The Impact of Salt Marsh Hydrogeology on Dissolved Uranium

A Thesis
Presented to
The Academic Faculty

by

Samuel D Sibley Jr.

In Partial Fulfillment
of the Requirements for the Degree
Masters of Science in Earth and Atmospheric Sciences

Georgia Institute of Technology
May 2004

The Impact of Salt Marsh Hydrogeology on Dissolved Uranium

Approved by:

Dr. Carolyn D. Ruppel, Advisor

Dr. Herbert L. Windom

Dr. Martial Taillefert

May 13, 2004

ACKNOWLEDGEMENTS

This research was supported primarily by South Carolina Sea Grant under the auspices of the Land Use Change and Ecosystem Study (LU-CES) program. The LU-CES project is sponsored by the Coastal Ocean Program, National Ocean Service, National Oceanic and Atmospheric Administration, through the South Carolina Sea Grant Consortium, under grant number NA960PO113, with C.R. as the Georgia Tech principal investigator. Some equipment and supplies and support for field assistants were also provided by a NSF Long-Term Ecological Research program for the Georgia Coastal Ecosystems grant to C.R. (OCE9982133). The views expressed in the thesis are those of the author and his advisor and do not represent either NOAA or the National Science Foundation.

Several people contributed to the work presented in this thesis. I'd like to thank Dr. Carolyn Ruppel for continued support and guidance and Dr. Herb Windom for his assistance in hypothesis development and for his generous allotment of laboratory space and ICP-MS time. I'd like to recognize Dr. Martial Taillefert for his prudent suggestions during project development, for use of his laboratory bench space and equipment and for his thoughtful manuscript revisions. No data could have been acquired during this investigation without the long hard hours of field work logged by the following individuals: Justin Bartlett, Patrick Fulton, Luis Castillo, and Phillip Straus, Jeremy Merrill, Amy Eisin and Brian Dolan.

In addition, I'd like to thank Paul Drewes, Frank Melendez and Paul Conrad (USGS, Water Resources, South Carolina District) for assistance retrieving stage data and for background regarding the calculation of freshwater discharge in tidally influences systems; Billy Moore (University of South Carolina) for his insight and conversation at project meetings and in the field; Jack Blanton (Skidaway Institute of Oceanography), Francisco Andrade and Adelaide Ferreira (University of Lisbon) for generating hypsometric relationships and for assistance applying them to generate system volume estimates; Sam Walker (University of South Carolina) for performing the time-consuming GIS analysis required to generate system-specific salt marsh areas; and Debbie Wells for training and for assistance with sample preparation at SKIO.

Most importantly, I'd like to thank my friends in Atlanta and Athens, my fiancé, Alicia, and my parents, Sam and Nancy, for keeping me centered socially and mentally and for continuing to motivate the completion of this thesis. The support and occasional distraction provided by these individuals made my experience at Georgia Tech fulfilling and memorable.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

As part of the South Carolina Sea Grant Consortium LU-CES program, we quantified U removal and investigated the efficacy of uranium as a quantitative tracer of groundwater discharge in a headwater salt marsh of the Okatee River, Bluffton, SC. Determining the magnitude of U removal is important for advancing U as a tracer of paleo-oceanic conditions. Since salt marsh groundwater is typically enriched in nutrients and other biologically and chemically reactive species, quantifying groundwater discharge from marshes is critical for constraining local and global biogeochemical cycles and for understanding the ability of salt marshes to modify the chemistry of important species in surface waters.

We hypothesized that water-column U(VI) was removed by tidally-induced advection of surface water into permeable, anoxic salt marsh sediments, a process resulting in bacterially-mediated precipitation of insoluble $U(IV)O_2$ and/or sorption of uranium to iron-oxides at the oxic/anoxic sediment interface. Furthermore, we suggested that hydraulic pressure gradients established by marsh-surface tidal inundation and seasonally-variable rainfall promote the discharge of salt-marsh-processed, uranium-depleted groundwater to tidal creeks, producing the surface-water U-removal signal.

Groundwater and surface water data revealed non-conservative uranium behavior. We documented extensive uranium removal from shallow marsh groundwater and seasonally variable uranium removal from surface waters. These observations allowed for the calculation of seasonally-dependent salt marsh uranium removal rates. On a yearly basis, our removal rate (58 to 104 μmol m^{-2} $year^{-1}$) reemphasized the importance of anoxic coastal environments as U sinks. When extrapolated globally, our removal estimate (24 ± 14 Mmol yr^{-1}) supported a missing or underestimated U source or an imbalance in the global oceanic U budget in favor of removal. An imbalanced oceanic U budget is plausible since, during interglacial periods, oceanic U concentrations may decrease due to increased temperature and intertidal area, both of which favor removal.

High uranium removal, high barium concentration water observed seeping from creek banks at low tide supported our hypothesis that groundwater discharge must contribute to uranium removal documented in tidal surface waters. Average site groundwater provided an analytically reasonable endmember for explaining uranium depletion in surface water. This observation encouraged our use of three endmember mixing models for estimating the fraction of surface water with presumed a groundwater signature. Our discharge estimates of 8 to 37 L m^{-2} day^{-1} agreed closely with previously published salt marsh values. Seasonality in discharge rates can begin to be explained by seasonal patterns in rainfall, tidal forcing, and marsh surface bioturbation. Although more work is required to validate U as a groundwater tracer, the results of this study are promising and suggest that U may be an effective quantitative tracer of groundwater discharge from salt marshes.

CHAPTER 1

INTRODUCTION

1.1 Uranium in Salt Marshes

Uranium (U) and its decay series daughters have been, and continue to be, of great value as chronometers and tracers of oceanic processes. Consequently, the marine geochemistry of U has been the subject of intense study for many years. U is an ubiquitous trace element that typically behaves conservatively (with respect to changes in salinity) in marine surface waters (Ku et al., 1977; Windom et al., 2000), principally due to the strong complexes the uranyl ion (UO_2^{2+}) forms with carbonates (e.g., $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$, UO_2CO_3). Uranyl-carbonate complexes are extremely important since they greatly increase the solubility of U(VI) minerals, facilitate U(IV) oxidation, and limit the extent of U(VI) adsorption (Langmuir, 1997). Uranyl-phosphate complexes can also be important in phosphate-rich environments (Sandino and Bruno, 1992). Despite U's typically conservative behavior, in certain coastal environments, including the study site for this investigation, nonconservative U behavior has been observed (Church et al., 1996, Windom et al., 2000).

Globally, the average oceanic U concentration is a remarkably constant 3.3 ± 0.2 $\mu g\ l^{-1}$ for a salinity of 35 (Ku et al., 1977, Chen et al., 1986), with the ^{238}U nuclide composing more than 99% of the marine U inventory. The remaining 1% is mostly ^{235}U (Dunk et al., 2002). In all oxygenated waters, U is present primarily in the +VI oxidation state. Conversely, in subsurface and sedimentary environments where oxygen is absent, U can be reduced to the +IV valence. Under appropriate condition, this process occurs slowly through abiotic interactions with ambient reduced species like S^{2-} or Fe^{2+} (Wersin et al., 1994; Liger et al., 1999). On the other hand, U is reduced efficiently by a number of iron and sulfate reducing bacteria (Lovely et al., 1991; Fredrickson et al., 2000) that are widespread in the natural environment (Barnes and Cochran, 1993; Abdelouas et al., 2000) (see Windom p. C-5). Unlike other redox active metals (e.g., Fe and Mn), which are solubilized by reduction, reduced U primary forms insoluble oxides, the minerals uraninite (UO_2) and pitchblende (UO_2 (am)) (Langmuir, 1997). For this reason, U is often referred to as a "reverse redox species."

Whether U reduced in marine sediments is preserved or released back to solution depends upon sediment and bottom water redox conditions. Reduced U(IV) minerals exposed to dissolved oxygen are readily oxidized to soluble U(VI) species and released from sediments (Shaw et al., 1994, Zheng et al., 2002). Considering this dependence, several recent studies have examined U's efficacy as a paleotracer of oceanic surface water productivity and sediment/bottom water redox character (Chaillou et al., 2002; Mangini et al., 2001; Nameroff et al., 2002; Pailler et al., 2002). Theoretically, sediment layers enriched in uraninite could reflect ancient bottom water and sediment anoxia since insoluble uraninite may be buried and preferentially preserved during periods of dominantly reducing conditions (Shaw et al., 1994).

Despite all that is known about aqueous geochemistry of U, its application in process-oriented studies is limited by a lack of quantitative understanding of its global sources and sinks (Swarzenski et al., 1999; Dunk et al., 2002; Zheng et al., 2002). For example, with regard to U sources, the role of groundwater in delivering dissolved U to the ocean remains uncertain (Dunk et al., 2002), and only a few studies have compiled global assessments of riverine U transport (Palmer and Edmonds, 1993; Windom et al., 2000). Conversely, although the removal of U from seawater has been widely studied (Barnes and Cochran, 1993; Church et al., 1996; Swarzenski et al. 1999; Klinkhammer and Palmer, 1991; Zheng et al., 2002; Windom et al., 2000) and is thought to be dominated be the reduction of U in oceanic sediments, several mechanisms may be involved (Dunk et al., 2002), and their relative importance is still largely unknown (Swarzenski et al., 1999; Dunk, 2002). In particular, few studies have examined the importance of suboxic intertidal coastal environments like salt marshes and mangrove forests in the removal of oceanic U.

Globally, salt marsh and mangrove environments occupy 3.8 x 10^{11} m^2 (Woodwell et al., 1973) and 1.8 x 10^{11} m^2 (Spaulding, 1997), respectively. Located at the interface of land and sea, these fringing ecosystems are above and below ground mixing zones of fresh and saline waters. Because of their unique position in the landscape and active biogeochemical cycling, salt marshes are biologically productive environments and are capable of significantly modifying the chemistry of ambient waters (e.g., by removing and supplying nutrients to surface waters). Since the regions surrounding salt marshes are among the most rapidly developing areas in United States, salt marshes are often important in assuaging anthropogenic impact to the coastal environment. Furthermore, because salt marshes and intertidal environments are more aerially extensive during interglacial periods, their influence on surface waters may be particularly important for understanding interglacial-glacial time-scale changes in ocean chemistry (Windom et al., 2000).

Several recent studies provide evidence of significant U removal in estuaries associated with salt marshes and mangrove forests (Maeda and Windom, 1982; Sarin and Church, 1994; Carroll and Moore, 1994; Shaw et al., 1994; Church et al., 1996; Windom et al., 2000). With each tidal cycle, U in sea water is delivered to these chemically and biologically active environments, where it can be removed from surface waters. In both the Savannah and Ogeechee River salt marsh estuaries, Maeda and Windom (1982) observed extensive U removal for samples collected during summer months, especially during low flow conditions. In fact, they concluded that both estuaries were net sinks for oceanic uranium, since, based on the shapes of U salinity profiles, U-removal rates must exceed the riverine input rate of U. Sarin and Church (1994) presented data showing the removal of U from the Chesapeake and Delaware bays. In both systems, U showed seasonally variable depletion at low salinities (< 5 psu) followed by conservative mixing. These authors demonstrated removal during spring (April) and summer (July and August) months. Shaw et al (1994) also observed depleted U in Chesapeake Bay waters beginning in April and continuing through October. Carroll and Moore (1994) documented strong U removal at salinities < 12 psu, followed by conservative mixing, for the Ganges-Brahmaputra mixing zone. Removal in this setting was limited to low discharge periods, when the low-salinity region of the mixing zone was spatially coincident with the coastal fringing mangrove forests.

Chesapeake Bay surface water samples collected by Church et al. (1996) demonstrated that intertidal salt marshes could be strong sinks for U at all salinities. They observed non-conservative U behavior during summer months and increased removal with higher tides. Finally, Windom et al. (2000) presented data on the behavior of uranium in eight different global estuaries. Their review showed that uranium mixed conservatively in most estuarine systems although they observed significant uranium removal in the Savannah estuary for all sampling periods (February through August).

Several mechanisms have been suggested to explain the observed removal of U from estuarine surface waters. U may be removed with particles from low-salinity regions by flocculation of humic substances and/or metals oxides or by biological uptake (Maeda and Windom, 1982; Sarin and Church, 1994; Shaw et al., 1994; Church et al., 1996). Particle-associated U could then be deposited with salt marsh sediments, buried, and, under the appropriate conditions, reduced. The chemical characteristics of the fresh-water/saline-water transition zone lend support to this hypothesis: The depression of pH, pe, and alkalinity in upper estuaries might destabilize the dominant uranyl carbonate complex, enhancing U complexation with water column solids (Church et al., 1996). Furthermore, the upper estuarine zone is typically associated with a region of elevated productivity supporting biological uptake by plankton or biodetritus (Shaw et al., 1994).

Tidal flooding of the marsh surface may also contribute to U removal. Favoring this hypothesis is the summertime increase in salt marsh surface acidity (resulting from the oxidation of sulfide), which could destabilize the dominant uranyl carbonate complex (Church et al., 1996), and elevated U concentrations observed in surface sediment extractions (Church et al., 1994; Summerton, 1992). Another important observation is the positive correlation between tide height and U removal (Church et al., 1996). U in tidal water that infiltrates creek banks or the marsh surface could adsorb to metal oxides at the oxic/anoxic interface (Barnes and Cochran, 1993; Shaw et al. 1994), thereby increasing removal. This mechanism would be especially effective during spring and summer periods when marsh surface area increases and surface sediments are oxidized due to active bioturbation.

The mechanisms discussed above rely mainly on sorptive processes to explain U removal. However, the reduction of U could contribute much more to removal in estuaries (and other anoxic coastal environments) than previous studies have suggested. Diffusion of U to organic-rich suboxic and anoxic oceanic sediments followed by microbially-mediated reductive precipitation of UO_2 is considered the dominant sink for oceanic U (Klinkhammer and Palmer, 1991, Barnes and Cochran, 1993, Dunk et al., 2002). With this in mind, Windom et al. (2000) and Carroll and Moore (1994) hypothesized that uranium removal in salt marsh and mangrove estuaries was the product of anaerobic, microbially-mediated processes occurring in intertidal sediments. Windom et al. (2000) further suggested that the circulation of tidal water through salt marshes, a process driven by tidal inundation, would be an efficient way to deliver oceanic uranium to anoxic sediments for processing. The efficacy of this process should be enhanced by subsequent advection of pore waters through salt marsh sediments, which would allow uranyl complexes to penetrate to deeper sediments before reduction, making seasonal reoxidation is less likely.

Several lines of evidence suggest that microbial processes probably play a fundamental role in the removal of U in coastal environments. Several recent laboratory studies have shown that pure cultures of environmental iron- and sulfate-reducing bacteria can efficiently reduce U(VI) to U(IV) (Lovely et al., 1991; Lovely and Philips, 1992; Lovely et al., 1993). Barnes and Cochran (1993) used sediment incubations to show that U-removal was correlated to sulfate reduction. Summerton (1992) observed significant enhancement of U in South Australian salt marsh soils compared to inland soils, consistent with the recent incorporation of U. The U-content was highest from samples collected from organic-rich sediment layers with actively reducing microbial populations, indicated by the strong odor of H_2S. Since salt marshes and mangrove forests are active biogeochemical settings dominated by sulfate reducing bacteria and exhibiting compressed redox stratification (Howarth and Teal, 1979), highly reducing conditions typically exist close to the marsh surface. Circulation of tidal water through salt marshes introduces U to the reducing marsh subsurface, where sulfate- and iron-reducing bacteria that are also capable of reducing U are abundant (Lovely et al., 1991, Barnes and Cochran, 1993; Abdelouas et al., 2000). The reduction of U in salt marsh sediments would leave pore- and groundwaters that discharge to the tidal creek at low tide U-depleted. If this mechanism is active, the extent of documented surface water U removal should correlate with shallow groundwater discharge. In practice, removal may be a product of all the processes discussed above, with the importance of any given mechanism and the overall magnitude of removal changing with the physical, biological and chemical characteristics (e.g., temperature, salinity, tidal amplitude, microbial activity, marsh productivity and permeability, etc.) of each particular environment.

In addition to the uncertainty surrounding U removal mechanisms in coastal settings, several associated and important unknowns warrant further investigation. First, the literature contains only three quantitative estimates of U removal (Church et al., 1996; Windom et al., 2000; Dunk et al., 2002). Windom (2000) predicted a uranium removed rate of ~70 μmol m^{-2} $year^{-1}$ for southeastern United States salt marsh estuaries. This compares to a rate of 15 μmol m^{-2} $year^{-1}$ determined by Church et al. (1996) for Delaware salt marshes. Dunk et al. (2002) used data by Carroll and Moore (1994) to generate an additional removal estimate of 30 μmol m^{-2} $year^{-1}$ for mangrove forests of the Ganges-Brahmaputra mixing zone. While these estimates are of the same order of magnitude, the associated uncertainties are considered to be quite large (Dunk et al., 2002). These uncertainties can mostly be attributed to the lack of published removal estimates, the uncertainty of the seasonal pattern and extent of U removal, and the inherent physical and chemical variability of the coastal environment.

Also, although U removal clearly varies with season, no previous study has collected and analyzed a continuous series of estuarine profiles or quantified the seasonal changes in U removal in salt marshes or mangrove forests. Previous studies grouped datasets, ignoring seasonal distinctions (Windom 2000), and/or sampled infrequently, so that a continuous seasonal evaluation of removal was not possible (Sarin and Church, 1994; Church et al., 1996). In another study, the researchers sampled a setting where removal was limited to very specific flow conditions, preventing a meaningful seasonal comparison (Carroll and Moore, 1994).

This study addresses these uncertainties by documenting and quantifying the seasonally-variable removal of U in a salt marsh-dominated South Carolina, USA tidal creek. We generate additional local and global U-removal estimates that consider a more comprehensive and continuous surface water dataset. Furthermore, by sampling both surface- and groundwater, we gain insight into the potential importance of surface water circulation though salt marshes for U removal. Based on the idea that surface water cycling through salt marshes is affecting U removal, we hypothesize that the U distribution in surface water may be a tracer for surface- and groundwater exchange and shallow pore-/groundwater discharge. We conclude this thesis by discussing the validity of this argument and by using a simple mixing model to calculate both the fraction of tidal creek water with a groundwater source and the groundwater discharge rate for the study area's headwaters region. The inclusion of some of the more enigmatic data is meant to provoke additional interest in this area of research.

1.2 Site Description

The study area is located in the lower coastal plain region of South Carolina (Beaufort County) near the headwaters of the Okatee River system. Specifically, the site straddles state route 278, which connects Interstate 95 with Hilton Head Island (Figure 1.1). The Okatee River is a small tidal creek (5-10 m wide, 1-3 m deep). Between August 2002 and July 2003 the Okatee accepted a total estimated freshwater flow of 6.4 to 7.7 x 10^6 m^3 $year^{-1}$. Discharge from the Okatee feeds the Colleton River, which flows into the Chechessee River en route to the Port Royal Sound. Measured along the flow path of these tributaries, the site is approximately 40 km from mouth of the Port Royal Sound. During the 2002 calendar year, the site experienced an average tidal amplitude of 2.13 ± 0.39 m, with a maximum of 2.88 m (USGS Real-time Data, station 02176575). This large tidal range is typical for the South Atlantic Bight region. The salinity of the tidal creek, measured near the USGS gaging station during 8 field campaigns spanning 10 months, typically varied between 0 (at low tide) and 25 psu (at high tide), although values as high as 38 were recorded during the first sampling trip in August 2002. Roughly 1 km upstream of the site, saline tidal influence diminishes,

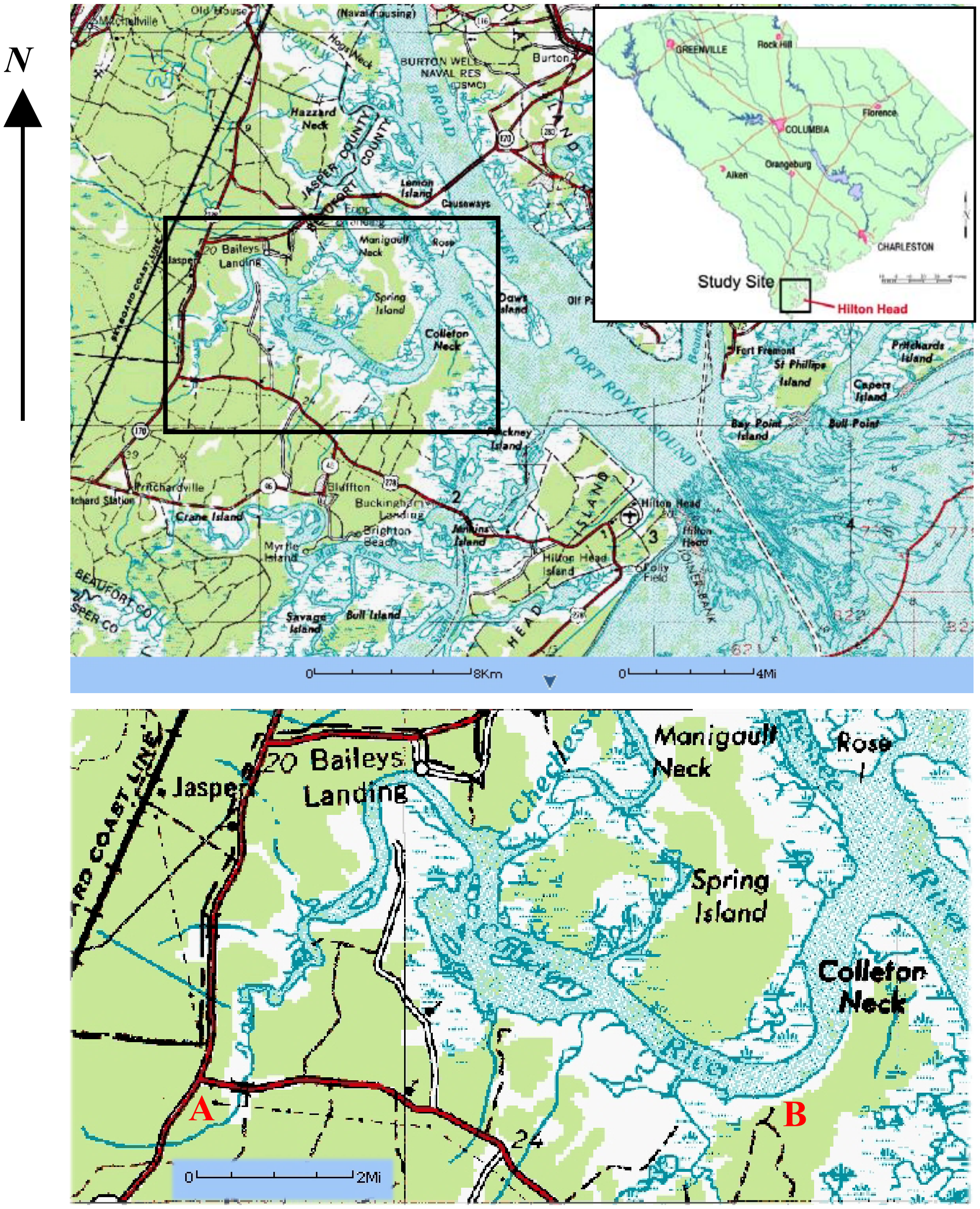

Figure 1.1 Site diagram. The points marked A and B in the lower figure represent our study site and the Waddell Mariculture Center, respectively.

and upland vegetation dominates riparian areas, implying a nearly fresh groundwater/ surface water system.

The Okatee river system is surrounded by extensive salt marsh. For the headwaters area near the study site, the width of the salt marsh varies between 35 m to greater than 200 m. Based on United States Geological Survey (USGS) and National Wetland Inventory (NWI) land-use/land-cover data, between 2785 and 2865 hectares of non-forested, tidal wetland surround the Okatee River above its confluence with the Colleton River (S. Walker, pers. comm.., 2003).

Three species of vegetation dominate the Okatee salt marsh: *Spartina alterniflora*, glasswort (*Salicornia*), and *Juncus roemerianus*. These species exhibit a consistent zonation, based on a complex variety of factors, including elevation, frequency and duration of inundation, soil texture, nitrogen availability, sulfide concentration, and soil moisture content, permeability and salinity (Clewell, 1997). The large tidal amplitude of the region favors an extensive zone of *Spartina* extending from the tidal creek toward the upland, with a limited zone of *Juncus* at the marsh's upland edge (Clewell, 1997). Tidal inundations flood *Spartina* zones daily or almost daily, with tall *Spartina* proliferating at lower elevations and in softer sediments and short *Spartina* growing at higher elevations and in firmer sediments. *Juncus* usually grows adjacent to the upland-marsh boundary, but does occasionally grow closer to the tidal creek in the study area. Glasswort is generally found between *Spartina* and *Juncus* stands in hypersaline soils, which typically occur proximal to the upland, where tidal inundation is more sporadic and where stranded ponds of tidally introduced water may take days to evaporate.

During our investigation, we installed eleven monitoring wells along three salt marsh transects, each positioned roughly perpendicular to the tidal creek and upland (Figure 1.2): Transect 1, consisting of monitoring wells (MW) 01n, 01s, 02, and 03, is located 60 meters south of the route 278 on the east side of the tidal creek; Transect 2 (wells 04 and 05) is located 120 meters south of route 278 on the west side of the tidal creek; and Transect 3, located 200 meters north of route 278, bridges the tidal creek, with wells 06 – 09 on the west side and well 10 on the east. Well locations sample different salt marsh terrain chosen primarily based on differences in dominant vegetation. All wells draw from a heterogeneous surficial aquifer that has confined and unconfined components, depending on local lithologies. Geographical well locations and other well/transect specific information are provided in Table 1.1 and Appendix A, Table A.1.

Site-specific stratigraphic information was obtained from continuous core logs recovered during well installation. Sediments are heterogeneous; typically 1-2 meters of organic rich, fine textured sediments cap a complex of clay, clay-/fine-sand, and sporadic layers of more permeable materials such as coarse sand and small gravel. Core logs and aerial photographs suggest that past meandering of the tidal creek has significantly influenced shallow marsh statigraphy. Occasional down-core layers of coarse sand and small gravel point to the existence of former stream channels that are now remote from the creek's main channel (Figure 1.3). Former channels, along with permeable-sediment outcroppings visible during low tide, probably provide conduits for significant subsurface groundwater flow to surface waters (Whiting and Childers, 1989; Portnoy et al., 1998; Jahnke et al., 2003). In most cases, the penetration of shallow wells was stopped at a local confining layer, consisting of brittle green clay. Fragments of this clay, presumably rip-off clasts, are present in several cores as well as in current creek bottom sediments.

Table 1.1
Well parameters and well transect information. Additional well specifications are provided in an expanded table in Appendix A.

Well ID	Distance[a]	Distance[b]	Elevation[c]	Plumb Depth[d]	North Latitude[e]	West Longitude
Okatee Transect 1 (South of South Carolina Route 278 bridge)						
MW01S	3	50	0.058	2.51	32 17.308	80 55.738
MW01N	3	50	0.070	2.74	32 17.307	80 55.739
MW02	17	40	0.210	1.79	32 17.309	80 55.731
MW03	2	40	0	1.81	32 17.316	80 55.748
Okatee Transect 2 (South of South Carolina Route 278 bridge)						
MW04	0	75	0	1.63	32 17.284	80 55.792
MW05	20	55	0.043	2.36	32 17.286	80 55.803
Okatee Transect 3 (North of South Carolina Route 278 bridge)						
MW06	2	69	0.600	2.04	32 17.477	80 55.774
MW07	2	110	0.000	3.32	32 17.474	80 55.748
MW08	2	155	0.113	1.65	32 17.470	80 55.722
MW09	2	198	0	1.98	32 17.464	80 55.693
MW10	1	NM	NM	2.34	32 17.451	80 55.68

[a] Distance (m) from proximal creek bank at bank full stage.
[b] Approximate distance (m) from upland/marsh boundary.
[c] Transect-specific elevation (m); wells of different transects were not connected during surveys.
[d] From ground surface (m).
[e] Determined using hand held GPS unit (accuracy ~ 5 m).

