



# The Mobility of Rare Earth Elements and Redox Sensitive Elements in the Groundwater/Seawater Mixing Zone of a Shallow Coastal Aquifer

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(Received in final form: 12 November 2003)

**Abstract.** The concentrations of Rare Earth Elements (REE) and Redox Sensitive Elements (RSE) were measured in groundwaters along a transect of the forest-marsh interface of a surficial aquifer system in North Inlet, SC. The well transect extended from a forest recharge area across the marsh and tidal creek to a tidal recharge area of beach ridge. The concentrations of the RSE (Fe, Mn, and U) were consistent with reducing conditions through the transect. Fe was present at concentrations ranging from a few micromolar to greater than one hundred micromolar in most wells. U was depleted with respect to salinity predicted concentrations, indicating removal with respect to the seawater endmember. Dissolved Mn concentrations were generally low in all wells, indicating no significant solid source of Mn (as MnOx) in this system. When extrapolated to a global scale, estimates of U removal during seawater exchange with the aquifer solids equaled 10–20% of the total riverine dissolved U input flux. REE concentrations in the forest recharge area were high in shallow wells, and showed a light enriched fractionation pattern, characteristic of soil leaching by Natural Organic Matter (NOM) rich waters. A decrease in REE concentration with depth in the forest wells coupled with a trend towards Heavy REE (HREE) enriched fractionation pattern indicated removal of the REE coincident with NOM and Dissolved Organic Carbon (DOC) removal. The saline waters of the beach ridge wells show a Light REE (LREE) enriched fractionation pattern and have the highest overall concentrations of the REE, indicating a significant REE source to the seawater endmember waters. The concentration gradients along the beach ridge flow path indicate a large source in the deep wells, and net export of dissolved REE to the tidal creek system and the coastal ocean. Ultrafiltration experiments indicate a transition from a colloidal dominated reservoir for the REE in the forest wells to a colloidal and dissolved reservoir in the beach ridge wells. The ultrafiltration data coupled with a correlation with Dissolved Inorganic Carbon (DIC) release suggest that there is diagenetic mobilization of an REE rich organic carbon phase in the saline endmember wells. We suggest here that degradation of this relic terrestrial organic carbon and REE rich phase results in the export of dissolved REE equal to or exceeding river inputs in this region.

**Key words:** coastal aquifer, Rare Earth Elements, Redox Sensitive Elements

## 1. Introduction

Recent studies indicate that the chemical export associated with groundwater seawater mixing can exceed river fluxes for a number of trace elements (Moore, 1996;

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Shaw et al., 1998). In these studies, Ra and Ba concentrations revealed excesses that could not be accounted for by riverine input. While the volume of freshwater discharge is likely small compared to riverine sources, the exchange of seawater through surficial aquifers can be comparable to river fluxes. Concentrations for many constituents in these saline groundwaters are elevated by as much as several orders of magnitude over river waters. Moore (1999) has coined the term “subterranean estuary” to describe this active mixing zone between fresh aquifer water and seawater. This mixing zone responds strongly to saltwater intrusion and sea level rise. Saltwater intrusion brings the mixing zone of the subterranean estuary inland, altering the chemistry and driving diagenetic alteration of solid phases. Potential interactions between salt marsh groundwater and intruding seawater, from saltwater intrusion or tidal creeks, may cause salt marshes to contribute significantly to the chemical exchange with the coastal ocean. Studies of Redox Sensitive Elements (RSE like U, Fe and Mn) indicate that salt marsh systems are sites of very active diagenetically driven exchange between groundwaters and local coastal waters (Church et al., 1996; Snyder et al., in press; Sundby et al., this volume). Church et al. (1996) suggest that U removal in salt marshes balances as much as 10% of the U river flux on a global scale. Similarly, Tachikawa et al. (2003) suggest that REE flux via groundwaters/seawater exchange may balance an oceanic deficit for Nd in their current global Nd mass balance. The importance of chemical exchange rates and diagenetic alteration in these systems takes on greater import in the context of the high discharge of DIC to coastal waters (Cai et al., 2003; Shaw, 2003). In this study we investigate the behavior and inventories of dissolved inorganic “tracer” species to elucidate the potential impact of diagenetic reactions occurring in salt marsh aquifers.

Rare earth elements (REE) have been used as process tracers in a variety of natural waters, including fresh groundwaters, rivers, estuaries, oceans, lakes and porewaters. However, REE have not yet been studied at the saltwater-freshwater interfaces in subterranean waters. In estuaries, REE undergo significant modification, including >90% decrease in concentration with a typical shift to a heavy REE (HREE) enriched signature (Sholkovitz, 1992); whereas, in subterranean estuaries, the same modification may not occur. Three characteristics define the utility of REE as process tracers: absolute concentrations, fractionation patterns, and anomalous behavior of select REEs. As a group, the REE have a very similar solution chemistry. The lanthanide contraction leads to a gradual decrease in ionic radius across the REE series, causing gradual changes in the strength of solution complexation. The HREE typically form stronger complexes and remain in solution; whereas, light REE (LREE) are more easily scavenged and removed from solution by adsorption onto settling particles. The source of the REE in natural waters is weathering of source rock. Weathering should lead to REE ratios in water similar to the source rock; however, variations in the strength of solution complexation and the affinity for particles cause fractionation to occur. Fractionation becomes evident when REE concentrations of a water mass are divided by REE concentrations in

the source rock (in this work North American Shale Composite, NASC). Shale normalized (SN) REE concentrations can be expressed as a fractionation pattern representing all of the REE or through a shale-normalized (SN) LREE/HREE ratio, such as  $(Nd/Yb)_{SN}$ .

REEs are trivalent in solution under normal conditions. Two of the REEs, Cerium (Ce) and Europium (Eu), undergo changes in oxidation state in specific environments. Eu is reduced in hydrothermal vents and volcanic regions; but this does not occur in passive margins such as coastal South Carolina. Ce, on the other hand, is readily oxidized to  $Ce^{4+}$ , which is extremely particle reactive and easily removed from solution. This anomalous behavior [relative to neighboring La, Pr and Nd leads to fractionation patterns depleted in Ce] is the norm in seawater (Sholkovitz et al., 1992). The relative depletion or excess of cerium versus what would be expected from La and Nd is termed the "Cerium Anomaly".

In this study the REEs and RSE are used as process tracers in a transect of wells in the salt marsh system in North Inlet SC. Krest et al. (2000) have completed a study of nutrient dynamics in many of the same wells sampled in this study. Krest et al. (2000) determined that subterranean mixing at the fresh water/seawater interface in this coastal salt marsh system is an area of significant nutrient input to the coastal ocean through submarine seawater exchange (as submarine groundwater discharge). The physical processes through which mixing occurs was further delineated by Gardner and Reeves (2002) who identified three distinct groundwater flow paths in this groundwater/seawater mixing zone along the well transect samples in this study. The patterns reflect: (1) Horizontal flow in the (fresh) forest side of the transect; (2) Upwelling at the forest-marsh interface; and (3) Downwelling on the eastern (saline) side of the transect.

This study will present REE and RSE data for a number of the same wells used in the studies of Krest et al. (2000), Gardner and Reeves (2002), Cai et al. (2003) and Goni and Gardner (this volume).

## 2. Methods

The REEs in all groundwater samples were preconcentrated and analyzed using isotope dilution ICPMS after the method of Shaw et al. (2003). Briefly, a filtered, acidified sample was transferred into a centrifuge tube and spiked with enriched isotopes of four REEs ( $^{142}Ce$ ,  $^{145}Nd$ ,  $^{161}Dy$  and  $^{171}Yb$ ). Nd, Dy, and Yb were chosen due to their representative nature of light, middle and heavy REE; whereas, Ce was chosen due to its unique oxidation chemistry. In this work, the amount of sample and spike varied due to the wide range of concentrations found in groundwaters. A spiked sample was allowed to sit a minimum of one day to come to equilibrium. After equilibration, a small amount (typically less than 50  $\mu L$ ) of clean aqueous Ammonia was added to the centrifuge tube to induce the precipitation of  $Mg(OH)_2$  as a carrier phase for the REEs. The precipitate was washed and centrifuged with two 500  $\mu L$  aliquots of deionized water to remove any residual Ba

and sea salts that may have been included in the precipitate. Finally, the precipitate was dissolved in 10% HNO<sub>3</sub> for ICPMS analysis. Concentrations of all spikes were determined by reverse isotope dilution ICPMS. Concentrations were divided by North American Shale Composite values to provide SN fractionation patterns. Ba and U were measured by isotope dilution (ID) ICPMS using enriched isotopes of <sup>135</sup>Ba and <sup>236</sup>U after methods described in Shaw et al. (1994, 1998). Fe, and Mn were determined spectrophotometrically after methods described in Sholkovitz et al. (1992).

