**Rare Earth Element Cycling in a Sandy Subterranean Estuary in
Florida, USA**

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Abstract

Rare earth element (REE) analyses were performed on 77 water samples and 5 sediment samples from the Indian River Lagoon system along the east coast of Florida. Groundwater samples were collected using nine multi-level piezometers installed along a shore-normal transect of the sandy subterranean estuary. Surface water samples were collected from Eau Gallie River and Crane Creek, the water column of the Indian River Lagoon above each piezometer, and the coastal Atlantic Ocean at Canova Beach. The REE concentrations of lagoon surface and subterranean estuary waters indicate that geochemical reactions within the subterranean estuary play a substantial role in the local REE cycle. The submarine groundwater discharge (SGD) flux of REEs calculated by using a modified form of the 1-dimensional vertical-flow equation is comprised of a nearshore heavy REE (HREE) enriched advective source chiefly composed of terrestrial SGD, and a light REE (LREE) and middle REE (MREE) enriched source that originates from reductive dissolution of Fe(III) oxides/oxyhydroxides in the subterranean estuary and subsequent transport by bioirrigation to the overlying lagoon. The total SGD flux of REEs reveals that this sandy subterranean estuary is a source for light and middle REEs and a sink for the heavy REEs to coastal waters. The SGD Nd flux is estimated at $7.69 \pm 1.02 \text{ mmol day}^{-1}$, which is roughly equivalent to the effective local river flux to the Indian River Lagoon. Although our re-evaluated SGD flux of Nd to the Indian River Lagoon is lower than an earlier estimate, it represents a substantial input to the coastal ocean and thus provides additional insights into the global oceanic Nd budget and the “Nd Paradox”.

1. Introduction

Surface water estuaries are known to be sites of rare earth element (REE) cycling and fractionation due to the mixing of fresh river waters and saline ocean waters (Sholkovitz, 1993; 1995, Sholkovitz and Szymczak, 2000). These systems represent the transition zone between continental weathering processes and export through river discharge and the open ocean. Seawater induced coagulation of colloids along the salinity gradient in estuaries is responsible for the removal of a large part of the REE inventory coming from the continent (Sholkovitz, 1993; 1995, Sholkovitz and Szymczak, 2000). Colloidal coagulation also causes the fractionation of the REEs with the order of removal being LREE (Light Rare Earth Elements) > MREE (Middle Rare Earth Elements) > HREE (Heavy Rare Earth Elements) (Sholkovitz, 1995). In addition to the removal of colloidal REEs, release of REEs in the order of LREE > MREE > HREE occurs as suspended river particulate matter enters the mid to high salinity region of a surface estuary (Sholkovitz, 1995).

Recently, research into REE cycling in subterranean estuaries suggests the mixing of terrestrial and marine groundwaters, more commonly referred to as submarine groundwater discharge (SGD), displays similar behavior to REEs in surface estuaries (Duncan and Shaw, 2003; Johannesson et al., 2011; Kim and Kim, 2011). Submarine groundwater discharge is operationally defined as all water that flows from the seafloor to the overlying marine water column on the continental margin regardless of the origin or composition of the fluid (Burnett et al., 2003). Furthermore, SGD can be composed of both groundwaters of terrestrial origin as well as marine circulation of seawater through coastal aquifer sediments (e. g. Kelly and Moran, 2002; Taniguchi et al., 2004; Michael

et al., 2005; Smith et al., 2008). Rare earth element fractionation patterns of SGD commonly display HREE and MREE enrichments that result from geochemical interactions with the sediments in the subterranean estuary (Duncan and Shaw, 2003; Johannesson et al. 2011; Kim and Kim, 2011). Previous work in the Indian River Lagoon, FL, suggests that the dissolution of Fe(III) oxide/oxyhydroxide mineral coatings on the aquifer sediments is a net source of LREEs and MREEs to SGD, and hence, the overlying surface estuary (Johannesson et al., 2011). Although LREEs and MREEs are released in the mid to high salinity regions of both surface and subterranean estuaries, the mechanism for REE release in the subterranean estuary of the Indian River Lagoon appears to be due to redox changes, unlike the salinity induced release in surface estuaries (Sholkovitz, 1995; Johannesson et al., 2011).

Interest in the fluxes of REEs are due, in part, to the “Nd Paradox” which points to an apparent decoupling of the Nd concentrations and isotope ratios in the ocean. In the ocean, REEs exhibit nutrient-like water column profiles that indicate scavenging from surface waters by particulate matter and subsequent regeneration at depth (Bertram and Elderfield, 1993; Goldstein and Hemming, 2003). These two processes lead to a progressive increase in REE concentration in deep waters as a function of thermohaline circulation and implies relatively long oceanic residence times for REEs (e.g. on the order of 10^4 years; Goldstein and Hemming, 2003). However, oceanic Nd isotope compositions vary within individual ocean basins for different water masses (e.g. North Atlantic Deep water, Antarctic Intermediate Waters, etc.), as well as between the different oceans (i.e. Atlantic, Indian, Pacific), indicating that the residence times of Nd,

and the REEs in general, must be similar to or less than the mixing times of the oceans (i.e. 500-1500 yrs; Broecker and Peng, 1982; Goldstein and Hemming, 2003).

A “missing” flux of $\sim 5.6 \times 10^7$ moles year⁻¹ of Nd with a $\epsilon_{\text{Nd}}(0)$ of -9.2 is needed in order to reconcile the “Nd Paradox” (Tachikawa et al., 2003; Arsouze et al., 2009). Many suggestions for the missing flux of Nd have been proposed including a greater atmospheric dust flux to the ocean, and/or greater dissolution of the dust in seawater, release from particulates in high salinity regions of estuaries, and diffusive flux from sediment porewaters (e.g., Jeandel et al., 1995; Elderfield and Sholkovitz, 1987; Sholkovitz, 1995; Sholkovitz and Szymczak, 2000; Zhang et al., 2008). None of these processes appear to have the necessary magnitude and Nd isotopic composition to balance the oceanic Nd budget (Johannesson and Burdige, 2007). However recent work suggests that a process referred to as “boundary exchange” may be able to account for much of the missing Nd flux. Boundary exchange includes all sediment-water interactions that occur on the continental shelf without reference to any specific process (Lacan and Jeandel, 2005; Jeandel et al., 2007). Consequently, elucidating the specific physicochemical or biogeochemical processes that may comprise boundary exchange are required to better understand the transfer of REEs from the continents to the oceans and to quantify the reactions involved in the exchange.

One possible boundary process is SGD. For example, Johannesson and Burdige (2007) evaluated the possible contribution of Nd from SGD to the global ocean using estimated mean Nd concentrations and $\epsilon_{\text{Nd}}(0)$ values for global SGD, and they reported terrestrial SGD Nd fluxes that were within a factor of 2 to 8 of the “missing Nd” flux of Tachikawa et al. (2003). However, Johannesson and Burdige (2007) did not measure Nd

in actual SGD, nor did they specifically examine the marine component of the SGD Nd flux. Nonetheless, the mixing of the terrestrial and marine components of SGD can promote geochemical reactions within the coastal aquifers that can mobilize nutrients and trace elements into solution, which are then discharged to the coastal ocean with SGD (e.g., Kelly and Moran, 2002; Duncan and Shaw, 2003; Charette and Sholkovitz, 2006).

Here we examine the REE concentrations in groundwaters from a subterranean estuary beneath the Indian River Lagoon on Florida's Atlantic Coast. Previously, we developed a simple box model to evaluate the SGD fluxes of REEs to overlying surface waters based on a limited REE dataset (Johannesson et al., 2011). In this contribution we augment our initial database by inclusion of additional groundwater samples that provide higher spatial resolution of REE concentrations within the entire subterranean estuary. The increased spatial resolution affords a more quantitative modeling approach, and an improved estimate of the SGD fluxes of REEs to the lagoon surface waters.

2. Field Site

The Indian River Lagoon study site is located near Melbourne, Florida, and is bounded to the north by the Eau Gallie River and to the south by Crane Creek (Fig. 1). The lagoon is a microtidal system (< 10 cm; Smith, 1993) where there is minimal exchange with the Atlantic Ocean except through three inlets (Sebastian, Ft. Pierce, and St. Lucie) at the southern end of the lagoon. The residence time of water near the study site is estimated to be ~18 days, whereas residence times can be as high as a year in the northern reaches of the lagoon (Smith, 1993).

The hydrostratigraphy of the region consists of Pleistocene beach ridges that surround the lagoon and the Holocene Anastasia Formation (Surficial Aquifer), which is composed of interbedded layers of quartz sand and minor coquina that underlie the entire lagoon (Scott, 1992). Underlying the Anastasia Formation is the Miocene Hawthorne Group confining unit, which consists of sand, marl, clay, carbonate, and phosphate layers (Miller, 1986). The Hawthorne Group is the upper confining layer for the Oligocene limestones and dolostones of the underlying Upper Floridan Aquifer System. The exchange of water between the Upper Floridan and Surficial Aquifers is negligible at the study site because of this confining unit (Miller, 1986). Within the shallow subterranean estuary of the Indian River Lagoon, porosity ranges from 37% to 45%, and hydraulic conductivity ranges from 10^{-4} to 10^{-10} m s⁻¹ in the upper 300 cm, but is more uniform (10^{-4} to 10^{-8} m s⁻¹) in the top 70 cm (Hartl, 2006; Smith et al., 2008).