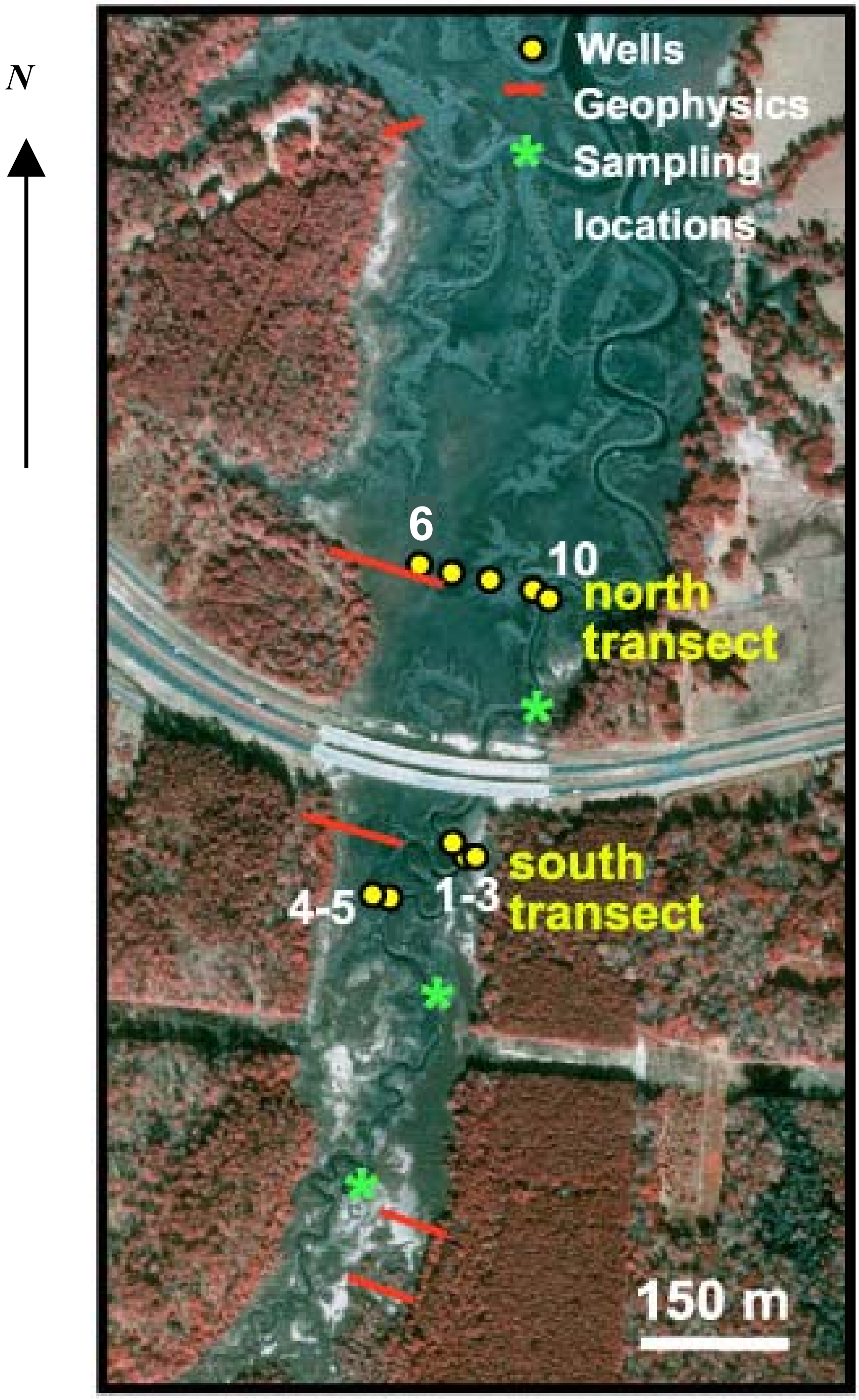

Figure 1.2 Large scale site diagram (expansion of point A, Figure 1.1). This map shows the positions of monitoring wells (circles) sampled during this study as well as the locations of various other physical field surveys conducted at the site. "Sampling locations" refer to work by other researchers.

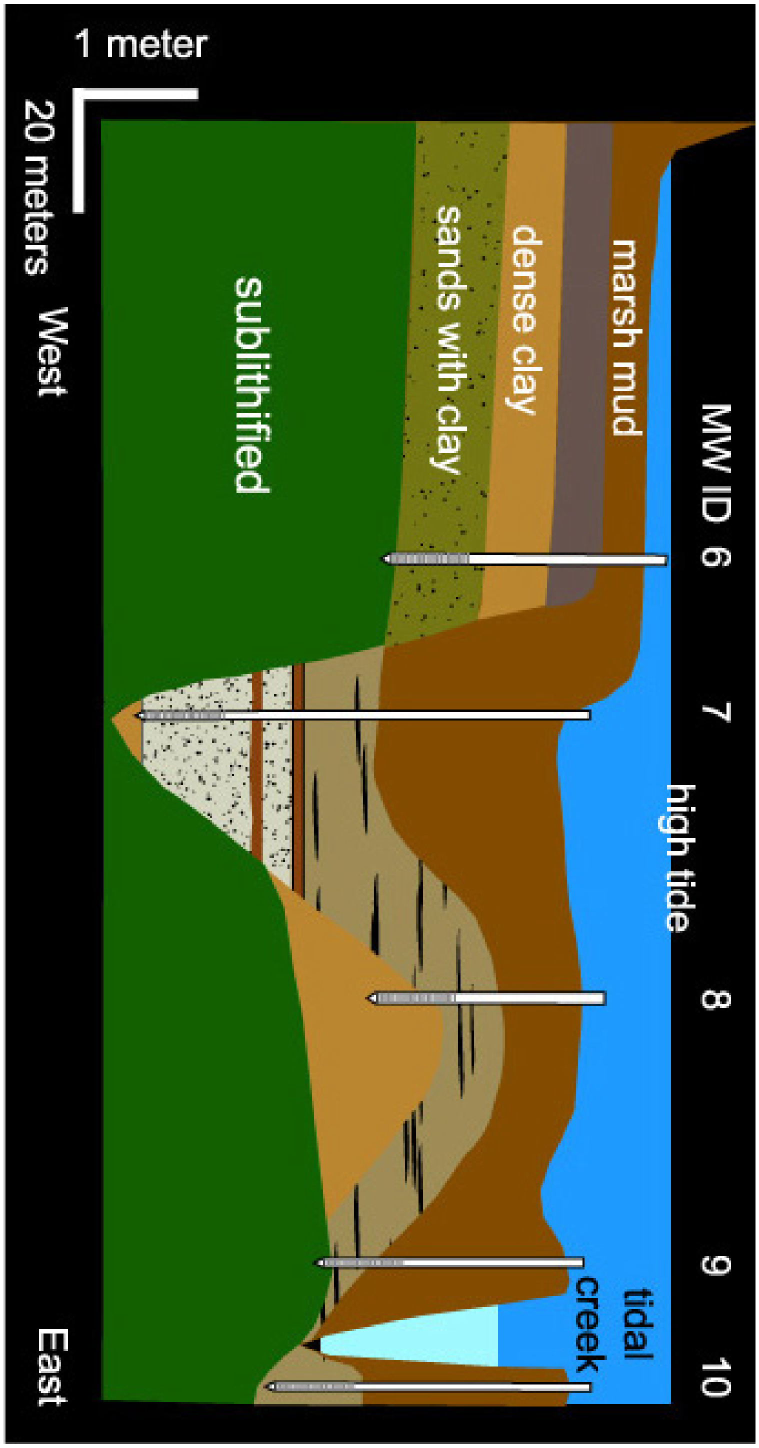

Figure 1.3 Conceptualized sediment cross-section for transect 3 (north transect; MWs 6 though 10 from left to right). The cross-section is based on simplified stratigraphic information from continuous core logs obtained during well installation. This figure illustrates the heterogeneity of the salt marsh subsurface and suggests the importance of past meandering of the tidal creek for determining the character of shallow marsh sediments.

CHAPTER 2

METHODS

2.1. Chapter Summary

This chapter describes the techniques employed during this investigation. We begin with a summary of monitoring well installation and sediment core recovery/analysis and follow with a description of field sampling and laboratory protocol. We conclude with a brief discussion of hydrologic methods utilized for supplementary site characterization and a description of geochemical laboratory experiments performed to support our hypothesis.

2.2. Monitoring Well Installation/Stratigraphic determination

We installed monitoring wells along three transects oriented roughly perpendicular to the tidal creek during two field excursions in January and May, 2002. The installation technique was designed for minimum disruption of the sediments and aquifer(s) and involved vibrating a 7.62 cm (4”) O.D. (1.65 mm wall thickness) aluminum pipe to the depth of refusal (2.2 to 3.6 m). The aluminum pipe was subsequently extracted and a 5.08 cm (2”) O.D. Schedule 40 PVC monitoring well consisting of a 3.81 cm (0.125’) conical well point, a 0.61 m (2’) length of machine-slotted (0.152 mm/0.006”) high-flow screen, and two to three 1.52 m (5’) solid “riser” sections was pushed into the open borehole. For MW06, we placed clean filter sand in the annular space around the screened interval. For all other wells, the marsh sediment collapsed around the screen and no filter sand was required. As necessary, excavated sediment was used to backfill the borehole around the riser, with care taken to avoid bridging the annular space.

Well completion involved installation of a thick (~ 30 cm) attapulgite seal overlain by a quick-drying concrete surface pad to prevent annular flow. Subsequently, the riser section was extended 2 – 5 ft (depending on elevation/tidal range) above the marsh surface and then encased with a 10.2 cm (4”) O.D. segment of PVC for wellhead protection. We developed each well by high rate pumping until the water ran clear or the well went dry.

We obtained continuous stratigraphic information for recovered sediment cores by splitting the cores lengthwise with a circular saw and identifying dominant layers by color, sediment type, grain size, mineralogy, and presence or lack of fresh organic material. We did not rigorously correct the sediment core lengths for compaction.

2.3. Geochemical Sampling

2.3.1. General Considerations

We collected samples during 8 field trips between August 2002 and June 2003. Field trips were planned to roughly coincide with full or new moon periods and thus the highest monthly tides. As discussed later, this strategy permitted us to target sampling periods when the degree of uranium removal from the tidal creek water should be nearly maximum (Church et al., 1996).

Surface water and groundwater samples were collected during each field trip, with sporadic marsh runoff/groundwater seepage (MRO/GS) sample collections. MRO/GS samples were typically collected near low tide from rivulets draining the marsh surface or from location of apparent groundwater seepage along the creek bank. We obtained MRO/GS samples to provide initial anecdotal evidence for various uranium removal mechanisms and to motivate later laboratory investigation. We collected additional surface water samples from the Colleton River (accessed from the Waddell Mariculture Center dock) during each field trip and seasonally from freshwater sources supplying the Okatee headwater area to constrain higher salinity estuarine chemistry and to determine best-available endmember concentrations for mixing calculations. All equipment (bottles, syringes, filters, tubing, etc.) was rinsed/equilibrated with sample before final collection, and trace metal grade pipette tips and nitric acid were used. However, we did not employ strict trace metal free methodology, since the chemical species of interest are typically not contaminants of concern on the materials utilized. To verify this assumption, we used a range of filter, bottle, acid, and tubing blanks to confirm that the samples were free of contamination.

2.3.2. Groundwater

We obtained groundwater samples using a variable-speed peristaltic pump equipped with rigid polyethylene tubing and a length of Tygon tubing fitted within the pump head. Using a slow pumping rate (~0.25 L/minute), wells were first purged of ~ 1 well volume. Subsequently, groundwater was redirected through the bottom of a flow cell that housed a conductivity, salinity, and temperature (CST) probe (WTW MultiLine P3 pH/Conductivity meter, equipped with TetraCon 325 probe for CST determination, calibrated before each field trip). Once the instruments' readings stabilized (usually within 5 minutes), a sample was pumped directly into a 50 ml all polypropylene/polyethylene (pp/pe) syringe (Fortuna), which was rinsed 3 times with fresh groundwater, and filtered using 25 mm, hydrophilic 0.45 μm PTFE filters (Millipore, Millex LCR25mm). The first 5 ml of filtrate was used to rinse new 60 ml polypropylene bottles of any existing debris and discarded. The remaining 45 ml sample was filtered and acidified to ~ 1 % HNO_3 (TraceMetal grade, Fisher Scientific) for uranium and barium determinations.

Additional samples for iron and phosphate analyses were collected using the same protocol and stored in 15 ml Falcon tubes. All samples were stored cold and in the dark until analysis, within 3 days for iron and phosphate and approximately one month for uranium. Samples from August 2002 through March 2003 were analyzed at one time for barium in March 2003. Subsequent samples were analyzed for barium in the same time-frame as uranium.

Due to the limited hydraulic conductivity of the formations intersecting the screened intervals of several of the wells, we took special care while purging wells to assure that samples were as representative as possible and originated in the adjacent aquifer. All groundwater samples, with the exception of MWO6, which contained iron-sulfide precipitate, were generally clear and particle free; all samples filtered quickly and easily.

2.3.3 Surface Water

Surface water was collected near the USGS stage gage platform, immediately southeast of the Rte 278 bridge, during each field trip. We monitored tidal creek salinity with a CST probe and collected several samples spanning the full range of available salinity during a unique diurnal tidal cycle. To ensure the accurate determination of salinity and temperature, creek water was first collected in a ridged polypropylene plastic cup for measurement and then withdrawn from that receptacle using an all pp/pe syringe. The sample was then filtered and stored using the same protocol described for uranium and barium groundwater samples. During filtration, CST was measured on the volume of creek water remaining in the plastic cup. Unlike groundwater samples, surface water samples were usually olive green/brown and often (especially at salinities ~ < 5 psu) difficult to filter. As a result, sample volumes ranged from 45 ml (at higher salinities) to 15 – 20 ml at salinities < 5 psu. Samples collected sporadically from fresh water sources and routinely from the Colleton River were processed identically to tidal creek samples.

2.3.4. Marsh Runoff and Suspected Groundwater Seepage

Several times during our investigation, we collected water seeping from creek banks during low tide and running off the marsh along preferential flow pathways after high tide. For these samples, water was drawn directly from small rivulets with an all pp/pe syringe and filtered and stored using the same protocol described for uranium and barium groundwater samples. For in-situ measurements, the CST probe was placed in areas of "pooling" discharge and allowed to equilibrate. Like surface water samples, MRO/GS samples were particle-rich and difficult to filter.

2.4. Geochemical Analysis

All samples collected during this investigation were analyzed for uranium and barium concentrations in Dr. Herb Windom's laboratory at the Skidaway Institute of Oceanography using isotope dilution inductively coupled plasma/mass spectrometry (ID ICP/MS). The technique is modified from the barium method of Klinkhammer and Chan (1990) and involves spiking an aliquot of sample with an appropriate volume of ^{235}U- or ^{138}Ba-enriched isotope solution. For a given sample, the concentration of the more abundant naturally occurring isotope (^{238}U and ^{135}Ba) is initially predicted based on sample salinity and the assumption of conservative mixing, and spike is added to achieve a measured isotope ratio (^{235}U/^{238}U or ^{138}Ba/^{135}Ba) close to unity. Following spike addition and a variable dilution (depending on sample salinity), samples were analyzed on a VG-Elemental PQII Plus ICP/MS by repeated scanning over the desired mass range (e.g., for U, 233.6 to 239.4 amu). Accuracy and precision were determined by analyzing blanks and samples of known U or Ba concentration placed at the beginning of each run and after every ten samples. The accuracy of U and Ba analysis was typically ± 5%. Precision, measured as the standard deviation of known replicate samples, was ≤ 0.04 ppb and ≤ 0.2 ppb for U and Ba, respectively. Because of its exemplary performance, the ID ICP/MS technique was recently applied in the certification of a standard reference material for the Canadian Research Counsel (Windom et al., 2000).

Total dissolved iron and inorganic phosphate were determined colorimetrically for all groundwater samples collected during, and subsequent to, the March 2003 field campaign. Ion was determined using a modified ferrozine technique after Stookey

(1970), where all dissolved iron is reduced to ferrous before analysis by spiking the sample with hydroxylamine and storing for 24 hours. Phosphate was measured using the standard acidified molybdate reagent and an ascorbic acid reductant (Grasshoff et al., 1999). Phosphate samples with high sulfide contents (based on the characteristic odor) were acidified (10 μl, 5 N HCL) and purged with N_2 for 15 minutes to minimize H_2S interference (Standard Methods 1999).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Introduction

This chapter presents geochemical results and interpretation of 8 months of investigation in the headwater area of the Okatee River, South Carolina. Results are discussed based on analyte (temperature, salinity, uranium, barium, total iron, and dissolved inorganic phosphate) for surface- and groundwater samples. We then present the results for marsh run off and groundwater seepage samples.

3.2. Geochemistry: Surface- and Groundwater

3.2.1. Temperature

We measured temperature on all groundwater and surface water samples collected during and after the August 30, 2002 sampling trip. The temperature of groundwater samples ranged from 12.2°C (MW01n, Jan 03) to 30.9°C (MW02, Oct 02). For surface water samples, temperatures ranged from 5.6°C (January 2003, rising tide, salinity = 17.1 psu) to 30.2°C (falling tide, October 2002, salinity = 19.5 psu). For all surface water samples collected, temperature increased with salinity. In general, for a given salinity, the temperature of falling tide samples exceeded those collected during the rising tide. We attribute this finding to radiative heating of tidal waters on the marsh surface during flooding tide.

Groundwater and surface water temperatures in the Okatee headwaters showed significant seasonal variation, with maximum and minimum values occurring in October and January, respectively. The large temperature fluctuations observed should result in major seasonal changes in the biogeochemical cycling of the salt marsh system, since chemical reaction rates typically double for every 10ºC increase in temperature (Connors, 1990). Groundwater temperatures showed a dampened, though apparently in phase, response to seasonal fluctuations of fresh (salinity < 1) and Colleton River surface water temperatures (Figure 3.1).

Depending on their location in the marsh, some wells showed a more dramatic response to surface water temperature variations. In general, forcing was most pronounced in wells from Transect 1 (01n, 01s, 02, and 03), with fluctuations generally greater than the site average (Figure 3.2). With the exception of MW04, fluctuations in Transects 2 and 3 were generally less pronounced than the site average, particularly in MWs 07 and 10, which showed significantly dampened responses to the seasonal rise in surface water temperatures (Figures 3.3 and 3.4). The limited response of these wells to seasonal temperature variations suggests the continuous influence of groundwater from a deeper or more upland source, where physical and chemical characteristics remain relatively constant throughout the year.

3.2.2. Salinity

Using a WTW MultiLine P3 pH/Conductivity meter, we obtained salinity data for every sample collected during this investigation except those acquired on August 8, 2002 trip. Salinities for these latter samples were measured in the lab using a refractometer.

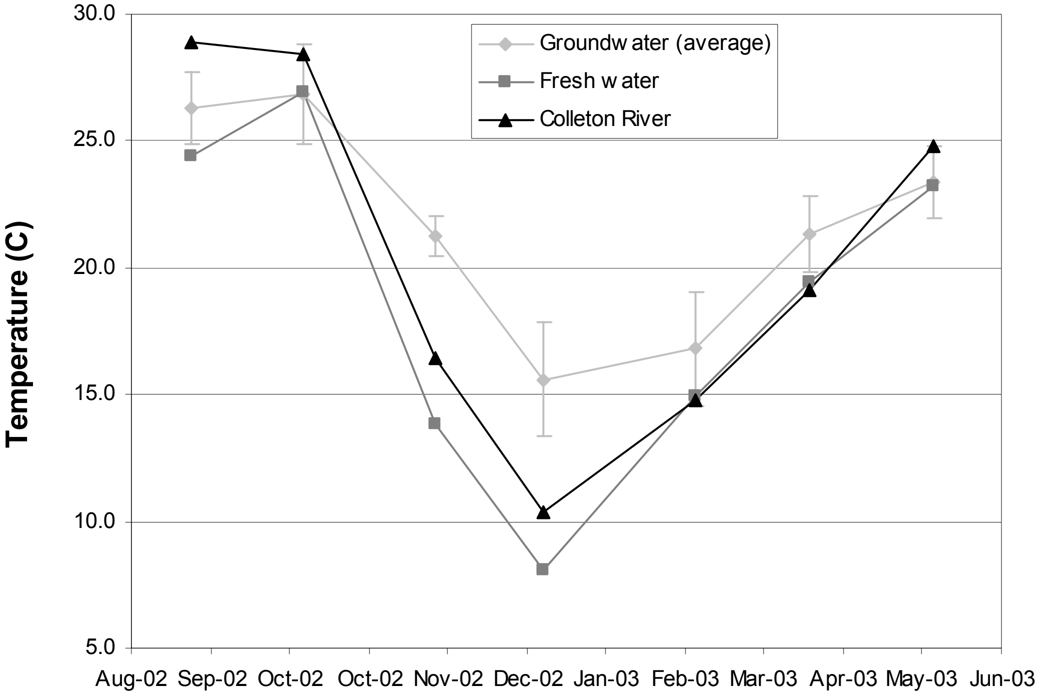

Figure 3.1. Seasonal groundwater and surface water temperatures for August 30, 2003 to June 3, 2003 sampling events. Groundwater values represent the average of all wells sampled during a given field outing (maximum n = 11). Fresh water values represent single measurements taken from endmember samples or from low salinity (< 1) creek samples. Saline surface water samples were collected from the Colleton River during each field trip. Seasonal fluctuations are apparent, with groundwater showing a dampened response to changes in surface water temperatures. Error bars on groundwater concentrations are ± 1 standard deviation.

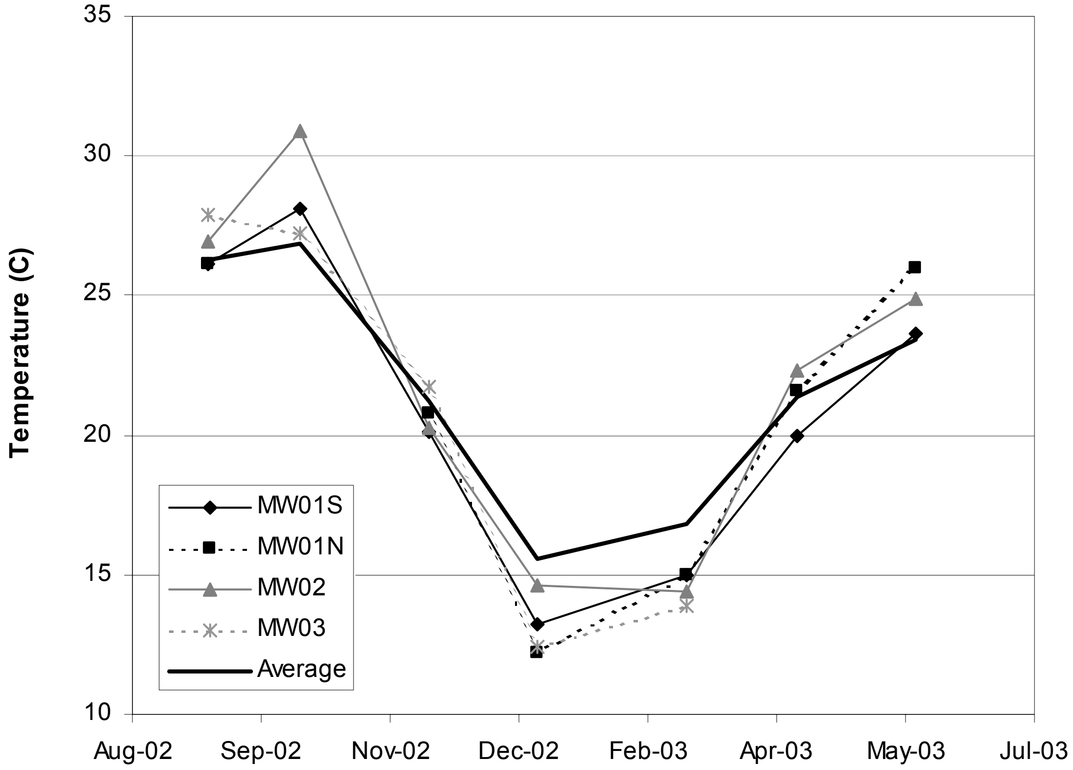

Figure 3.2 Seasonal variation in transect 1 groundwater temperatures for August 30, 2003 to June 3, 2003 sampling events. Wells from transect 1 showed a more dramatic response to surface water temperature variations than average site groundwater (n = 11). MW03 was not samples after March 2003.

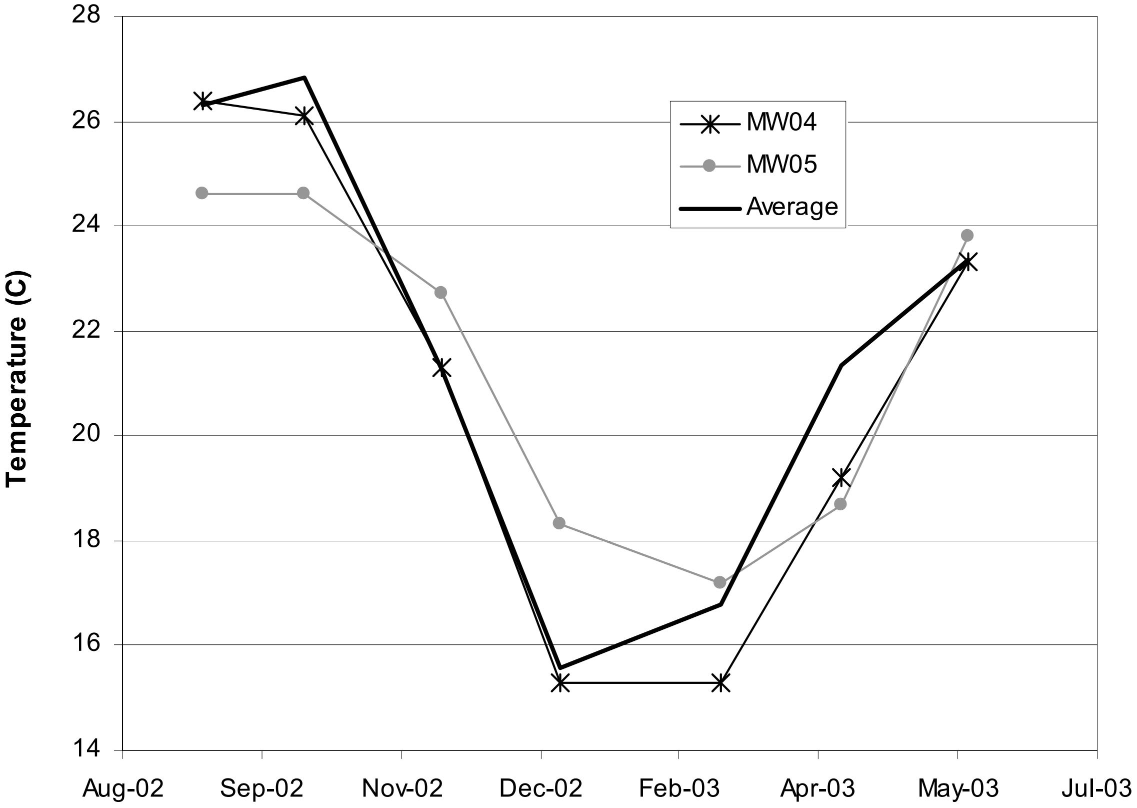

Figure 3.3 Seasonal variation in transect 2 groundwater temperatures for August 30, 2003 to June 3, 2003 sampling events. MW04 showed similar variation to average site groundwater, while MW05 displayed a dampened response.