Ultrafiltration experiments were performed on a series of samples from the shallow, forest wells and the deep, ocean side wells. Unfiltered samples were stored on ice immediately after collection. On sub-sample consisting of 500  $\mu$ l of the sample was pipetted into 4000 Dalton (4 kD) centrifuge filters and separated by centrifugation. A second subsample was filtered using a cleaned 0.22  $\mu$ m syringe filter. After filtration, the 4 kD filtrate and the 0.22  $\mu$ m filtrate fractions were analyzed for REE by ICPMS as described above. REE inventories in the different size fractions were determined by difference. The <4 kD fraction is termed "truly dissolved", 4 kD to 0.22  $\mu$ m is the colloidal fraction. Filter membranes were washed with generous amounts of deionized water to minimize contamination; and filter blanks were determined to verify the cleaning procedure. It was necessary to keep membranes wet after the cleaning step to avoid failure; thus, the wash step immediately preceded the filtration.

### 3. Study Area

The main part of this study was conducted at the North Inlet National Estuarine Research Reserve in Georgetown, South Carolina. The well transect (Transect D, Figure 1) was chosen because it transects a range of physiochemical mixing zones as well as a range in vegetation types. Transect D has been the focus of a number of studies; thus, the geochemistry, geology, and hydrology of the region is well known. Complete descriptions of this study area can be found elsewhere, Gardner and Reeves (2002), Krest et al. (2000), Cai et al. (2003) and Goni and Gardner (this volume). The transect extends 260 meters from an upland forest through Juncus and Spartina marsh, across Crabhaul Creek, ending at a sandy, partially forested beach ridge on the east side of the creek (Figure 2). The upland forest and the Beach ridge are topographic highs (~2 meters of total elevation) compared to the creek, resulting in zones of high hydraulic potential at the ends of the transect with the low at the creek. Sample points were installed at multiple depths below the marsh surface (0.62, 1.2, 2.4, 3.6 and 4.8 m) at the 30 well stations across the marsh and are numbered according to their distance from station 0 in the forest.

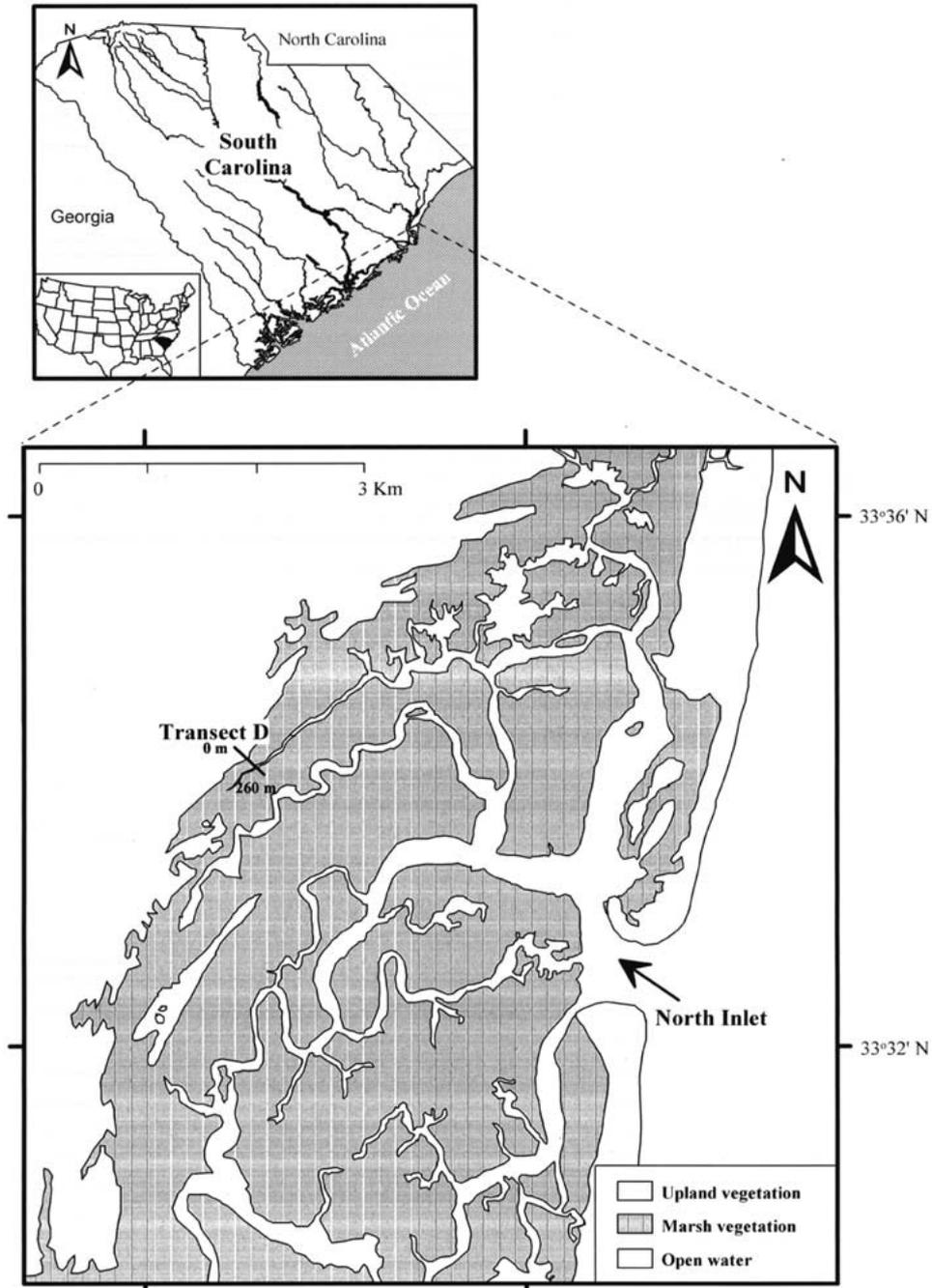


Figure 1. Map of the North Inlet showing Well Transect D.

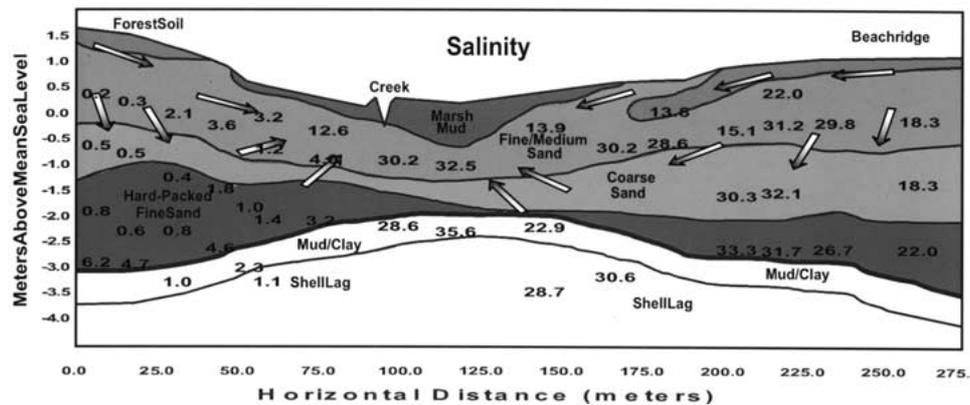


Figure 2. Composite of salinity data for the Well Transect D. Data is presented as a composite of several sampling trips.