Freshwater inputs to the Indian River Lagoon include two small rivers (Eau Gallie River and Crane Creek), urban storm runoff, direct rainfall, and SGD (Martin et al., 2007). Previous studies have determined SGD fluxes at the study site and shown that the magnitude of the terrestrial SGD flux decreases with increasing distance offshore, becoming negligible at the freshwater-saltwater seepage face (Martin et al., 2007). The discharge of terrestrial SGD as a function of distance offshore follows the relationship:

$$\omega = 0.16 - 0.0064 x \quad (1)$$

where ω is the flow rate of terrestrial SGD in cm day⁻¹ and x is the distance offshore in meters (Martin et al., 2007). Terrestrial SGD mixes with circulated lagoon waters (i.e., the marine SGD component) at the seepage face and is subsequently released to overlying lagoon waters. Martin et al. (2007) computed a total SGD flux of 117 m³ day⁻¹

per meter of shoreline with only 0.02 to $0.9 \text{ m}^3 \text{ day}^{-1}$ per meter of shoreline of that flux being terrestrial SGD. Hence, marine SGD accounts for most of the groundwater discharged to the Indian River Lagoon.

The lithostratigraphy of the upper 300 cm of the subterranean estuary consists of quartz sands with Fe(III) oxide/oxyhydroxide minerals typically coating the sand grains (Hartl, 2006; Roy et al., 2010). Roy et al. (2010) collected six sediment cores from the subterranean estuary located ~1 m north of each multi-level piezometer (i.e., multisamplers; Martin et al., 2003) used to collect groundwater (i.e., EGN-0, 10, 20, 22.5, 30 and CIRL-39; see Fig. 1). The convention is EGN-0 for 0 m and so forth out to EGN-30 for 30 m offshore, whereas CIRL-39 is located 250 m offshore. All sediment cores except CIRL-39 had a top layer of black sulfide-rich sediment overlying orange sediments coated with Fe(III) oxide/oxyhydroxide minerals (Roy et al., 2010, 2011). The thickness of the black sulfide-rich sediment increases offshore, ranging from ~17 cm at EGN-0 (shoreline) to a thickness of ~68 cm at EGN-30. Roy et al. (2010) were not able to determine the depth of the black sediment layer at CIRL-39, but a deeper core taken at approximately the same site showed the layer to extend to at least 250 cm below seafloor (cmbsf) (Hartl, 2006). The gradual thickening of the black sulfide sediments with distance offshore is thought to reflect the gradual inundation of the subterranean estuary as sea level rose over the last 250 years (Roy et al., 2010).

3 Methods

3.1 Sample Collection

Groundwater samples for REE analysis were collected in April 2007 from a 30-m long transect of eight multi-level piezometers (at 0, 5, 10, 15, 17.5, 20, 22.5, and 30 m) and from one multi-level piezometer located ~250 m from the shoreline (Martin et al., 2007; Fig. 1). Before the samples were collected from each multisampler, water was pumped into an overflow cup and specific conductivity, dissolved oxygen, temperature, and salinity were monitored until these parameters stabilized. Once stable, ~60 mL of water was filtered through a 0.45 μm in-line filter cartridge (GEO-TECH, polyether sulfone membrane) and collected in acid cleaned HDPE bottles. All surface and groundwater samples for REE analysis were acidified to $\text{pH} < 2$ with ultra-pure HNO_3 . Along with the REE samples, waters were collected for major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and for major anion samples (Cl^- and SO_4^{2-}). Major cations samples were acidified with a drop of ultra-pure HNO_3 , but the major anions were not acidified. Water samples were collected for the Eau Gallie River and Crane Creek in March 2009 and Canova Beach in March 2012 by a similar method employing 0.45 μm filter (Gelman Science, polyether sulfone membrane), followed by acidification with ultra-pure HNO_3 .

Five representative sediment samples (one gram each) from the Indian River Lagoon subterranean estuary were also analyzed for REEs from cores previously collected and described in Roy et al. (2010). Sediments taken from EGN-0 at 205-207 cmbsf and from EGN-22.5 at 185-187 cmbsf consist of orange colored sediments characterized by abundant Fe(III) oxide/oxyhydroxide coatings on quartz grains. Multisamplers EGN-0 at 2-4 cmbsf and CIRL 39 at 5-7 cmbsf are black sediments containing Fe-sulfide minerals. Sediments from EGN-22.5 at 50-52 cmbsf consist of gray sediments from the transition zone in the sediment cores between the Fe(III)

oxide/oxyhydroxide coated sediments and the Fe-sulfide-rich sediments (Roy et al., 2010).

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 DX500) at the University of Florida. Major solutes for the Eau Gallie River, Crane Creek, and Canova Beach were also measured by ion chromatography (Dionex DX300) at Ohio State University following the procedure of Welch et al. (1996). Alkalinity was determined by standard titration methods during sample collection on site. Dissolved sulfide, $\text{S}(-\text{II})$, concentrations were measured spectrophotometrically during sample collection using the Methylene Blue method (Cline, 1969; Eaton et al., 1995). Dissolved Fe and Mn concentrations were determined by high-resolution (magnetic sector) inductively coupled plasma mass spectrometry (HR-ICP-MS, Finnigan MAT Element II) at the University of Florida by monitoring ^{56}Fe and ^{55}Mn (Roy et al., 2010). Samples were diluted by a factor of 50 in 5% (v/v) ultra-pure HNO_3 and spiked with rhodium as an internal standard.

Water samples for REE analysis were 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 in order to separate the REEs from the major salts (e.g., Greaves et al., 1989; Johannesson et al., 2011). Two 3-mL acid rinses of 1.75 M ultra-pure HCl and 2 M ultra-pure HNO_3 were performed to elute Fe and Ba, respectively, from the columns. The REEs were then eluted from the column into a Teflon[®] beaker with 10 mL of 8 M

ultra-pure HNO_3 . Each sample was subsequently evaporated to dryness on a hot plate, and taken up in 10 mL of a 1% v/v ultra-pure HNO_3 solution for analysis.

Approximately 0.2 g of each sediment sample was placed in a Teflon[®] digestion tube and mixed with 5 mL of ultra-pure HF following the procedure of Tang et al. (2004). The digestion tube with a watch glass covering the top was placed in a DigiPREP MS[®] digestion system (SCP Science; Champlain, NY) and allowed to reflux at 90°C for ~2 hours and then evaporated to dryness. Ten mL of ultra-pure HNO_3 was subsequently added to the digestion tube and evaporated to dryness, and a final 5 mL of ultra-pure HF was added before the mixture was allowed to evaporate to near dryness. The remaining residue was taken up in 2 M ultra-pure HCl and then loaded on a Bio-Rad Econo-Pac column packed with 8 mL of Bio-Rad[®] AG 50 W-X8 (100-200 mesh, hydrogen form) cation-exchange resin to separate the REEs from the major salts. Two acid rinses of 2 M ultra-pure HCl (35 mL) and 2 M ultra-pure HNO_3 (20 mL) were performed to elute Fe and Ba, respectively. Fifteen mL of 8 M ultra-pure HNO_3 was used to elute the REEs from the column, and the eluted solution was collected into a 30 mL Savillex[®] beaker. A small aliquot of the solution was diluted to a factor of 10,000 in preparation for analysis.

Each sample was spiked with ^{115}In at 1 ppb for use as an internal standard and analyzed for the REEs by HR-ICP-MS (Thermo Fisher Element II) at Tulane University. We monitored ^{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 mode and monitored ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , and ^{145}Nd in low and medium-resolution mode. Although many of these isotopes are free of isobaric interferences, monitoring them in medium or high-resolution mode in addition to low-resolution mode provides an

additional check for potential interferences especially for the Eu isotopes and the HREEs. BaO⁺ species that form in the plasma stream can interfere with the Eu isotopes, and LREEO⁺ and MREEO⁺ species formed in the plasma can cause interferences with HREEs. Monitoring in high-resolution mode results in the separation of the REE peaks from those of the interfering oxides. The HR-ICP-MS was calibrated with a series of REE calibration standards (5, 20, 100, 500, 1000 ng kg⁻¹). Analytical precision of REE analyses was always better than 5% relative standard deviation (RSD), and generally better than 2% RSD.

3.3 REE solution complexation

Modeling REE solution complexation for the broad salinity range of Indian River Lagoon waters (Table 1) was performed using a combined specific ion interaction and ion-pairing model (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. [CO₃²⁻]_F, [SO₄²⁻]_F) used in the modeling were calculated via SpecE8 in the Geochemist's Workbench[®] (release 7.0; Bethke, 2008), employing the thermodynamic database from PHRQPITZ (Plummer et al., 1989).

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272 **3.4 REE SGD Flux Calculation**

273 The SGD flux model for each of the naturally occurring REEs is based on a
 274 modified form of the 1-dimensional vertical-flow equation that accounts for diffusion,
 275 advection, and non-local mass transfer processes (Meile et al., 2001; Smith et al., 2008).
 276 For each individual REE, we have:

$$277 \quad J = \phi D_s \frac{\partial C}{\partial z} - v\phi C + \int_z^0 \alpha(z)\phi(C_z - C_{SW})dz = J_{diff} - J_{adv} + J_{bio} \quad (2)$$

278 where ϕ is porosity (0.37 ± 0.04 ; Smith et al., 2008), C is the concentration of a given
 279 REE in the porewaters (pmol kg^{-1}), t is time (days), z is depth (cm; positive upward), D_s
 280 is the bulk sedimentary diffusion coefficient corrected for tortuosity ($\text{cm}^2 \text{ day}^{-1}$), v is the
 281 seepage velocity (cm day^{-1}), $\alpha(z)$ is the depth-dependent (non-local) mass transfer
 282 coefficient (day^{-1}), C_z is the porewater concentration of a given REE at a given depth z
 283 (pmol kg^{-1}), and C_{SW} is the concentration of a given REE in the water that circulates
 284 through the sediments from the marine endmember (i.e. overlying lagoon water). A
 285 positive total flux (J) represents a release of a given REE from the sediments into the
 286 Indian River Lagoon, whereas a negative total flux indicates that the REE is sequestered
 287 in the sediments of the subterranean estuary (Eq. 2). The model does not identify or
 288 quantify the uptake mechanisms for REEs in the subterranean estuary.