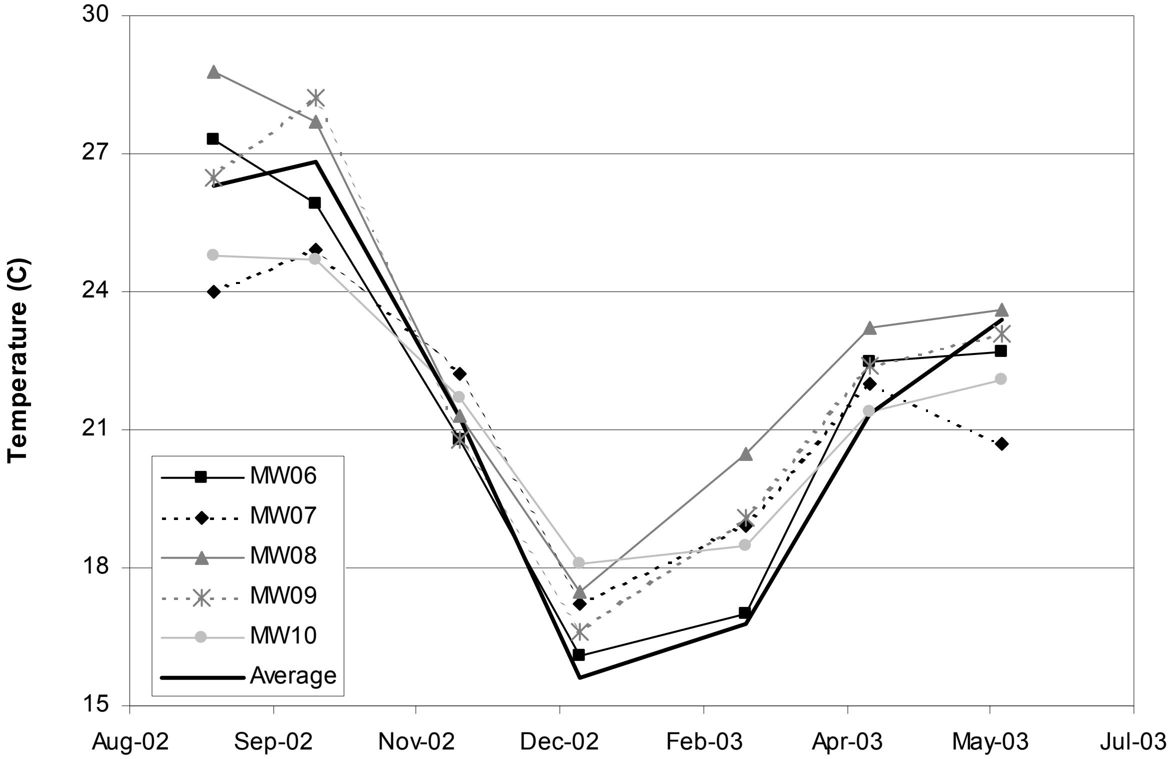

Figure 3.4 Seasonal variation in transect 3 groundwater temperatures for August 30, 2003 to June 3, 2003 sampling events. In general, wells from transect 3 showed a dampened response to surface water temperature changes compared to the average groundwater temperature at the site. This was especially apparent in MWs 07 and 10 during summer 2002 and spring/summer 2004 sampling events.

The salinity of surface water samples varied with both the tidal cycle and the season (Table 3.1). We observed salinities from 0.5 to 38 psu during high tide measurements and from 0 to 8 psu during low tide measurements. These variations can be attributed to several interacting factors, including season, recharge events, rate of evapotranspiration, degree of groundwater discharge, and tidal range. For example, the August 8, 2002 creek samples (8 – 37.7 psu) were highly saline, probably due to seasonally high temperatures and low precipitation, compared to August 30, 2002 samples (0 – 0.5 psu), which were collected during a major storm event. In general, we recorded salinities of less than 1 psu for samples collected during low tide.

Additional surface water samples were collected seasonally from two freshwater tributaries of the Okatee River and routinely from the Colleton River at the Waddell Mariculture Center, Bluffton, SC. The salinity of Colleton River samples ranged from 25.2 (June 03) to 36 (Aug 8, 2002).

Table 3.1.
Salinity range, number of samples, and tidal stage for tidal creek samples and salinity of individual Colleton river samples for surface water collected between August 2002 and June 2003.

	8-Aug[a]	30-Aug[b]	7-Oct	26-Nov[b]	5-Jan	4-Mar[b]	3-June	16-Apr
Range (psu)	8 - 37.5	0 - 0.5	0.7 - 23.7	0.1 - 14.4	0.5 - 22.2	2.4 - 13.3	0.2 – 16.5	0.2-15.5
n =	8	8	10	10	11	4	10	11
Stage	Falling/ Rising	Falling	Falling	Rising	Falling	Falling	Falling	Falling
Colleton R. (psu)	36	34.4	30.4	28.3	29.2	28.8	26.3	25.2

[a] Salinity measured with refractometer.
[b] Recent or active rain event.

For groundwater samples collected from monitoring wells, salinities varied between 21.3 and 52.8 psu, with maximum and minimum values observed in MW02

(October 2002) and MW01n (June 2003), respectively. Krest et al. (2000) and Shaw et al. (1998) measured similar salinities (25 – 40) for shallow groundwater samples collected from a North Inlet, SC salt marsh. Table 3.2 lists the salinities for all groundwater samples collected during this investigation. In general, monitoring wells 01s, 02 through 04, and 06 tended to have higher salinities, with average values between 33.2 (MW04) and 48.6 (MW02), than wells 01n, 05 and 07 through 10, which showed averages between 26.5 (MW07) and 29.7 (MW08). With the exception of MW01n, lower salinity wells were located in tall *Spartina alterniflora*, lower elevation zones. Such areas were proximal to the tidal creek and are probably more strongly affected by tidal exchange and/or local groundwater discharge. However, salinity variations at our site could not be explained by marsh elevation or proximity to the tidal creek alone.

For example, MW01n, which is located ~1 m from, and ~30 cm deeper than, MW01s, is unusual in that pumping apparently affected its chemistry. When we collected our first groundwater samples, MW01s and MW01n had identical salinities. Over time, salinity in 01n decreased considerably while salinity in 01s remained relatively constant. It should be noted that MW01n is closer to the creek as a result of foot traffic that caused slumping of the bank in the area. It is possible that this disturbance increased the connection between the creek and the well. It is also possible that the somewhat deeper formations intersected by MW01n's screened interval (the brittle green phosphate-rich clay layer and specifically the coarse sandy sediment on top of this formation) are more permeable and have connection with the tidal creek or a lower, somewhat fresher groundwater reservoir. In addition, MW04, located along transect 2 (southwestern transect) and adjacent to the creek bank in tall *Spartina*, showed anomalously high salinity given its position in the marsh and the general trend of groundwater salinity at the site. This well sustained a higher pumping rate than most other wells at the site, which implies that it intersects a high permeability formation. Inspection of the creek bank near MW04 at very low tide revealed an outcropping coarse sediment layer beneath an overhanging clay layer. This coarse sediment layer was similar in appearance and approximate elevation to coarse, permeable layers observed in MW04 and MW05 sediment cores and may represent former creek-bottom sediments.

Table 3.2.
Shallow groundwater salinities (psu), averages, and standard deviations for all samples collected from August 2002 to June 2003.

	Salinities (psu)									
	9-Aug[a]	31-Aug	6-Oct	25-Nov	6-Jan	5-Mar	17-Apr	4-June	Average	St Dev
MW01S	39	38.4	37.2	36.8	37	36	34.9	34.9	36.8	1.5
MW01N	39	36.6	31.7	26.3	27.4	24.4	22.4	21.3	28.6	6.5
MW02	50	49.3	51.9	46.6	52.8	50.5	46.8	41.1	48.6	3.7
MW03	35	34.9	35.1	37	38.2	39	NS	NS	36.5	1.8
MW04	35	34.5	33.2	33.3	33.5	31.4	32.2	32.4	33.2	1.2
MW05	NS	27.9	26.6	27	27.7	27.3	27.8	27.9	27.5	0.5
MW06	38	37	35.2	35.7	35.7	34.5	35	34.9	35.8	1.2
MW07	28	27	25.8	26	26.4	26	26.4	26.5	26.5	0.7
MW08	35.5	32.7	25.5	27	29.5	29.9	28	29.1	29.7	3.2
MW09	NS	29	28.2	28.1	28.9	28.3	28.8	28.8	28.6	0.4
MW10	29	28.4	26.9	27.1	27.2	26.4	26.6	26.9	27.3	0.9
Average	36.5	34.2	32.5	31.9	33.1	32.2	30.9	30.4		
Average (w/o MW02)	34.8	32.6	30.5	30.4	31.2	30.3	29.1	29.2		

NS Well was not sampled.
[a] Salinity measured with a refractometer post-sampling in laboratory.

In most wells, we observed limited variability in salinity. MWs 01s, 01n, 02, 03, and 08 showed the most variability in salinity, with standard deviations of 1.5, 6.5, 3.7, 1.8, and 3.2 psu, respectively. All other wells had standard deviations less than 1.2 psu. In general, the seasonal pattern of salinity change varied depending on standard deviation; wells with lower standard deviations showed relatively consistent, but small, seasonal variation, while wells with higher standard deviations showed inconsistent seasonal changes. Figures 3.5 and 3.6 illustrate the variability and seasonality of salinity for these groupings of wells.

Figure 3.7 illustrates the positive correlation between the standard deviations of temperature and salinity for a given well and each well's average salinity. As is well established, groundwater in the Southeastern U.S. is usually colder than saline surface water during the summer and warmer than surface water connected to the ocean during winter. To explain the correlation in Figure 3.7, we postulate that, as the influence of seasonally variable forcing factors, such as evapotranspiration, precipitation, and tidal exchange, increases, the seasonal temperature variation observed in well samples will also increase. On the other hand, wells that exhibit more consistent physical and chemical properties must be less influenced by such forcing factors or more strongly influenced by a groundwater source of relatively consistent character.

3.2.3. Uranium

Background on Surface Water Mixing

We determined uranium concentrations using Isotope Dilution-Inductively Couple Plasma Mass Spectrometry (ICPMS) for all samples collected during this investigation. Our data analysis hinges on quantifying the difference between measured uranium concentrations and those predicted by the conservative mixing of saline and freshwater endmembers. In systems exhibiting salinity gradients, site mixing curves are often used to study the behavior of aqueous species, including U. When the relationship

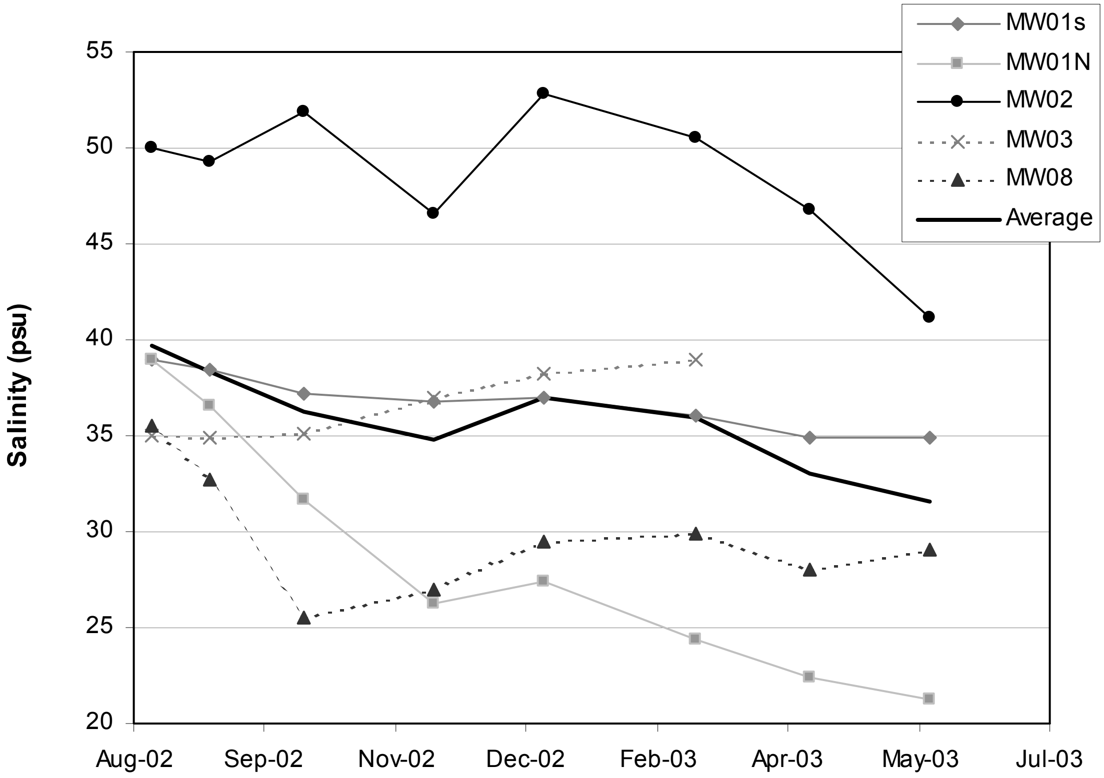

Figure 3.5 Variability of salinity in groundwater samples from wells showing standard deviation greater than 1.2 psu. With the exception of MW08, “more variable” wells were located along transect 1 and displayed inconsistent seasonality, suggesting a more complex set of governing factors when compared to “less variable” wells.

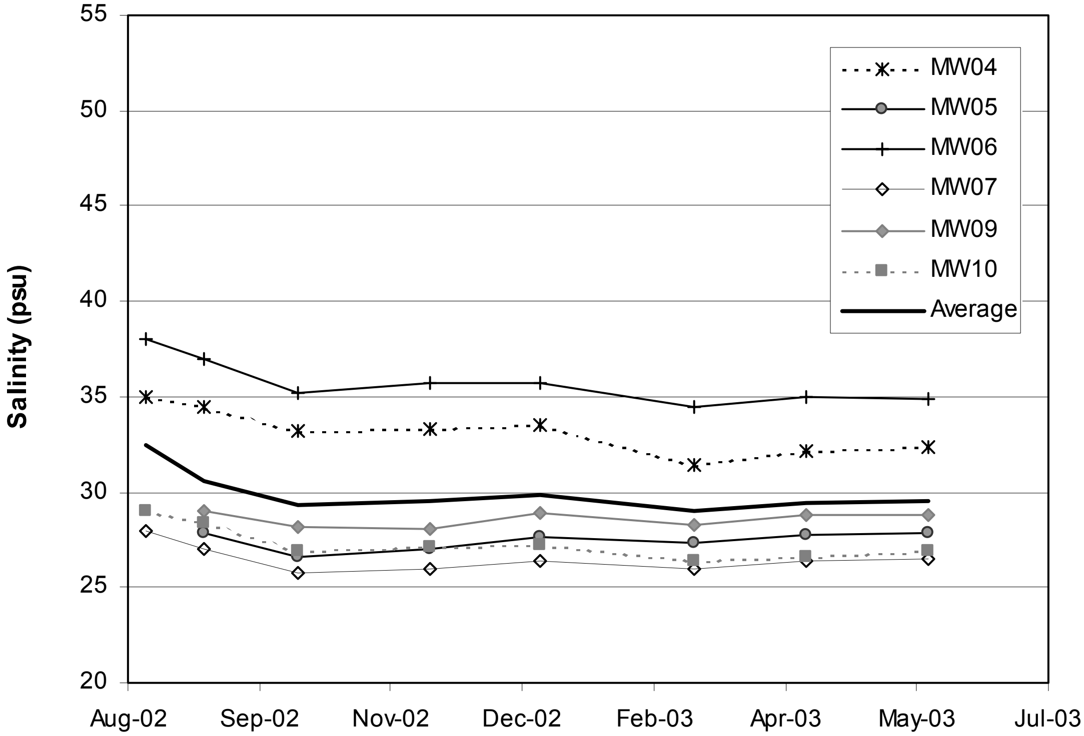

Figure 3.6 Variability of salinity in groundwater samples from wells showing standard deviation less than 1.2 psu. The scale from figure 4.5 is maintained for comparison. "Less variable" wells were located along transects 2 and 3 (lower marsh) and displayed consistent seasonality and limited variability. These wells must be more isolated from seasonal forcing agents (i.e., variable air and surface water temperatures and surface water salinity) or strongly influenced by a groundwater source with relatively constant physical and chemical properties.

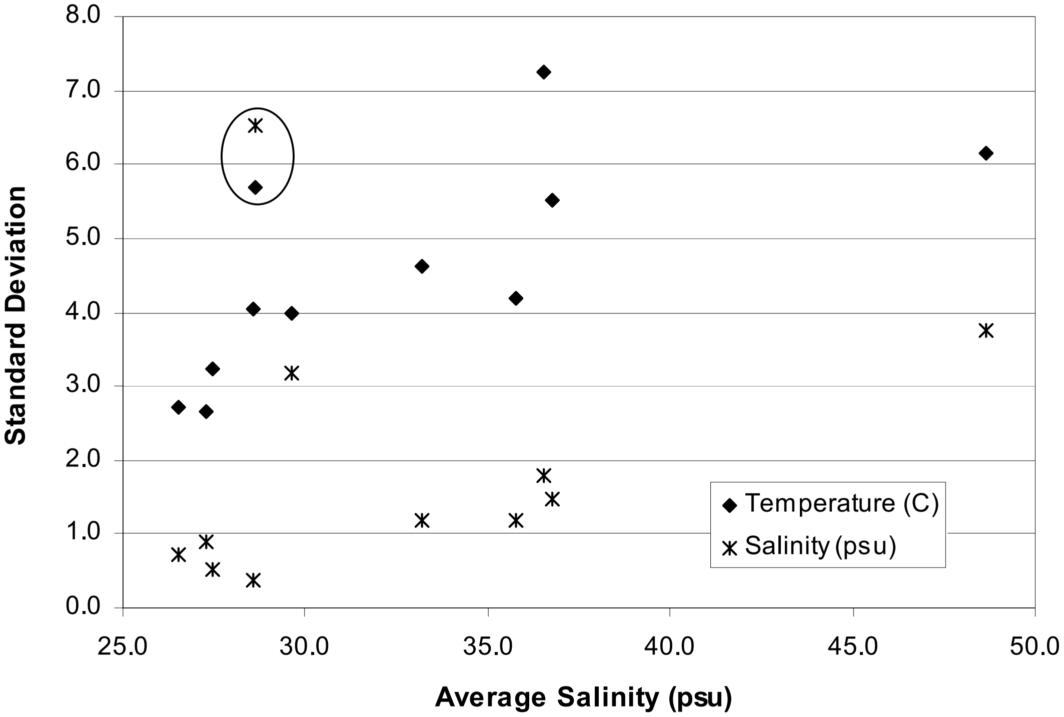

Figure 3.7 The standard deviations of temperature (^{o}C) and salinity (psu) versus average salinity for monitoring wells. Though not particularly strong, these positive correlations demonstrate the less-variable nature of lower salinity groundwater in the Okatee salt marsh. MW01n (circled) exhibited unusual freshening over the course of our investigation, resulting in large standard deviations in salinity and temperature compared to wells of similar salinity.

between U and salinity is linear, conservative mixing (or simple dilution) is assumed. On the other hand, when the mixing curve is concave up or concave down, U removal or addition is respectively inferred.

The interpretation of mixing diagrams and the accuracy of corresponding data analyses depends strongly on the saline endmember employed (Toole at al., 1987; Carroll and Moore, 1994). However, choosing this endmember is often difficult, especially when sampling in the higher salinity region of an estuarine system is limited. In some cases, a lower salinity endmember may describe mixing in a system more accurately than the accepted open ocean uranium concentration (Toole et al., 1987; Sarin and Church, 1994; Shaw et al., 1994; Church et al., 1996). Physical factors (i.e., tidal amplitude, tidal-prism volume, freshwater-discharge magnitude) determining the mixing behavior and residence times of water in different tributaries (or within a given tributary) of an estuary probably exert the most control over whether this is the case.

Table 3.3 lists the seawater and freshwater endmember concentrations used to determine seasonal conservative mixing trends for uranium. We determined the freshwater endmember concentration as the average of 5 samples collected over 8 months from two fresh water tributaries feeding the Okatee headwaters. We adopted the Colleton River value (point B, Figure 1.1) corresponding to each sampling event as a variable saline endmember. In doing so, we assure that removal is not overestimated and corresponds to processes occurring within the Okatee River's salt marsh system alone. Removal estimates based on higher salinity endmembers would include the effects of removal processes occurring in the lower estuary and along the continental shelf (Sarin and Church, 1994).

Table 3.3.
Endmember salinities and uranium concentrations for the conservative mixing of uranium in the Okatee river estuarine system.

	Date	Salinity (psu)	Uranium (ppb)
Fresh water	NA	0	0.10[a]
Colleton River	August 9, 2002	36	2.78
	August 31, 2002	34.4	2.78
	October 6, 2002	30.4	2.54
	November 25, 2002	28.3	2.59
	January 6, 2003	29.2	2.55
	March 5, 2003	28.8	2.38
	April 17, 2003	26.3	2.06
	June 3. 2003	25.2	1.86
Ocean[b]	NA	35	3.26
		36.2	3.46

[a] Standard deviation of 0.02 ppb.
[b] After Windom et al., 2000.
NA Not applicable

Surface Water

Uranium concentrations for nearly all tidal-creek samples fell below the variable conservative mixing line defined by Colleton River samples (Figure 3.8), documenting uranium removal from the water column. Samples collected in early-August 2002 at high tide are a notable exception. These samples had higher salinities and U concentrations than our Colleton River endmember sample for the same sampling event. The mechanism responsible for addition is unclear, but may be related in part to bioturbation. For northeast pacific and northeast Atlantic oceanic sediments, Zheng et al. (2002) concluded that bioturbation remobilized up to two-thirds of the authigenic U formed by exposing authigenic U to oxidizing conditions. It is also possible that our Colleton River endmember, which was chosen out of convenience, was not appropriate for this sampling event (e.g., if the salinity and U concentration of the true system endmember was actually greater than the Colleton River sample employed, higher salinity samples would show

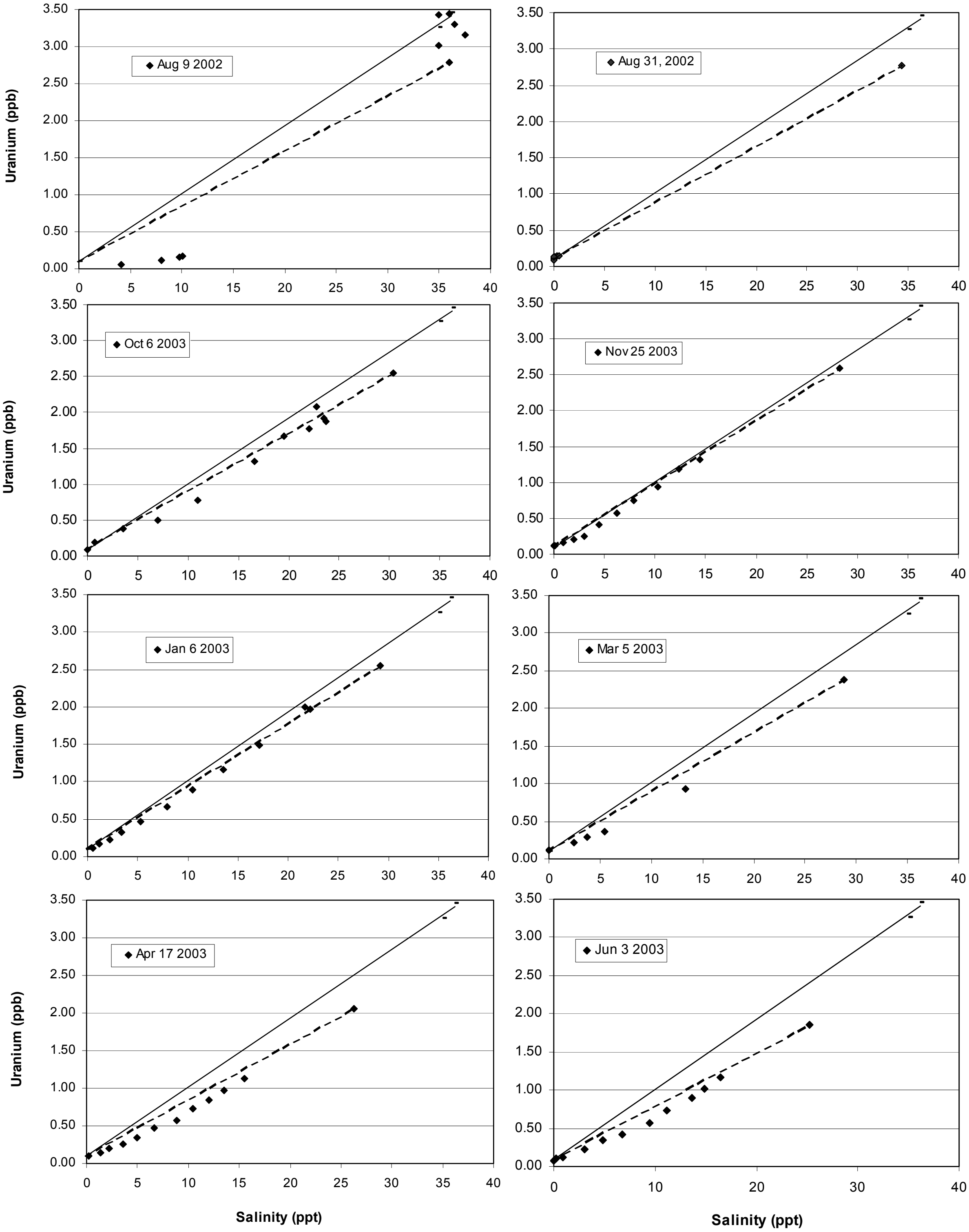

Figure 3.8 Surface water uranium concentrations for all sampling events, August 2002 through June 2003. The graphs illustrate the accepted freshwater/open ocean uranium dilution line (after Windom et al., 2000) and the dilution lines constrained by the saline Colleton River samples. In general, the uranium concentrations observed fall below these lines, suggesting removal from solution. November through June samples clearly demonstrate the seasonality of removal. August 31, 2002 samples were collected during a major storm event. Thus, all headwater tidal creek samples had salinity < 1 psu.

false addition). In stark contrast, the remaining lower-salinity early-August 2002 tidal creek samples showed the largest U-removal fractions observed for our entire investigation.

In general, removal (as a percentage) was greatest at low salinities (< ~ 7 psu) and decreased as creek-sample salinities converged with Colleton River endmember salinities. Church et al. (1996) and Maeda and Windom (1982) suggested that U-removal at low salinity may be due to water-column processes, including interaction with colloidal organic matter and metal oxides. In addition, marsh groundwater, which carries a significant removal signature, is advected to surface waters preferentially at low tide and should contribute to observed low-salinity removal. If reduced iron is carried in groundwater discharge, oxidation to Fe^{+3} and coprecipitation with dissolved U may also contribute to removal. The larger residence time of lower salinity headwaters, resulting from repeated "ponding" of fresh discharge by flooding tidal waters, should enhance the observed removal signal generated by these processes.

For November – June 2003, surface water U distributions could be approximated by a 2nd-order polynomial that included all data points or by a linear least-squares fit above salinity ~ equal to 7psu. Both approaches generated R^2 values > 0.99. However, the lack of higher salinity samples prevented us from further constraining this relationship. Overall, the shape of U-removal distributions was probably dependent on both physical (e.g., variations in fresh water flow, tidal prism volume, flow velocities, groundwater discharge rates and water residence time) and chemical factors.