## 4. Results

### 4.1. SALINITY AND FLOW PATHS

Figure 2 presents a 2D cross section of D transect including measured salinities at discrete depths. Arrows are used to indicate the general direction of the hydraulic potential (from high to low) based on earlier measurements of hydraulic potential from Gardner and Reeves (2002). Salinities generally increase going east (seaward) along the transect (from 0 to 260 m). The transect begins in a coastal forest that is primarily recharged via precipitation with little or no loss due to evapotranspiration. Hydraulic potentials from Gardner and Reeves (2002) indicate a zone of upwelling on the western side of the creek beginning at the forest edge (from ~34 to ~76 m) as well as a deep zone of upwelling extending to 147 m. In contrast, the hydraulic potential on the eastern side of the creek indicates general downwelling associated with drainage along the hydraulic gradient and a mixture of tidal recharge and precipitation.

The forest to marsh section of transect D reflects a fresh water to brackish water transition in both the horizontal and vertical dimensions along the flow paths (Figure 2). Shallow wells (1.2 and 2.4 m) remain relatively fresh ( $S \leq 2.0$ ) in the 0–50 m section of the transect. Deeper wells, particularly at the Mud/Clay confining layer, are more saline ( $S = 4.5\text{--}6.0$ ) in this same region showing some vertical stratification. A marked increase in salinity occurs at the creek edge in both shallow and deep wells.

The sharp transition in salinity at the creek denotes a transition to salinity ranging from 20–30 in the wells adjacent to the creek on the seaward side. Salinities remain higher east of the creek, in the range of  $S = 13\text{--}30$  in the shallow wells, and nearing 35 in some of the deeper wells. Overall there is a gradient in salinities with depth, indicating some stratification within the tidewater dominated section of the aquifer.

## 5. Redox Sensitive Elements (RSE)

The concentrations of the RSE were measured as indicators of diagenetic mobilization of solid oxide phases (as dissolved Fe, Mn) and of removal of U under reducing conditions. Logistical limitations prevented us from collecting samples for sulfide analysis synoptic with all of our sampling trips. However, dissolved sulfide measurements made by the Moore group indicated reducing conditions (as measurable sulfide) in all of their well samples from this location (Duncan, 2002). The sulfide concentration in waters at the forest marsh transition ranged from 10–250  $\mu\text{mol/kg}$  (0–30 m) and decreased to a less than 60  $\mu\text{mol/kg}$  in the wells out to the creek (30–100 m). Sulfide concentrations were highest coincident with the sharp salinity gradient adjacent to the creek (100–175 m), ranging from 15–1100  $\mu\text{mol/kg}$ . Sulfide concentration was generally lower in the remainder of the transect (175–260 m) ranging from 30–80  $\mu\text{mol/kg}$ .

Dissolved Fe is present in the wells at the forest edge of the well transect (0–25 m) at concentrations ranging from 10 to 70  $\mu\text{mol/kg}$  (Figure 3a; except within the impermeable layer). Dissolved Fe remains elevated in the intermediate depth wells ( $\sim$ 10 to 140  $\mu\text{mol/kg}$ ) to the edge of the salinity transition (50–75 m), except in the shallowest wells where concentrations are typically less than 10  $\mu\text{mol/kg}$ . Fe concentrations remain low at most depths in the wells adjacent to the creek (75–175 m). Fe concentrations are generally higher in the beach ridge end of the transect (175–275 m), ranging from 11–51  $\mu\text{mol/kg}$  in the intermediate depth wells. There is no clear trend with depth or along flow paths in this section of the transect.

Dissolved Mn concentrations are generally low ( $<10$   $\mu\text{mol/kg}$ ) throughout the transect (Figure 3b). The highest observed Mn concentration occurs at the shallow forest edge (11  $\mu\text{mol/kg}$ ) but decreases to near zero both horizontally and vertically along the flow path. The concentrations remain low ( $<3$   $\mu\text{mol/kg}$ ) adjacent to the creek, only increasing to 3–7  $\mu\text{mol/kg}$  at the beach ridge section of the transect.

Dissolved U concentration is discussed in the context of the expected salinity normalized concentrations to aid in the elucidation of sources and sinks. The shallow forest wells showed slightly elevated U concentrations for these very low salinity waters, with the concentrations decreasing along the flow path, coincident with increasing salinity. The U concentration remained low ( $<0.1$   $\text{nmol/kg}$ ) through the salinity mixing zone to the creek (50–100 m) (Figure 3c). The U concentration increased across the salinity front, but was depleted with respect to the concentration that would be predicted by salinity. The U concentration range remained generally low ( $<3$   $\text{nmol/kg}$ ) adjacent to the creek (with only 1 sample approaching the salinity predicted concentration). The U concentrations in all of the beach ridge section of the transect (175–275 m) were depleted with respect to that predicted by the high salinities in these wells.

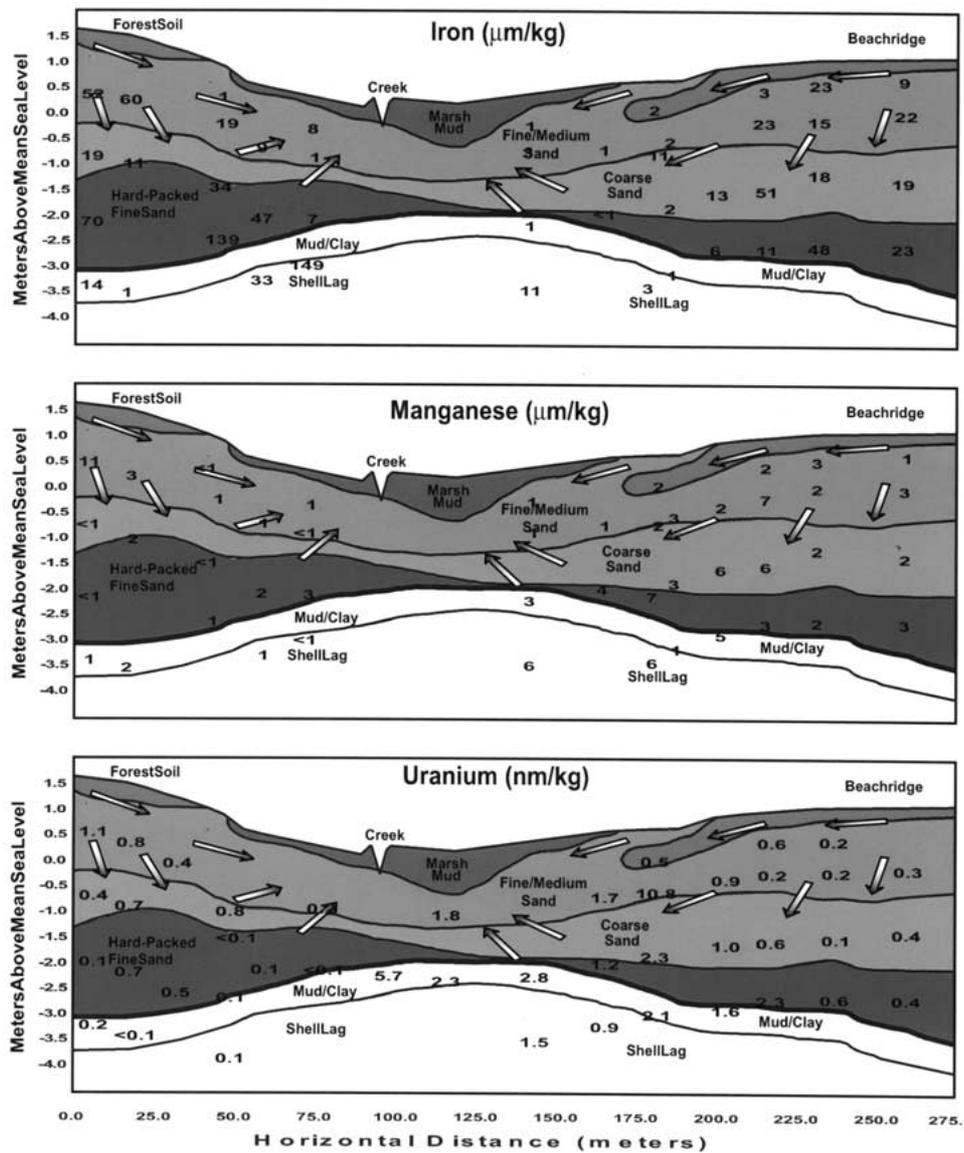


Figure 3. Composite of Fe data in  $\mu\text{mol/kg}$  (a), Mn data in  $\mu\text{mol/kg}$  (b), and U data in nmol/kg (c), for the Well Transect D. Data is presented as a composite of several sampling trips.