289 The bulk sedimentary diffusion coefficient of a given REE (D_s) is estimated by
 290 dividing the molecular diffusion coefficient (D_{SW} ; Li and Gregory, 1974) for the specific
 291 REE in seawater by the tortuosity factor (θ^2) determined via the Weissberg relationship
 292 (i.e., Burdige, 2006). Only the diffusion coefficients for La and Yb are available, limiting
 293 the quantitative computation of diffusive fluxes to these two REEs. Nonetheless, the

diffusive fluxes for La and Yb were estimated using Fick's First Law modified for sediments (Eq. 3):

$$J_{diff} = -\phi \frac{D_{SW}}{\theta^2} \frac{\partial C}{\partial z} \quad (3)$$

where $\partial C / \partial z$ is the concentration gradient of La or Yb across the sediment-water interface (e.g., Berner, 1980; Burdige, 2006). This gradient is estimated as $\Delta C / \Delta z$ where ΔC is the concentration difference between the shallowest pore water sample and the lagoon waters, and Δz is the depth in the sediments of this pore water sample. The advective flux of a given REE is calculated using an average of the seepage velocities (v) determined at the field site (Smith et al., 2008). The integrated advective and diffusive fluxes for the subterranean estuary are then determined by integrating the fluxes at the individual sites from 0 to 30 m offshore using a trapezoidal approximation method.

The integral term in Eq. 2 represents the flux attributed to non-local mass transfer or irrigation processes, J_{bio} . In the Indian River lagoon system, irrigation processes are primarily biologically induced (i.e., bioirrigation) because of the limited wave and tidal action at the site. The term $\alpha(z)$ is the exponential depth-dependent irrigation component (Boudreau, 1984):

$$\alpha(z) = \alpha_0 e^{\alpha_1 z} \quad (4)$$

where α_0 is the irrigation intensity (day^{-1}) at the sediment-water interface and α_1 is the depth-attenuation coefficient (cm^{-1}). The values for α_0 and α_1 were obtained by averaging the values reported in the appendix of Smith et al. (2008). The bioirrigation flux of REEs for the entire subterranean estuary is also estimated by the trapezoidal approximation in the same manner as the diffusive and advective fluxes.

316 The Smith et al. (2008) transport model is fitted to observed ^{222}Rn porewater data
 317 using seepage velocity (v) and irrigation coefficients (α_0 and α_1) as fitting parameters.
 318 Goodness of fit between the model and data was tested using a χ^2 and sensitivity analysis
 319 was performed using Monte Carlo simulations, where an average of 72% of runs
 320 converged on the same minimum χ^2 . Based on these sensitivity results, 90% confidence
 321 intervals were placed on the fitting parameters to provide an estimate of uncertainty.
 322 This 90% confidence interval yields the uncertainty of the irrigation (or non-local
 323 exchange) rates on the fate and transport of the REEs. Meile et al. (2001) demonstrated
 324 that the values for α_0 and α_1 are not dependent on the geochemical species used to
 325 determine them; therefore, the irrigation coefficients determined by ^{222}Rn data are valid
 326 in determining REE fluxes.

328 4. Results

329 4.1 REE Concentrations

330 Rare earth element concentrations are reported in Table 2 along with shale
 331 normalized Yb/Nd ratios, pH, Cl, Fe, and Mn concentrations for all 77 water samples
 332 from the Indian River Lagoon system. Surface water REE concentrations in the Indian
 333 River Lagoon decrease with increasing distance offshore. For example, the Nd
 334 concentration in waters from 5 m offshore (EGN-5 WC, where WC indicates water
 335 column sample) is 638 pmol kg^{-1} , whereas surface water 250 m offshore (CIRL-39 WC)
 336 has a Nd concentration of 164 pmol kg^{-1} . Nonetheless, the general decrease in REEs with
 337 increasing distance offshore exhibits two local maxima at EGN-17.5 WC and EGN-22.5
 338 WC, where the Nd concentrations are 389 and 354 pmol kg^{-1} , respectively.

Groundwaters of the Indian River Lagoon system exhibit the same trend of decreasing REE concentrations with increasing distance offshore, although considerable scatter exists in the concentrations, especially for groundwater collected from piezometers closest to shore (Table 2). The lowest Nd concentrations are observed in groundwater from CIRL-39 located 250 m offshore, where concentrations range from 82.5 to 242 pmol kg⁻¹. The groundwater Nd concentrations from CIRL-39 contrast with those of groundwater in the EGN-0 profile, where Nd ranges from 417 to 954 pmol kg⁻¹. The highest porewater concentrations of Nd in the Indian River Lagoon subterranean estuary occur at EGN-22.5, where Nd reaches concentrations of up to 2410 pmol kg⁻¹. During our sampling the EGN-22.5 multisampler was located at the front of the freshwater-saltwater interface where mixing of terrestrial SGD and circulating marine SGD occurs (Martin et al., 2007).

Shale normalized REE plots for all surface water and porewater samples collected from the Indian River Lagoon are presented in Fig. 2. All surface waters and porewaters are enriched with HREE relative to LREE ($\text{Yb/Nd}_{\text{PAAS}} > 1$); however, the degree of enrichment varies in the Indian River Lagoon system with HREE enrichment generally decreasing with increasing distance offshore (Fig. 2). Porewater samples from EGN-0 and the onshore beach well have the highest enrichments in HREEs with an average $\text{Yb/Nd}_{\text{PAAS}}$ of 33, whereas those at CIRL-39 have an average $\text{Yb/Nd}_{\text{PAAS}}$ ratio of 2.85. The REE pattern in the lagoon surface waters overlying the transect exhibits similar HREE enrichments to the underlying porewaters ($\text{Yb/Nd}_{\text{PAAS}}$ from 29.3 at EGN-5 to 3.53 at CIRL-39; Table 2). The coastal seawater sample (i.e. Canova Beach) exhibits a comparatively flat shale-normalized REE pattern that most closely resembles the REE

patterns of porewaters from the CIRL-39 multisampler located 250 m offshore as well as Eau Gallie River water (Fig. 2). The Canova Beach REE pattern also lacks a large negative Ce anomaly common to open ocean seawater.

Rare earth element concentrations and shale-normalized REE patterns of sediments from the Indian River Lagoon subterranean estuary are presented in Table 3 and Fig. 3. All sampled sediments are depleted in the REEs relative to PAAS and have slight enrichments in the HREEs relative to the LREEs ($\text{Yb/Nd}_{\text{PAAS}}$ ranging from 1.12 to 1.70). Because the subterranean estuary consists of sandy sediments, the depletion in REEs relative to PAAS in these sediments likely reflects the low REE content in quartz, which acts to dilute the REE contents relative to shale composites (Taylor and McLennan, 1985; Götze et al., 2004). Rare earth element patterns in Indian River Lagoon sediments likely reflect those of other phases such as Fe(III) oxide/oxyhydroxide coatings, clay minerals, and/or possibly Fe sulfide minerals (Tang and Johannesson, 2006; Willis and Johannesson, 2011).

4.2 Porewater REEs

Porewater Nd and Yb concentrations do not appear to exhibit similar trends as Fe and Mn except for piezometers EGN-15 and EGN-30 (Roy et al., 2010; Fig. 4). However, porewater maxima for Nd, Yb, Fe, and Mn increase with depth with increasing distance offshore, ranging from the sediment-water interface at EGN-0 to about 200 cmbsf at EGN-30 (Fig. 4). The subsurface maxima for porewater Nd and Yb concentrations correspond to the approximate positions within the subterranean estuary where terrestrial SGD mixes with marine SGD as indicated by Cl^- concentrations (Fig. 4). The plots of Fe,

Mn, Nd, Yb in the subterranean estuary against salinity, using the Cl^- concentrations as a proxy for salinity, show non-conservative mixing for all four elements (Fig. 5). However, the magnitude and range Fe, Nd, and Yb concentration show a general decrease as salinity increases across the subterranean estuary, whereas Mn shows higher concentrations in brackish water (i.e. Cl^- concentrations between 62 and 300 mmol kg^{-1}) than both fresh and marine porewaters (Fig. 5). Samples with salinities consistent with brackish waters exhibit some of the highest concentrations of all four elements despite the general decreasing trend for Fe, Nd, and Yb. These particular samples are located at piezometers EGN-5, 10, 22.5 and 30 and, in most cases, are found within the mixing zone of terrestrial and marine groundwaters within the subterranean estuary.

