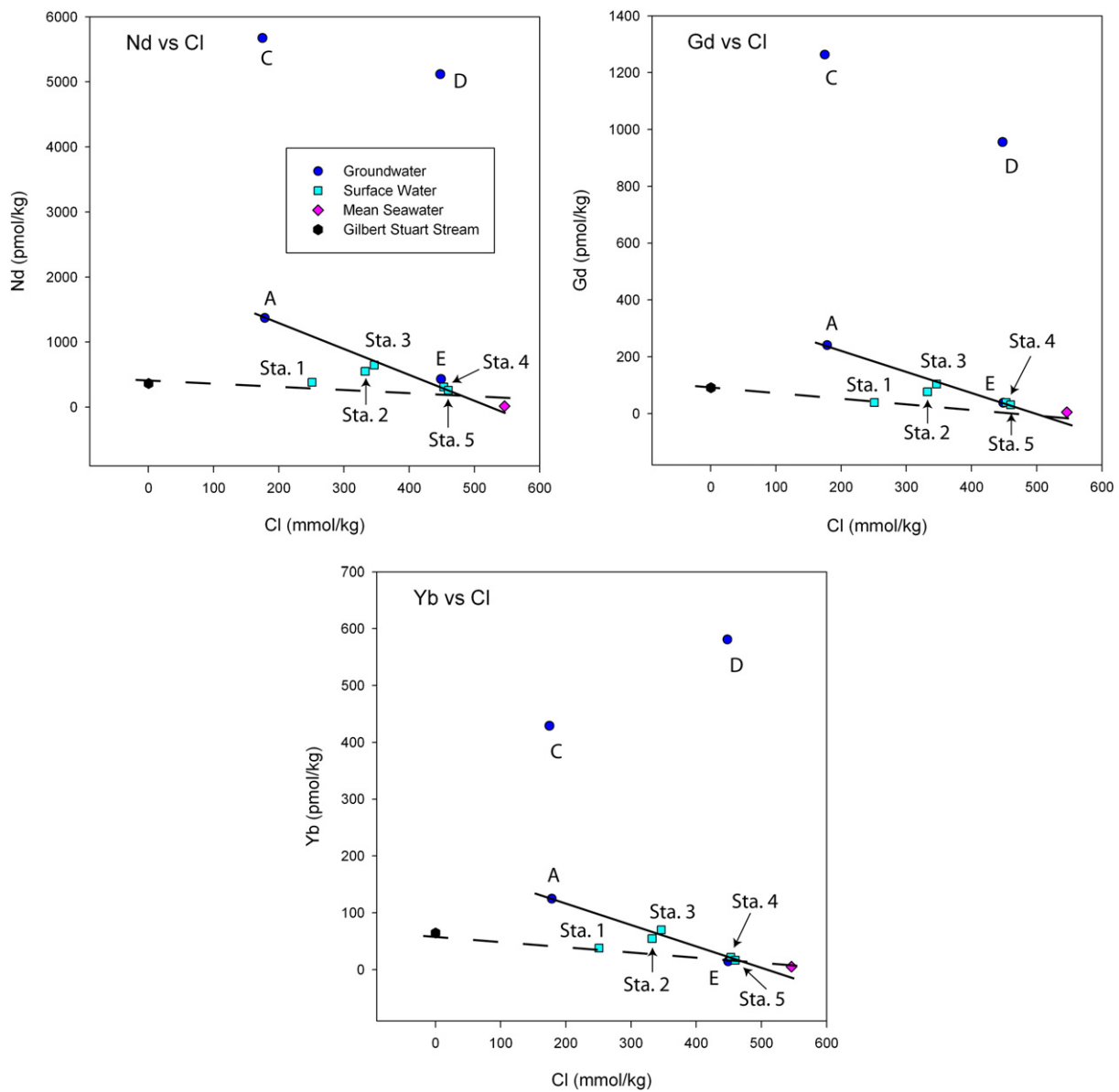


Fig. 4. REE vs. Cl^- plots for Nd, Gd, and Yb for surface and groundwaters of the Pettaquamscutt estuarine system. Because no major ion data was available for the Gilbert Stuart Stream, the average Cl^- concentration for the Connecticut River is used ($0.23 \text{ mmol kg}^{-1}$; Douglas et al., 2002). Groundwater B values are not shown in this plot due to the fact that these values are much higher than the other samples. Mean seawater values for Nd, Gd, and Yb are calculated from data in Piepgras and Jacobsen (1992), Westerlund and Öhman (1992), Sholkovitz et al. (1994), German et al. (1995), Nozaki and Zhang (1995), Zhang and Nozaki (1996), and Nozaki and Alibo (2003). Solid lines represent the mixing lines that demonstrate surface waters from Sta. 2 and 3 are a mixture of groundwater A and Rhode Island Sound waters (Sta. 5). The dashed line suggests that the northern most Pettaquamscutt surface water (Sta. 1) can be explained as an ~50:50 mix of Gilbert Stuart Stream and Rhode Island Sound (Sta. 5).

and MREE-phosphate coprecipitates (i.e., $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$) and groundwater sample A is also supersaturated with respect to HREE-phosphate minerals of the same form. In addition, all the Pettaquamscutt Estuary groundwaters, except for sample B and D, are supersaturated with respect to hydroxyapatite (log (SI) values of 0.037, 4.21, and 7.36 for A, C, and E, respectively). Although fluorapatite is the most common form of apatite in the environment (Deer et al., 1992; Klein, 2002), because we did not measure F^- concentrations in