## 6. Rare Earth Elements (REE)

Results for the REE are presented as shale (NASC) normalized patterns as a function of piezometer depth at the well sites sampled. Well positions are presented superimposed on the aquifer topography including arrows indicating gradients in hydraulic potential (approximate flow paths). Figures 4a–d present data collected on four sampling trips over a range of seasonal conditions, 4 May 1999, 25 Janu-

ary 2001, 5 July 2001 and 15 October 2001. The data are presented in a form approximating a 2D concentration map in order to present trends along gradients in hydraulic potential.

Waters from shallow well samples (0.62, 1.23 and 2.46 m) along the transition zone from forest to the upper marsh edge (0–50 meters along the transect), are REE enriched with respect to regional surface waters (Table I). Shallow forest well waters are enriched by as much as 30 times for the LREEs and up to 5 times for the HREEs when compared to fresh endmember waters from Winyah Bay, adjacent to North inlet (Duncan, 2002). The REE fractionation pattern in these waters range from flat to a LREE enriched pattern. A negative Ce anomaly is seen in a few of the shallowest waters, but is not observed consistently in these wells. The LREE enriched pattern is usually found in waters containing the highest overall REE concentrations. This trend is consistent for all sampling trips. Waters collected from the deeper wells (3.70 and 5.54 m) in the forest/marsh transition zone have much lower REE concentrations when compared to the shallow wells, resulting in concentrations more comparable to coastal seawater samples in the region. The fractionation pattern in the deeper wells ranges from flat to slightly HREE enriched in the 3.70 m well to a seawater like HREE enriched pattern in the deepest well (5.54 m). There is no observable Ce anomaly in the patterns of these deeper well samples.

The saline wells on the eastern side of the creek are all enriched in REE when compared to local seawater samples (Figures 4a–d, Table I). The fractionation patterns are consistently flat to LREE enriched. In contrast to the forest/marsh transition wells, the concentrations and LREE enrichment increased with depth in most of these wells. This is most pronounced in the wells at the eastern end of the transect (175–260 m) where the concentrations may range several orders of magnitude in a single vertical well profile.

Size partitioning of the REEs was determined for eight water samples along the transect by ultrafiltration (Figure 5). Two operationally defined fractions, 0.22  $\mu\text{m}$  to 4 kD and <4 kD were processed as indicators of colloid association by the REEs.

At the forest/marsh transition (0 m), the 0.22  $\mu\text{m}$  to 4 kD (colloidal) size fraction accounts for the majority of the REE inventory. The fractionation pattern in the colloidal fraction is predominantly LREE enriched. In contrast, the “dissolved” fraction (<4 kD) of the forest/marsh transition is a smaller fraction of the total REE inventory with a flat pattern. In wells from 22–167 m, the colloidal fraction is still the bulk of the REE inventory, but fractionation pattern is flat. The fractionation pattern of the “dissolved” fraction wells 33–167 m is flat to slightly HREE enriched. In the eastern section of the transect (189–239 m), the patterns of both size fractions become more LREE enriched and the concentrations of each phase converge (though the colloidal fraction is still higher). In the two easternmost wells, the concentration and fractionation pattern of the “dissolved fraction” is comparable to the colloidal fraction in the most enriched forest side well.

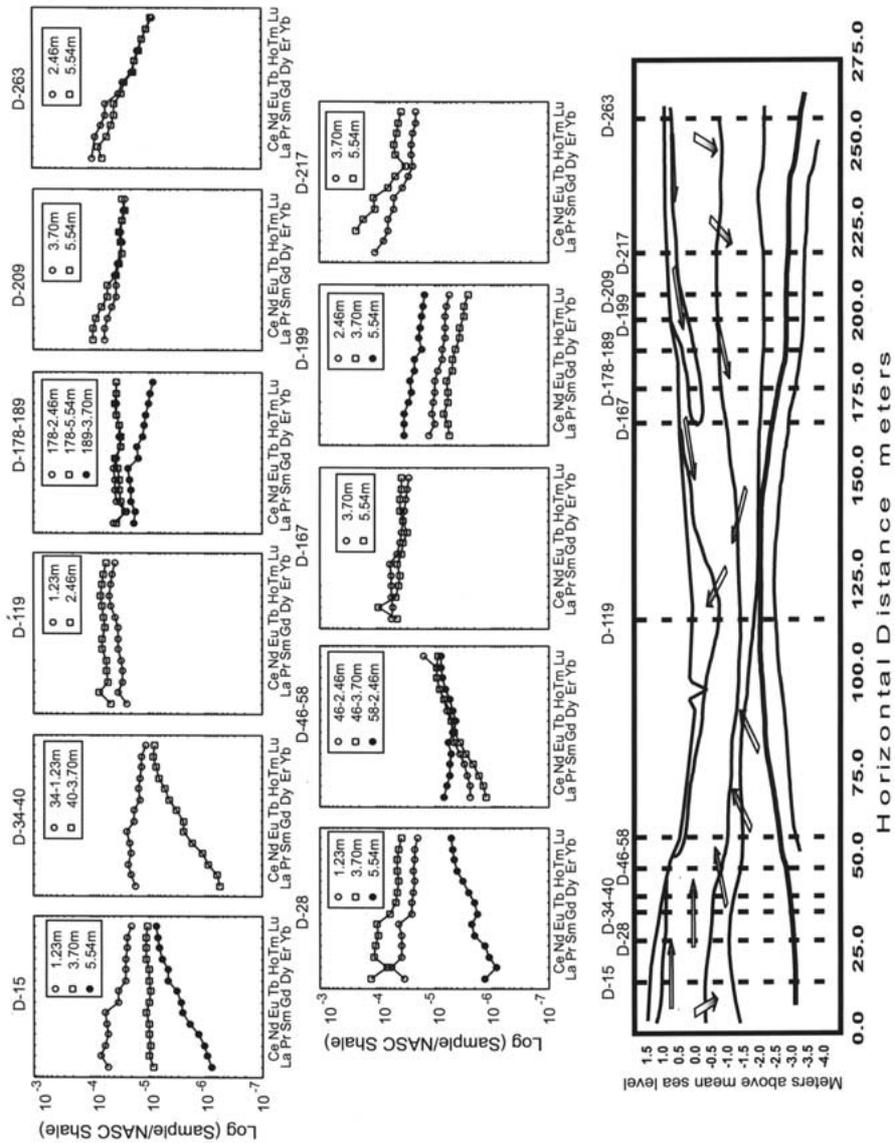


Figure 4. Shale normalized REE data from sampling trips in May 1999 (a), January 2001 (b), July 2001 (c), and October 2001 (d).