In order to test for a correlation between Fe and two REEs (Nd and Yb), the Bonferroni correction method was applied to determine the Spearman's rank correlation coefficient of the 10,000 sample bootstraps at each individual piezometer. This bootstrapping technique is considered more reliable because it does not require the assumption of a theoretical sample distribution. For the majority of the piezometers, there appears to be no significant correlation between Fe and the REEs in the subterranean estuary. However, there are three piezometers (EGN-15, 22.5, and CIRL-39) that have a significant correlation at the 80% level for Fe and Nd. Furthermore, the correlations of Fe and Nd for EGN-15 and 22.5 are significant at the 95% level. Correlations are significant for Fe and Yb at the 80% level for EGN-10 and 17.5 and at the 90% level for EGN-30.

4.3 REE Solution Complexation

REE solution complexation modeling results for Eau Gallie River, Crane Creek, and Canova Beach are shown along with previously published modeling results for terrestrial SGD, total SGD, and the Indian River Lagoon water column (i.e., Johannesson et al., 2011; Fig. 6). Model predictions indicate REEs are predominately complexed with carbonate ions (i.e. LnCO_3^+ and/or $\text{Ln}(\text{CO}_3)_2^-$, where Ln indicates any of the lanthanides) in all waters of the Indian River Lagoon. More specifically, for waters with neutral pH (i.e., Eau Gallie River, Crane Creek, and terrestrial SGD), REEs chiefly occur in solution as carbonato complexes (LnCO_3^+), whereas the dicarbonato complex ($\text{Ln}(\text{CO}_3)_2^-$) dominates in the higher pH waters of the lagoon. Furthermore, REEs are predicted to chiefly occur as carbonato complexes in total SGD, except for Yb and Lu, which primarily occur as dicarbonato complexes. Modeling for the Canova Beach sample suggests that for the LREEs, a substantial portion is in the free metal form (i.e. 20 to 40% occurring as Ln^{3+}) and complexed with sulfate ions (10 to 20% as LnSO_4^+). The model predictions for REEs complexed in the free metal and sulfate forms for Canova Beach waters are much higher than those predicted for open ocean water (i.e., Millero, 1992), which is most likely because Canova Beach waters have a lower pH than that of the open ocean water (7.46 vs. 8.1, respectively).

4.4 SGD Flux Calculations

Diffusive fluxes of all REEs are several orders of magnitudes lower than the calculated advection and bioirrigation fluxes for these elements in Table 4; therefore, REE diffusive fluxes are considered to be negligible compared to advective and bioirrigation fluxes in the Indian River Lagoon. All REEs exhibit positive advective

fluxes from the subterranean estuary into the overlying waters of the Indian River Lagoon, whereas bioirrigation results in a positive flux for the LREEs and MREEs (i.e. La through Tb) and a negative flux for the HREEs (i.e. Dy through Lu). Total REE fluxes indicate that SGD is a source of REEs to the Indian River Lagoon except in the case of the four heaviest REEs, Er, Tm, Yb, and Lu. These HREEs exhibit either no net total SGD fluxes to the overlying water column (i.e., Er, Tm) or negative fluxes (i.e., Yb and Lu; Table 4). The negative SGD fluxes for Yb and Lu indicate that the subterranean estuary acts as a sink for Yb and Lu. These results suggest that bioirrigation plays an important role in sequestering the HREEs within the sediments of the subterranean estuary.

5. Discussion

5.1 SGD REE fluxes

The total SGD flux of REE calculated using the modified form of the 1-dimensional vertical-flow equation (eq. 2) are approximately an order of magnitude lower than those calculated using the simple three box model presented in Johannesson et al. (2011). In the specific case of Nd, the recomputed total SGD flux ($9.4 \pm 1 \text{ mmol day}^{-1}$) is similar to the local, effective river flux for Nd to the lagoon of $12.7 \text{ mmol day}^{-1}$ (Johannesson et al., 2011). The computed SGD fluxes in Table 4 suggest advection and bioirrigation differentially affect the REE fluxes delivered to the water column from the subterranean estuary. Specifically, the advective flux is enriched in HREEs, which may suggest that the advective flux primarily consists of fresh (i.e., terrestrial) groundwater that is commonly highly enriched in the HREEs (Fig. 2). The HREE enriched patterns of terrestrial SGD are likely the result of a number of factors including the adsorption of

REEs onto Fe(III) oxides/oxyhydroxides (Quinn et al. 2004, 2006a,b), which are the predominant mineral coating on aquifer sands within the near shore sediments (Roy et al., 2010, 2011), and aqueous complexation with strong ligands such as the carbonate ion (Fig. 6). The competition for dissolved REEs between surface sites on minerals like Fe(III) oxides/oxyhydroxides and dissolved ligands like the carbonate ion has been shown to fractionate the REEs in natural waters leading to enrichments in the HREEs compared to LREEs (Byrne and Kim, 1990; Koeppenkastrop and DeCarlo, 1992; Quinn et al., 2004). Specifically, the formation of strong aqueous complexes with carbonate ions preferentially stabilizes HREEs in solution, lowering the activity of the free metal ion, e.g., $[\text{Lu}^{3+}]_F$, and thus inhibiting its adsorption onto mineral surface sites compared to LREEs and, to a lesser extent, MREEs (Quinn et al., 2004, 2006a,b; Tang and Johannesson, 2010; and references therein). Hence, the combination of surface and solution complexation processes acting on the REEs can explain the HREE enriched patterns of nearshore SGD as well as the HREE enrichment of the advective REE flux.

Johannesson et al (2011) suggested that REEs are coupled to the Fe cycle in the Indian River Lagoon which is supported by the similar non-conservative mixing behavior across the subterranean estuary (Fig. 5). Previous research has shown that the reduction of Fe (III) oxide/oxyhydroxide coatings on the aquifer sands likely releases previously sorbed and/or coprecipitated LREEs and MREEs into solution (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989, 1992). The bioirrigation component of the total SGD flux, as well as the total SGD flux, exhibits positive fluxes of LREEs and MREEs from the subterranean estuary into the overlying lagoon water column (Table 4). However, the negative bioirrigation and total SGD fluxes computed for HREEs (Yb and Lu) suggest

the sediments of the Indian River Lagoon estuary act as a sink for these REEs (Eq. 2; see also Johannesson et al., 2011). These results differ from earlier porewater studies of the Chesapeake Bay, Virginia, and Buzzard's Bay, Massachusetts, that found positive porewater fluxes to the overlying water column for all the REEs (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; 1992).

Total SGD fluxes of Nd, Gd, and Yb, along with their component advective and bioirrigation fluxes at each piezometer are plotted as a function of distance from shore in Fig. 7. The highest SGD fluxes for Nd and Gd occur at EGN-5, 5 m from the shoreline. As distance increases offshore, SGD fluxes for Nd and Gd dramatically decline by up to a factor of 50 (Fig. 7). All advective SGD fluxes for Nd and Gd are positive, reflecting transport out of the subterranean estuary and into the overlying Indian River Lagoon water column. In contrast, the bioirrigation fluxes for Nd and Gd at 15 m and 22.5 m offshore (multisamplers EGN-15 and EGN-22.5) are negative, indicating the removal of Nd and Gd from solution. The negative bioirrigation fluxes result in negative total SGD fluxes at these two sites (Fig. 7). The bioirrigation flux for Yb is negative (i.e., into the subterranean estuary sediments) for the majority of piezometers sampled, resulting in a negative total SGD flux for Yb.

5.2 REE concentrations and fractionation patterns within the subterranean estuary

Previous work in the Indian River Lagoon has showed that binary mixing of terrestrial SGD with lagoon water that has circulated through the sediments cannot account for these elevated REE concentrations in total SGD (Johannesson et al, 2011). Instead, these observations indicate that porewater-sediment geochemical reactions

occurring in the subterranean estuary are likely responsible for the elevated REE porewater concentrations (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; 1992). Mean REE porewater concentrations from each piezometer are normalized to the average REE content in the five sediment samples from the subterranean estuary (Fig. 8). An outstanding feature of this figure is the overall flattening of the sediment-normalized REE fractionation patterns in the porewaters with increasing distance offshore. The gradual flattening of the sediment-normalized REE patterns of Indian River Lagoon also support the notion that the sediments of the subterranean estuary act as sink for HREEs within the Indian River Lagoon System. An exception to this trend are the porewaters from EGN-22.5, which have sediment normalized LREE and MREE values that are 10-fold higher than porewaters from the closest mutisamplers, EGN-20 and EGN-30, and exhibit shale-normalized Yb/Nd ratios that are more similar to the nearshore porewaters. The substantially higher sediment-normalized LREE and MREE values for porewaters from EGN-22.5 compared to nearby porewaters further indicate that the freshwater-saltwater interface within the subterranean estuary is an important region where LREEs and MREEs are mobilized from the sediments to the porewaters.

The apparent preferential release of LREEs and MREEs at the freshwater-saltwater interface within the Indian River Lagoon subterranean estuary may be due to the increase in salinity occurring across the seepage face. Introduction of higher salinity marine waters to the subterranean estuary may induce desorption of metals, such as the REEs, from mineral surface sites via ion-exchange reactions involving the major cations (Moore, 1999). For example, previous studies demonstrate REEs release from suspended sediments in the mid to high salinity regions of surface estuaries owing to displacement

of REEs from sediment surfaces by Ca and Mg (Sholkovitz, 1993, 1995; Sholkovitz and Szymczak, 2000). Increasing salinity in the subterranean estuary may also act to suppress the adsorption of REE onto mineral surface sites, which is expected to affect LREEs such as Nd more than HREEs like Yb, owing to the formation of stronger aqueous complexes of the HREEs. For example, Tang and Johannesson (2010) report that with an increase in ionic strength, REE adsorption onto Fe(III) oxide/oxyhydroxide-coated quartz sand is suppressed, with LREE and MREE adsorption exhibiting a greater degree of suppression than the HREE. In this sense, increasing concentrations of dissolved solutes like Ca and Mg likely outcompete REEs for adsorption sites on aquifer sediment mineral surfaces leading to salinity-induced desorption of LREEs and MREEs relative to the HREEs in the subterranean estuary.