Like others (Shaw et al., 1994; Sarin and Church, 1994; Church et al., 1996), we observed seasonally variable uranium removal in tidal creek samples, with larger removal occurring during the spring, summer, and early fall (March – October), and lower removal occurring during the winter (November – January). The steadily increasing removal with season is more clearly illustrated when U deficits for creek samples are calculated versus the dilution line constrained by the open ocean U endmember (Figure 3.9). The large seasonal U-depletion observed for Colleton River samples (Table 3.4) suggests active U removal outside the Okatee/Colleton River system as well.

Table 3.4.
Statistics associated with the apparent conservative behavior of uranium at salinity > ~ 7 and removal values for Colleton River samples and for extrapolated endmember values.

Month	U range (> 7psu)	n	Equation [b]	R^2	Colleton [U] (ppb)	% removal[c]	% removal[d]
08/09/02	4.1 - 37.5	10	No Linear Portion	NA	2.78	23	NA
08/31/02	34.4	1	NA	NA	2.78	19	NA
10/06/02	7 - 30.4	9	0.0891x - 0.1419	0.982	2.54	17	11.4
11/25/02	7.9 - 28.3	5	0.0907x + 0.0251	0.999	2.59	9	4.8
01/06/03	7.9 - 29.2	7	0.0906x - 0.0476	0.997	2.55	13	7.0
03/05/03	13.3 - 28.8	2	0.093x - 0.3045	NA	2.38	18	12.2
04/17/03	8.9 - 26.3	6	0.0846x - 0.1729	0.999	2.059	22	17.0
06/03/03	9.5 - 25.2	6	0.0817x - 0.1964	0.999	1.86	27	20.7

[a] Rain event

[b] Least-squares linear extrapolation (sal > 7 psu)

[c] For Colleton River samples, relative to the accepted open ocean endmember

[d] For an extrapolated endmember (sal=35 psu), relative to the accepted open ocean endmember

For example, when a linear trend is cast through samples with salinity > 7 psu and extrapolated to 35 psu, we can define an extrapolated, or effective, oceanic endmember concentration. Values for this extrapolated endmember diverged from the open ocean value with increasing temperature and the approach of summer (Table 3.4). This trend was most apparent for the November 2002 through June 2003 time series, when

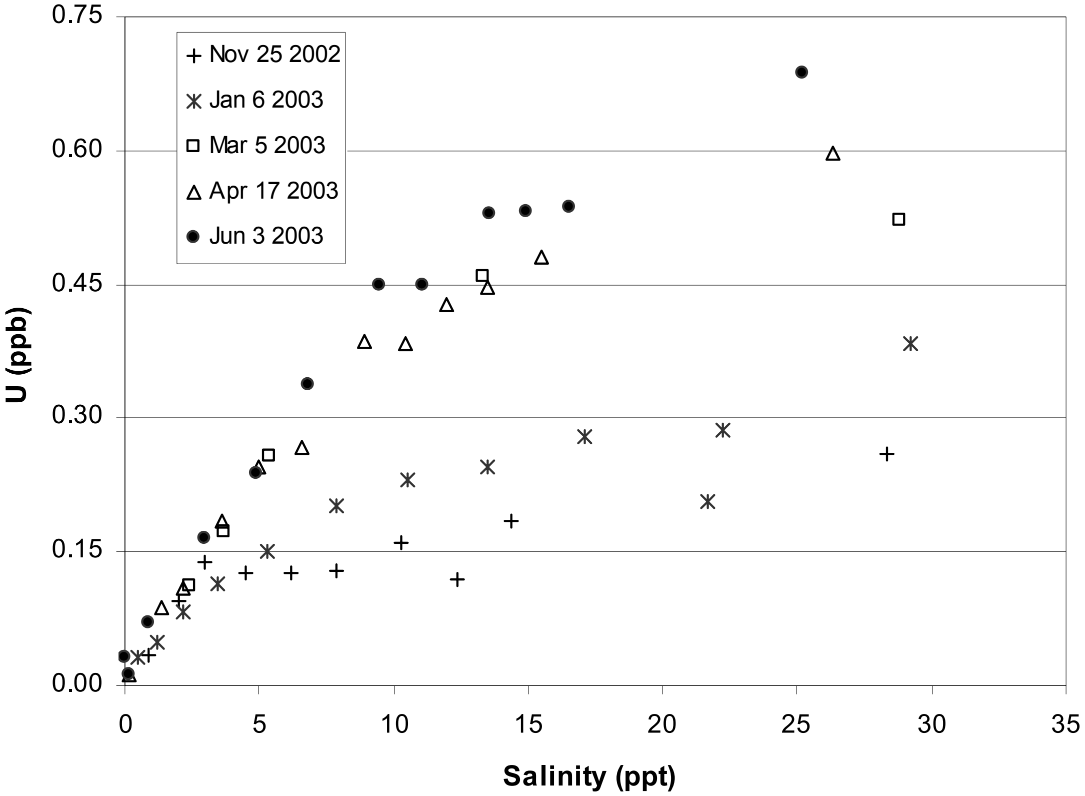

Figure 3.9 Uranium deficit (U predicted – U observed) vs. salinity for surface water samples collected between November 25, 2002 (minimum observed uranium removal) and June 3, 2003 (our last sampling period). The U deficit was calculated by comparing creek samples with the dilution line constrained by the open ocean U endmember rather than the lower salinity Colleton River endmember. Data collected during this time period and interpreted in this way clearly show the steady and consistent increase in uranium removal with season.

extrapolated endmember values demonstrated 4.8 to 20.7 percent depletion. Similar values were reported by Sarin and Church (1994) and Shaw et al. (1994) for the Delaware/Chesapeake Bay system. High-salinity removal may result from diffusion of uranium into coastal reducing sediments (Klinkhammer and Palmer, 1991; Barnes and Cochran, 1993; Shaw et al., 1996), tidal-circulation/groundwater discharge in the lower estuary or along the continental shelf (Windom et al. 2000), or from the cumulative effect of removal occurring within other tidal tributaries feeding the Port Royal Sound.

Uranium is usually transported through the low salinity region of estuaries in the colloidal size fraction (Swarzenski et al., 1995; Andersson et al., 2001), which by definition is included in our dissolved (< 0.45 microns) size fraction, and through the higher salinity region in the dissolved size fraction as a strong carbonate complex (Langmuir, 1997). To determine whether interactions with water-column particulate matter might explain observed uranium removal, we collected filtered and unfiltered samples over a tidal cycle in June 2003. A strong, salinity-dependent interaction between U and particulate matter (i.e., a large U concentration in unfiltered samples at low salinity) would suggest adsorption and deposition as a plausible U-removal mechanism. However, unfiltered uranium concentrations were only slightly higher than those in filtered samples (Figure 3.10). This was true at all salinities and for our endmember samples, suggesting a small, consistent particulate U presence in the water column, but no obvious salinity-dependent U/particulate matter interaction. The fact that unfiltered U concentrations are slightly larger than filtered concentrations at all salinities suggests that uranium associated with particulate matter is not available for desorption induced by changes in ionic strength. This implies the presence of a low-concentration, mineral-

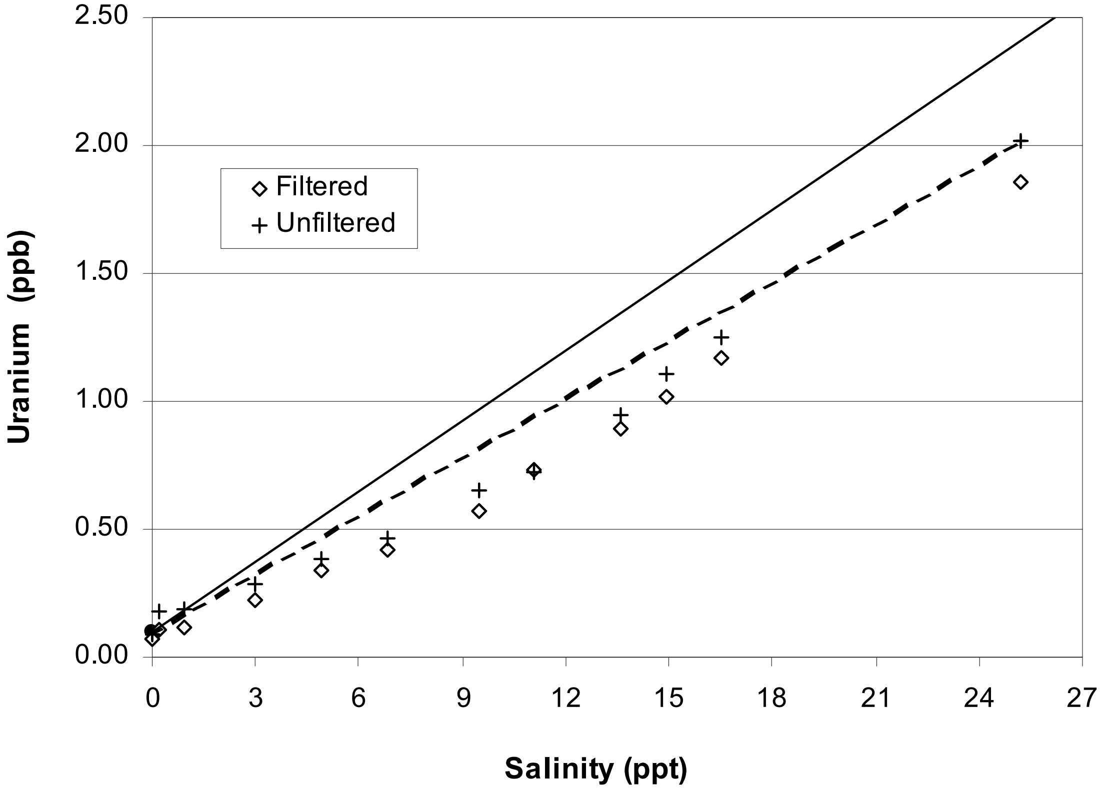

Figure 3.10 Filtered versus unfiltered uranium concentrations for surface water samples collected on June 3, 2003. The graphs illustrate the accepted freshwater/open ocean uranium dilution line (after Windom et al., 2000) and the dilution lines constrained by the saline Colleton River samples (dashed). Since the differences in uranium concentrations between filtered and unfiltered samples are small, sorption of uranium to particulates in the water column can not explain the magnitude of observed removal and does not appear to be important for removal in the Okatee river tidal system.

matrix- or possibly a biologically-bound (Shaw et al., 1994) uranium presence in the water column. All together, these data suggest that sorption to large particles is probably not an important removal mechanism for dissolved uranium in the Okatee river. However, they do not provide direct information on the colloidal size fraction, which, through aggregation and interaction with the marsh surface, could still be involved with removal processes (Church et al., 1996; Langmuir, 1997; Swarzenski et al., 1995).

Groundwater

Table 3.5 lists uranium concentration and calculated removal for all groundwater samples collected during this investigation. Groundwater uranium concentrations were uniformly low, with a range of 0.02 ppb (MW04, November 2002) to 2.97 ppb (MW06, April 2002). For a given well, concentrations varied little (Figure 3.11), with no apparent seasonal trend. Groundwater samples demonstrated dramatic U removal, with an average removal fraction of 0.86 (Figure 3.12). When MW06, which had a removal fraction of only 0.31, is treated as an outlier, average removal increases to 0.92. Low groundwater concentrations were expected based on the observed prevalence and seasonal persistence of highly reducing conditions in marsh sediments and the documented efficiency of anaerobic uranium removal processes (Lovely et al., 1991; Barnes and Cochran, 1993). Other processes, such as sorption to iron oxides at the oxic/anoxic interface (Barnes and Cochran, 1993) and abiotic reduction by sulfide, may also contribute to the low observed groundwater concentrations in a limited way (Wersin et al., 1994).

MW06 consistently exhibited high ferrous iron concentrations and imperceptible H_2S odor and yielded particulate FeS during purging/sampling. Therefore, the higher uranium concentrations (lower removal fractions) documented in this well may be the

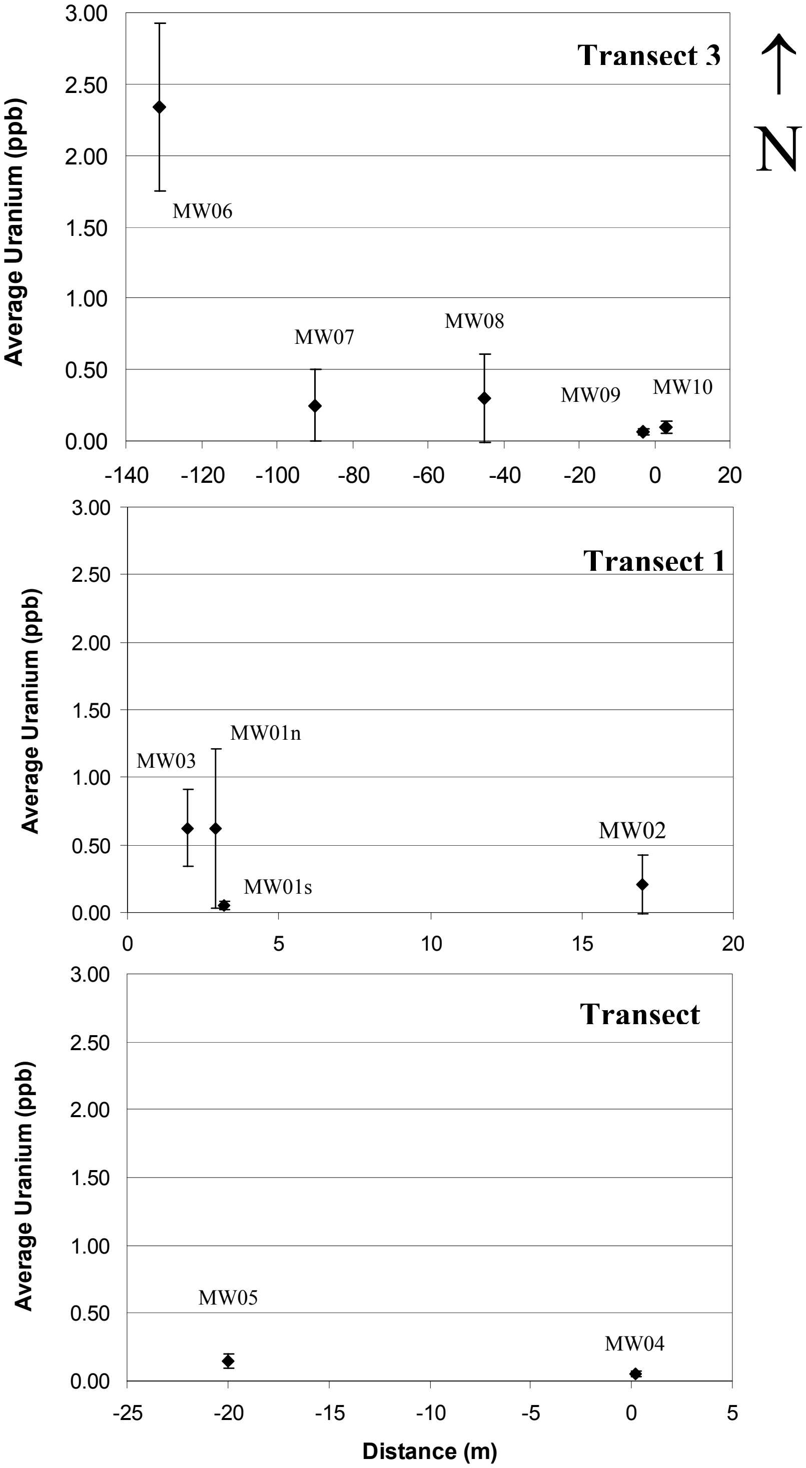

Figure 3.11 Groundwater uranium concentrations across sampling events for our three sampling transects versus approximate distance from the tidal creek bank (x = 0; values increase moving east). Error bars are plus and minus one standard deviation. Uranium concentrations were generally low and showed little variability, except for MWs 01n, 03 and 06. In all cases, higher concentrations wells were located on firm marsh, at higher relative elevations than other wells, and in stands of short spartina or glasswort.

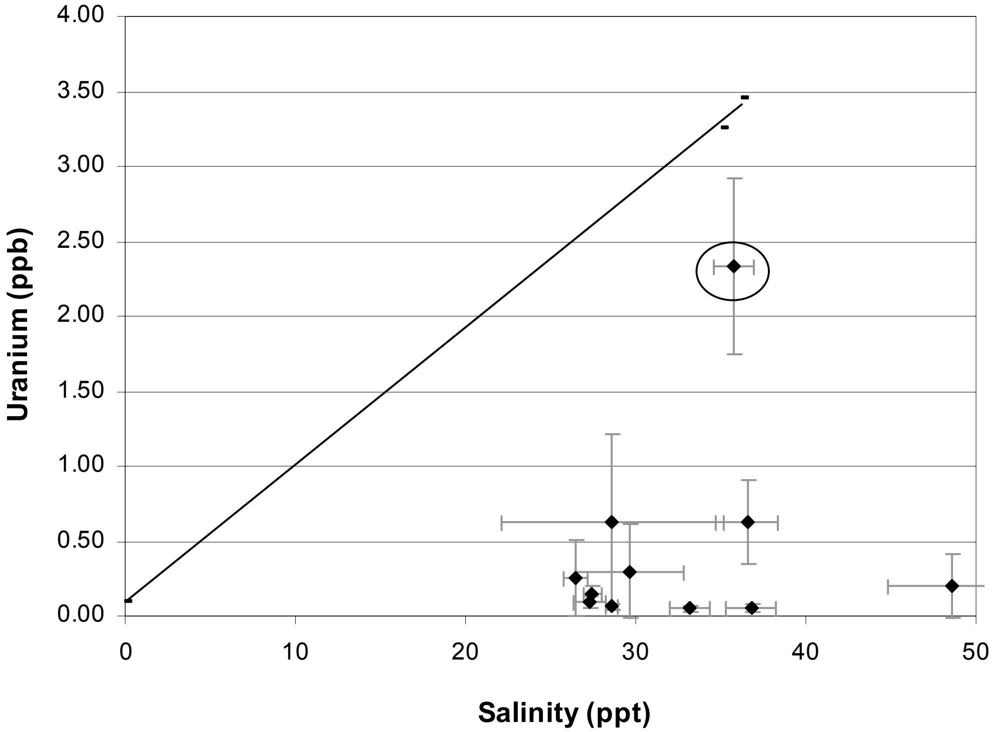

Figure 3.12 Average groundwater uranium concentrations versus salinity. With the exception of MW06 (circled), groundwater samples from all wells showed extensive removal compared to the concentrations predicted by conservative mixing of fresh- and open ocean waters. The high salinity point represents MW02, which was shallow and located in a salt flat.

product of U-release from iron oxides during ferric iron reduction or an unfavorable redox environment (Barnes and Cochran, 1993). For example, Barnes and Cochran (1993) found U-removal in marine sediments that was linearly related to sulfate reduction rates. Thus, large FeS and Fe^{+2} concentrations observed in MW06 may poise the redox potential surrounding the well's screened interval at a larger, less favorable value for microbial reduction (Klinkhammer and Palmer, 1991; Barnes and Cochran, 1993). However, this conclusion is speculative, as debate regarding the optimal chemical environment and redox potential for U-reduction is ongoing, with several authors finding evidence for uraninite formation at higher pEs correlated with Fe reduction (Abdelouas et al., 2000; Zheng et al., 2002).

Groundwater uranium concentrations were not correlated with other measured parameters (e.g., salinity, phosphorus, total iron, pH or barium concentration). Since the marsh subsurface demonstrates considerable heterogeneity, our wells probably do not sample continuous groundwater flow pathways. Thus, potential correlations are likely obscured.

Table 3.5.
Uranium concentrations and percent removals for all groundwater samples collected from August 2002 to June 2003.

		9-Aug	31-Aug	6-Oct	25-Nov	6-Jan	5-Mar	17-Apr	4-June	Average	St Dev
MW01s	**Uranium (ppb)**	**0.05**	**0.05**	**0.06**	**0.04**	**0.03**	**0.12**	**0.04**	**0.03**	**0.05**	**0.03**
	Removal fraction	99	99	98	99	99	97	99	99	99	1
MW01n	**Uranium (ppb)**	**1.98**	**0.69**	**0.28**	**0.24**	**0.40**	**0.17**	**0.81**	**0.43**	**0.62**	**0.59**
	Removal fraction	49	81	91	91	85	93	65	80	79	15
MW02	**Uranium (ppb)**	**0.10**	**0.10**	**0.12**	**0.73**	**0.20**	**0.10**	**0.14**	**0.14**	**0.20**	**0.21**
	Removal fraction	98	98	98	84	96	98	97	97	96	5
MW03	**Uranium (ppb)**	**1.11**	**0.83**	**0.46**	**0.55**	**0.40**	**0.41**	**NS**	**NS**	**0.63**	**0.28**
	Removal fraction	68	76	87	85	90	89	NA	NA	87	11
MW04	**Uranium (ppb)**	**0.04**	**0.07**	**0.05**	**0.02**	**0.03**	**0.09**	**0.04**	**0.05**	**0.05**	**0.02**
	Removal fraction	99	98	98	99	99	97	99	98	99	1
MW05	**Uranium (ppb)**	**NS**	**0.22**	**0.22**	**0.13**	**0.09**	**0.12**	**0.10**	**0.12**	**0.14**	**0.05**
	Removal fraction	NA	92	92	95	97	95	96	96	95	2
MW06	**Uranium (ppb)**	**2.76**	**1.32**	**2.04**	**2.38**	**1.71**	**2.72**	**2.97**	**2.76**	**2.33**	**0.59**
	Removal fraction	27	64	42	33	52	21	15	21	34	17
MW07	**Uranium (ppb)**	**0.05**	**0.07**	**0.07**	**0.07**	**0.77**	**0.44**	**0.27**	**0.25**	**0.25**	**0.25**
	Removal fraction	98	98	97	97	71	83	90	90	91	10
MW08	**Uranium (ppb)**	**1.05**	**0.20**	**0.20**	**0.18**	**0.14**	**0.12**	**0.16**	**0.33**	**0.30**	**0.31**
	Removal fraction	70	94	92	93	95	96	94	89	90	8
MW09	**Uranium (ppb)**	**NS**	**0.11**	**0.08**	**0.06**	**0.05**	**0.07**	**0.05**	**0.04**	**0.06**	**0.02**
	Removal fraction	NA	96	97	98	98	98	98	99	98	1
MW10	**Uranium (ppb)**	**0.05**	**0.08**	**0.17**	**0.06**	**0.07**	**0.09**	**0.07**	**0.16**	**0.09**	**0.04**
	Removal fraction	98	97	94	98	97	97	97	94	97	2

NS Not sampled
NA Not applicable

3.2.4. Barium

We determined barium concentrations using Isotope Dilution-ICPMS for all samples collected during this investigation. Like uranium, our data analysis relies on quantifying the relationship between observed barium concentrations and the concentrations predicted by the conservative mixing of seawater and freshwater endmembers. Table 3.6 gives the endmember concentrations used to determine conservative barium mixing behavior. We determined the freshwater endmember concentration as the average of 4 samples collected over 8 sampling trips from two fresh water tributaries feeding the Okatee headwaters. We used the Colleton River value collected during each sampling trip as a variable saline endmember. The open ocean saline endmember concentrations used in diagrams was taken from Shaw et al. (1998).

Barium concentrations in surface water were typically less than 35 ppb, although anomalously high values (36 – 86 ppb) were recorded during our first sampling trip (August 9, 2002). Compared to uranium, the behavior of barium in surface water was complex, showing both removal and addition (with respect to simple dilution curves) in the low salinity (< 10 psu) zone and addition at higher salinities in Colleton River endmember samples (Figure 3.13). In general, we observed dramatic, very low salinity (< 0.5 psu) barium removal followed by gradual release to solution over the 1 – 10 psu salinity range, consistent with the sorption/desorption of barium from suspended particulate matter and the findings of Stecher and Kogut (1999). Samples collected in early August 2002, October 2002, and April and June 2003, showed addition compared to mixing curves between 5 and 10 psu, followed by approximately conservative mixing. Samples collected in January and March 2003 converged with the conservative mixing trend for salinities greater than 10 psu, consistent with barium behavior observed in other estuaries (Coffey et al., 1997; Shaw et al., 1998; Stecher and Kogut, 1999; Nozaki et al., 2001). Uniquely, our November 2002 samples showed very low salinity removal, followed immediately by conservative mixing, with no evidence for the salinity induced release of barium from suspended particles expected in estuarine environments. The variable barium behavior documented by surface water samples suggests that several

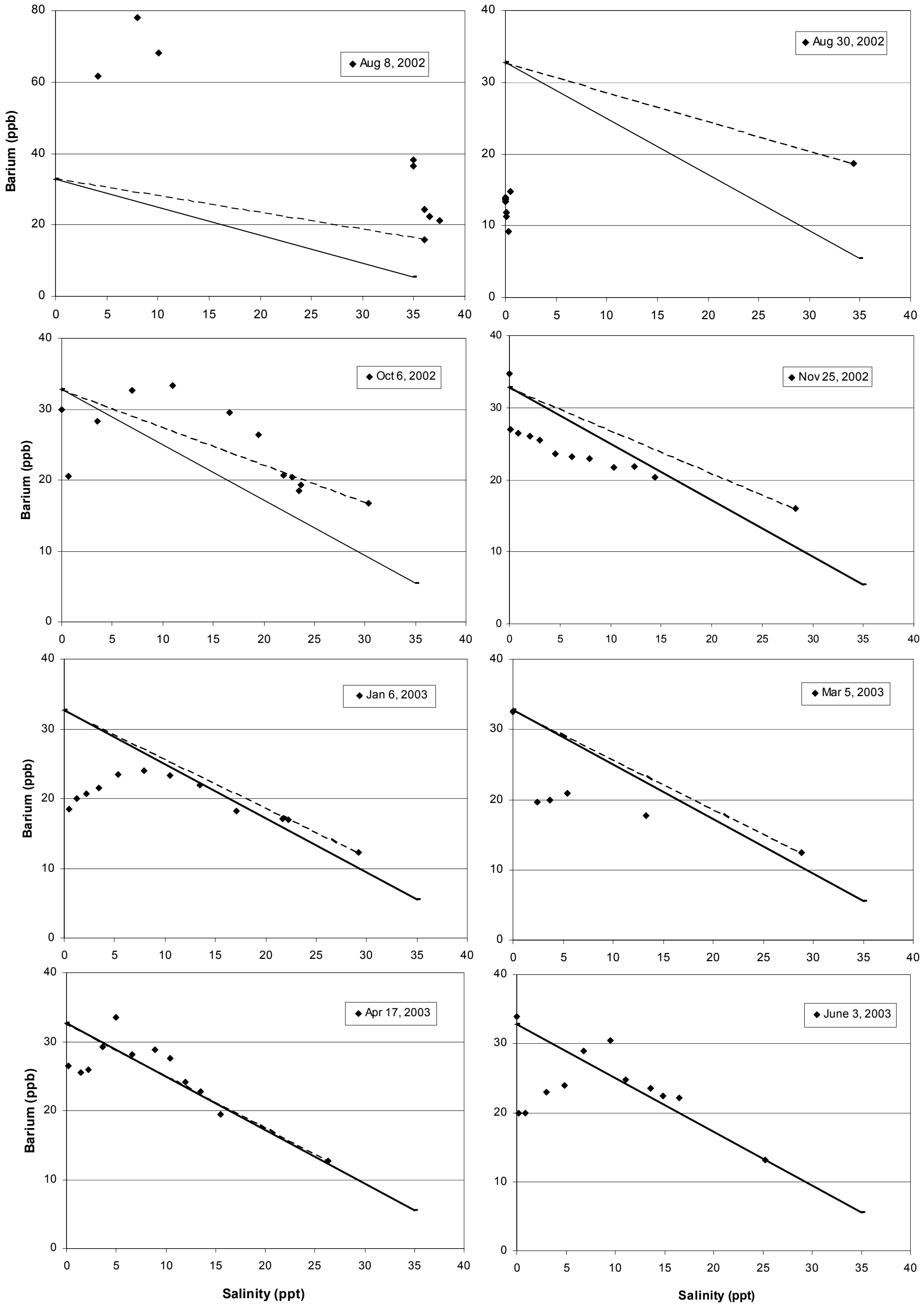

Figure 3.13 Surface water barium concentration versus salinity. This figure illustrates the complex behavior of barium in the tidal creek headwaters of the Okatee River. Barium showed dramatic low salinity (< 0.5 psu) removal, followed by release from suspended particulate matter and, in most cases, conservative mixing. Samples collected in early August 2002, October 2002 and in April and June 2003 showed excess barium (addition) in the 5 – 10 psu range. Uniquely, November 2002 samples show removal followed immediately by conservative mixing.

seasonally-dependent processes interact to control dissolved barium concentrations in the Okatee/Colleton River system.