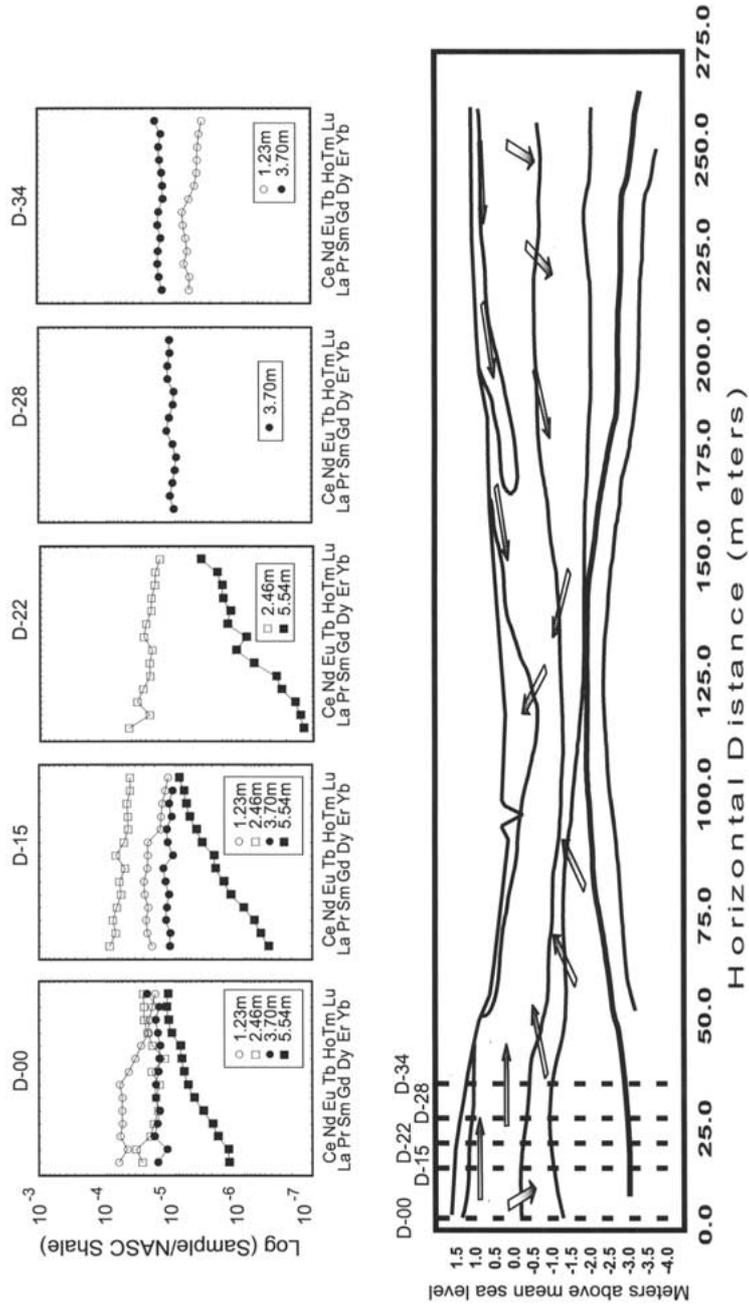


Figure 4b.

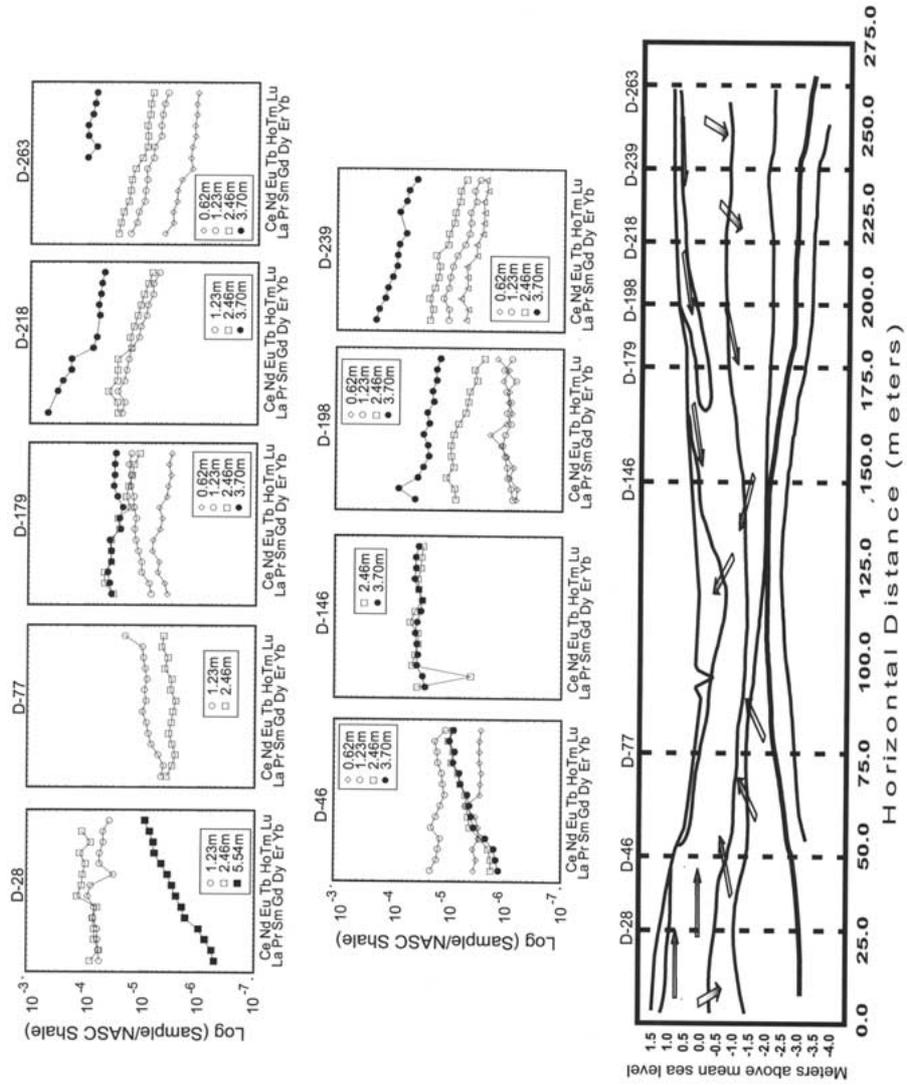


Figure 4c.

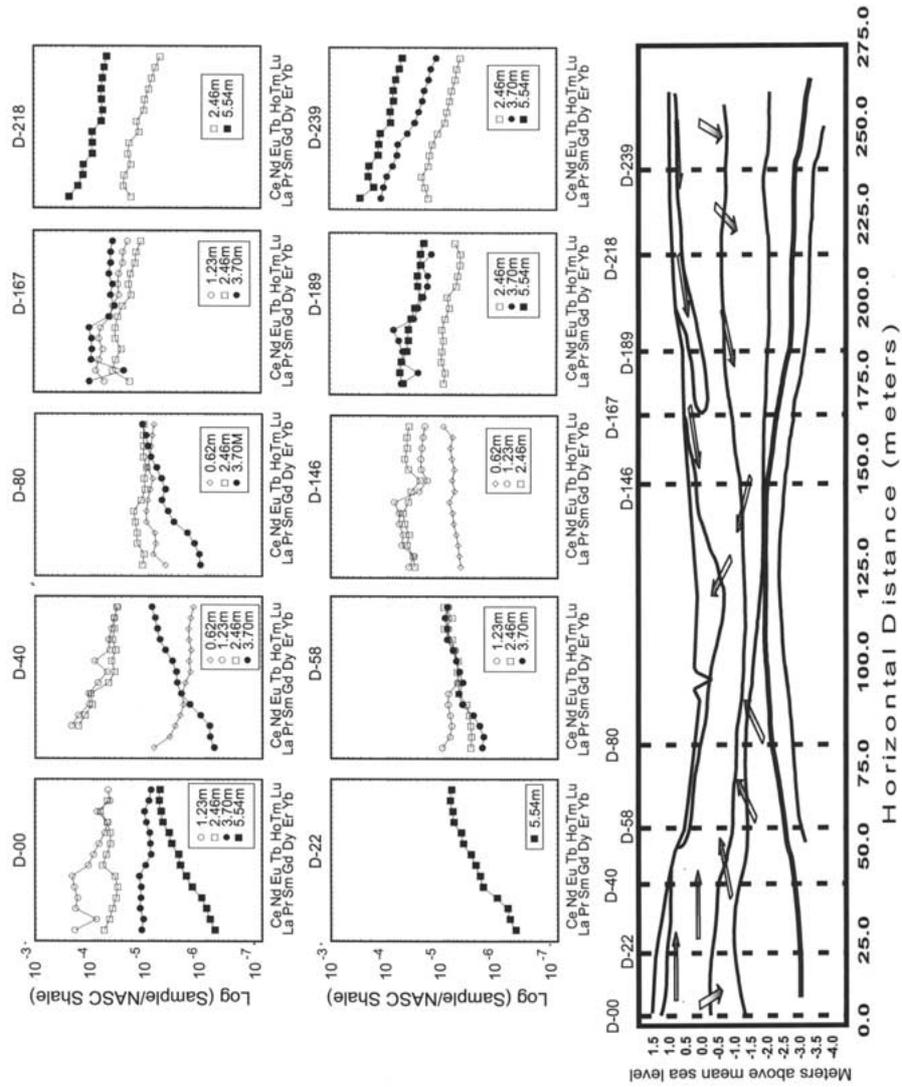


Figure 4d.