However, salinity effects alone cannot explain the general flattening of the normalized REE fractionation patterns with increasing distance offshore because they do not fully account for the decrease in HREE concentrations with distance offshore (Fig. 8). Furthermore, Johannesson et al. (2011) note a weak correlation between REE concentrations and salinity in the Indian River Lagoon, which suggests other geochemical processes are also required to produce the REE fractionation patterns. The likelihood that salinity changes are not the primary mechanism influencing REE cycling in the Indian River Lagoon is further supported by the wide range of Nd and Yb concentrations measured in porewaters with similar Cl^- concentrations (Fig. 5).

5.3 Coupled REE and Fe cycling

Johannesson et al. (2011) suggest that geochemical reactions controlling Fe cycling are responsible for REE mobilization in the subterranean estuary of the Indian River Lagoon. The mixing curves provide some evidence that REE cycling is may be coupled to that of Fe (Fig. 5). The distribution of Nd and Yb concentrations in porewaters from each piezometer is shown in Fig. 9 along with the Fe production zone (i.e., via reductive dissolution of Fe(III) oxides/oxyhydroxides) and the Fe sink zone (i.e., Fe(II) removal by adsorption and sulfide mineral precipitation) in the subterranean estuary as conceptualized by Roy et al. (2011). The Fe production and Fe removal zones were delineated based on a reactive transport model for Fe in the subterranean estuary assuming all groundwater flow at each piezometer is vertical and upward (Roy et al., 2011). As groundwater flows upwards through the subterranean estuary, it traverses through an anoxic zone where Fe(III) oxides/oxyhydroxides within the sediments are reduced releasing Fe(II) to the porewaters (Fe production zone), followed by an intermediate zone where some of the dissolved Fe(II) is subsequently re-adsorbed onto remaining Fe(III) oxides/oxyhydroxides in the sediments (Fe sink zone), and finally through sediments near the sediment-water interface where DOC- and SO_4^{2-} -rich circulating lagoon water drives sulfate reduction and subsequent precipitation of FeS minerals (Fe-sulfide zone; Roy et al., 2011). The reactive transport model developed by Roy et al. (2011) does a relatively good job of reproducing the dissolved Fe concentrations in the subterranean estuary. Furthermore, bioirrigation transports oxygenated lagoon waters into the subterranean estuary sediments, and this oxygen can locally influence the Fe cycle by oxidizing Fe(II) and S(-II), and ultimately drive Fe(III) oxide/oxyhydroxide precipitation and FeS dissolution, respectively.

The superimposition of the results of the Fe reactive transport model on the
 porewater Nd and Yb profiles for the Indian River Lagoon subterranean estuary further
 supports the notion that REE cycling in the subterranean estuary is likely coupled to the
 Fe cycle (Fig. 9). The concentration maxima for Nd and Yb at multisamplers EGN-15
 through EGN-30 are located within the Fe production zone, suggesting release of sorbed
 or co-precipitated REEs as a result of the reductive dissolution of Fe(III)
 oxide/oxyhydroxide minerals within the sediment (Fig. 9; Johannesson et al., 2011; Roy
 et al., 2011). As mentioned previous, there is some statistical evidence that Nd and Yb are
 significantly correlated to Fe in a few of the wells further offshore. The concentrations of
 Nd and Yb decrease in the Fe sink zone where the REEs are likely re-adsorbed onto
 Fe(III) oxides/oxyhydroxides within the sediments. In the Fe-sulfide (FeS) zone, Nd and
 Yb porewater concentrations are relatively constant, suggesting that dissolved REEs are
 not affected by precipitation of Fe-S minerals. Nearer to shore, the porewater
 concentration maxima for Nd and Yb (i.e., EGN-0, 5, and 10) occur near the sediment-
 water interface, and within the FeS zone (Fig. 9). Because Fe is not being released by
 reductive dissolution of Fe(III) oxides/oxyhydroxides in the Fe-sulfide zone, the increase
 in REE concentrations in nearshore porewaters from the sediment-water interface must
 reflect a different source or process, such as the horizontal inflow of HREE-enriched
 terrestrial SGD.

The modern Fe cycle in the Indian River Lagoon subterranean estuary is thought
 to be a consequence of glacial-interglacial changes in sea level (Roy et al., 2010, 2011).
 Specifically, during the previous sea-level low stand that characterized the Last Glacial
 Maximum (~ 18 - 22 kyr bp; Bradley, 1999), the subterranean estuary was located further

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4 591 offshore, and under these conditions the quartz sands that make up the current
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6 592 subterranean estuary were subaerially exposed, which allowed Fe(III)
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9 593 oxides/oxyhydroxides precipitates to form, coating these sands and leading to their
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11 594 orange color. As the glaciers receded, these sediments were flooded by the rising sea,
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14 595 which facilitated the reduction of the Fe(III) oxides/oxyhydroxides coatings as labile
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16 596 dissolved organic carbon of marine origin was circulated through the sands (Roy et al.,
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19 597 2010; Dorsett et al., 2011). The dissolved Fe(II) produced by reductive dissolution of
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21 598 Fe(III) oxides/oxyhydroxides in the production zone of the subterranean estuary is
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24 599 subsequently transported upward by SGD into the sulfate reduction zone and precipitated
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26 600 as Fe-sulfide minerals forming a black layer within the sediments (Hartl, 2006; Roy et al.,
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29 601 2010; 2011). Lastly, bioirrigation circulates the overlying lagoon waters containing
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31 602 dissolved oxygen through these sediments, which causes the dissolution of the FeS
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36 604 Rare earth elements were likely adsorbed onto the Fe (III) oxide/hydroxide sand
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46 608 compared to HREEs in the presence of strong complexing ligands such as carbonate ions
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48 609 and/or organic ligands (Quinn et al., 2004; 2006a,b; Tang and Johannesson, 2005), the
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55 612 prevailed, reductive dissolution of the orange, Fe(III) oxide/oxyhydroxide coated
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solution. Such a scenario is consistent with the gradually flattening of the REE patterns
 with distance offshore in the Indian River Lagoon (Fig. 2), as well as in previous studies
 that noted a preferential release of LREE and MREE during estuarine sedimentary
 diagenesis (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; 1992). Because the
 pH of Indian River Lagoon porewaters is less than 8, the Fe(III) oxide/oxyhydroxide
 coatings on aquifer sediments will exhibit a weak positive surface charge (Dzombak and
 Morel, 1990). Consequently, Fe(III) oxides/oxyhydroxides remaining in the subterranean
 estuary are expected to sequester the HREEs, which chiefly occur in the porewaters as
 negatively charged HREE dicarbonato complexes, whereas the LREEs and MREEs,
 which occur as positively charged carbonato complexes, will remain in solution and be
 transported with flowing groundwater (Kochinsky and Hein, 2003; Tang and
 Johannesson, 2005; Johannesson et al., 2011). Adsorption of HREE dicarbonato
 complexes onto the surfaces of the remaining Fe(III) oxide/oxyhydroxide coatings is
 consistent with the computed negative SGD fluxes for the HREEs (Table 4; Fig. 7).

As Fe(II) precipitates with sulfide in the subterranean estuary, the REEs appear to
 remain in solution and are transported into the overlying water column of the Indian
 River Lagoon (Johannesson et al, 2011). No statistically significant relationship exists
 between porewater REE and S (-II) concentrations ($R^2 = 0.021$ and 0.033 for Nd and Yb,
 respectively). Furthermore, the constant Nd and Yb concentration in the FeS zone of the
 subterranean estuary suggests that the REEs are decoupled from the Fe cycle during Fe-
 sulfide precipitation (Fig. 9). If a relationship exists between REEs and dissolved sulfide,
 a decrease in the REE concentrations upward in the FeS zone should be found. Naveau et
 al. (2006) demonstrated that Eu(III) adsorbs onto air-oxidized pyrite surfaces but not

fresh, unoxidized pyrite surfaces. More recently, Morgan et al. (2012) demonstrated in a laboratory experiment that there is little interaction between the REEs and FeS minerals. These observations suggest that Fe-S minerals exposed to the oxygenated surface waters of Indian River Lagoon could potentially sequester REEs near the sediment-water interface. Additional, higher resolution sampling of porewaters from the sediment-water interface may provide greater insights into the possible role that Fe-S minerals play in REE cycling in the Indian River Lagoon.