the Pettaquamscutt waters, we cannot evaluate the saturation indices for this mineral. Nevertheless, we interpret the supersaturation of Pettaquamscutt Estuary groundwaters with respect to hydroxyapatite as evidence that these waters are also likely supersaturated with respect to fluorapatite. Taken together the saturation index calculations suggest that REE-phosphate minerals like rhabdophane and florencite, and/or REE-bearing apatite, control the solubility limits of the REEs in groundwaters from the Pettaquamscutt subterranean estuary.

Anthropogenic phosphorus may also influence the REE patterns of the Pettaquamscutt groundwaters by enhancing the precipitation of phosphate minerals. Wastewater from industrial activities in the Narragansett Bay has added excess phosphorus to the waters for 200 years (Nixon et al., 2008). Although industry in the region has decreased since its height during the early to mid-20th century, septic tanks, which are another source of phosphorus, are used extensively in the region for residential waste disposal (Nixon et al., 2008). The addition of phosphorus that escapes from septic tanks into local groundwaters could potentially enhance the LREE removal from groundwaters relative to MREEs and HREEs because: 1) LREEs are typically more abundant than MREEs and HREEs; and 2) the solubility products for LREE-phosphates are lower than the corresponding MREE- and HREE-phosphates (Jonasson et al., 1985; Liu and Byrne, 1997; Centiner et al., 2005).

Another process that likely exerts important controls on dissolved REE concentrations in the Pettaquamscutt subterranean estuary is the