Table 3.6.
Endmember salinities and barium concentrations for the conservative mixing of barium in the Okatee river estuarine system.

	Date	**Salinity (psu)**	**Barium (ppb)**
Fresh water	NA	0	33[a]
Colleton River	August 9, 2002	36	16
	August 31, 2002	34.4	19
	October 6, 2002	30.4	17
	November 25, 2002	28.3	16
	January 6, 2003	29.2	12
	March 5, 2003	28.8	12
	April 17, 2003	26.3	13
	June 3. 2003	25.2	13
Ocean[b]	NA	35	5.49

[a] Standard deviation of 2.1 ppb.
[b] Shaw et al. (1998).
NA Not applicable

Like uranium, barium concentrations for measured (Colleton River) and extrapolated (calculated for 35 psu) endmembers deviated from the values expected based on the conservative mixing of fresh and saline surface waters. Unlike uranium, Colleton River endmember samples showed addition, but no discernable seasonal trend, with values progressively converging with the expected (fresh-water/open-ocean) dilution line over the 11-month course of our investigation (Table 3.7). Extrapolated endmember values varied from 150% addition to 17% depletion between November 2002 and June 2003. Sarin and Church (1994) and Shaw et al. (1994) also reported excess barium in endmember values for the Delaware/Chesapeake Bay system.

Table 3.7.

Statistics associated with the conservative behavior of barium at salinity > ~ 10 and addition values for Colleton River samples and for extrapolated endmember values.

Month	[Ba] (ppb) range (> 10 psu)	n	Equation[b]	R^2	Colleton [Ba] (ppb)	% addition	Predicted [Ba] (salinity 35)	% addition
08/09/02	16 -68	7	No linear portion	NA	16	238	NA	NA
08/31/02	19	1	NA	NA	19	213	NA	NA
10/06/02	17 - 33	8	No linear portion	NA	17	84	NA	NA
11/25/02	16 - 22	4	-0.3346x + 25.426	0.975	16	49	13.7	150
01/06/03	12 - 23	6	-0.5741x + 29.249	0.974	12	23	9.2	67
03/05/03	12 - 18	2	-0.3438x + 22.321	NA	12	20	10.3	87
04/17/03	13 - 28	5	-0.8626x + 34.741	0.941	13	4	4.6	-17
06/03/03	13 - 25	5	-0.851x + 35.049	0.975	13	0	5.3	-4

[a] Rain event

[b] Least-squares linear extrapolation (sal > 10 psu)

To obtain a basic estimate of the particulate versus dissolved load of barium in the tidal creek, we collected parallel filtered (dissolved; < 0.45 μm) and unfiltered (total Ba) samples during our last field campaign (June 2003). Dissolved and total barium concentrations differed significantly at salinities less than 10 (Figure 3.14). Unlike uranium, which showed little affinity for the particulate phase at low salinities, particles exerted significant control over dissolved barium concentration in the low salinity region of the tidal creek. At higher salinities, however, the concentrations of barium in filtered and unfiltered samples were nearly equal and typically close the conservative mixing line. The unexpected Total Ba addition observed at low salinities is noteworthy. This signature of excess Ba may be associated with input from groundwater discharge (see below) followed by immediate sequestration by particles. Such a signal would not have been observed or predicted had we not collected samples for Total Ba analysis. This

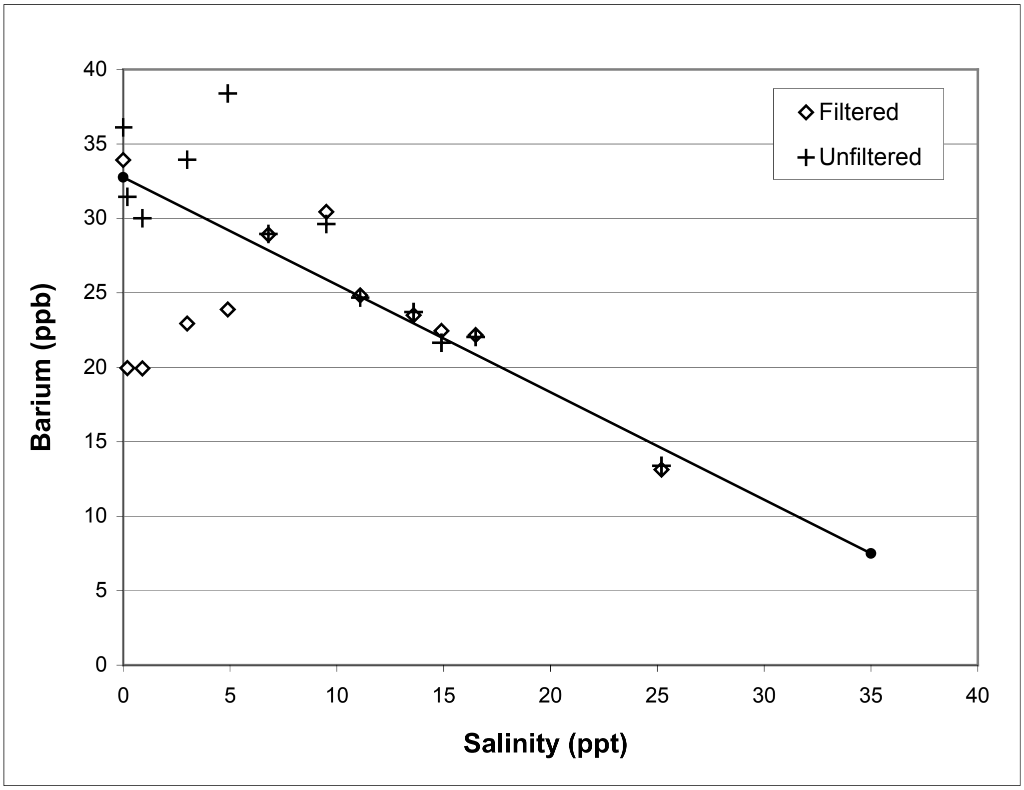

Figure 3.14 Surface water barium concentration versus salinity for filtered and unfiltered samples collected June 3, 2003. Unlike uranium, reactions between dissolved barium and particulate material in the water column significantly affected observed barium concentrations. This interaction was most pronounced below a salinity of ~ 7 psu. Above this salinity, filtered and total barium concentrations were approximately equal. Above a salinity of about 10 psu, total barium and dissolved barium concentrations were close to those predicted by conservative mixing.

finding emphasizes the importance of understanding metal/particle estuarine dynamics and analyzing more than one empirical size fraction when investigating estuarine surface water processes.

Shallow marsh groundwater generally contained much higher barium concentrations than surface water, with a range of 37 ppb (MW01n in June 2003) to 381 ppb (MW10 on Aug 30, 2002) (Figure 3.15). Shaw et al. (1998) observed similar barium concentrations (27 – 109 ppb) in groundwater collected from shallow monitoring wells in a North Inlet, SC salt marsh (salinity 25 – 40 psu). We observed the highest average barium concentration (197.4 ± 75.9 ppb) in MW10 and the lowest average value in MW01n (54.3 ± 15.3 ppb). The site average, computed from all of the groundwater samples collected, was 85.2 ± 42.8 ppb. The elevated barium concentrations observed during this study can be interpreted as a large addition relative to the conservative mixing of surface waters (Figures 3.16). Shaw et al. (1998) describe the possible mechanisms leading to the enrichment of barium in coastal groundwater. Briefly, aquifer solids are first enriched via interactions with fresh, barium-rich surface- and/or groundwaters. Similar to its estuarine chemistry, available barium is subsequently desorbed from these solids with exposure to saline tidal waters. Additional barium could be supplied via diagenetic release from barium-containing metal oxide phases, the dissolution of authigenic barite, and/or the decomposition of barium-rich organic material.

We did not observe seasonality in groundwater barium concentrations, although seven of the eleven wells (01s, 01n, 04, 05, 06, 08, 10) showed study-period maximums during the August 30, 2002 sampling event. Other than a weak positive correlation with phosphorus, groundwater barium concentrations were not correlated with any of the other

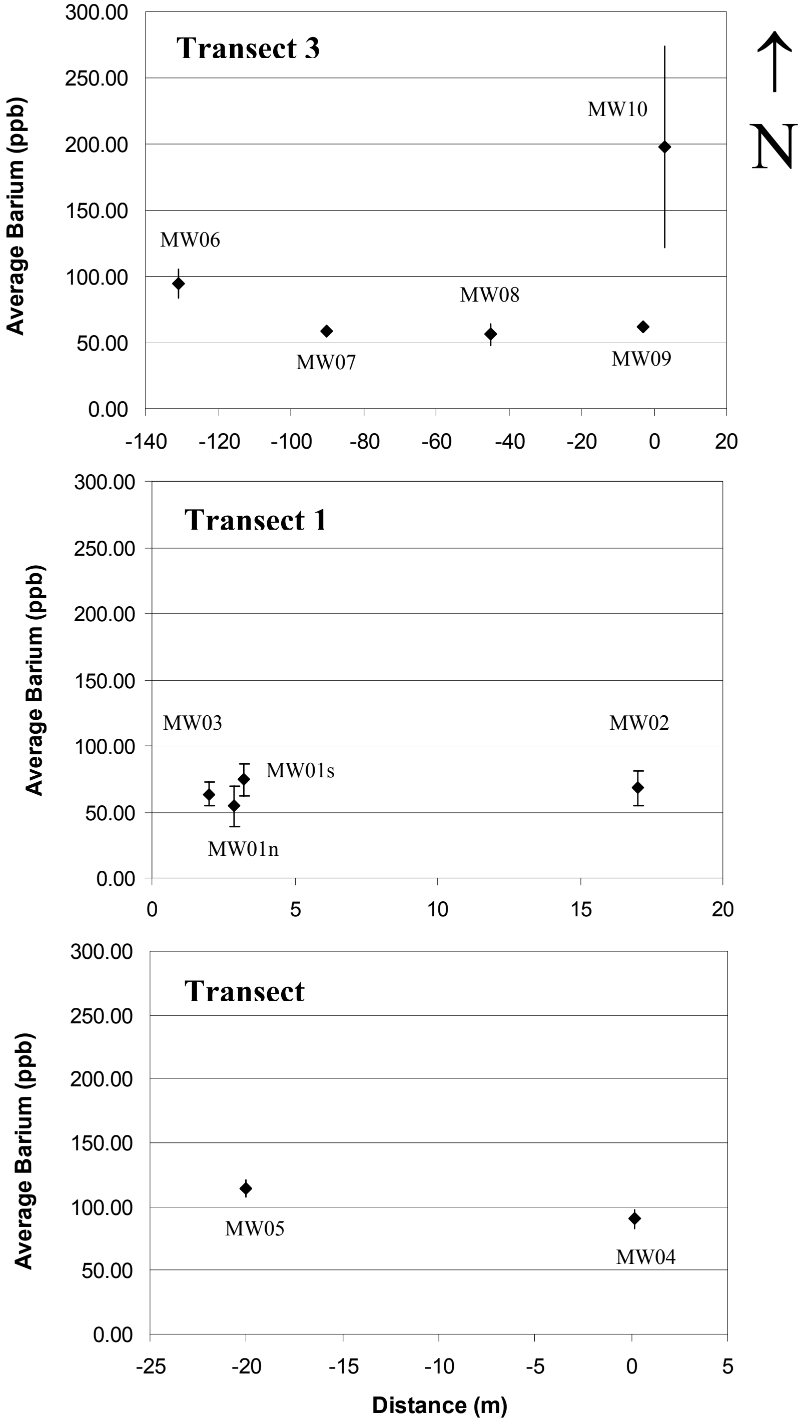

Figure 3.15 Average groundwater barium concentrations across sampling events for Okatee headwater monitoring wells vs. well distance (m) from the proximal tidal creek bank (x = 0; values increase moving to the east). Error bars are ± 1 standard deviation. Barium concentrations in groundwater were consistently higher than those in surface water. With the exception of MW10, barium concentration showed little variation over the August 2002 – June 2003 sampling period.

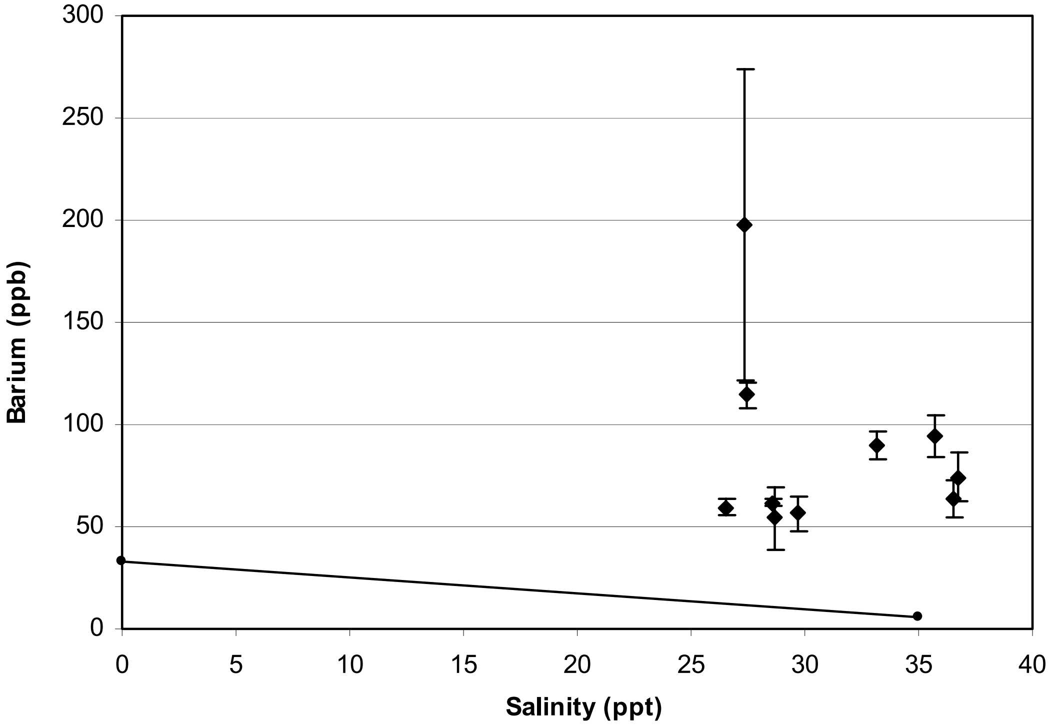

Figure 3.16 Average groundwater barium concentration versus salinity. Error bars represent ± 1 standard deviation. Concentrations display a large addition compared to those predicted by the conservative mixing of fresh- and sea waters.

chemical species we measured. However, the large difference observed between groundwater and surface water barium concentrations provides a reliable indication of the source of water seeping into the tidal creek at low tide.

3.2.5. Total Iron and Dissolved Inorganic Phosphate

We determined total iron and dissolved inorganic phosphate concentrations colorimetrically for all groundwater samples collected from the March 2003 field campaign through the final field trip in June 2003. Because of the anoxic character of subsurface salt marsh environments, we suspect that most of the iron detected in groundwater samples was present in the +2 oxidation state. The presence of hydrogen sulfide in most of the groundwater samples collected from the site suggests the absence of more energetically favorable electron acceptors and supports this conclusion. As shown in Figure 3.17, total iron concentrations were extremely low (less than 1 μM) except in MWs 01s, 02, 03 and 06, with average values of 127, 34.0, 2.14, and 137 μM, respectively. MW06 was located on firm ground at the boundary between the low (short *Spartina*, sulfide-rich) and high (tall *Spartina*) marsh and yielded black, iron sulfide precipitate during purging and sampling of the well. This finding suggests that MW06 samples a redox transition zone.

Phosphate concentrations (Figure 3.18) were qualitatively correlated with the presence of sulfide. We observed high phosphate concentrations (22.5 – 73.5 μM) in samples containing particulate or gaseous sulfide (transects 2 and 3; i.e., MWs 04 through MW 10), and very low phosphate concentrations (0.09 – 3.94 μM) in the remaining four wells (MWs 01s, 01n, 02, and 03; transect 1).

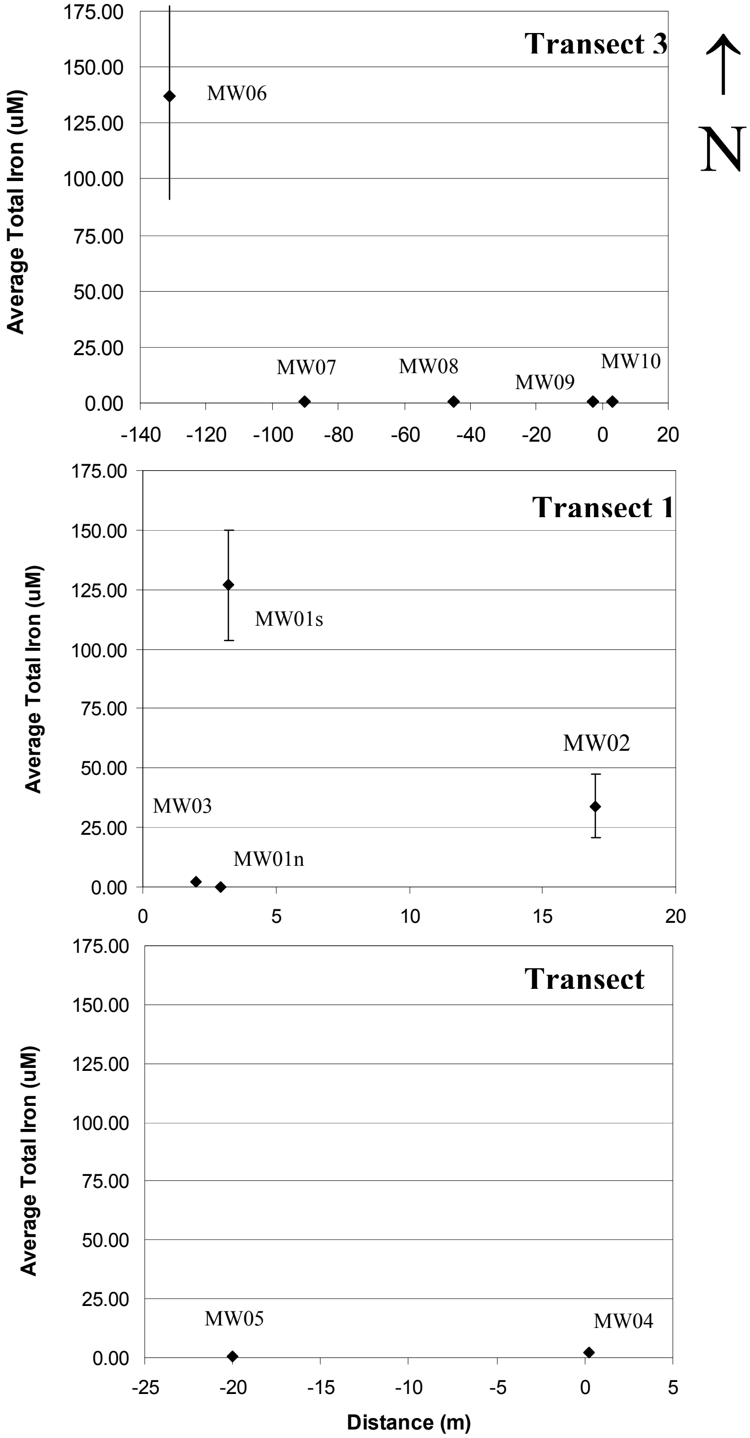

Figure 3.17 Average groundwater total iron concentrations vs. distance from the proximal tidal creek bank (x = 0). Total iron concentrations were extremely low with the exception of three wells, MW01s, MW02, and MW06. These wells were located on firm ground in higher marsh areas, closer to the upland. MW06 contained iron sulfide particulates. Iron concentrations showed no correlated with any of the other variables measured during this investigation.

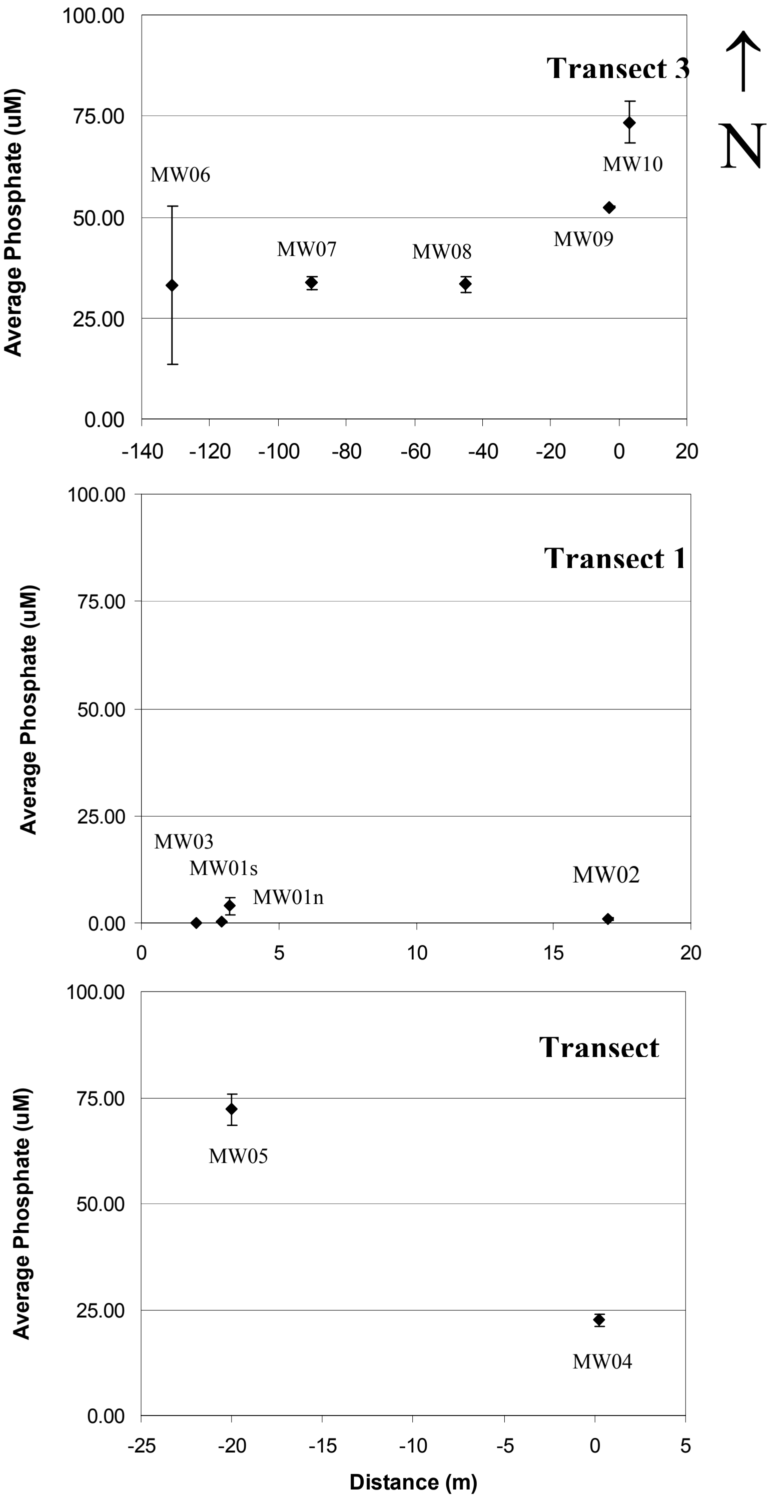

Figure 3.18 Average groundwater dissolved inorganic phosphate. Phosphate concentration appeared to correlate with the presence of gaseous or particulate sulfide: we observed the highest phosphate concentrations in wells that possessed the characteristic odor of hydrogen sulfide (MWs 04, 05, and 07 – 10) or sulfide particulates (MW06). Phosphate concentrations correlated loosely with barium as well.

3.3. Marsh Run Off and Groundwater Seepage (MRO/GS)

We collected several samples of water running off the marsh surface and seeping from the creek bank at low tide. These samples were taken to determine how interactions with surface and subsurface sediments affect surface water chemistry and to provide anecdotal evidence for uranium-removal mechanisms. Table 3.8 provides collection information, salinity, and uranium and barium concentrations for marsh runoff/groundwater seepage (MRO/GS) samples. The uranium concentrations of MRO/GS samples clustered together based on their removal extents (Figures 3.19 and 3.20). Samples that plotted near average groundwater uranium concentrations, implying a similar degree of uranium removal, also showed high barium concentrations, suggesting a groundwater source. These results imply that the discharge of uranium-depleted groundwater to surface water during periods of favorable hydraulic head gradient (i.e., low and falling tides) must contribute to the observed uranium removal. High barium and low uranium concentrations in surface waters have been invoked previously as evidence of groundwater discharge to coastal environments (Shaw et al., 1998; Swarzenski et al., 2001).

For samples that grouped closely with surface water uranium concentrations in Figure 3.20, barium concentrations were expectedly low, uranium depletion was on par with the flooding tidal water, and the samples clearly reflected surface run off with minimal additional U removal. Whether some of the observed uranium removal in these samples resulted from reactions with surface sediments remains unclear. However, samples collected from the tidal creek water column during the rising tide demonstrated similar salinities and uranium removal values as these MRO/GS samples. Therefore, it is

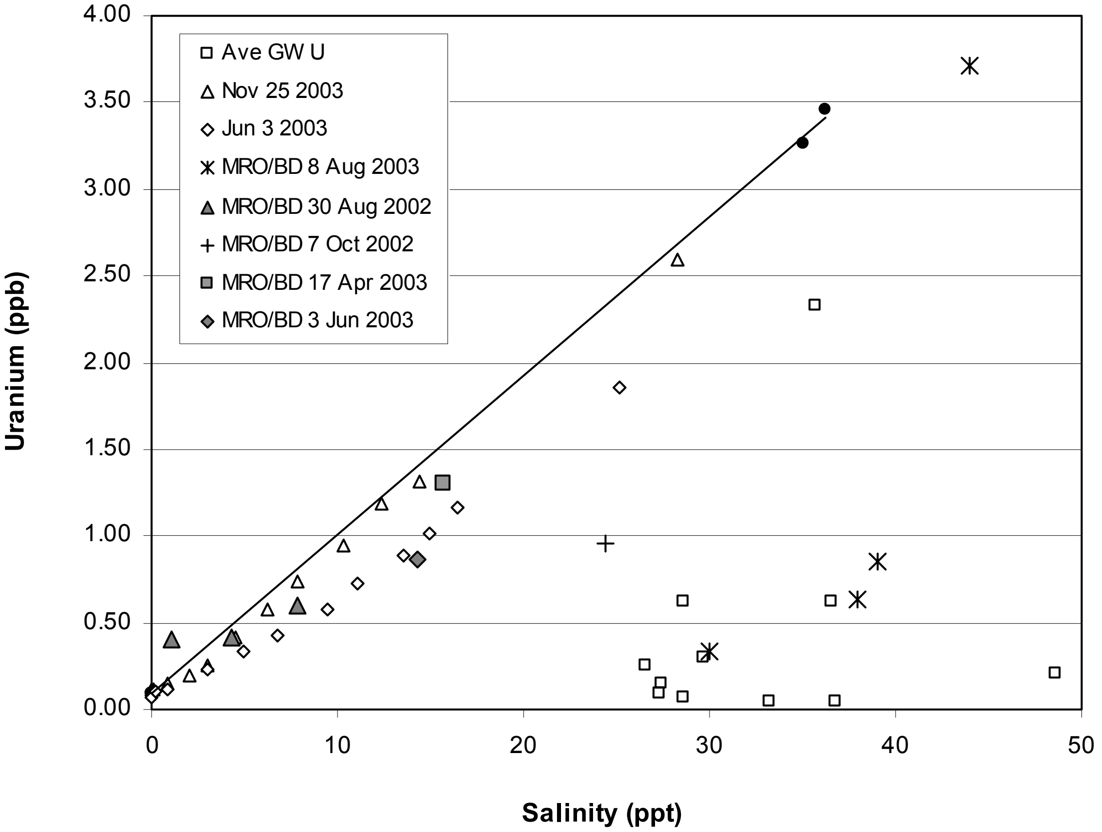

Figure 3.19 Average groundwater (all samples), surface water from November 2002 (minimum observed U removal) and June 2003 (maximum removal for 2003 sampling period), and marsh runoff/bank discharge (MRO/BD) uranium concentrations. During collection, we attempted to obtain samples of water running off the marsh or discharging from the creek bank. With the exception of the October 2002 sample, all MRO/BD samples grouped with either surface- or groundwater samples. This observation points to the different sources of the water samples. The fact that several of the samples collected grouped with average groundwater uranium samples indicates that uranium depleted groundwater is actively discharging from creek banks in the Okatee headwaters during low tide. Furthermore, the observation that marsh run off samples group with surface water uranium concentrations indicates that no significant additional depletion of uranium occurred as a result of the flood-tide water's contact with the marsh surface, at least over a diurnal tidal cycle.