5.4 Implications for the Global SGD Flux of Neodymium

Submarine groundwater discharge is an important source of LREE and MREE to the coastal waters of the Indian River Lagoon (Table 4). As such, SGD may represent an important source of REEs to the oceans in other regions of the globe (e.g., Johannesson and Burdige, 2007; Kim and Kim, 2011, 2014). The Canova Beach sample also suggests that SGD from the Indian River Lagoon may impact these coastal waters as they have REE concentrations and fractionation patterns that more closely resemble those of the Indian River Lagoon waters than open-ocean seawater. Nonetheless, it is important to note that the Indian River Lagoon is not representative of all subterranean estuaries. Like surface water estuaries, tidal variations, geology, and climate can influence the geochemical reactions associated with the subterranean estuary. The Indian River Lagoon is microtidal and its subterranean estuary remains submerged, which promotes the reductive dissolution of Fe (III) oxides/oxyhydroxides in sediments and subsequent release of REEs to the porewater (Roy et al., 2010, 2011). Kim and Kim (2011) note that groundwaters discharging to the coastal waters of Jeju Island, South Korea, display

MREE-enriched fractionation patterns, which contrasts with the HREE enriched fractionation patterns of Indian River Lagoon groundwaters. The computed Nd-SGD flux to the coastal water of Jeju Island is $120 \pm 60 \text{ mol day}^{-1}$, which is five orders of magnitude greater than the SGD Nd flux we estimate for the Indian River Lagoon (i.e., $9.4 \pm 1 \text{ mmol day}^{-1}$).

To estimate the potential rate at which REEs may be released to porewaters by reductive dissolution of the Fe(III) oxide/oxyhydroxide coatings on quartz sands in Indian River Lagoon sediments, we approximated the amount of Nd bound to these Fe(III) oxide/oxyhydroxide coatings, and multiplied this value by the Fe production rate estimated for these sediments of $1.99 \text{ } \mu\text{mol cm}^{-2} \text{ yr}^{-1}$, which assumes a formula of $\text{Fe}(\text{OH})_3$ for Fe(III) oxides/oxyhydroxides in the sediments (Roy et al., 2011). The average Fe(III) oxide/oxyhydroxide content of the orange sediments from the Indian River Lagoon is estimated, from leaching experiments, to be 0.2 wt.%, or $1.87 \times 10^4 \text{ } \mu\text{mol Fe kg}^{-1}$ of sediment (Roy et al., 2010). The Nd bound to Fe(III) oxide/oxyhydroxides (i.e., $8.01 \pm 4.1 \text{ } \mu\text{mol Nd kg}^{-1}$ sediment) is calculated by subtracting the average Nd content of the black sediment samples ($6.16 \pm 2.7 \text{ } \mu\text{mol kg}^{-1}$; EGN-22.5 2-4 cmbsf and CIRL-39 5-7 cmbsf), which are assumed to have no Fe(III) oxide/oxyhydroxides present (Roy et al., 2010, 2011), from the average Nd content of the orange and grey sediment samples ($14.2 \pm 3.1 \text{ } \mu\text{mol kg}^{-1}$; EGN-0 205-207 cmbsf, EGN 22.5 50-52 cmbsf, and EGN-22.5 185-187). These simple calculations indicate that the mole ratio of Nd to Fe in orange sediments from the Indian River Lagoon is on the order of $4.3(\pm 2.2) \times 10^{-4}$, which when multiplied by the Fe production rate, suggests a Nd release rate during reductive dissolution of Fe(III) oxides/oxyhydroxides of $\sim 0.9 \pm 0.4$

nmol Nd cm⁻² yr⁻¹. Although, there are no published Nd release rates for the highly permeable sediments of Jeju Island, these sediments are composed of easily-weathered basalt fragments that are expected to contain higher REE contents than quartz, which is the dominant mineral in Indian River Lagoon sediments, and the Fe(III) oxides/oxyhydroxides that coat the quartz (e.g. Price et al., 1991; Götze et al., 2004; Leybourne and Johannesson, 2008; Kim and Kim, 2011, 2014). Because of the differences in aquifer mineralogy and calculated Nd SGD fluxes, it seems likely that the Nd release rate for the Jeju Island sediments exceeds the Nd release computed here for Fe reduction within Indian River Lagoon sediments.

6. Conclusion

We assessed the SGD fluxes of REEs to coastal waters of the Indian River Lagoon by modeling advective transport and bioirrigation in sediments of the underlying subterranean estuary. An advective flux composed of HREE-enriched terrestrial SGD was identified that discharges near the shoreline (within 10 m of the shore), whereas a bioirrigation flux composed of MREE-enriched marine SGD occurs within the subterranean estuary starting ~15m offshore. The marine SGD source of REEs driven by bioirrigation originates from the reductive dissolution of Fe (III) oxide/hydroxides and subsequent release of sorbed or coprecipitated REEs. LREEs and MREEs released to the porewaters by reduction of Fe(III) oxides/oxyhydroxides in the subterranean estuary form positively charged, carbonate complexes (LnCO₃⁺) in solution that are transported to the overlying lagoon waters. However, HREEs released by this process occur chiefly from negatively charged dicarbonate complexes (Ln(CO₃)₂⁻) in porewaters, which readily

adsorb to surface sites on remaining Fe (III) oxides/oxyhydroxides within the
subterranean estuary sediments.

Our Nd-SGD flux to the Indian River Lagoon is equivalent to the effective local
river flux of Nd to the lagoon, 9.4 ± 1 mmol day⁻¹. The several order of magnitude
differences between the Nd-SGD flux from the Indian River Lagoon in Florida, and Jeju
Island, South Korea, may reflect differences in aquifer mineralogy and Nd release rates,
and demonstrates the need for additional studies of REE-SGD fluxes from subterranean
estuaries with differing sediment characteristics (e.g. mineralogy) to constrain the global
Nd-SGD flux. In addition to studying the REE cycling and fluxes globally, the Nd
isotopic composition of coastal groundwaters is needed to understand the total impact
that submarine groundwater discharge has on Nd in the oceans and paleoceanographic
investigations.

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Table 1. Geochemical composition of the waters from the Indian River Lagoon system used in the REE complexation modeling. Major solutes are reported in mmol kg⁻¹ and ionic strength (*I*) is reported in mol kg⁻¹.

	pH	Ca	Mg	Na	K	Cl	SO ₄	Alk ^b	<i>I</i>
Lagoon Water Column ^a	8.41	8.68	–	321	6.87	338	17.7	2.61	0.402
Terrestrial SGD ^a	7.13	1.72	0.70	10.8	0.20	4.67	0.50	2.90	0.014
Total SGD ^a	7.19	10.6	–	200	3.45	335	11.7	3.87	0.266
Eau Gallie River	7.10	3.24	0.68	5.42	0.08	7.74	0.61	3.62	0.017
Crane Creek	7.12	3.91	0.99	6.27	0.09	9.10	0.71	4.44	0.021
Canova Beach	7.46	7.03	64.0	514	10.5	521	31.1	2.08	0.728

^aMean values, see Table 2 in Johannesson et al. (2011) for details

^bReported as HCO₃⁻.

Table 2. REE concentrations (pmol kg^{-1}) presented for all surface and groundwaters in the Indian River Lagoon System along with pH, Cl (mmol kg^{-1}), Mn and Fe ($\mu\text{mol kg}^{-1}$). WC indicates the water column samples collected above each piezometer. For each piezometer, the porewater samples are presented as a function of depth (cmbsf) into the underlying sediment.

	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)PAAS	pH	Cl	Fe ^a	Mn ^a
Beach Well		1120	2380	309	1310	301	101	514	104	938	327	1760	448	4950	1260	51.8				
EGN 0 2	15	167	428	49.8	417	83	22.1	117	21.4	242	101	691	197	2220	533	72.8	6.78	1.74	0.027	0.28
EGN 0 3	25	167	409	51.8	437	110	30.5	149	25.9	247	83.2	456	117	1090	222	34.1	6.76	1.73		0.18
EGN 0 4	35	578	1230	162	785	182	54.3	217	35.6	264	84.4	485	122	1130	220	19.8	6.75	1.79	0.23	0.13
EGN 0 5	55	791	1640	215	954	213	62.0	234	40.5	301	90.8	534	142	1370	272	19.6	7.04	1.75	0.009	0.00
EGN 0 6	75	592	1220	156	674	138	40.7	147	27.8	195	54.1	343	97.2	890	164	18.1	7.08	1.79		0.06
EGN 0 8	115	391	830	104	568	112	25.6	117	21.5	155	40.5	314	80.8	692	123	16.7	7.22	1.76	0.11	0.10
EGN 5 WC		559	1050	151	638	121	34.8	127	23.8	181	75.9	523	140	1390	317	29.8	8.63	242	0.38	0.11
EGN 5 1	7	1280	2690	340	1420	278	74	290	48.8	325	101	566	136	1310	288	12.6	8.27	265	2.38	0.22
EGN 5 2	15	432	872	111	496	99.3	34.5	110	21.0	128	44.2	294	77.3	708	151	19.6	7.32	196	1.04	1.42
EGN 5 3	25	448	892	113	500	98.6	32.7	98.4	20.7	97.8	27.2	166	40.9	331	61.3	9.08	7.11	62	1.50	1.50
EGN 5 4	35	640	1300	159	695	123	36.0	107	16.9	94.6	17.0	116	26.2	217	38.8	4.28	7.25	16.7	2.21	1.05
EGN 5 5	55	229	435	54.4	262	55	19.8	63.8	10.1	76.4	20.2	155	39.1	343	66.5	17.9	7.26	59.0	6.61	0.92
EGN 5 7	95	214	404	51.1	248	48	15.6	50.2	7.47	54.6	11.9	90.8	20.3	155	25.7	8.56	7.39	3.70	1.13	0.59
EGN 5 8	115	179	335	41.0	214	40	12.9	39.2	5.80	47.9	10.9	86.2	19.5	150	23.7	9.57	7.31	3.31	1.90	0.55

^aFe and Mn data taken from Roy et al. (2010)

Table 2. con't.