reductive dissolution of Fe(III) oxides/oxyhydroxides contained within the sediments. Previous work has demonstrated that Fe(III) oxides/oxyhydroxides can exhibit MREE enriched, shale-normalized REE fractionation patterns, and as a consequence, reductive dissolution of these mineral phases could impart a MREE enriched signature to the waters by releasing relatively more of the MREEs compared to LREEs and HREEs upon dissolution (Johannesson and Lyons, 1995; Johannesson and Zhou, 1999; Protano and Riccobono, 2002). Furthermore, positive Ce anomalies found in groundwater samples C and D may be evidence for the reductive dissolution of Fe(III) oxides/oxyhydroxides due to the fact that positive Ce anomalies are noted in marine ferromanganese crusts and nodules (Elderfield, 1988; Byrne and Sholkovitz, 1996; Bau, 1999). Rare earth elements in groundwaters from the Pettaquamscutt Estuary correlate well with dissolved Fe^{2+} (R^2 value of 0.97 for Nd, Gd, and Yb; Tables 1 and 2) but exhibit weaker relationships with total dissolved Fe (R^2 value of 0.70 for Nd, Gd, and Yb Tables 1 and 2). These correlations, however, are controlled solely by one sample with much higher REE concentrations (groundwater B). High DOC values in groundwater samples C and D may inhibit the precipitation of Fe-sulfide minerals by the formation of Fe-organic complexes (Luther et al., 1992), which further complicates the interpretation of these relationships. Geochemical modeling employing Geochemist's Workbench® (release 7.0; Bethke, 2008) suggests that groundwaters C and D are supersaturated with respect to Fe-sulfides yet they have the highest dissolved sulfide concentrations. We interpret the strong positive correlation of S(-II) and DOC ($R^2 = 0.92$; Table 1) in the Pettaquamscutt groundwaters as evidence for the inhibition of Fe-sulfide precipitation by Fe-organic complexation.

5.2. Controls on REE in surface waters

The shale-normalized REE fractionation patterns of Pettaquamscutt surface waters and plots of individual REE concentrations as a function of Cl^- concentrations, all suggest that mixing of SGD, Gilbert Stuart Stream waters, and Rhode Island Sound waters occurs within the surface estuary (Figs. 2 and 4). Moreover, except for Station 1, the surface waters of the Pettaquamscutt Estuary fall along mixing lines when individual REEs are plotted vs. the corresponding Cl^- concentrations. Here we use either Gilbert Stuart Stream water or groundwater A as the freshwater endmembers and Rhode Island Sound as the marine endmember (i.e., the Station 5 water; Fig. 4). The REE data are also consistent with the Pettaquamscutt Estuary not being well mixed over its entire length. Specifically, the REE data suggest that surface waters from Stations 2 and 3 are mixtures of equal parts groundwater A and Rhode Island Sound water (Station 5), but surface water at Station 4 is dominated by the influx of water from Rhode Island Sound (Fig. 4). Kelly and Moran (2002) noted that the residence time of water north of Station 3 was greater than the tidal cycle, whereas surface waters south of Station 3 are well-mixed due to complete water exchange over one tidal cycle. The observations of Kelly and Moran (2002) and those presented in this study are in agreement with the general structure of the Pettaquamscutt Estuary, which consists of a northern, fjord-like portion (north of Station 3) that contains two deep (~15–20 m), anoxic saline basins that do not mix with the estuary except during relatively rare overturn events, and a shallow (<2 m) southern portion that is well mixed (Gaines and Pilson, 1972). The surface water at Station 1 falls in the middle of the mixing line between the Gilbert Stuart Stream and Rhode Island Sound waters (Fig. 4), which likely reflects the proximity of Station 1 to the mouth of the Gilbert Stuart Stream (Fig. 1).

Based on the geographic distribution of the glacial deposits (see Schafer, 1961a,b; Nowicki and Gold, 2008), as well as the cross plots for Nd, Gd, and Yb, as a function of Cl^- concentrations, we suggest that groundwater discharging to the northwestern portions of the Pettaquamscutt Estuary (groundwater A) accounts for the majority of the SGD to this estuary. Groundwater A is the only groundwater sample

from the subterranean estuary that plots along the mixing line for the Pettaquamscutt Estuary (Fig. 4). Groundwaters from both sites C and D have REE concentrations that plot well above the mixing line indicating that these groundwaters, despite their high REE concentrations, likely contribute little to the REE budget of the Pettaquamscutt Estuary. The variation in the physical characteristics of the surficial aquifer materials may explain why only groundwater A appears to influence the REE budget of the surface estuary waters. Specifically, in the north-west portion of the Pettaquamscutt Estuary from where groundwater A was collected, surficial sediments are composed of highly permeable glacial outwash deposits and undifferentiated ice contact deposits consisting of poorly sorted gravel, cobbles, and pebbles (Schafer, 1961a; Nowicki and Gold, 2008). In contrast, the eastern and southern portions of the estuary where groundwaters C and D were collected are underlain by a ground moraine deposit composed of compacted till (Schafer, 1961b; Nowicki and Gold, 2008). The compacted till contains gravel, sand, and silt, which specifically makes it less permeable than the glacial outwash and undifferentiated ice contact deposits of the northwestern portion of the Pettaquamscutt watershed.