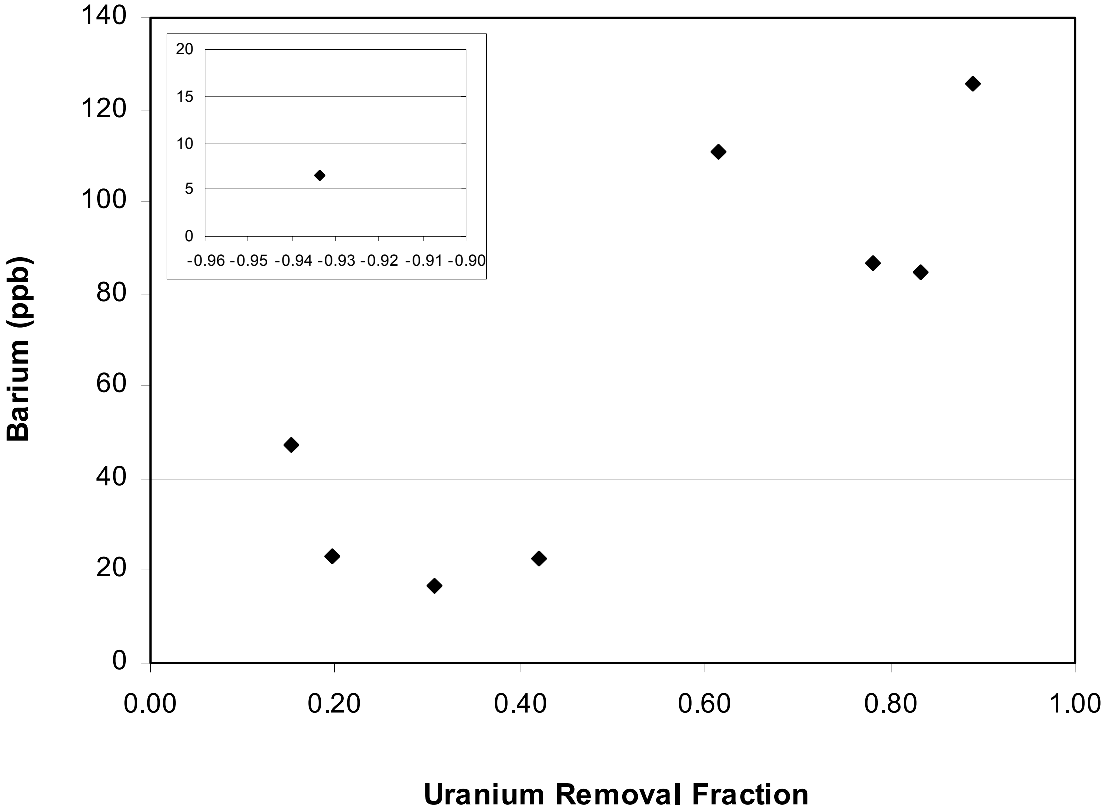

Figure 3.20. Fraction of U removal versus barium concentrations (ppb) for marsh run off/groundwater seepage (MRO/GS) samples. Samples group in low removal, low barium, or high removal, high barium clusters. Given the groundwater barium enrichment observed during this study (and others), this figure lends additional support for the conclusion that groundwater is seeping into the creek bank at low tide and is likely contributing to the observed water-column uranium deficit. One MRO/GS sample from the August 2002 collection period is not presented, as low sample volume precluded barium analyses. The sample illustrated by the inset, collected during a rain event, demonstrated small addition (negative fraction removal) and extremely low barium concentrations.

likely that most of the uranium removal observed in marsh runoff samples occurred prior to flooding of the marsh surface in the Okatee headwaters. Initial estimates of surface water residence time for the Okatee system cluster around 3 days (W. Moore, pers. comm.., 2003). This suggests that U removal in marsh runoff samples would likely need to be larger for marsh surface processes to account for the depletion observed in surface water samples.

Table 3.8. Salinities, uranium and barium concentrations, uranium removal fraction and field notes for MRO/GS samples.

Date/ID	Salinity (psu)	Uranium (ppb)	U removal fraction[a]	Barium (ppb)	Description from field book written during sample collection
Aug0802-1	30	0.33	0.89	126	Collected near transect 1, approximately at low tide, from a point on the creek bank near the low water level. This sample appeared to be concentrated discharge from the bank.
Aug0802-2	39	0.85	0.78	87	Collected near transect 1, approximately at low tide, from a point on the creek bank near the low water level. Tidal creek salinity at time of collected was ~ 9 psu.
Aug0902-1	44	3.71	0.15	47	Collected from rivulets on the marsh surface adjacent to MW01s.
Aug0902-2	38	0.63	0.83	85	Collected near transect 1, approximately at low tide, from water apparently draining a thin sandy layer in the creek bank. Discharge was clear (at least compared to the other MRO/GS samples).
Aug3002-1	1.1	0.40	-0.93	7	Collected from rivulets on the marsh surface adjacent to MW01s. Sample was rusty colored appeared to originate near a glasswart and *Juncus* stand. Sample is mostly rain water (it was raining all day during collection, and fairly heavily in the morning) running of the marsh surface.
Aug3002-2	4.3	0.41	0.21	NA	Collected in concentrated surface runoff zone within a stand of high *Spartina* behind MW10. Sample was collected just before high tide.
Aug3002-3	7.9	0.60	0.31	17	Collected in the same location as Aug3002-1, during the falling tide. The salinity in creek never rose above 1 psu, so, most likely, this sample consists of fresh water that flooded the marsh and mixed with salty pore waters.
Oct0702	24.4	0.95	0.61	111	Collected ~20 m south of MW01s @low tide. Rivulets originating from horizontal crack in creek bank sediments. A veneer of very fine clean sand is on top of the mud near the creek bottom. This sand may have washed out of the creek bank.
Mar1703	15.7	1.30	0.20	23	Collected sample of surface marsh run off from unvegetated boundary (~ 1 m wide) between low and tall *Spartina* near MW06. There was less than 1 cm of standing water left on the marsh surface.
Jun0303	14.3	0.86	0.42	23	Collected from surface water pooled in a crab hole ~ 3 m south of MW05. Observed that marsh surface was quite dry, suggesting that it had not been flooded recently. In fact, the tide did not crest the marsh on this day, suggesting that the sample had been "incubating" in the crab hole for some time with out exchanging with the flooding tide.

[a] Removal fraction is based on comparison of observed sample concentrations with conservative behavior assuming the accepted open ocean saline endmember.

NA Not analyzed

CHAPTER 4

U REMOVAL AND GROUNDWATER DISCHARGE CALCULATIONS

4.1. Overview

This study was motivated by recent evidence supporting uranium removal from surface water in anoxic coastal environments such as salt marsh and mangrove (Church et al., 1996; Windom et al., 2000; Carroll and Moore, 1993). These results challenged established ideas about uranium cycling and highlighted gaps in knowledge about uranium geochemistry and the importance of coastal uranium removal processes. In particular, information concerning the mechanism and magnitude of U removal in coastal settings is needed to further constrain the global uranium budget and to evaluate the efficacy of U as a tracer for coastal processes (Windom et al., 2000).

In this section, we use observed seasonal surface-water U mixing trends to calculate U removal from a salt marsh-influenced tidal creek. In addition, we investigate the role played by the marsh subsurface in U removal. Specifically, we address the potential importance of surface water cycling though marsh sediments. Because dissolved uranium can be removed from solution by microbially-mediated anaerobic processes operating in coastal settings (Lovely et al., 1991; Barnes and Cochran, 1993), we believe that the circulation of tidal water through salt marsh sediments should be an efficient mechanism for removing dissolved uranium from surface waters. Because this circulation would result in the discharge of salt-marsh-processed, uranium-depleted groundwater to the creek, we propose that the extent of uranium removal observed in surface waters might be indicative of the magnitude of surface water and shallow groundwater exchange occurring in the system. We conclude this section by estimating the contribution (percentage and rate) of groundwater discharge required to simulate observed surface water removal trends.

4.2. Estuarine Salt Marsh Uranium Removal Rates

In this study, we have documented seasonally variable uranium removal from surface waters, confirming the pattern of uranium removal observed in similar coastal settings (Church et al., 1996; Windom et al., 2000). Although the available data set permits only a general assessment of the importance of various U removal mechanisms, we were able to generate quantitative estimates of U removal using information obtained from mixing curves.

We calculated the rate of U-removal from the Okatee/Colleton river system using three independent methods. These approaches rely on quantifying the difference between predicted conservative and observed nonconservative behaviors of U documented by U-salinity surface water profiles, which themselves are dependent on the use of appropriate and accurate fresh and saline endmembers. It is important to reemphasize that we used a variable lower salinity saline-endmember (collected routinely from the Colleton River at the Waddell Mariculture Center) instead of the accepted open ocean endmember to constrain mixing in our system. This technique should isolate the removal occurring in the Okatee/Colleton River system upstream from the Waddell Center from the dramatic removal occurring in other portions of the estuary and/or along the continental shelf (Section 4.2.3).

4.2.1. Method 1: Effective Freshwater Endmember Approach (EFEA)

We determined U-removal first with an Effective Freshwater Endmember Approach (EFEA), which is described by the following equation (after Li and Chan, 1979):

$$R = Q(I - U_F), \tag{4.1}$$

where Q is the river discharge (m^3 month^{-1}), U_F is the observed freshwater U endmember (µg m^{-3}), and I is the U-axis intercept of a line tangent to the high-salinity (typically > 8 psu) region of mixing and represents an "effective" freshwater endmember (µg m^{-3}) (Figure 4.1). Thus, removal is calculated by multiplying the difference between the effective and actual freshwater endmembers by the freshwater discharge for a given time period. Resulting values are subsequently normalized by system salt marsh area. For yearly removal estimates, I and Q were calculated as the average extrapolated U-intercept from our 8 datasets and the sum of the freshwater discharge occurring over the study period, respectively. The EFEA avoids the ambiguity and difficulty associated with calculating estuarine hydrologic variables and residence time.

The determination of freshwater discharge in equation 4.1 was not straightforward. The on-site USGS gauge is tidally influenced, obscuring freshwater discharge, and there are no gauges upstream of the site. In the past, freshwater discharges have been determined by averaging net discharge (positive and negative values) values over a daily or weekly period (Paul Drewes, USGS, pers. comm., 2003). However, this procedure leads to inconsistent and sometimes negative daily or weekly discharge estimates since the large tidal exchange dominates the freshwater discharge to the system. Instead, based on the shape of typical discharge vs. time plots for the system and on field

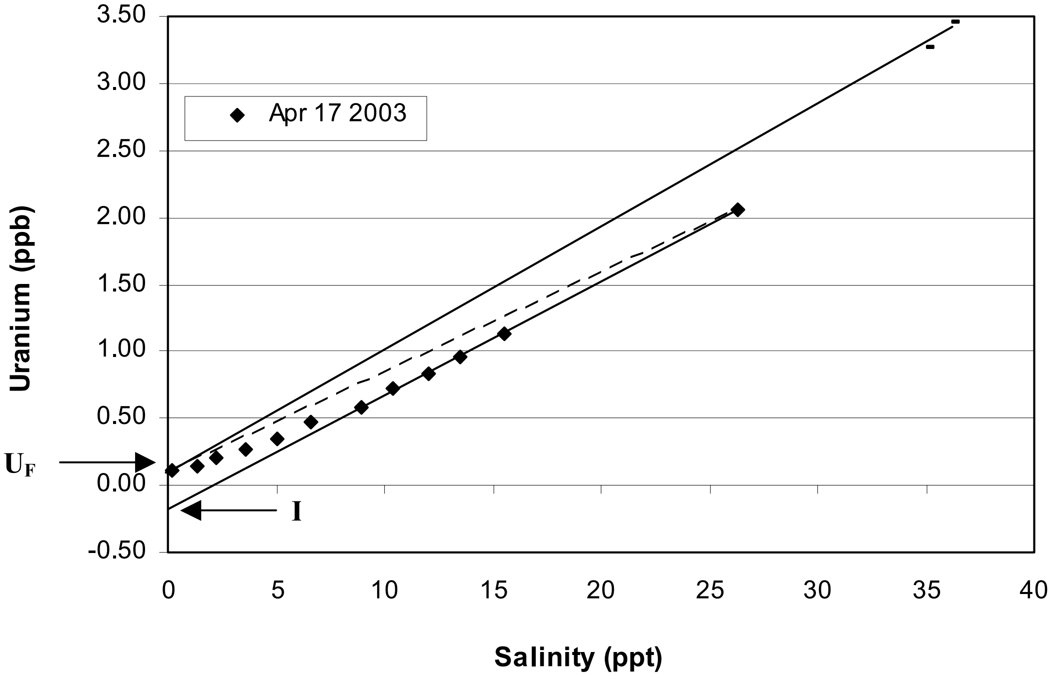

Figure 4.1 Derivation of the effective fresh water endmember used for calculating U removal rates. The graphs illustrate the accepted freshwater/open ocean uranium dilution line (after Windom et al., 2000), the dilution lines constrained by the saline Colleton River samples, and the tangent of the high-salinity (> 8 psu) region of mixing for exemplary data. U_F is the observed freshwater U endmember (μg m^{-3}), and I is the U-axis intercept, which represents an "effective" freshwater endmember (μg m^{-3}). Removal rate is calculated by multiplying the difference between the effective and actual freshwater endmembers by the freshwater discharge for a given time period. Resulting values are subsequently normalized by salt marsh area.

observations that creek water was typically fresh (i.e., < 1 psu) at low tide, we estimated average daily freshwater discharge using data collected just before the reversal of the creek's flow direction. Using 15-minute-interval discharge data provided by the USGS (Water Resources, South Carolina District), we estimated freshwater discharge in two ways: (1) by selecting the single discharge value determined for 1/2 hour before the reversal of tidal velocity and (2) by averaging the four values calculated for the 75-minute to 30-minute period before the reversal of tidal velocity. For the second method, the data recorded 15 minutes before tide reversal were excluded due to the influence of the impending flood-tide. Discharge values (typically 2 per day due to the semi-diurnal nature of the tidal cycle) were subsequently averaged over 1 month periods. Both methods produced similar freshwater discharge values (Figure 4.2).

4.2.2. Method 2: Mass Balance Approach (MBA)

The second U-removal estimate was based on a simple mass-balance approach (MBA). We derived the following equation for daily removal:

$$R = \frac{2\left(\mathrm{V_{TP}U_{TP}} - \mathrm{V_{TP}U_{TP}}\left(1-\alpha\right)\right)}{T_{res}}, \qquad (4.2)$$

where α is the average fraction of U-removal from surface water, V_{TP} is the tidal prism volume entering the Okatee/Colleton River system (m^3), U_{TP} is the U concentration of tidal prism water, and T_{res} is the approximate residence time of water in the tidal creek system. The entire expression is multiplied by two to account for the low tidal prism volume estimate, as described below. As in the EFEA approach, values are subsequently normalized for salt marsh area.

The fraction U-removal (α) was calculated from U-salinity mixing relationships

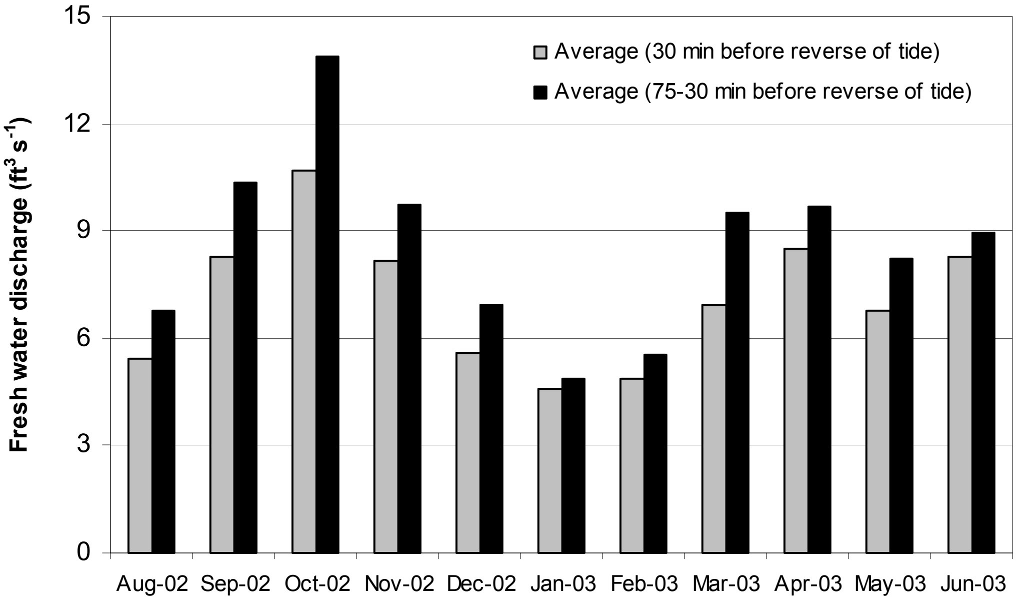

Figure 4.2 Freshwater discharge estimates for August 2002 to June 2003. Using 15-minute-interval total discharge data calculated and provided by South Carolina USGS, we estimated freshwater discharge two ways: by selecting the single discharge value determined for 1/2 hour before the reversal of tidal velocity and by averaging the four values calculated for the 75-minute to 30-minute period before the reversal of tidal velocity. The data point 15 minutes before tide reversal was excluded due to the influence of the impending flood-tide. On average, estimates generated using the latter approach were ~ 20% greater.

by comparing observed and expected concentrations and averaging calculated removal fractions for all samples having salinity greater than 8 psu. Low salinity samples were excluded in this calculation due to unreasonably high removal estimates resulting from low U concentrations. The T_{res} value of ~3 days was approximated independently by W. Moore (pers. comm., 2004) using radium isotope data and J. Blanton (pers. comm., 2004) using hydrographic methods. For yearly estimates, we use the average of R and U_{TP} values determined for individual sampling events and multiply the equation by 365 days. The small difference between the total-U and dissolved U data for June suggests a minimal interaction between U and particulate matter in the Okatee. In addition, except for a few abnormally high salinity samples collected in August 2002, none of the U-salinity profiles demonstrated U-addition relative to the system-specific mixing relationships. Therefore, we ignore U release and particulate-export in our simple mass balance.

Like our first calculation, the accuracy of the MBA estimate is dependent on both chemical and physical data. In particular, the estimate depends on the accuracy of the tidal prism volume calculation. Unfortunately, like freshwater discharge values, this value was not readily available. Therefore, we derived a partial system volume by integrating a hypsometric relationship produced for the Okatee watershed by J. Blanton and colleagues (Blanton, pers. comm., 2003) from a stage of 0 to 2.13 m (the mean tidal height calculated for the Okatee River gaging station over the 2002 calendar year). The hypsometric data were only generated for the upper portion of the Okatee River, extending from the headwaters to “Bailey’s Landing,” and therefore cover half or less of the areal extent of the marsh system of interest (See figure 1.1). Therefore, the tidal prism volume we calculate is probably 2 (or more) times smaller than the actual tidal prism volume.

The MBA assumes a constant U concentration saline endmember. Since the salinity and therefore U concentration of the Colleton River endmember certainly change over the course of the tidal cycle, the implicit assumption that this endmember is constant is not valid. However, based on the presumed salinity change of a given tidal cycle in this portion of the estuary (~5 psu), we estimate the effects of changing U concentrations on resulting removal calculations to be small (10-20%) relative to the overall uncertainty of the method.

In summary, because of the added uncertainties associated with the MBA removal calculation, this estimate should be taken as an order-of-magnitude approximation until more accurate data can be obtained. As will be shown below, the values obtained using this approximation are sufficient for a general consideration of removal processes and for comparison with estimates determined using the first method.

4.2.3. Method 3: Effective Saline Water Endmember Approach (ESEA)

By analogy to EFEA, another suitable method for determining U removal is an Effective Saline water Endmember Approach (ESEA). In practice, the MBA is quite similar to EFSA. However, we can derive a more specific formulation as follows (figure 4.3):

$$R = \frac{2\mathrm{Q}(\mathrm{E}-\mathrm{U_S})365}{T_{res}}, \tag{4.3}$$

where Q denotes the estimated tidal prism volume (m^3), U_S is the average saline water uranium endmember concentration (10.3 μmol m^{-3}) measured at the Colleton River, T_{res}

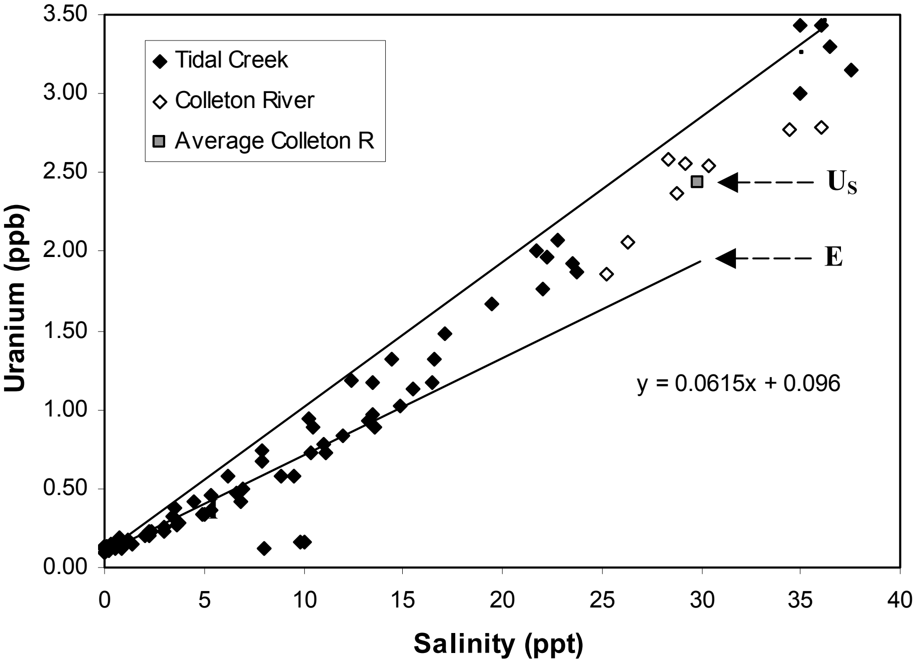

Figure 4.3 Derivation of the effective saline water endmember used for calculating yearly U removal rates. The graph illustrates the accepted freshwater/open ocean uranium dilution line (after Windom et al., 2000) and the trend line cast through *all* low- and mid-salinity (<15 psu) data points collected during this investigation to the average Colleton River endmember salinity (29.8 psu). U_S is the average saline water U endmember concentration (10.3 µmol m^{-3}) measured at the Colleton River, and E is the effective saline endmember (8.11 µmol m^{-3}), which was determined by extrapolation of the trend line. Removal rate is calculated by multiplying the difference between the effective and actual freshwater endmembers by the tidal prism volume. The result is then multiplied by two to account for our low tidal prism estimate and by 365 to express removal over the year. Finally, we normalize by the system's average salt marsh area.

represents the approximate residence time of water in the tidal creek system (~3 days), and *E* is the effective saline endmember (8.11 μmol m^{-3}). *E* was determined by extrapolating a trend line through all low- and mid-salinity (<15 psu) data to the average Colleton River endmember salinity (29.8 psu). The equation is multiplied by two to account for the low tidal prism estimate (discussed above) and by 365 to express removal over the year. Final estimates are normalized by the system's average salt marsh area. Because data from all seasons are represented in the extrapolation, the integrated yearly estimate is derived.

4.2.4. Removal Estimates

Seasonal and yearly U-removal estimates determined using the first two approaches are given in Tables 4.1 and 4.2. Note that only yearly estimates were determined with the ESEA. Yearly U removal computed using the MBA (58 μmol m^{-2} $year^{-1}$) and ESEA (104 μmol m^{-2} $year^{-1}$) were two orders of magnitude larger than those computed with the EFEA (0.37 μmol m^{-2} $year^{-1}$), but compared well with published estimates of 16 to 70 μmol m^{-2} $year^{-1}$ (Church et al., 1996; Dunk, 2002; and Windom et al., 2000). Despite differences in the magnitude of estimates, seasonal trends calculated with all three methods were in good agreement with those observed in U-salinity mixing trends. High temperature, enhanced chemical and biological activity, and low discharge all favor a large removal signal for August 2002.

Table 4.1. U removal estimates based on freshwater discharge and effective freshwater U endmember concentrations [$R=Q(I-U_r)$]. Values are normalized by the average computed salt marsh area (2.82×10^7 m^2). Results were obtained using the larger freshwater discharge estimate (average of computed discharge values 30 to 75 minutes before flood tide). The use of smaller discharge estimates decreases all predictions by ~20%.

Sampling Date[a]	I[b]	Fresh water discharge (m^3 month^{-1})	Removal Rate[c]
August 9, 2002	-0.737	512370	15.2 (0.064)
October 6, 2002	-0.142	1053314	8.9 (0.037)
November 25, 2002	-0.0251	714131	3.1 (0.013)
January 6, 2003	-0.0476	367386	1.9 (0.0079)
March 5, 2003	-0.305	722690	10.3 (0.043)
April 17, 2003	-0.173	711643	6.8 (0.029)
June 3, 2003	-0.196	655935	6.8 (0.029)
Yearly Estimate	-0.225[d]	7674878[e]	87.5 (0.37)[f]

[a] Data extrapolated to estimate removal for entire month.

[b] U-axis intercept determined from extrapolation of higher salinity U-salinity data.

[c] µg m^{-2} month^{-1} (µmol m^{-2} month^{-1}).

[d] Average of U-axis intercept from the 7 applicable fiend campaigns.

[e] Sum of monthly freshwater discharge estimates (75m – 30m values) for August 2002 – July 2003.

[f] µg m^{-2} year^{-1} (µmol m^{-2} year^{-1}).

Table 4.2. U removal estimates based on approximate tidal prism volumes and percent U removal calculated from U-salinity relationships for salinity > 8 psu. Values are normalized by the average computed salt marsh area (2.82×10^7 m^2). These initial calculations use an approximated tidal prism volume of 5.6×10^6 m^3.