Table 1. REE concentration in selected surface and groundwater samples (pmol/kg)

REE	Upper Winyah Bay S = 6.4 Sept 1998	Seawater off Winyah Bay/North Inlet Sept 1998	Upper Winyah Bay S = 0.0 Feb 2000	Seawater off Winyah Bay/North Inlet Feb 2000	Transect D-0 depth 1.23 m S = 0.2 Oct 2001	Transect D-0 depth 5.54 m S = 6.2 Oct 2001	Transect D-0 depth 0.62 m S = 13.9 Oct 2001	Transect D-218 depth 5.54 m S = 31.7 Oct 2001
La	$1.53 \times 10^3$	$7.40 \times 10^1$	$8.22 \times 10^2$	$5.74 \times 10^1$	$5.03 \times 10^4$	$1.73 \times 10^2$	$1.28 \times 10^3$	$5.97 \times 10^4$
Ce	$4.23 \times 10^3$	$7.72 \times 10^1$	$1.85 \times 10^3$	$1.19 \times 10^2$	$4.24 \times 10^4$	$4.29 \times 10^2$	$2.75 \times 10^3$	$8.59 \times 10^4$
Pr	$4.61 \times 10^2$	$1.59 \times 10^1$	$2.23 \times 10^2$	$1.38 \times 10^1$	$1.10 \times 10^4$	$5.46 \times 10^1$	$3.21 \times 10^2$	$7.65 \times 10^3$
Nd	$1.85 \times 10^3$	$5.78 \times 10^1$	$9.37 \times 10^2$	$5.17 \times 10^1$	$4.19 \times 10^4$	$2.76 \times 10^2$	$1.44 \times 10^3$	$3.12 \times 10^4$
Sm	$3.82 \times 10^2$	$1.02 \times 10^1$	$1.82 \times 10^2$	$1.08 \times 10^1$	$8.72 \times 10^3$	$7.41 \times 10^1$	$2.89 \times 10^2$	$3.96 \times 10^3$
Eu	$8.98 \times 10^1$	4.23	$4.6 \times 10^1$	2.7	$2.01 \times 10^3$	$1.99 \times 10^1$	$6.37 \times 10^1$	$8.42 \times 10^2$
Gd	$4.70 \times 10^2$	$1.31 \times 10^1$	$2.84 \times 10^2$	$3.16 \times 10^1$	$4.31 \times 10^3$	$1.04 \times 10^2$	$3.02 \times 10^2$	$3.50 \times 10^3$
Tb	$6.74 \times 10^1$	2.19	$3.89 \times 10^1$	4.7	$5.80 \times 10^2$	$1.83 \times 10^1$	$3.95 \times 10^1$	$3.97 \times 10^2$
Dy	$3.96 \times 10^2$	$1.41 \times 10^1$	$2.17 \times 10^2$	$2.84 \times 10^1$	$2.74 \times 10^3$	$1.43 \times 10^2$	$2.62 \times 10^2$	$2.22 \times 10^3$
Ho	$7.87 \times 10^1$	3.33	$4.63 \times 10^1$	6.6	$4.62 \times 10^2$	$3.40 \times 10^1$	$5.09 \times 10^1$	$4.95 \times 10^2$
Er	$2.28 \times 10^2$	$1.19 \times 10^1$	$1.41 \times 10^2$	$1.97 \times 10^1$	$1.10 \times 10^3$	$1.19 \times 10^2$	$1.54 \times 10^2$	$1.37 \times 10^3$
Tm	$3.12 \times 10^1$	2.07	$1.98 \times 10^1$	3.1	$2.40 \times 10^2$	$1.83 \times 10^1$	$2.30 \times 10^1$	$1.85 \times 10^2$
Yb	$2.01 \times 10^2$	$1.14 \times 10^1$	$1.20 \times 10^2$	$1.82 \times 10^1$	$9.04 \times 10^2$	$1.24 \times 10^2$	$1.35 \times 10^2$	$1.09 \times 10^3$
Lu	$2.94 \times 10^1$	1.91	$1.81 \times 10^1$	8.5	$1.55 \times 10^2$	$1.91 \times 10^1$	$3.08 \times 10^1$	$1.56 \times 10^2$

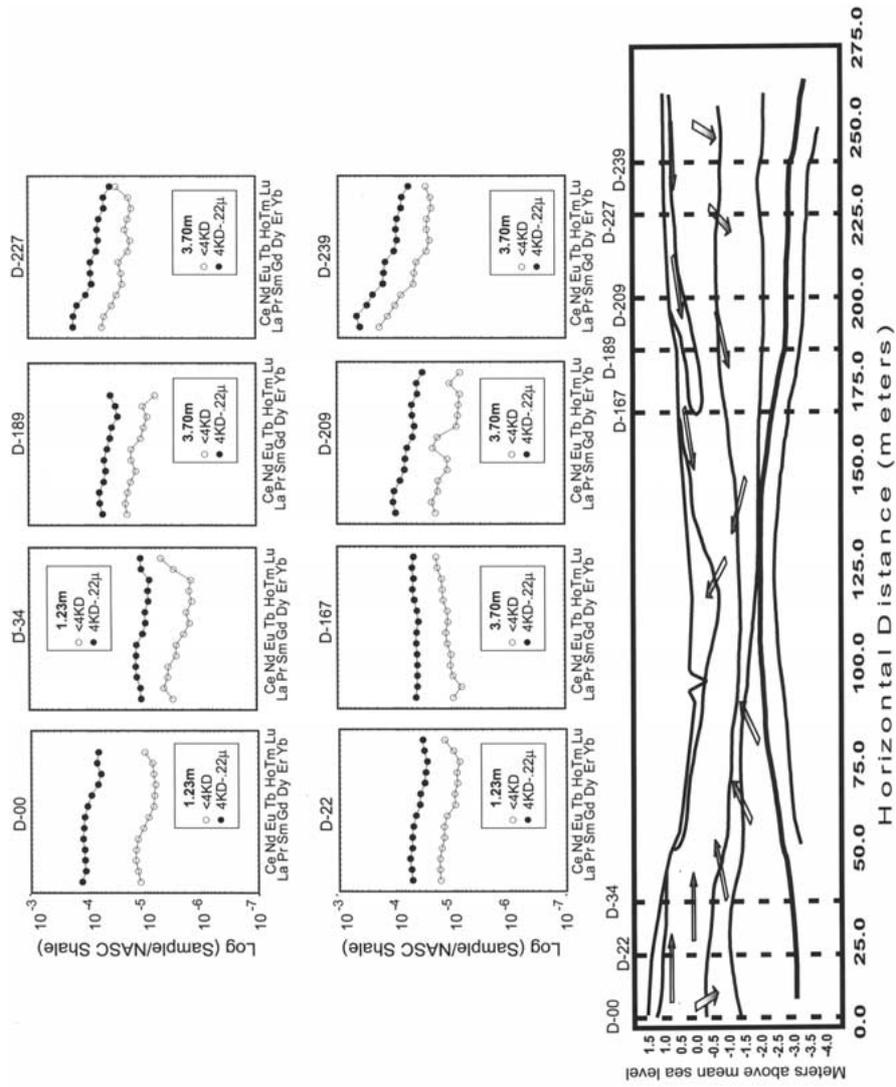


Figure 5. Shale normalized REE size fraction data from sampling trips in May 2002.