We performed two different simulations, one for the northern, fjord-like portion of the estuary, and the other for the well-mixed southern part of the estuary. In each case the simulations were set up to reproduce the REE concentrations and shale-normalized REE fractionation patterns of Pettaquamscutt Estuary surface waters from the northern (Stations 2 and 3) and southern (Station 4) parts of the estuary by mixing groundwater A, Gilbert Stuart Stream, and Rhode Island Sound (i.e., Station 5) waters in various proportions (Table 4). For both model simulations, equal portions of groundwater A and Gilbert Stuart Stream water were used because Kelly and Moran (2002) reported that the volume of groundwater discharged to the Pettaquamscutt is roughly equal to the volumetric discharge from the Gilbert Stuart Stream. Rhode Island Sound water was subsequently titrated into various mixtures of equal proportions of groundwater A and Gilbert Stuart Stream to best reproduce the shale-normalized REE patterns of surface

Table 4

Major element and REE data employed in the mixing model in the form entered into the React Program of the Geochemist's Workbench® (release 7.0; Bethke, 2008). Major element concentrations are all in mmol kg^{-1} except for P ($\mu\text{mol kg}^{-1}$). REE concentrations of Groundwater A are in nmol kg^{-1} . Surface water REE concentrations (Gilbert Stuart Stream and Rhode Island Sound) are in pmol kg^{-1} .

	Groundwater A ^a	Gilbert Stuart Stream ^b	Rhode Island Sound ^c
pH	6.49	6.89	8.04
Ca	2.22	0.35	5.46
Mg	20.8	0.28	55.1
Na	149	0.03	437
K	3.32	0.03	9.01
Cl	179	0.23	460
HCO_3^-	8.41	0.69	2.28
SO_4^{2-}	5.47	0.072	26.9
P	1.96	0.63	1.23
La	1.40	453	211
Ce	2.06	350	398
Pr	0.31	95.3	43.9
Nd	1.37	367	259
Sm	0.25	73.9	32
Eu	0.035	12.2	4.4
Gd	0.24	91.4	31.5
Tb	0.04	16.5	4.87
Dy	0.25	94.6	37.4
Ho	0.047	22.3	5.13
Er	0.14	64.5	16.7
Tm	0.02	10.6	2.58
Yb	0.13	64.8	16.5
Lu	0.019	24.8	2.21

^a P concentration is from Kelly and Moran (2002).

^b Major element data is average Connecticut River values from Douglas et al. (2002). P data is from Gaines and Pilson (1972).

^c Major element and REE data from Sta. 5 are used for Rhode Island Sound. P data for Rhode Island are the values reported by Pilson (1985) for Narragansett Bay.

waters of the northern and southern parts of the Pettaquamscutt Estuary. Because of the differences in the hydrodynamics between the northern, fjord-like and southern well-mixed parts of the estuary, the mixing models required substantially different amounts of Rhode Island Sound water to best reproduce the shale-normalized REE patterns of Pettaquamscutt Estuary waters.

Fig. 5 presents the results of the mixing simulations. A satisfactory match for the majority of the REEs (i.e., MREEs and HREEs) was obtained for the northern, fjord-like part of the Pettaquamscutt Estuary by employing a mixture of 25% groundwater A, 25% Gilbert Stuart Stream, and 50% Rhode Island Sound water (Fig. 5a). Here, the average REE concentration of surface waters from Stations 2 and 3 was used in the model. The model does a good job of reproducing the MREE and HREE concentrations and their associated, shale-normalized ratios, but performs poorly for the LREEs (i.e., La–Sm). Nonetheless, the enhanced

removal of the LREE predicted by the model is not entirely unexpected owing to the much lower solubility product values for the LREE-phosphate phases compared to the MREE- and HREE-phosphate phases (Liu and Byrne, 1997). The possible reasons for the discrepancy in the removal of LREEs by phosphate phases between the mixing model and the actual data are discussed below.