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)PAAS	pH	Cl	Fe	Mn
EGN 10 WC		155	369	31.1	296	49.9	8.54	57.9	11	95.5	22.6	102	21.3	109	45.7	8.58	8.58	344		0.02
EGN 10 1	7	678	1380	177	747	135	36.3	123	17.9	112	22.0	101	22.6	197	42.7	3.62	7.17	230	1.22	0.96
EGN 10 2	15	171	367	32.7	277	45.7	8.49	70.2	9.02	99.8	16.4	82.1	16.5	170	31.6	8.41	7.13	132	1.96	0.98
EGN 10 3	25	121	275	24.7	231	29.1	5.87	37	5.45	64.5	11.3	50.1	8.44	95.4	17.9	5.66	7.34	13.3	2.18	0.71
EGN 10 4	35	490	1010	125	550	102	28.3	86.2	11.9	90.5	14.9	63.6	15.9	143	28.5	3.56	7.32	8.07	3.78	0.60
EGN 10 5	55	141	312	26.6	227	35	3.73	41.1	8.13	74.6	14.8	55.8	12.2	120	18.8	7.23	7.31	4.52	0.84	0.55
EGN 10 6	75	319	637	80.3	368	65.5	19.0	56.5	7.93	59.3	10.2	54.3	14.4	123	22.6	4.57	7.29	4.06	1.00	0.45
EGN 10 7	95	318	647	80.1	352	61.8	16.7	49.9	6.47	44.5	6.84	38.3	10.3	91.5	16.7	3.56	7.29	4.02	0.82	0.43
EGN 10 8	115	137	307	27.5	217	28.1	3	30.2	5.36	47.9	9.06	42.7	9.71	84.4	14.5	5.32	7.38	4.03	0.24	0.44
EGN 15 WC		300	574	74.5	362	71.4	21.0	91.0	17.0	114	30.5	131	28.3	239	52.7	9.06	8.47	354	0.18	0.12
EGN 15 1	7	226	417	53.2	275	52.8	18.3	70.8	13.7	97.7	27.1	112	24.8	205	44.5	10.2	7.59	257	0.97	0.89
EGN 15 2	15	217	402	51.3	255	50.2	18.4	65.1	13.4	95.4	27.3	110	23.9	190	40.2	10.2	7.24	314	0.96	1.03
EGN 15 3	25	206	369	84.5	314	46.6	15.4	57.7	12.6	106	32.3	126	25.7	184	34.5	8.01	7.2	107	2.92	1.19
EGN 15 4	35	216	396	51.5	262	51.9	18.4	61.7	14.3	122	36.7	142	28.6	202	35.9	10.5	7.25	47.9	3.52	1.11
EGN 15 5	55	486	963	126	565	118	35.4	117	22.9	166	40.4	145	28.8	201	35.6	4.87	7.27	39.1	5.14	1.10
EGN 15 6	75	583	1130	148	652	134	37.6	132	24.2	178	42.5	148	31.5	219	38.1	4.60	7.24	37.7	5.93	1.22
EGN 15 7	95	373	735	96.1	452	84.3	26.1	88.4	17.4	151	42.5	152	30.4	226	41.4	6.86	7.44	5.71	2.91	0.56
EGN 15 8	115	687	1380	183	862	186	49.6	163	30.1	253	62.0	222	48.4	364	63.6	5.79	7.39	5.91	6.51	0.58

Table 2. con't.

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)PAAS	pH	Cl	Fe	Mn
EGN 17.5 WC		345	694	80.5	389	70.7	18.8	84.1	13.0	95.3	23.1	107	21.6	194	41.1	6.86	8.57	349		0.06
EGN 17.5 1	7	360	724	81.8	414	74.9	21.2	89.0	14.0	99.7	21.9	89.7	17.1	147	29.8	4.87	7.85	355	0.82	0.47
EGN 17.5 2	15	355	706	104	435	74.5	19.7	85.5	13.1	90.3	19.8	77.5	14.1	124	24.4	3.91	7.45	344	1.62	0.80
EGN 17.5 3	25	410	774	90.2	447	83.7	22.0	103.9	15.6	114	26.7	103	17.1	141	26.3	4.33	7.4	265	0.59	0.81
EGN 17.5 4	35	268	516	56.4	298	56.5	15.8	75.9	13.2	99.4	23.7	88.6	13.8	106	18.7	4.89	7.34	227	0.19	0.72
EGN 17.5 5	55	437	845	98.0	462	93.5	27.7	123	21.8	161	39.0	134	21.9	148	23.4	4.40	7.3	153	1.57	0.95
EGN 17.5 6	75	367	708	79.6	389	72.3	18.5	79.1	13.1	97.9	21.0	74.3	12.2	87.9	13.3	3.10	7.3	77.5	9.08	0.82
EGN 17.5 7	95	176	343	37.0	215	36.1	10.1	43.9	8.18	64.2	14.7	53.6	8.54	62.4	10.1	3.98	7.42	9.19	13.0	0.54
EGN 17.5 8	115	608	1240	165	731	139	36.6	144	26.3	164	38.9	120	18.4	105	17.8	1.97	7.48	7.89	9.71	0.53
EGN 20 WC		157	294	33.2	191	33.1	13.0	50.1	7.48	62.9	15.1	65.2	10.8	101	20.8	7.29	8.13	370		0.13
EGN 20 1	7	238	436	51.3	268	50.8	16.1	70.6	11.0	88.6	21.5	79.7	13.3	105	18.3	5.38	7.27	330	0.84	0.71
EGN 20 2	15	213	389	45.3	245	46.3	15.0	69.2	11.5	99.1	25.5	97.6	15.2	120	21.0	6.69	7.26	330	0.91	0.61
EGN 20 3	25	180	321	35.9	212	38.1	14.8	63.5	11.2	96.2	24.9	95.9	15.7	123	21.3	7.97	7.23	215	2.38	0.84
EGN 20 4	35	254	463	55.2	286	55.9	18.4	73.0	12.5	105	26.0	99.4	17.0	131	21.4	6.26	7.2	155	1.89	0.83
EGN 20 5	55	181	329	33.3	214	37.8	14.6	66.0	12.5	123	34.2	137	26.7	198	32.3	12.7	7.22	230	2.17	0.77
EGN 20 6	75	259	462	55.6	298	58.5	18.8	75.5	13.3	125	32.8	130	25.1	172	25.2	7.89	7.37	121	12.8	0.92
EGN 20 7	95	138	227	25.0	164	29.8	10.0	42.5	7.78	79.7	21.4	89.1	19.1	132	19.7	11.0	7.31	55.6	18.5	0.84
EGN 20 8	115	126	222	23.1	155	21.2	7.04	27.3	4.29	41.8	9.3	37.7	8.2	60.8	9.72	5.39	7.28	8.23	21.2	0.56

Table 2. con't.

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)PAAS	pH	Cl	Fe	Mn
EGN 22.5 WC		245	520	54.3	354	61.2	8.01	60	12	139	27.7	143	18.9	196	35.1	7.59	8.31	334	0.056	0.11
EGN 22.5 3	6	141	289	27.5	258	50.5	5.6	45.9	8.69	73.2	14.4	64.7	10.2	93.4	12.3	4.96	7.43	352	1.57	0.94
EGN 22.5 5	66	367	523	55.4	401	69.6	15.6	119	14.6	143	37.4	150	22.8	168	28.7	5.73	7.23	273	13.4	1.17
EGN22.5 6	106	677	1430	171	773	131	24.1	139	17.5	99.1	26.7	88.6	16.8	104	15.3	1.85	7.11	192	286	2.90
EGN 22.5 7	146	617	1260	155	715	116	28.4	122	16.3	112	32.0	135	22.3	188	24.8	3.60	7.09	222	262	2.60
EGN 22.5 8	186	1680	2880	362	2410	481	39.2	464	87	961	354	1700	361	2490	434	14.2	7.15	240	196	2.46
EGN 30 WC		141	228	16.6	127	20.0		36.8	6.59	48.5	13.2	48.0	9.48	71.7	11.7	7.76	8.34	363	0.054	0.10
EGN 30 1	10	92.5	161	19.9	116	21.4		31.0	5.65	39.4	11.0	38.5	8.20	61.0	10.0	7.20	7.82	353	1.13	0.39
EGN 30 2	30	104	185	19.9	118	16.2		29.9	5.74	41.8	7.17	40.5	8.49	57.7	9.02	6.72	7.98	324	2.33	0.58
EGN 30 3	50	125	187	22.1	120	17.7		35.9	6.69	55.1	12.8	68.9	9.86	102	17.1	11.7	7.78	323	6.16	0.64
EGN 30 6	150	248	427	31.5	239	33.3		55.3	10.6	97.5	28.4	169	30.4	258	38.2	14.8	7.77	300	226	2.63
EGN 30 7	190	322	550	55.6	327	58.3		81.7	13.0	89.8	26.7	98.6	20.6	143	20.8	6.00	7.23	297	235	2.61
EGN 30 8	230	101	182	19.2	110	22.5		27.4	6.64	68.9	19.6	95.8	17.5	115	21.6	14.3	7.39	295	232	2.64

Table 2. con't.