## 7. Discussion

### 7.1. CHEMICAL EXCHANGE WITH COASTAL WATERS

The diagenetic reactions in the salt marsh aquifer result in a source for REEs and a sink for U with respect to coastal seawater. However, the significance of this REE source and U sink can only be determined based on an estimate of the amount of seawater cycled through the salt marsh aquifer. The synoptic response of the hydraulic potential (as water height in the piezometers) to tidal forcing suggests that there is a significant variation in the total volume of seawater contained in the aquifer on a daily basis (Gardner, personal communication). The gradients observed along flow paths in the well transect suggest that the tidal response supports advective mixing in these wells. We can estimate the effect of this process on chemical exchange using the volume exchange estimate made by Krest et al. (2000) in the North Inlet salt marsh system. Krest et al. (2000) estimated a volume exchange of aquifer waters of  $10\text{--}20 \text{ l m}^{-2} \text{ d}^{-1}$  based on Ra isotope inventories. This estimate is approximately two orders of magnitude higher than the estimate of net flow due to recharge offered by Gardner and Reeves (2002). The difference lies in the mechanism that drives the exchange and hence the definition of water exchange. The net exchange due to recharge along the hydraulic potential is a net water flux. In contrast, the exchange based on Ra isotope inventory reflects an equivalent volume of water needed to account for the chemical exchange due to advective mixing. In our case even if we assume that the net flow of fresh water is near zero for each tidal cycle, the chemical alteration of the water that enters and leaves the aquifer can account for a very large net chemical exchange. Thus, the exchange estimate based on chemical exchange (Krest et al., 2000) is more useful for our study.

The magnitude of the U sink (on a per liter basis) can be estimated as the difference between the expected U concentration based on salinity and the U concentration observed (after Shaw et al., 1994). Using the well data from the Eastern side of the salinity transition (east of the creek), we get an average U deficit of  $8 \text{ nmol U/kg}$  of groundwater in the high salinity region. This yields an estimate of  $80\text{--}160 \text{ nmol m}^{-2} \text{ day}^{-1}$  when coupled with the exchange estimate of Krest et al. (2000). This is 1–2 times the estimate of U removal in the Canary Creek salt marsh system in Delaware Bay studied by Church et al. (1996). Church et al. (1996) concluded that removal occurred in the creek water column as a result of several possible factors (including complexation with NOM and coprecipitation with Fe oxides). It is possible that mixing of creek waters with NOM rich reducing groundwaters accounts for the removal that we observe in North Inlet. While the role of flow into permeable marsh sediments was not part of the Church et al. (1996) study, the surprising agreement between our results reinforce the original conclusions made by Church et al. (1996). Clearly, marsh sediments are a significant sink for elements such as U, that can be sequestered by NOM or removed under reducing conditions.

Rivers are assumed to be the primary source of REEs to the coastal ocean, so we use a comparison with local river input to evaluate the significance of the REE source from the salt marsh aquifer. We put the estimate of  $10\text{--}20 \text{ l m}^{-2} \text{ d}^{-1}$  in the context of local river flow by multiplying by the area of salt marshes in South Carolina ( $\sim 1800 \text{ km}^2$ ). This approach yields a volume exchange of 18–36 billion liters of seawater cycled through the marsh aquifer per day, comparable with 20–40% of the river input to the area (Duncan, 2002). Comparison of the concentration of REEs in the saline wells indicate one to two orders of magnitude enrichment over coastal seawater (Table I), so it is valid to consider the bulk of the inventory as a diagenetic input. This assumption allows us to make a qualitative comparison of river endmembers in the region to endmember concentrations in the well waters. The saline (downwelling) waters of the beach ridge side of the transect range in REE concentrations from near high-end river endmembers in the surface wells to a factor of 30 enrichment over river endmembers for the LREE fraction. The saline wells where we have measured the “<4-kD” fraction are enriched over the river endmember by factors ranging from 2 to 10 for the LREEs. The fate of this highly concentrated, LREE enriched water is unknown. Water moving deeper may, as Gardner and Reeves (2002) hypothesize, flow further eastward and interact with Bly Creek, the next tidal creek to the east. It seems likely that this downwelling mass, already at high salinity, may not undergo processes seen in surface estuaries (significant salting out, coagulation, adsorption onto particles). If this water mass remains in the subsurface, it is likely that it is being transported in the direction of the coastal ocean, this being the primary flow direction of aquifers on the east coast. Though this is a qualitative comparison, the contribution of REEs to the coastal ocean from the enriched aquifer waters is comparable if not greater than that of local rivers. Put in the context of the global distribution of salt marsh systems, this finding may require a reevaluation of REE sources to the world’s oceans. The question we address here is whether the REE enrichment is derived from a terrestrial source or a recycled marine source.

## 7.2. REE DYNAMICS AT FOREST/MARSH TRANSITION

The flow path predicted by the hydraulic gradient in the forest marsh transition (0–50 m) is the initial mixing zone of fresh water with the salt wedge. This salinity increase is greatest as a function of well depth. This zone is comparable to the upper estuary in terms of ionic strength increase, but differs dramatically in terms of redox conditions and chemical loading (as both dissolved and colloidal phases).

The REE fractionation pattern of the shallow forest wells is unusual for the dissolved REEs but is typical for the particulate and/or colloidal phase. Work by Viers et al. (2000) and Dia et al. (2000) in organic-rich river waters and groundwaters suggest that a LREE enriched or flat fractionation pattern may be a common feature of water masses dominated by high levels of organic matter. For the Kalix River, Ingri et al. (2000) found large temporal variations in the REEs associated with

organic matter. Further, they observed a LREE enriched to flat shale normalized pattern in the colloidal phase ( $<0.45 \mu\text{m}$ ) similar to our observation.

The data from the shallow forest wells suggests that the REE signature is attained rapidly in the shallow soil (upper 1–2 m). The forest/marsh transition wells are primarily recharged by rain events, as water from high tide does not transgress into the forest. Gardner and Reeves (2002) have shown that water level response in the wells is rapid following a rain event, suggesting high soil permeability in this system. The LREE enriched fractionation pattern of these terrestrial waters reflects preferential leaching of the solid phase (Ingri et al., 2000). It is likely that the presence of significant loading of DOC and NOM has increased the rate of weathering of a LREE enriched source, accounting for both the fractionation and high concentrations (Dupre et al., 1996). Increased weathering has been observed in the Congo River basin and Cameroon from organic-rich waters that result in elevated REE concentrations (Viers et al., 2000). Another potential explanation is that natural organic matter preferentially binds the LREEs. Most complexation models do not include organic matter and therefore its potential importance in complexing REEs may be underestimated. Recent work using experimentally determined parameters suggests that organic matter may be the dominant complexing ligand in some freshwater environments with the complexation being greater for the LREE than the HREE (Moermond et al., 2001). One final potential explanation is that the REE signature in these wells reflects a severely weathered source. The HREE are more soluble and thus more easily weathered. It is possible that the HREE have been removed from the source rock, leaving a LREE enriched source.

Our ultrafiltration work was conducted in an effort to measure the truly dissolved phase and determine the origin of the REE enrichment. Clearly the colloidal material that passes through the  $0.22 \mu\text{m}$  filter yields a combined colloidal and dissolved inventory as reflected in Figures 4a–d). Fractionation patterns of the  $<4$  kD (truly dissolved) and  $4$ – $0.22 \mu\text{m}$  fractions (Figure 5) suggests a LREE enriched colloidal phase in the fresh source water.

The gradient in REE concentration coupled with the high REE concentrations in the colloidal size fraction suggests a significant terrestrial REE source in these NOM rich fresh waters. The change in concentration along the flow path also suggests an overall REE removal process that preferentially removes the LREE rich fraction of the REE load. This is consistent with removal processes in the estuarine mixing zone where the characteristic HREE enriched seawater pattern is formed (Sholkovitz, 1992). The REE concentration gradient probably reflects preferential removal of the LREE colloidal fraction of the groundwater REE load. In contrast to an estuarine system, this removal occurs under anoxic conditions; thus, there appears to be no removal of Fe or Mn associated with oxide formation, but colloid aggregation may still be significant in the deep forest marsh transition wells. The initial increase in ionic strength in the 0–5 salinity-mixing zone is probably responsible for the adsorption (or aggregation) of terrestrial source DOC and NOM onto solid phases. This process results in the formation of the organic carbon (and

REE) rich solid phase. The long-term fate of the organic carbon rich solid phase may control the net REE export from the aquifer. The fate of the REE (especially LREE) and organic carbon rich solid phase that results from the observed removal process is not known. However, as physiochemical regimes change with saltwater intrusion, the reactivity of the phase may change. Hedges et al. (1997) postulated that the reactivity of terrestrial organic carbon could change from refractory, in terrestrial waters, to labile upon transport to the sea. Such a process may also occur as saline waters intrude into deposits of terrestrial organic carbon, having a dramatic effect on the mobility of the reservoir of the associated REE inventory. Further, a large change in pH and ionic strength may alter the solubility of humic material and contribute to mobility of associated REE.