The mixing model for the southern portion of the Pettaquamscutt Estuary was performed identically as for the northern part except that the mixing proportions of the three endmembers required to best reproduce the REE concentrations and shale-normalized REE patterns of surface water from Station 4 were substantially different than for surface waters from the northern part of the estuary. Specifically, the best match was obtained for a mixture of 2.5% groundwater A, 2.5% Gilbert Stuart Stream, and 95% Rhode Island Sound water (Fig. 5b). Again, the mixing simulation was unable to match the LREE

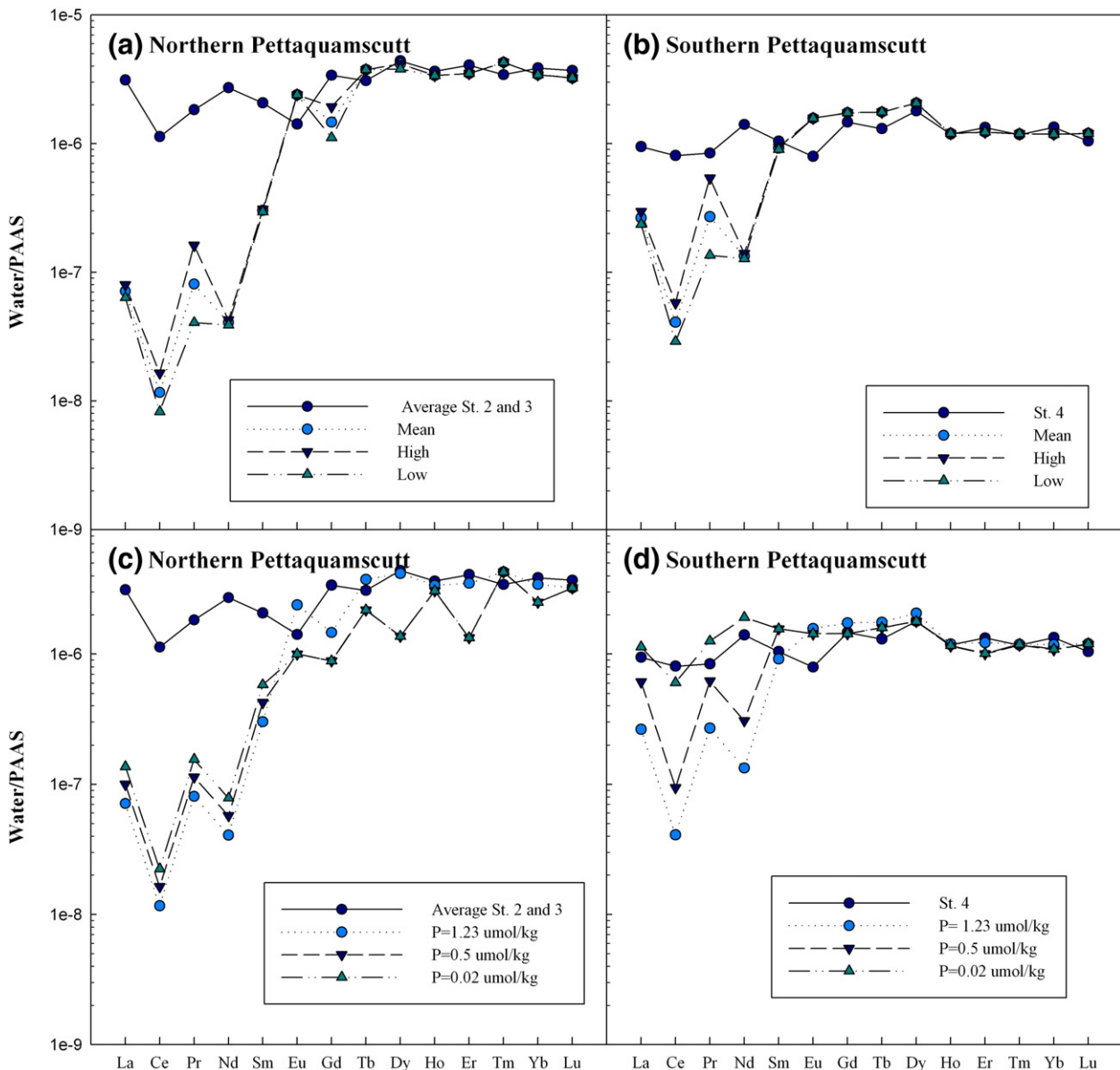


Fig. 5. Panels (a) and (b) are the REE fraction patterns resulting from the mixing model for the Northern and Southern portions of the Pettaquamscutt Estuary, respectively compared to their representative REE patterns. The mixing model in the Northern Pettaquamscutt is 25% groundwater A, 25% Gilbert Stuart Stream (Sta. R), 50% Rhode Island Sound. The mixing model in the Southern Pettaquamscutt is 2.5% groundwater A, 2.5% Gilbert Stuart Stream (Sta. R), 95% Rhode Island Sound. Mean, high, and low refer to the solubility product values for REE-phosphate phase used in each modeling simulation. The solubility products for the high and low simulations are the mean plus and minus the standard deviations reported in Liu and Byrne (1997), respectively. Panels (c) and (d) are the results of the sensitivity analysis on the affect of P concentration to the mixing model for the northern and southern Pettaquamscutt Estuary.

concentrations and shale-normalized ratios of Station 4 water, but does a reasonable job of reproducing the MREE and HREE concentrations (Fig. 5b).

To evaluate whether the mixing proportions suggested by the REEs are reasonable, we compare the model predicted Cl^- concentrations to the measured Cl^- for the surface waters. The REE mixing simulation for the southern Pettaquamscutt Estuary produced a Cl^- concentration of 441 mmol kg^{-1} that is roughly equivalent to the concentration of Station 4 (453 mmol kg^{-1} ; Table 1), which we sought to reproduce with this mixing simulation. For the northern portion of the estuary, the predicted Cl^- concentration of 275 mmol kg^{-1} is somewhat lower than the average concentration of Stations 2 and 3 ($\sim 340 \text{ mmol kg}^{-1}$; Table 1). The difference in Cl^- between the model and data for the northern part of the estuary may be due to the use of Connecticut River Cl^- data in place of the Gilbert Stuart Stream. Despite the discrepancy between the model output and the actual Cl^- data from the northern Pettaquamscutt Estuary, we submit that the model results are reasonable to a first approximation when considering the constraints on available data (i.e., lack of Cl^- data for Gilbert Stuart Stream).

The apparent over-prediction of LREE removal by phosphate phases may be due to the use of P concentrations in the model calculations that are higher than the true values in Rhode Island Sound. The P data reported by Pilson (1985) are from a site in the Narragansett Bay located north of Rhode Island Sound; therefore, the value may not be representative of the P concentrations in the sound. In order to test the sensitivity of the mixing model to P concentrations, four additional simulations were run using the mean values of the solubility products of REE-phosphate phases from Liu and Byrne (1997) with P concentrations of 0.5 mmol kg^{-1} and $0.02 \text{ mmol kg}^{-1}$ (detection limit for P analyses; Pilson, 2013) for both portions of the estuary (Fig. 5c, d). The results of these simulations are presented with the shale-normalized REE fractionation patterns from the first simulation described above (i.e., P concentration of $1.23 \text{ mmol kg}^{-1}$) and the measured data for the surface waters (Fig. 5c, d). For the northern portion of the Pettaquamscutt Estuary, the mixing model predicts enhanced LREE removal relative to the actual data at all P concentrations (Fig. 5c). In the southern Pettaquamscutt Estuary, the mixing model with a P concentration of 0.5 mmol kg^{-1} still shows enhanced LREE removal; however, at $[\text{P}] = 0.02 \text{ mmol kg}^{-1}$, the model predictions for all 14 naturally occurring REEs are substantially improved and closely match the actual measured concentrations (Fig. 5d). The results of the sensitivity analysis presented here suggest that the P in the Rhode Island Sound endmember must be at the detection limit ($0.02 \mu\text{mol kg}^{-1}$) and that the P in the Gilbert Stuart Stream and groundwater sample A influences the mixing model in the Northern Pettaquamscutt.