Sampling Date[a]	Colleton R. [U][b]	% Removal	Removal Rate[c]
August 9, 2002	2.78	19	2231 (9.4)
October 6, 2002	2.54	5	540 (2.3)
November 25, 2002	2.59	3	360 (1.5)
January 6, 2003	2.55	4	463 (1.9)
March 5, 2003	2.38	19	1836 (7.7)
April 17, 2003	2.06	16	1337 (5.6)
June 3, 2003	1.86	15	1131 (4.8)
Yearly Estimate	2.44[d]	12[e]	13827 (58)[f]

[a] Data extrapolated to estimate removal for entire month.

[b] µg L^{-1}; system-specific saline endmember approximation.

[c] µg m^{-2} month^{-1} (µmol m^{-2} month^{-1})

[d] Average of Colleton River concentrations for all field campaigns.

[e] Average of % U removal for 7 applicable field campaigns.

[f] µg m^{-2} year^{-1} (µmol m^{-2} year^{-1}).

That MBA and ESEA estimates correlate well with observations is expected since they are derived from a direct measure of removal based on mixing-curve calculations. EFEA estimates, on the other hand, are based on an indirect measure of removal (extrapolated y-intercept) that is affected by processes occurring both within and outside the system. EFEA estimates are also extremely sensitive to subtle changes in the slope of the trend lines cast through data points. For example, variations in U concentration and salinity of our Colleton River endmember affected the slope of the trend lines used to predict the effective fresh water endmember, I (see table 3.4 and figure 3.1), in an inconsistent way across season (i.e., expected removal variation with season suggest that trend line slopes should decrease with the coming winter and increase with the approach of summer, resulting in less negative and more negative I values, respectively). Furthermore, it is clear that estimates derived from the EFEA depend closely on the magnitude of freshwater discharge, a parameter that was difficult to estimate and that may have little true influence on U removal.

Although this study does not seek to assess the validity of various U-removal mechanisms, some additional consideration of this issue is warranted. Since other removal estimates for U have been based on the EFEA (Windom et al. 2000; Dunk, 2002), it is important to address why the values we derived using this approach are so low. The EFEA as expressed in this study was first employed by Li and Chan (1979) for determining Ba release from particles at low salinity. Several factors support the suitability of the EFEA for Ba-release calculations: The major source of Ba to estuarine systems is freshwater discharge; Ba removal/release is clearly dependent on colloidal/particulate induced processes and, thus, on freshwater/saline water interactions;

and high salinity conservative mixing of Ba makes the approach simple to apply.

In contrast, the EFEA is less applicable for U removal calculations since the major source of U is the open ocean, and particulate interactions are probably not a significant mechanism for removal. Therefore, removal estimates based on freshwater discharge volumes have the potential to be misleading, and this method should be applied cautiously and probably limited to environments where freshwater discharge is clearly associated with element-removal. We note that low removal rates derived from the EFEA are unlikely to have resulted from uncertainty associated with the freshwater discharge estimates, which would have to be incorrect by two orders of magnitude to explain the deviations between calculated removals.

Two of our three approaches generated U removal estimates that were larger, although of similar orders of magnitude, than those previously in the literature. Church et al.'s (1996) determined a U removal of 16 µmol m^{-2} $year^{-1}$ for a lower Delaware Bay salt marsh (Canary Creek, Lewis, Delaware) using the MBA. The difference between their estimate and our larger ones probably results from temperature and tidal-range differences between field sites and possibly from variations in marsh biogeochemical cycling, invertebrate burrowing, freshwater composition (i.e., DOM and metal-oxide content), and hydrologic properties of marsh sediments. For example, the tidal amplitude for their Delaware Bay study site varies between 1 and 1.5 m (Windom et al 2000), compared to a tidal range of ~ 1.8 to 2.5 m for our study site. These authors documented highest removal when the marsh surface was flooded, which occurred only during spring tides, whereas the surface of the Okatee salt marsh is inundated frequently. The consistency of surface-flooding observed during many sampling trips to the Okatee marsh supports this conclusion.

Using the EFEA, Windom et al. (2000) determined a U-removal rate of 70 µmol m^{-2} yr^{-1} for the Savannah River estuary, located within 40 km south of our field site. However, they normalized the calculated removal value by 20% of the computed salt marsh area, which increases their estimate on an areal basis. When normalized by full marsh area for comparison with our results, the Windom et al. (2000) removal value is recalculated to 15 µmol m^{-2} $year^{-1}$. Based on the low estimates generated by the EFEA in the our study, the Windom et al. (2000) estimate may suffer from a similar, though less dramatic, negative bias. Because they compute removal using the full yearly discharge of an entire estuarine system, rather than that of a small tidal tributary, their result isn't as low (relatively) as the one we determined using EFEA. All things considered, the published estimate for the Savannah River estuary (normalized by 20% of the system's marsh area) compares well with the results we obtain from the Okatee system in this study and is probably more accurate than the recalculated version of their estimate normalized by the full marsh area.

Dunk et al. (2002) recently reviewed information pertaining to global U budget calculations. Using data from Carroll and Moore (1994) for the Ganga-Brahmaputra mixing zone and an EFEA, they predicted removal of 30 µmol m^{-2} yr^{-1} for mangrove forests. Considering the estimates by Church et al. (1996) and Windom et al. (2000), the uncertainty associated with U behavior in other estuaries, and the lack of knowledge about removal processes, they assigned salt marsh and mangrove systems a U-removal rate of 20 ± 10 µmol m^{-2} yr^{-1}. When determining this removal rate, the authors deemed Windom et al.'s (2000) estimate of 70 µmol m^{-2} $year^{-1}$ high, since it documents year-round removal with limited winter-time measurements. However, our MBA and ESEA estimates are both several times larger than Dunk's conservative removal and can be rationalized by considering site characteristics that favor removal.

As in the study of Windom et al. (2000), our site is located in the zone of maximum expected average tidal range of the South Atlantic Bight and in a region of high temperature and vigorous chemical and biological activity. These characteristics should lead to not only higher removal but also to the extension of the seasonal removal capacity of marshes. Although low winter removal rates were clearly documented by this study, removal estimates are averaged over the whole year and are still much larger than previously suspected. Large average tidal ranges should enhance the communication between surface- and groundwater by making high-tide surface water infiltration and advection across the tidal creek bank and low-tide shallow groundwater discharge more favorable. These hydrologic processes are suspected to increase removal of uranium. The frequent inundation of the salt marsh in the study area, a phenomenon connected both to the large tidal range and low average elevation of the marsh relative to mean high tide, may also enhances removal through the surficial processes proposed by Church et al. (1996). The high average temperatures in the study area enhance microbially-mediated biogeochemical processes previously invoked for U-removal. The long warm season extends the impact of the active observed macrofauna burrowing, a process that radically alters near-surface permeability and surface water infiltration (Hughes et al., 1998), facilitating U(VI) transport to reducing sediments, thereby affecting U removal. Thus, the rates of U removal we calculate, though large, are probably reasonable and imply that salt marshes in subtropical areas play a greater role in U removal than proposed by Dunk et al. (2002).

This study reemphasizes the importance of anoxic coastal environments for U removal and suggests a larger impact than previously documented in the literature. Although extrapolation of these results to a global scale requires caution, these new estimates do have significant implications for the global U budget. Specifically, the results increase the Dunk et al. (2002) published estimate of total removal beyond the margin of error cited in their study. Averaging published removal values and including a conservative estimate of 58 μmol m^{-2} yr^{-1} from this study, we determine a global U removal rate of 24 ± 14 Mmol yr^{-1} when taking into account the combined global area of salt marsh (3.8×10^{11} m^2) and mangrove (1.8×10^{11} m^2) systems (Woodwell et al., 1973; Spaulding, 1997). The new estimate is twice that generated by Dunk et al. (11.2 ± 5.6 Mmol $year^{-1}$). Considering all the sources and sinks for U described by Dunk et al., our approximation, if correct, supports a missing or underestimated U source or an imbalance in the global U budget in favor of removal. For example, during interglacial periods, oceanic U concentrations probably decrease due to increased temperature and intertidal area, both of which favor removal.

4.3. Uranium as a tracer for groundwater discharge in salt marsh and estuarine systems

4.3.1 Background

Increasing coastal population and growing evidence for the importance of solute transport by groundwater pathways have focused research attention on quantifying the role of groundwater in water- and chemical-cycling in salt marshes and other coastal environments (Moore, 1999; Windom and Niencheski, 2003). The advective discharge of groundwater through permeable salt marsh sediments is well documented (Whiting and Childers, 1989; Malcolm and Sivyer, 1997; Krest and Moore, 2000; Jahnke et al., 2003). Pressure gradients produced by upland recharge of rain water induce groundwater flow through the salt marsh. This flow is facilitated and enhanced if permeable formations extend far enough into the upland (Jahnke et al., 2003; Tobias et al., 1998). Alternatively, advection can be promoted by hydraulic pressure gradients established by the flooding of marsh surfaces and the saturating of sediment pore waters and macrofauna burrows. At low tide, this saturated sediment mass can be several meters above creek water levels and can generate significant flows through permeable sediments to the tidal creek (Whiting and Childers, 1989; Hughes et al., 1998; Jahnke et al., 2003). Accordingly, maximum discharge should occur during spring tide periods, when both the highest and lowest water levels of the month are typically observed. In both cases, the salinity of discharging groundwater is often similar to estuarine surface waters due to the consistent delivery of sea salts to shallow aquifers by flood tides (Jahnke et al., 2003).

Salt marsh groundwater, which includes pore water and recycled surface water (Cable et al., 1997; Moore, 1999), is typically enriched in nutrients and other biologically and chemically reactive constituents (e.g., ammonia, nitrate, silicate, phosphate, etc.) compared to surface water (Whiting and Childers, 1989; Portnoy et al. 1998; Moore, 1999; Jahnke et al., 2003; Windom and Niencheski, 2003). Thus, groundwater discharge from salt marshes can result in significant chemical fluxes to surface waters that can have a major influence on the biology and chemistry of the coastal ocean. It follows that quantifying the magnitude of groundwater discharge is critical for determining the role of salt marshes in local and global biogeochemical cycles, understanding the ability of salt marshes to modify the chemistry of important species in surface waters, and predicting the impact of land-use change on the coastal ecosystem. Furthermore, accurate discharge (and species flux) estimates are required to quantify the importance of salt marshes in the coastal landscape and, thus, to make data-based policy decisions regarding marsh preservation and management of adjacent upland areas.

Coastal groundwater discharge rates are difficult to determine and often poorly quantified. Spatially-variable, high-permeability sediment layers control the distribution of groundwater discharge in salt marshes (Jahnke et al., 2003; Whiting and Childers, 1989; Portnoy et al., 1998). Considering the well-documented heterogeneity of salt marsh sediments and flow systems, it is not surprising that commonly-used, localized “seepage or flux” meters fail to consistently capture advective flow signals and often produce uncertain estimates. For example, using benthic flux chambers, Jahnke et al. (2003) documented highly variable fluxes of groundwater containing silicate, phosphate, and ammonium in the Satilla River estuary (GA, USA) and noted that flow was missed by many of their deployments. Similar results have been reported by Whiting and Childers (1989) for a North Inlet, SC salt marsh, Portnoy et al. (1998) for discharge into

Nauset Marsh estuary (Cape Cod, Massachusetts), and Cable et al. (1997) for groundwater input into St. George Sound, Florida. Thus, despite the demonstrated importance of GW advection, a lack of quantitative certainty in many settings limits the prediction of solute/chemical fluxes and the completion of species mass balances.

One approach to minimize uncertainties in groundwater discharge predictions involves the use of tracer elements. Natural geochemical tracers that have limited sources and that are influenced by well-understood processes are promising tools for quantifying groundwater discharge from salt marshes and other coastal sediments. Tracers employ a system-wide (vs. localized) approach, which aims to integrate the discharge signal in surface water over the entire region of interest, minimizing the effects of environmental heterogeneity. Moore (1999) described the "subterranean estuary," a below ground mixing zone of fresh meteoric water and recycled saline surface water. This coastal feature has fundamental importance for estuarine chemistry and mimics processes occurring in surface water estuaries. Fortuitously, biogeochemical conditions (e.g., high ionic strength and reducing conditions) characterizing the subterranean estuary enhance/deplete the concentrations of several different tracer elements in groundwater compared to concentrations predicted by the conservative mixing of surface waters (Moore, 1999; Swarzenski et al., 2001; Windom and Niencheski, 2003). The discharge of shallow marsh groundwater has the apparent effect of changing the expected surface water behavior of applicable tracers. Ideally, the difference between observed and predicted concentrations can be quantified to estimate pore-/groundwater discharge.

Moore (1999) and others have suggested several potentially valuable tracer elements for marsh groundwater discharge, including Ba, CH_4, ^{222}Rn, and Ra isotopes. In particular, Moore has pioneered an approach involving Ra isotopes. In several studies, spanning globally diverse environments (e.g., Brazil, Southeastern United States, India, etc.), Moore and coworkers (1993, 1996, 2000, etc.) have used Ra isotopes to quantify groundwater discharge and pore-water/water column exchange, nutrient fluxes, and system residence times. Other studies have also employed similar tracers to obtain qualitative evidence for groundwater and chemical fluxes. For example, Swarzenski et al. (2001) used several different chemical tracers of groundwater discharge, including the enriched tracers Rn, methane, Ba, and Ra and the depleted (reverse redox) tracers U, V, and Mo, to characterize the hydrogeology of a submarine spring off Crescent Beach, Florida.

Based on the results presented in this thesis, U appears to be a quantitatively useful tracer of groundwater in coastal environments. As noted above, an effective tracer should have limited sources and be influenced by specific processes. For U, the dominant source is flooding tidal waters from an oceanic endmember and the potentially important removal processes all involve tidally-driven surface-water interaction with and/or cycling through salt marsh sediments, resulting in the discharge of U-depleted groundwater back to surface waters.

During this investigation, we documented seasonally-variable U-removal from surface waters and consistently high U-removal (92%) in shallow marsh groundwater. In addition, we measured U-depleted/Ba-enriched water seeping from creek banks at low tide (Figure 3.20). These data suggest that the discharge of U-depleted marsh-groundwater contributed to observed surface water U-removal, and, therefore, that the extent of U removal documented in surface waters could be indicative of the magnitude of groundwater input. Figure 3.19, which illustrates the relationship between groundwater, surface water, and marsh-runoff/seepage sample U concentrations and salinity, supports this hypothesis and demonstrates that average site groundwater provides an analytically appropriate and potentially effective endmember for explaining uranium depletion in surface water. Together, these observations encouraged our use of three endmember mixing models constrained by salinity for quantifying the percent and rate of groundwater input to the Okatee/Colleton river system.

4.3.2 Mixing Model and Discharge Rate Calculations

The distribution of U in surface waters of the Okatee system (i.e., concentration vs. salinity) can be explained by the mixing of 3 chemically distinct endmembers: low-U-concentration fresh water, higher-U-concentration saline water (Colleton River), and low-U-concentration saline marsh pore-/groundwater. For each tidal creek surface water sample collected during this investigation, we solved the following set of equations (4-4, 4-5, and 4-6) for the fraction contribution of groundwater (f_{GW}, 4-7), fresh water (f_{FW}, 4-8), and Colleton River water (f_{CR}, 4-9):

$$S_{TC} = f_{GW}\left(S_{GW}\right) + f_{FW}\left(S_{FW}\right) + f_{CR}\left(S_{CR}\right) \tag{4-4}$$

$$U_{TC} = f_{GW}\left(U_{GW}\right) + f_{FW}\left(U_{FW}\right) + f_{CR}\left(U_{CR}\right) \tag{4-5}$$

$$f_{GW} + f_{FW} + f_{CR} = 1 \tag{4-6}$$

$$f_{GW} = \left(\frac{S_{TC}}{S_{GW}}\right) - f_{CR}\left(\frac{S_{CR}}{S_{GW}}\right) \tag{4-7}$$

$$f_{FW} = \left(\frac{U_{TC}}{U_{FW}}\right) - \left(\frac{S_{TC}U_{GW}}{U_{FW}S_{GW}}\right) + f_{CR}\left[\left(\frac{S_{CR}U_{GW}}{U_{FW}S_{GW}}\right) - \left(\frac{U_{CR}}{U_{FW}}\right)\right] \tag{4-8}$$

$$f_{CR} = \left[1 - \left(\frac{S_{TC}}{S_{GW}}\right) - \left(\frac{U_{TC}}{U_{FW}}\right) + \left(\frac{S_{TC}U_{GW}}{U_{FW}S_{GW}}\right)\right]\left[1 - \left(\frac{S_{CR}}{S_{GW}}\right) - \left(\frac{U_{CR}}{U_{FW}}\right) + \left(\frac{S_{CR}U_{GW}}{U_{FW}S_{GW}}\right)\right]^{-1} \tag{4-9}$$

where *S* and *U* denote salinity and uranium concentration, respectively, for tidal creek samples or endmembers described by the subscripts *TC* (tidal creek sample), *CR* (Colleton River endmember sample), *GW* (groundwater endmember), and *FW* (fresh water endmember).

We determined unique saline, and groundwater endmembers for each sampling event (Table 4.3). We approximated the saline endmembers as the salinity (S_{CR}) and U concentration (U_{CR}) of the single point collected from the Colleton River at the Waddell Mariculture Center and calculated the groundwater endmember as the site-average salinity (S_{GW}) and U concentration (U_{GW}) of all wells (excluding the hyper-saline MW02 and the elevated-U-concentration MW06). The same freshwater endmember (S_{FW}, U_{FW}) was used for each calculation and was determined as the average of 5 samples collected over 8 months from two fresh water tributaries feeding the Okatee headwaters. In instances where the use of endmember models is analytically inappropriate, negative contributions of one endmember or another will result. For most sampling events, the calculations generated positive contributions for all endmembers, suggesting that the result is physically plausible. However, physical plausibility does not prove that the results are correct.

Once a fraction groundwater was assigned to each tidal creek surface water sample, we calculated a marsh-normalized ground water discharge rate for the headwaters area, corresponding to each sampling event:

$$D = \frac{V_H f_{GW}}{A_{MH} T_{res}} \qquad (4\text{-}10)$$

where D is the groundwater discharge rate (L m^{-2} day^{-1}), T_{res} is the system water residence time (~3 days), f_{GW} is the average calculated fraction of surface water consisting of groundwater, and V_H and A_{MH} are the upper-Okatee tidal creek water volume (5.62 x 10^9 L) and salt marsh area (4.23 x 10^6 m^2), respectively. f_{GW} was calculated for each sampling event between October 2002 and June 2003 to determine seasonal groundwater discharge rates and represents the average of fractional groundwater contributions calculated for individual tidal creek samples with salinity $\geq$ 5 psu. Low salinity samples were excluded when determining the average groundwater fraction to reduce the quantitative impact of fresher water on the calculation (i.e., necessarily, as salinity approaches 0, the fractional groundwater contribution must approach 0 as well). Thus, the inclusion of low salinity points reduces the groundwater fraction predicted. In actuality, the effect of precluding low salinity samples was small (Table 4.4). V_H and A_{MH} were calculated by the same hypsometric relationship used for U removal calculations for the upper Okatee River (Section 4.2.2). Briefly, a site specific hypsometric curve (water area, m^2 vs. stage, m) derived by J. Blanton and colleagues (Blanton, pers. comm., 2003) was integrated from stage 0 to 2.13 m (the mean tidal range observed at the site) to estimate a mean water volume and a marsh area specific to the upper potion of the Okatee River (i.e., the region extending from the headwaters to

"Bailey's Landing," Figure 1.1). Thus, discharge values generated are appropriate for the upper Okatee River region.

Table 4.3.
Salinity and U concentrations for 3-endmember mixing calculations.

Date	Groundwater		Colleton River	
	Salinity (psu)	**U (ppb)**	**Salinity (psu)**	**U (ppb)**
August 9, 2002	34.4	0.62	36	2.78
August 31, 2002	32.2	0.26	34.4	2.78
October 6, 2002	30.0	0.18	30.4	2.54
November 25, 2002	29.8	0.15	28.3	2.59
January 6, 2003	30.6	0.22	29.2	2.55
March 5, 2003	29.9	0.18	28.8	2.38
April 17, 2003	28.4	0.19	26.3	2.06
June 3. 2003	28.5	0.18	25.2	1.86

4.3.3 Groundwater Contributions and Discharge Rates

Figure 4.4 illustrates the results of mixing calculations performed for October 2002 through June 2003 sampling events and shows the predicted fractions of groundwater, fresh water, and Colleton River water vs. salinity for each tidal creek sample. The clear seasonality documented in surface water U removal is expressed by a parallel seasonality in groundwater contribution to the system. This result was expected since the model as formulated must attribute removal to the groundwater endmember. Above salinity of ~5 psu and throughout the mid-salinity region, groundwater contributions stabilize. The fact that groundwater contributions are ~ constant throughout the mid-salinity region implies that the U tracer is acting to average the groundwater discharge signal over the system, as anticipated.

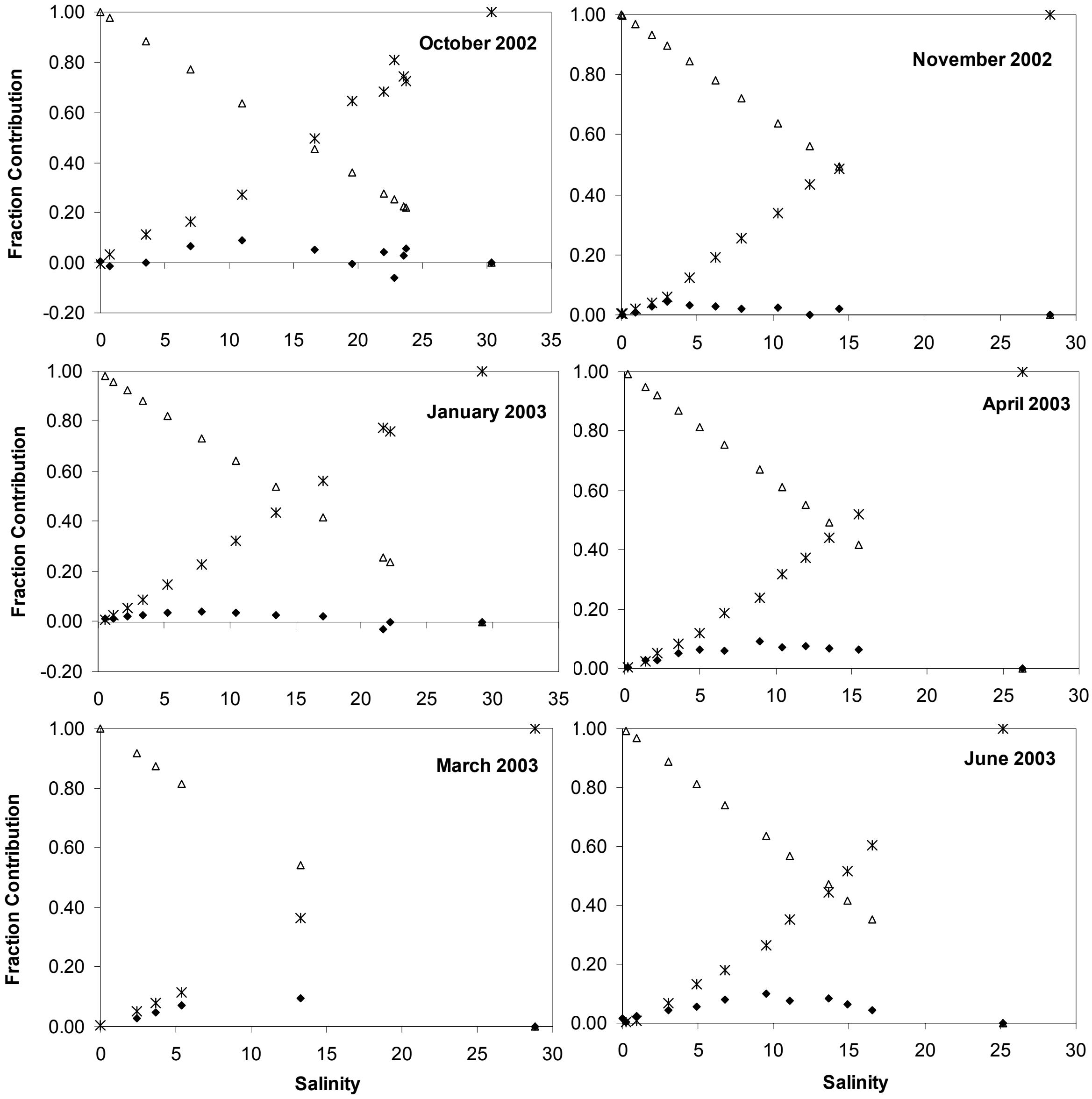

Figure 4.4 Predicted fractions of groundwater (♦), fresh water (Δ), and Colleton River water (∗) vs. salinity for tidal creek samples collected between October 2002 and June 2003. The groundwater contribution demonstrates a parallel seasonality to documented U removal.

Table 4.4.
Average groundwater contributions, determined from 3-endmember mixing calculations, and associated discharge rates calculated using eq. 4-10.

Date	**All Samples**[a]		**Salinity > 5 psu**[b]	
	GW fraction	Discharge[c]	GW fraction	Discharge[c]
August 9, 2002	*-0.03*	*-14*	*0.32*[d]	*140*
October 6, 2002	0.03	11	0.03	15
November 25, 2002	0.02	9	0.02	9
January 6, 2003	0.02	8	0.02	8
March 5, 2003	0.06	27	0.08	37
April 17, 2003	0.06	25	0.07	32
June 3. 2003	0.06	26	0.07	33

[a] Average groundwater fraction calculated using all tidal creek samples collected.

[b] Average groundwater fraction calculated using tidal creek samples with salinity > 5 psu

[c] L m^{-2} day^{-1}

[d] Groundwater contribution was calculated from excluding several high-tide, high salinity samples that showed apparent addition compared to the Colleton River endmember.

Table 4.4 gives average groundwater contributions, calculated from mixing results for each sampling event, and corresponding groundwater discharge values, determined from 5-10. Our discharge estimates of 8 to 37 L m^{-2} day^{-1} agree closely with previously published salt marsh values. Krest and Moore (2000) calculated that a groundwater discharge rate of 20 to 40 L m^{-2} day^{-1} was needed to account for the excess Ra inventory in a North Inlet, South Carolina tidal creek. For the same marsh, Whiting and Childers (1989) and Morris (1999) used direct seepage measurements and system salt balance calculations, respectively, to estimate a groundwater discharge between 7.8 to 28 L m^{-2} day^{-1}.