### 7.3. REE DYNAMICS IN WELLS ADJACENT TO THE CREEK

The wells adjacent to the creek (50–150 m) record the greatest lateral and vertical salinity gradients, going from 5–30 S in the space of tens of meters. In terms of an estuarine model of mixing, this is the zone where we would expect a significant increase in U associated with the seawater endmember and a general decrease in Fe, Mn, and REEs (particularly the LREEs). In contrast to these predictions, the low salinity waters of the forest side of the creek have the lowest REE concentrations and the characteristic HREE enriched seawater fractionation pattern. Again it is important to note the absence of a pronounced negative Ce anomaly. These wells intersect an upwelling zone, where waters from the deeper colloidal aggregation zone flow towards the shallower aquifer and the creek. Some of the highest dissolved Fe concentrations are observed in the deep forest wells, perhaps indicating reductive mobilization from a particulate phase. However, there is no indication of release of any associated REE inventory. Dissolved phase concentrations of U and Mn remain low in these well waters indicating no significant dissolution of a Mn oxide phase.

### 7.4. REE DYNAMICS IN THE TIDAL RECHARGE ZONE

The release of REEs in the deep saline wells of the seaward side Transect D indicates release from a substantial solid reservoir. The LREE enriched fractionation pattern of the resultant REE enriched waters is similar to the pattern observed in the shallow NOM rich waters of the forest side wells. The solid phase formed via removal of NOM and DOC in the deeper saline waters of the forest marsh transition (0–50 m) would be enriched in the LREEs based on the fraction removed from solution. Relic organic carbon rich deposits in the seaward side of the marsh may be a solid phase source for the observed release of REEs. The zone where these deposits occur would migrate as the freshwater/seawater transition zone followed the zone of seawater intrusion. The extent of saltwater intrusion into the sediments of Transect D has only occurred in the last 1500 years (R. Gardner personal com-

munication). This suggests that the transition zone that we observe at the beginning of the transect may have been further east in the recent past.

The general LREE enriched pattern in the deep saline waters of the transect, is also similar to what would be expected from the enrichment to a marine particle phase. The enrichment is expected to occur during the estuarine mixing/fractionation process (Sholkovitz, 1992). The important question we consider here is whether the observed enrichments reflect the decomposition of an enriched relic solid phase or the recycling of a marine solid particulate phase. The significance of this question lies both in the impact to the REE mass balance as well as the source of the DIC enrichments observed in these wells measured by Cai et al. (2003).

We first consider a recycled or relic marine solid phase as our source for the dissolved REE enrichments in wells of the seaward section of the marsh transect. As discussed by Sholkovitz (1992) the partitioning of dissolved REEs onto particulates during estuarine mixing results in the characteristic HREE enriched seawater pattern as well as a pronounced Ce anomaly. The resultant particulate phase will have a LREE enrichment relative to the detrital fraction of the particulate phase. Likewise we expect a strong positive Ce anomaly in this solid phase. In short we anticipate a solid source having a fractionation pattern that is a mirror image (on the horizontal axis) of the characteristic seawater REE pattern. A potential carrier phase for this REE enrichment would be the Mn and Fe oxide particle coatings that normally form as these elements precipitate during estuarine mixing. Degradation of the non-detrital component of this marine derived particulate phase would produce a dissolved enrichment showing an LREE enriched pattern with a pronounced positive Ce anomaly. We might also expect to see enrichments of Mn and Fe as well. The patterns we observe in the saline wells reflect a very large LREE enrichment, but generally lack the expected Ce anomaly. Likewise, there is little evidence of dissolution of a Mn or Fe oxide phase that might be the carrier for the REEs.

Other possible relic marine solid sources for the observed REE enrichments in well waters include apatites or carbonates. While apatite phases are not uncommon in this region, we have not observed a consistent and concurrent enrichment of phosphate in these well waters (Duncan, 2002), nor do we see evidence for the release of other associated species like U. Marine carbonates are very common in this aquifer system and their dissolution contributes to the observed DIC export at this site. However, the REE inventory in carbonates reflects that of the marine waters that they precipitated from. Thus they are unlikely to be the source for the very large enrichments we observe.

An alternative explanation is the degradation or release of a relic carbon rich phase. These relic phases probably formed during recent lower sea level stands when the freshwater extended further seaward than today. These relic zones of DOC adsorption/colloid aggregation represent a reservoir of refractory organic carbon. These can also be a significant reservoir for REE, as is the case in the recent zone of DOC and NOM precipitation at the forest/marsh interface. The change

in chemical environment in the aquifer may result in degradation or mobilization of some fraction of this organic rich material. The increased level of DIC found in these wells by Cai et al. (2003) suggests degradation of an organic phase and probably contributes to the DOC pool. The mobility of REE in these high salinity waters may reflect mobilization with, or complexation by, the resultant DOC. Similar observations have been made in salt marsh porewaters where complexation of  $\text{Fe}^{3+}$  with organic ligands supports the dissolved Fe inventory (Luther et al., 1996; Taillefert et al., 2000, 2002). This mechanism is consistent with the occurrence of dissolved Fe in the saline wells where dissolved sulfide should remove the Fe as a precipitate. The exact mechanism of REE mobilization in these wells is uncertain. However, the release of the REE load through degradation and/or mobilization of the relic carbon rich phase clearly supports a significant flux of terrestrial REE (and probably DIC) to the coastal ocean. The consequence of this flux to the global mass balance of REE is yet to be determined, but these results demonstrate the need to quantify chemical fluxes associated with groundwater/seawater exchange.

## 8. Conclusions

REE and RSE analysis of groundwater from a salt marsh reveal three distinct physicochemical regimes over a distance of only 260 m. These regimes coincide with determined groundwater flow patterns for the area. Low salinity, high NOM groundwaters exhibit high REE concentrations and a LREE enriched to flat fractionation pattern. The low salinity forest/marsh transition can be characterized as the site of shallow advective input of an REE rich colloidal phase and deep removal of that same phase. This transition zone resembles the upper estuary as a zone of aggregation/precipitation of colloids resulting in a solid reservoir. The area adjacent to the marsh creek is characterized by a very sharp salinity gradient, a large REE inventory that is not significantly diluted by saline source waters, and nearly complete removal of U in these anoxic waters. The seaward section of the transect has some of the highest REE concentrations ever reported for saline environments. The high concentrations and extreme LREE enriched fractionation pattern in this water is indicative of regeneration from a solid phase. Ultrafiltration substantiated this view in that  $\sim 30\%$  of the REE inventory lies in the "truly dissolved phase" suggesting a significant REE source to coastal waters. We suggest that the solid reservoir formed at the marsh transition can be mobilized as salt water intrudes into the transition zone. Estimates of exchange based on mixing data indicate that the marsh aquifer is a significant source for REEs (especially LREEs) to coastal waters, and a significant sink for seawater U.

## Acknowledgements

The authors would like to thank Dr. Bob Gardner for setting the well transect and for his insight into the hydrology of this salt marsh system. We would also like to

thank Dr. Jim Krest for his help in the sampling portion of this project, Dr. Willard Moore for his insightful suggestions, Dr. George Luther for his review and editorial handling of this manuscript, and the Baruch Institute for maintaining access to the field site. This work was supported by NSF Grant # OCE-9712298 (to W.S. Moore and T.J. Shaw).

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