The LREE removal in the mixing simulations may indicate that the solubility product data presented by Liu and Byrne (1997) are not appropriate for these calculations. These researchers assumed congruent REE-phosphate dissolution in their experiments, and consequently only measured the PO_4^{3-} concentrations, and not the corresponding REE concentrations, in their REE-phosphate dissolution experiments. Consequently, the substantially lower solubility products for the LREE-phosphates compared to MREE- and HREE-phosphates determined by Liu and Byrne (1997) could reflect the assumption of stoichiometric dissolution (e.g., Centiner et al., 2005). For example, the presence of trace amounts of phosphate impurities in the REE phosphate minerals used in the solubility experiments could alter the REE/P ratio in the dissolving fluid, leading to higher PO_4^{3-} than Ln^{3+} concentrations in the experimental solutions (Centiner et al., 2005). Furthermore, Köhler et al. (2005) noted that during apatite dissolution experiments, secondary phosphate minerals such as rhabdophane precipitated. Because rhabdophane has an affinity for the LREEs, the precipitation of LREE enriched secondary phosphates like rhabdophane during such experiments could affect the solubility constant calculations if stoichiometric dissolution is assumed.

Table 5The calculated SGD and river fluxes of REEs to the Pettaquamscutt in mmol day^{-1} .

	SGD flux ^a	River flux ^b
La	26.2 ± 11.0	45.3
Ce	38.4 ± 16.2	35.0
Pr	5.78 ± 2.44	9.53
Nd	25.6 ± 10.8	36.7
Sm	4.73 ± 1.99	7.39
Eu	0.65 ± 0.27	1.22
Gd	4.51 ± 1.90	9.14
Tb	0.75 ± 0.32	1.65
Dy	4.72 ± 1.99	9.46
Ho	0.88 ± 0.37	2.23
Er	2.64 ± 1.12	6.45
Tm	0.37 ± 0.16	1.06
Yb	2.33 ± 0.98	6.48
Lu	0.34 ± 0.15	2.48

^a Calculated using an average SGD flux of $6.8 \times 10^9 \text{ L yr}^{-1}$.

^b Flux calculated using a discharge of $1 \times 10^5 \text{ m}^3 \text{ day}^{-1}$ from Siffing (1997).