		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)PAAS	pH	Cl	Fe	Mn
	CIRL 39 WC	143	256	24.4	164	27.2		44.9	8.0	51.4	7.6	38.1	7.1	42.2	8.3	3.53	8.26	391		0.07
	CIRL 39 1	10	151	299	27.9	182	29.9	47.8	8.0	52.7	12.2	34.5	6.6	36.0	7.2	2.71	7.66	387	0.49	0.57
	CIRL 39 2	20	153	293	27.4	179	29.8	48.1	8.0	50.3	11.9	31.4	6.2	33.1	6.9	2.53	7.49	382	0.12	0.38
	CIRL 39 3	30	199	417	40.1	221	39.4	56.0	8.8	55.6	8.5	36.3	6.1	37.6	7.4	2.33	7.65	385	0.38	0.34
	CIRL 39 4	40	175	362	35.2	198	35.2	48.8	8.0	45.8	11.4	29.2	5.5	33.6	6.8	2.32	7.51	385	0.23	0.37
	CIRL 39 5	60	127	236	16.3	82.5	12.6	17.3	2.1	10.5	1.81	5.37	0.80	5.31	0.87	0.882	7.23	334		0.34
	CIRL 39 6	110	135	280	25.2	154	24.4	32.9	6.3	45.7	12.5	45.0	8.3	56.4	10.6	5.03	7.26	332	0.034	0.24
	CIRL 39 7	140	129	259	23.7	143	24.2	29.2	5.8	33.1	10.1	29.2	6.2	41.3	7.7	3.96	7.4	336	0.020	0.23
	CIRL 39 8	180	163	379	42.1	242	44.3	59.1	7.0	69.9	16.4	45.0	7.2	41.0	6.8	2.32	7.44	336		0.19
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd)PAAS	pH	Cl	Fe	Mn
	Eau Gallie River	320	742	117	627	180	82.5	268	39.7	250	59.7	201	35	291	60.3	6.35	7.1			
	Crane Creek	57.3	152	19.8	205	69.4	44.4	124	19.7	140	41.8	140	28.6	254	53.9	17.0	7.12			
	Canova Beach	1310	3320	353	1560	333	75.5	374	62.1	296.0	70.2	212	30.6	189	33.2	1.66	7.46			
	Mean Seawater ^b	25.2	7.4	3.5	17.9	3.6	0.91	5.4	0.74	6.04	1.5	5.52	0.76	5.4	0.91	4.1				

^bMean seawater concentrations 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), Nozaki and Alibo (2003).

Table 3. The REE contents reported in $\mu\text{mol kg}^{-1}$ of five sediments samples from the Indian River Lagoon subterranean estuary.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd) _{PAAS}
EGN-0 205-207 cmbsf	8.65	17.9	2.36	11.3	1.86	0.46	1.84	0.31	2.15	0.45	1.18	0.25	1.36	0.31	1.66
EGN 22.5 2-4 cmbsf	6.25	12.8	1.67	8.07	1.32	0.32	1.17	0.21	1.18	0.23	0.68	0.11	0.66	0.12	1.12
EGN 22.5 50-52 cmbsf	9.92	20.2	2.62	11.9	2.22	0.46	2.02	0.45	2.88	0.65	1.61	0.27	1.27	0.21	1.46
EGN 22.5 185-187 cmbsf	14.5	30.1	3.88	19.4	2.59	0.62	2.99	0.45	3.06	0.67	1.95	0.33	2.40	0.41	1.70
CIRL 39 5-7 cmbsf	4.92	4.80	4.79	4.25	5.70	4.92	4.30	6.34	5.79	5.86	4.92	4.81	3.05	2.92	1.50

Table 4. Computed SGD fluxes for REEs within the Indian River Lagoon system based on evaluation of equation 2.2. The total SGD flux for each REE (J_{total}) is composed of the computed advective flux ($-J_{\text{adv}}$) and the REE flux to the overlying water column from bioirrigation processes (J_{bio}). J_{diff} refers to the diffusive flux, which is considered negligible. The advective component ($-J_{\text{adv}}$) reflects the terrestrial SGD that discharges nearshore. The negative sign is used so that a positive $-J_{\text{adv}}$ represents REE transport out of the subterranean estuary to the overlying surface estuary. All fluxes are in units of mmol day^{-1} .

	J_{diff}	$-J_{\text{adv}}$	J_{bio}	$J_{\text{total}}^{\text{a}}$
La	0.0050	5.5±0.6	3.0±0.9	8.5±1
Ce	0.011	11±1	6.8±2	18±2
Pr	0.0014	1.4±0.2	0.76±0.3	2.2±0.3
Nd	0.0051	6.2±0.7	3.2±1	9.4±1
Sm	0.0010	1.2±0.1	0.72±0.2	1.9±0.2
Eu	0.00031	0.32±0.04	0.24±0.05	0.56±0.06
Gd	0.0010	1.3±0.1	0.76±0.2	2.0±0.2
Tb	0.00013	0.21±0.02	0.090±0.03	0.30±0.04
Dy	0.00038	1.5±0.2	-0.25±0.2	1.2±0.3
Ho	0.000038	0.43±0.05	-0.20±0.06	0.23±0.08
Er	-0.00032	2.3±0.3	-2.2±0.3	0.09±0.4
Tm	-0.000077	0.55±0.07	-0.55±0.08	-0.01±0.1
Yb	-0.00077	5.2±0.6	-6.4±0.9	-1.2±1
Lu	-0.00033	1.1±0.1	-1.6±0.2	-0.51±0.3

^a $J_{\text{total}} = -J_{\text{adv}} + J_{\text{bio}}$

Fig. 1 Panel A is the map of the Indian River Lagoon System on the Atlantic Coast of Florida, USA (Martin et al., 2007). The red circle is the approximate position of the coastal seawater sample taken at Canova Beach. Panel B shows the specific portion of the lagoon where the Eau Gallie North (EGN) transect is located and the CIRL-39 piezometer which is 250 m offshore from the mainland. The red circles represent the locations for the samples taken from Eau Gallie River and Crane Creek. Panel C shows the EGN transect and the locations of each piezometer represented by a light blue circle. The piezometers are labeled as EGN-X in which X refers the distance in meters from the shoreline (e.g. EGN-15 is located 15m from the mainland).

Fig. 2 Shale-normalized REE patterns for groundwaters and surface waters of the Indian River Lagoon. The groundwater and overlying lagoon waters are presented for each piezometer in a-I, whereas panel j shows the REE patterns for the two local streams (Eau Gallie River and Crane Creek), Florida Coastal seawater (Canova Beach) and mean, open ocean seawater. All water samples are normalized to Post-Archean Australian Shale (PAAS; Nance and Taylor, 1976). In addition, the mean shale-normalized Yb/Nd ratio for waters from each piezometer are included in each panel. Mean open ocean seawater was computed from data presented 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).

Fig. 3 Shale-normalized REE patterns (normalized to PAAS) for five sediment samples from the Indian River Lagoon subtterranean estuary.

Fig. 4 Depth profiles for Fe, Mn, Nd, and Yb concentrations in porewaters at each piezometer along the Eau Gallie North transect within the Indian River Lagoon subtterranean estuary. Dashed lines represent the sediment-water interface. Points above the dashed lines represent the overlying lagoon water concentrations of Fe, Nd, and Yb at each piezometer. Orange line represents fresh-brackish transition as determined by the Cl^- concentration (i.e., 62 mmol kg^{-1}) and the green line represents the brackish-marine transition ($\text{Cl}^- > 300 \text{ mmol kg}^{-1}$; Roy et al., 2010). The Mn points at EGN-20 represent 10x the measured concentrations and at EGN-22.5 and 30 100x the measured concentrations. Fe and Mn data is from Roy et al. (2010).

Fig. 5 Concentrations of (a) Nd, (b) Yb, (c) Fe, and (d) Mn plotted against Cl^- concentrations (proxy for salinity) across the Indian River Lagoon subterranean estuary. Fresh groundwater (GW) are samples with Cl^- concentrations $< 62 \text{ mmol kg}^{-1}$, brackish GW represents samples with Cl^- concentrations between 62 and 300 mmol kg^{-1} , and marine GW is defined as $\text{Cl}^- > 300 \text{ mmol kg}^{-1}$ (Roy et al., 2010). The overlying lagoon waters (Water Column) are also plotted for comparison. The break on the Fe axis in panel (d) represents a range in concentrations from 30 to $180 \mu\text{mol/kg}$.

Fig 6. Results for the REE complexation modeling for (a) Terrestrial SGD, (b) Total SGD, (c) the Indian River Lagoon water column, (d) Eau Gallie River, (e) Crane Creek, and (f) Canova Beach. Data for a-c are from Johannesson et al. (2011).

Fig. 7. Computed total, advective, and bioirrigation SGD fluxes for Nd, Gd, and Yb for each piezometer plotted versus distance offshore. Positive fluxes indicate discharge to the overlying surface estuary, whereas negative fluxes reflect losses to the subterranean estuary sediments.

Fig. 8 Rare earth element fractionation patterns for mean porewaters from each piezometer normalized to the average REE contents in sediments of the Indian River Lagoon subterranean estuary.

Fig. 9 Distribution of log [Nd] and [Yb] concentrations in porewaters of the Indian River Lagoon subterranean estuary superimposed with the conceptual Fe production and sink zones of Roy et al. (2011). The log [REE] scales for all piezometers is the same as EGN-0 except for CIRL-39. The orange dashed line represents the approximate upper boundary of the Fe production zone, which is defined by the Fe concentration maxima in each profile (Roy et al., 2011). The black dashed line represents the approximate upper boundary of the Fe sink zone defined by the bottom of the FeS –rich black sediment layer in each piezometer. The red dashed line refers to the 300 mmol kg⁻¹ Cl⁻ concentration line that represents the seepage face as defined by Roy et al. (2010).