5.3. Submarine groundwater discharge of REE to Rhode Island Sound

The SGD flux of each of the REEs to the Narragansett Bay/Rhode Island Sound was estimated following the same procedures described in Kelly and Moran (2002) for the SGD nutrient fluxes. Specifically, the volumetric flux of SGD ($6.8 \times 10^9 \text{ L yr}^{-1}$) used in our calculation is an average of the annual groundwater discharge to the Pettaquamscutt Estuary determined using the tidal prism, and the estimated Ra residence time of 8 days and 20 days by Kelly and Moran (2002). The shorter residence time of 8 days reflects a higher groundwater discharge rate necessary to account for the faster Ra removal due to tidal flushing (see Kelly and Moran, 2002, for details). Again, we assumed that the composition of groundwater A is representative of the bulk of the SGD to the Pettaquamscutt Estuary. The resulting estimates of the SGD flux of the REEs are presented in Table 5. The estimated SGD flux of REEs to the Pettaquamscutt Estuary ranges from 0.3 ± 0.1 to $38 \pm 16 \text{ mmol day}^{-1}$, with the SGD flux for Nd estimated as $26 \pm 11 \text{ mmol day}^{-1}$ (Table 5). The groundwater flux of Nd is roughly equivalent to the Nd flux from the Gilbert Stuart Stream ($36.7 \text{ mmol day}^{-1}$). The REE fluxes presented in Table 5 can be considered conservative estimates due to the fact that the REE concentrations of groundwater A are much lower than the REE concentrations of the other groundwaters sampled (Table 2). If the bulk SGD to the Pettaquamscutt Estuary has higher REE concentrations than those of groundwater A, then the SGD fluxes of REEs to the estuary would be even greater than the estimates presented in Table 5.

The results of the SGD REE flux calculations for the Pettaquamscutt Estuary compare well with the SGD REE fluxes calculated for the Indian River Lagoon in Florida, where we computed an SGD flux of $7.69 \pm 1.02 \text{ mmol day}^{-1}$ (Chevis et al., in review). The SGD fluxes of Nd at both of these sites are approximately equal to the local Nd flux of river water Nd fluxes into the estuaries, but the Nd flux to the Pettaquamscutt Estuary is over 3 times greater than that of the Indian River Lagoon. In comparison, the SGD Nd flux estimated by Kim and Kim (2011) for Jeju Island, Korea, is 5 orders of magnitude greater than the SGD Nd flux we estimate for the Pettaquamscutt Estuary (Table 5). The discrepancy is most likely due to the aquifer on Jeju Island being composed of young, easily weathered basaltic rock fragments as opposed to the glacial deposits derived from Late Proterozoic and Paleozoic rocks that characterizes the Pettaquamscutt Estuary watershed. Furthermore, these differences suggest that REE SGD fluxes are highly variable and depend on the structure and composition of the subterranean estuary.

6. Conclusions

The rare earth element fractionation patterns for all the Pettaquamscutt groundwater samples in this study have similar

MREE-enrichments despite a wide range in REE concentrations. The differences in pH among the Pettaquamscutt groundwaters influence the REE concentrations without causing fractionation among the REE suggesting that solution chemistry does not exert control on the REE fractionation patterns. Removal by colloidal material and reductive dissolution of Fe oxides-oxyhydroxides do not appear to be important processes controlling REE behavior in the Pettaquamscutt. The weathering of REE-bearing minerals such as apatite, accompanied by the precipitation of LREE-enriched secondary phosphate minerals such as rhabdophane, probably exerts more controls on the REE patterns of SGD within the Pettaquamscutt Estuary. The precipitation of the LREE-enriched phosphate minerals may be enhanced by the addition of anthropogenic phosphorus by septic tanks and remnants of industrial activities around Narragansett Bay.

Groundwater from the northwestern portion of the estuary appears to have the most influence on the REE patterns due to the higher discharge volume from highly permeable glacial outwash and undifferentiated ice contact deposits located in this portion of the Pettaquamscutt watershed. Even though Pettaquamscutt groundwaters do influence the surface water patterns, the surface water REE patterns have flat to HREE enriched fractionation patterns. The evolution of these surface water patterns is likely due to the continued precipitation of LREE-enriched phosphate minerals.

The estimated SGD flux of Nd to the Pettaquamscutt Estuary using REE concentration from the groundwater in the northwestern portion of the estuary is roughly equivalent to that of the Gilbert Stuart Stream. The similar fluxes from groundwater and river water to the Pettaquamscutt are consistent with the findings in our previous investigation of REEs in the SGD of the Indian River Lagoon in Florida, USA. The fact that the SGD flux is of the same order of magnitude as the Gilbert Stuart Stream points to the need for more REE and Nd isotopic studies in subterranean estuaries in order to establish a global SGD flux of Nd to be employed in determining the oceanic Nd budget.

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