Discharge values calculated for August 2002 should be ignored, since the 3-endmember mixing model inadequately described the data (Figure 4.5) and the number of

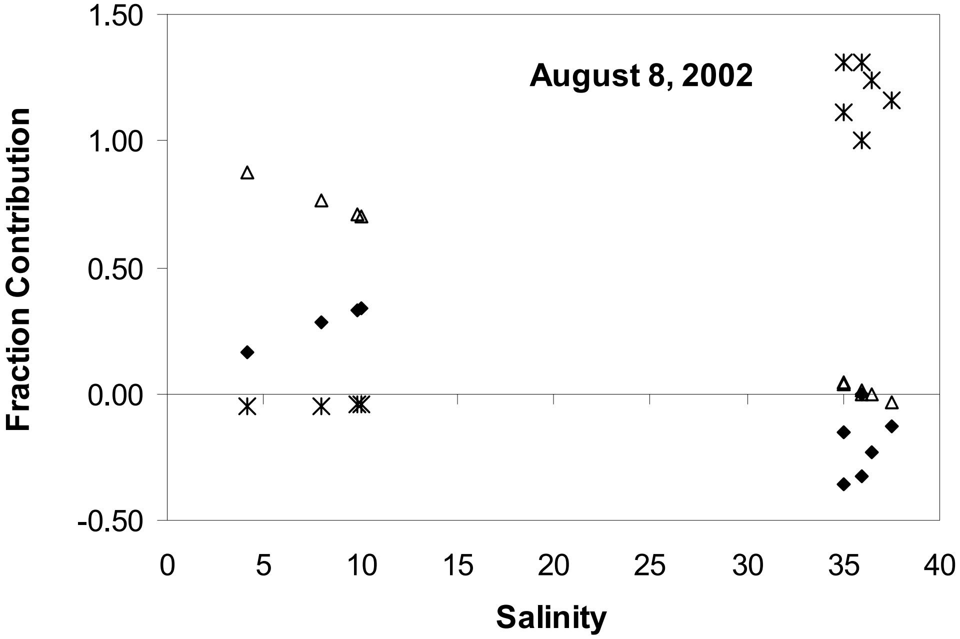

Figure 4.5 Predicted fractions of groundwater (♦), fresh water (Δ), and Colleton River water (*) vs. salinity for tidal creek samples collected on August 8, 2002. Addition of U to solution is expressed as a negative groundwater contribution. These data suggest that the 3-endmember mixing approach is not always a suitable way to describe U removal from solution.

data points describing mid-salinity mixing was small. This sampling period was unusual compared to the others due to observed U-addition in high-salinity tidal creek samples. The large groundwater contribution predicted for mid-salinity August 2002 samples suggests high discharge at low tide during this sampling period, but actual discharge calculations may or may not be valid. Additional research is required to understand the U behavior observed during this month and to determine whether results are anomalous.

4.3.4 Seasonality

Our calculations suggest broad seasonality in groundwater discharge, with higher values in the spring/summer (25 – 37 L m^{-2} day^{-1}) and lower values in the late fall and winter (8 – 15 L m^{-2} day^{-1}). Other studies have documented similar seasonality in the concentration of salt marsh groundwater tracers and for discharge rates. For example, Krest and Moore (2000) found that average tidal creek radium enrichment in the summer was approximately 2 times greater than that of winter. This seasonality is consistent for Ra enrichment in tidal creeks of the southeastern United States (Moore, 1996). In addition, Cable et al. (1997) used seepage meters to document seasonality in groundwater input into St. George Sound, Florida, with higher flows in summer (June through September) and lower rates in the winter (October through May). If we recall that the main factors influencing salt marsh groundwater discharge are tidal fluctuations leading to inundation of the marsh surface and precipitation leading to upland groundwater recharge (Cable et al., 1997; Hughes et al., 1998; Tobias et al., 2001; Jahnke et al., 2003), we can begin to rationalize the observed seasonality.

The morphology of tidal creek/salt marsh systems in the South Atlantic Bight is characterized by steep creek banks and shallow sloping marsh surfaces. Thus, once the tidal creek reaches bank-full conditions, subtle changes in maximum tide height may significantly change the area of salt marsh flooded during a tidal cycle. The extent of marsh surface saturation by flooding waters will change according. Subsequently, differences in average daily maximum tide height could result in seasonal differences in hydraulic pressure gradients resulting from flooding tidal water and, thus, the magnitude of groundwater discharge. In addition, seasonal differences in average daily tidal range could influence the final difference in elevation between saturated marsh surface sediments and tidal creek water levels at low tide, resulting in similar seasonal pressure gradients and groundwater discharge rates. Daily maximum tidal height and range data for the Okatee site from 2002 averaged over one month periods (Figure 4.6) both show maximum and minimum values for summer and winter periods, respectively. This seasonality follows the seasonality in the U-removal and calculated discharge rates and, if 2002 data are typical of general seasonal variations, suggests that more dramatic summertime tidal forcing may contribute to groundwater discharge seasonality.

In addition, precipitation data acquired by the USGS show that rainfall patterns show a rough positive correlation with U removal and calculated groundwater discharge rates (Figure 4.7). Cable et al. (1997) and Tobias et al. (2001) both attributed seasonal variations in salt marsh groundwater flow to precipitation patterns. In addition, Hughes et al. (1998) observed a significant groundwater response to rainfall in a Hunter River, Australia salt marsh. Thus, low winter precipitation at the site may have resulted in lower upland to tidal creek head gradients and reduced groundwater discharge. However,

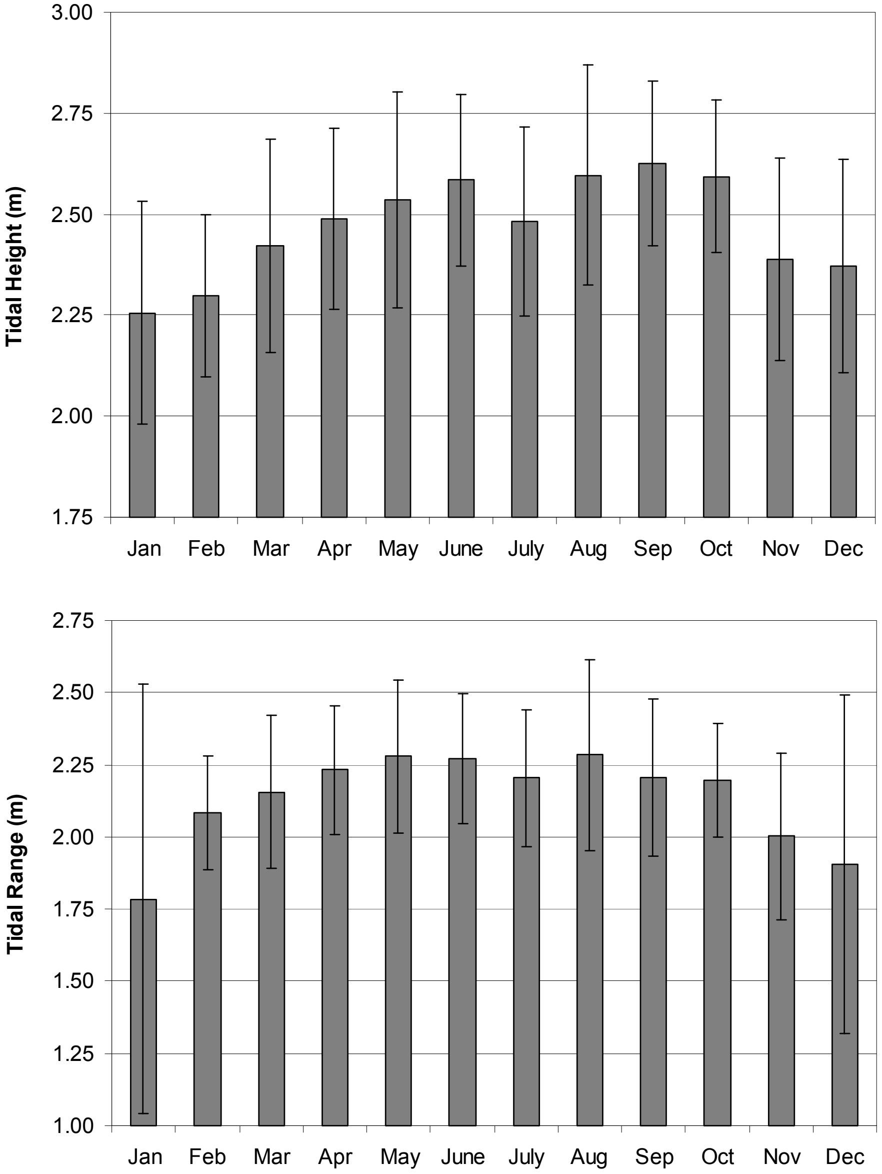

Figure 4.6 Average daily maximum tidal height and range by month for the Okatee River gaging station for 2002. Note the truncated y-axes. Error bars indicate 1 standard deviation. These plots illustrate the general seasonality of tidal forcing at our study site. This seasonality is similar to that observed for U removal and groundwater discharge estimates and, if 2002 data are typical, suggests that variations in tidal forcing may have influenced the magnitude of groundwater discharge.

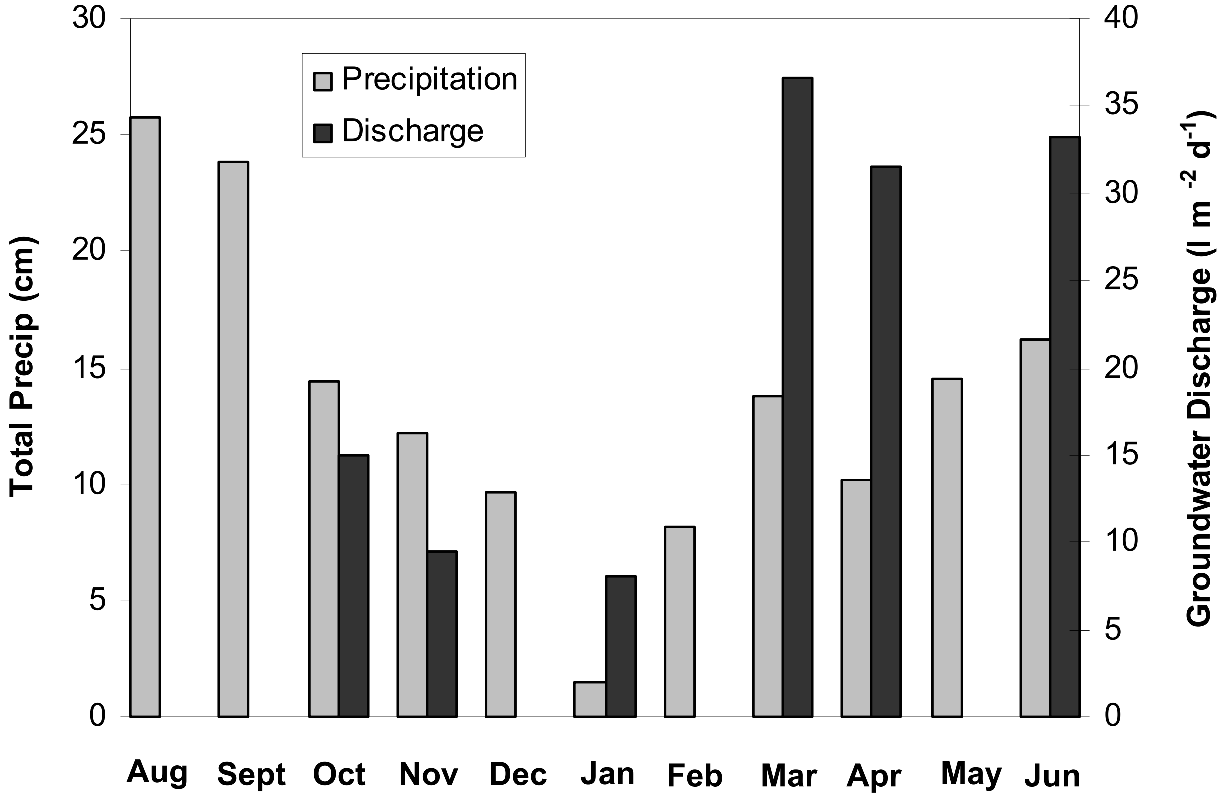

Figure 4.7 Total monthly precipitation recorded at the Okatee river gaging station and groundwater discharge calculated using the MBA for the period encompassing our study (August 2002 through June 2003). This plot illustrates the seasonality of precipitation at our study site. This seasonality shows a rough positive correlation with groundwater discharge estimates and suggests that variations in upland groundwater recharge may have influenced the magnitude of salt marsh groundwater discharge.

we note that the impact of upland recharge and pressure gradients may not be as important at our site as documented at other locations. Harvey and Odum (1990) stated that where low permeability units underlie marsh settings (as evidence suggests for at least part of the Okatee site) upland groundwater discharge to marsh sediment will normally be a much smaller component of water balance than tidal infiltration. Furthermore, Jahnke et al. (2003) stated that upland pressure gradients are more important when permeable marsh sediment extend into the upland. Upland wells installed adjacent to the west side of the site did reveal the presence of high permeability units, but the degree of hydraulic connectivity between these layers and sediments in the marsh is not clear, partially due to the complex sedimentation patterns at the site.

Seasonal variations in temperature and macrofauna activity certainly contribute to the seasonality of groundwater discharge rates as well. Higher summertime temperatures lead to increased biological and chemical activity and result in the opening of pore space (e.g., through the reduction of ferrous iron particles) and increased bioturbation, which enhances communication between surface water and subsurface permeable sediments. For example, Hughes et al. (1998) observed a 1 to 2 order of magnitude increase in marsh surface infiltration rate (from 0.01 to 0.1-1 m/day) resulting from the presence of crab burrows, with rates of burrows themselves averaging 11 m/day. Higher infiltration rates increase the volume of surface water retained by and cycled through marsh sediments during a given tidal cycle, resulting in increased hydraulic gradients and enhanced groundwater flow (Jahnke et al., 2003). During summertime, the effects of bioturbation and larger tidal forcing may act synergistically to promote groundwater discharge. Conversely, during winter months, lower surface- and bank sediment permeability resulting from geochemical pore clogging and the absence of bioturbation likely inhibit both delivery of U(VI) in surface water to microbially-active, reducing sediments and groundwater discharge to the tidal creek. Because the marsh subsurface remains reducing year-round and the extent of U removal in marsh groundwater is consistently high, if the seasonal change in marsh hydraulic conductivity described above is important, seasonal patterns of surface water U removal, groundwater discharge and Ra addition can be explained without invoking changes in subsurface microbial respiration rates (i.e., microbial U-removal rates).

4.3.5 Barium and Groundwater Discharge

Several authors have suggested Ba as another tracer of groundwater discharge to coastal waters (Shaw et al., 1998; Swarzenski et al., 2001; and Moore, 1999). Therefore, elevated Ba concentrations should have accompanied the depleted uranium signal in groundwater discharge at our study site. The data we collected do provide some evidence of Ba addition. As expected, site groundwater and bank discharge samples showed highly elevated Ba concentrations vs. salinity. Furthermore, low to mid salinity Ba addition observed in August and October 2002 and June 2003 tidal creek samples point to possible groundwater input to the system.

However, unlike uranium, the Ba profiles failed to reveal clear seasonality in addition and removal. In addition, observed Ba concentrations for the majority of surface water samples provided only limited evidence for groundwater input to the Okatee system, as Ba addition rarely corresponded directly to uranium depletion. For example, although Colleton River endmember U concentrations show clear seasonality, the Ba concentrations measured in the Colleton River decrease over the course of our investigation from high August 2002 values to values falling near the standard dilution line for Ba for June 2003. Furthermore, identical 3 endmember mixing calculations performed for Ba yield negative endmember contributions. Assuming that groundwater discharge is the ultimate source of the U-removal signal, observed dissolved (i.e., 0.45 μm filtered) Ba concentrations in the tidal creek were too low (or average groundwater Ba concentrations too high) when compared with documented U removal.

The discrepancy in the behavior of Ba in the system might be partially explained by its low- salinity particle reactivity (figure 3.13; Coffey et al., 1997; Stecher and Kogut, 1999, Nozaki et al., 2001). Since groundwater discharge in the system should occur preferentially at low tide, the character of the water receiving the discharge will determine whether or not the Ba signal is observed in filtered samples. Since the tidal creek at low tide was nearly fresh except during the first August 2002 sampling period, Ba discharged to the tidal creek in the headwaters (or any region where low tide water has salinity < ~ 8 psu) was likely sequestered by particulate matter, obscuring the groundwater discharge signal. The August 8, 2002 samples had salinity > 8 psu at low tide and showed dramatically elevated Ba concentrations. In this case, the groundwater discharged to the tidal creek at low tide entered higher salinity water, meaning that Ba addition was less masked by adsorption. Thus, both U and Ba surface water profiles supported groundwater discharge for this month.

Unfiltered sampled collected during the June 2003 field trip also showed excess Ba in the 5 – 10 psu range. These results were not observed in parallel filtered samples and are likely a product of groundwater discharge followed by immediate sequestration by particles. This signal would not have been observed had we not collected unfiltered samples for total Ba analysis. This finding emphasizes the importance of analyzing more than one empirical size fraction when investigating the behavior of particle-reactive metals in estuaries. Had we collected total Ba (i.e., unfiltered) samples during each of our outing, rather than just our last, correlations between U-depletion and Ba addition may have been more evident and stronger support for the importance of groundwater discharge may have been obtained.

CHAPTER 5

CONCLUSIONS

This study of salt marsh U biogeochemistry incorporated 8 months of surface- and groundwater sampling in a South Carolina USA tidal creek. We generated local U removal estimates and examined the efficacy of U as a tracer of groundwater discharge in coastal environments. U, a redox sensitive, low concentration constituent of all fresh and marine waters, has historically been considered a conservative element with regard to its estuarine transport. However, in agreement with recently observed removal of U from similar salt marsh tidal creeks (Church et al. 1994; Church et al., 1996; Windom et al., 2000), this thesis documents seasonally-variable removal of U from the Okatee/Colleton River system.

In general, removal (as a percentage) documented in this study was greatest at low salinities (< ~ 7 psu) and decreased as creek-sample salinities converged with saline endmember. Larger removal occurred during the spring, summer, and early fall (March – October), and lower removal occurred during the winter (November – January). Extensive, seasonally variable removal documented for Colleton River endmember samples suggested U removal occurring in other portions of the estuary or along the continental shelf. Consistently high U-removal and Ba addition in shallow marsh groundwater and U-depleted/Ba-enriched water seeping from creek banks at low tide showed that groundwater discharge was certainly contributing to the removal signal observed in surface water.

By sampling surface water, groundwater and bank seepage, we gained insight into the importance of surface water circulation though salt marshes for U removal. Because tidally driven surface-/groundwater circulation results in the discharge of salt-marsh-processed, uranium-depleted groundwater to the creek, we proposed that the uranium removal observed in surface waters could be quantified to estimate the magnitude of groundwater discharge occurring in the system. A similar approach employing Ra isotopes and pioneered by W. Moore (Moore, 1996; More, 1999) has been widely accepted. The graphical relationship between groundwater, surface water, and marsh-seepage U concentrations and salinity illustrated that average site groundwater was a suitable endmember for describing surface water uranium depletion. Therefore, we used three endmember mixing models to quantify the groundwater input required to simulate observed surface water U removal trends. To our knowledge, we are the fist employ this approach using U.

We calculated the rate of U-removal from the Okatee/Colleton river system using three independent methods that considered a more comprehensive surface water dataset than previous investigations. By using a variable lower salinity saline-endmember to constrain mixing in our system, we isolated the removal occurring in the Okatee/Colleton River from the removal occurring in other portions of the estuary and/or along the continental shelf.

Yearly U removal computed using the Mass Balance (58 μmol m^{-3} $year^{-1}$) and Extrapolated Saline Endmember (104 μmol m^{-3} $year^{-1}$) Approaches, which were both based on direct quantification of percent surface water U removal, compared well with published estimates of 16 to 70 μmol m^{-3} $year^{-1}$ (Church et al., 1996; Windom et al., 2000; and Dunk et al., 2002). The somewhat larger removal estimated in this study probably resulted from temperature and tidal-range differences between field sites and possibly from variations in marsh biogeochemical cycling, bioturbation, freshwater composition (i.e., DOM and metal-oxide content), and hydrologic properties of marsh sediments. Removal computed using our Extrapolated Freshwater Endmember Approach (0.37 µmol m^{-3} $year^{-1}$) was two orders of magnitude lower than the other estimates. This lower result was probably related to the approach's dependence on the magnitude of fresh water discharge entering the system, a quantity that apparently did not adequately describe removal.

Incorporating our more conservative 58 µmol m^{-3} $year^{-1}$ value with previously generated removals, we determined an extrapolated global U removal that was twice as large as the value derived by Dunk et al. (2002). Considering all the sources and sinks for U described by Dunk, our approximation, if correct, supports an imbalance in the global U budget in favor of removal or suggests a missing or underestimated U source. An imbalanced oceanic U budget is plausible since, during interglacial periods, oceanic U concentrations may decrease due to increased temperature and intertidal area, both of which favor removal. Overall, this study reemphasized the importance of anoxic coastal environments for U removal and suggested a larger impact than previously documented in the literature. U-removal estimates generated during this investigation will aid future attempts to constrain the global U budget and to employ oceanic sediment records to understand ancient ocean chemistry. However, our current removal calculations should be applied cautiously until more accurate system water and tidal prism volumes, necessary and important variable in our removal calculations, are determined.

Our groundwater discharge estimates of 8 to 37 L m^{-2} day^{-1} agreed closely with previously published salt marsh values of 7.8 to 40 L m^{-2} day^{-1} calculated using a variety of methods for the North Inlet, SC salt marsh (Krest and Moore, 2000; Whiting and Childers, 1989; Morris, 1999). In addition, our calculations suggested broad seasonality in groundwater discharge, with higher values in the spring/summer (25 – 37 L m^{-2} day^{-1}) and lower values in the late fall and winter (8 – 15 L m^{-2} day^{-1}). Other studies have documented similar seasonality in salt marsh groundwater tracers and discharge rates (Krest and Moore, 2000; Cable et al., 1997). The causes of seasonality in groundwater discharge, particularly for the seasonality predicted by tracer elements like Ra, are not clear. However, salt marsh groundwater discharge is probably most dependent on seasonal changes in tidal forcing, marsh biogeochemistry, precipitation and macrofauna activity (Cable et al., 1997; Tobias et al., 2001; Jahnke et al., 2003).

As in previous investigations (Whiting and Childers, 1989; Jahnke et al., 2003), groundwater discharge at our site was supported by spatially variable permeable sediment layers observed intersecting the tidal creek at low tide and in continuous sediment cores. Based on interpretation of sediment cores and aerial photos, past meandering of the tidal creek probably controls shallow marsh statigraphy and groundwater discharge pattern. Former creek bottom sediments likely provide permeable conduits for the advective transport of reduced marsh constituent to surface waters.

Several authors have suggested Ba as another tracer of groundwater discharge to coastal waters (Shaw et al., 1998; Swarzenski et al., 2001; and Moore, 1999). Therefore, elevated Ba concentrations should have accompanied the depleted uranium signal in groundwater discharge at our study site. Our surface water and seepage data, indeed, provided some evidence of Ba addition. However, unlike uranium, our Ba profiles failed to show clear seasonality in addition and were lower than expected based on U removal observed. Low surface water Ba concentrations can be understood, in part, by considering low-salinity interactions with particles.

The groundwater discharge signature for U in surface water is removal rather than addition. This is opposite of what is typically expected from tracer elements (e.g. Ra, Rd, CH_4, Ba, etc.) and is probably why U hasn't been employed previously in this manner. In addition, until recently, U has been a difficult and time consuming element to analyze for. However, with the advent of the rapid and accurate ID-ICPMS determination, and the growing number of regionally-dedicated ICP-MS machines, U can now be determined quickly and accurately. Therefore, U may prove to be a valuable tool in future studies of coastal systems. For now, groundwater discharge rates determined by this study will be applied by others working in the Okatee/Colleton river system to quantify the input of groundwater derived chemicals and nutrients to coastal waters, a topic of significant interest given the degree of land use change and anthropogenic impact occurring in coastal environments.

The value of the work presented in this thesis could be enhanced by some additional work. For example, before removal estimated determined by this study are accepted they should be recalculated using more accurate system water volume and tidal prism volumes. These volumes were not available at the time of publication, but may be attainable through queries of advanced surface water flow models currently being generated for the site. The analysis of additional higher salinity samples would have allowed us to determine if the small high-salinity addition observed in August 2002 samples is common or an artifact of our endmember choice. Therefore, future investigations should probably measuring higher salinity samples to constrain the behavior of U in the lower estuary and to determine appropriate system endmembers (i.e., endmember not based primarily on convenience of sampling location). The acquisition of surface water profiles for the Broad river, the main tributary feeding the Port Royal Sound, would have helped to determine whether the behavior observed in the smaller Okatee watershed was representative of the system in general. It is possible that local differences in lithology and marsh area could affect the processing of U in proximal watersheds. Finally, additional U removal estimates must be determined for marshes spanning different climates and geologies to generate more accurate global U-removal values.

The use of U as a tracer of groundwater discharge must still be validated. Most importantly, further research is required to determine whether seasonal fluctuations predicted by tracer elements and observed in this study (and in several studies by Moore and coworkers) represent true changes in groundwater discharge or factors altering tracer chemistry. Discharge estimates should be compared with estimates determined using physical hydrologic techniques and with estimates (in progress) by W. Moore using Ra profiles obtained for the same system. Validation of surface water removal trends and discharge calculations might also be possible using the flow model generated for the study region if U surface water profiles can be adequately simulated by assuming a specific rate of groundwater discharge into the tidal creek system. Since dissolved Ba was an inconsistent tracer of groundwater discharge in our system, any future attempts to correlate Ba concentrations in lower-salinity estuarine surface waters with discharge should include analysis of more than one empirical size fraction.

APPENDIX

Well ID	WELL INNER DIAMETER [cm]	Well Volume bgs [liters]	PLUMB DEPTH bgs [feet]	TOP SCREEN DEPTH bts [meters]	LENGTH OF SCREEN [meters]	BOTTOM OF SCREEN INTVL [meters]
Okatee South Transect						
MW01S	5.08	4.92	8.22	1.86	0.61	2.47
MW01N	5.08	5.37	8.97	2.09	0.61	2.70
MW02	5.08	3.50	5.86	1.14	0.61	1.75
MW03	5.08	3.55	5.94	1.16	0.61	1.77
MW04	5.08	3.19	5.33	0.98	0.61	1.59
MW05	5.08	4.63	7.74	1.71	0.61	2.32
Okatee North Transect						
MW06	5.08	4.01	6.69	1.39	0.61	2.00
MW07	5.08	6.51	10.88	2.67	0.61	3.28
MW08	5.08	3.23	5.40	1.00	0.61	1.61
MW09	5.08	3.88	6.48	1.33	0.61	1.94
MW10	5.08	4.58	7.66	1.69	0.61	2.30

Table A.1 Additional monitoring well parameters.

August 8 & 9, 2002 (Spring Tide)

Sample	Date	Time	Salinity (psu)	Uranium [ ] ppb	Barium [ ] ppb
FW	8-Aug	1630	4.1	0.06	62
WMC	8-Aug	845	36	2.78	16
BD/MRO1	8-Aug	1530	30	0.33	126
BD/MRO2	8-Aug	1550	39	0.85	87
BD/MRO3	9-Aug	1400	44	3.71	47
BD/MRO4	9-Aug	1530	38	0.63	85
MW01S	8-Aug	2000	39	0.05	89
MW01N	8-Aug	2030	39	1.98	65
MW02	8-Aug	1930	50	0.10	82
MW03	9-Aug	1545	35	1.11	47
MW04	9-Aug	2012	35	0.04	94
MW05	9-Aug	2005			
MW06	9-Aug	1900	38	**2.76**	99
MW07	9-Aug	1840	28	0.05	62
MW08	9-Aug	1734	35.5	1.05	47
MW09					
MW10	9-Aug		29	0.05	199
creek 1	8-Aug	1010	37.5	3.15	21
creek 2	8-Aug	1130	36	3.44	24
creek 3	8-Aug	1310	35	3.01	38
creek 4	8-Aug	1440	9.8	0.16	86
creek 5	8-Aug	1615	8	0.12	78
creek 6	8-Aug	1730	10.1	0.17	68
creek 7	8-Aug	1900	35	3.43	36
creek 8	8-Aug	2040	36.5	3.30	22

Table A.2 Data for samples collected on August 8 and 9, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

August 29, 30, & 31, 2002 (Neap Tide, Rain Event)

Sample	Date	Time	Temp (C)	Salinity (psu)	Uranium [ ] ppb	Barium [ ] ppb
FW	30-Aug	1020	24.4	0	0.10	13
WMC	29-Aug	1550	28.9	34.4	2.78	19
BD/MRO1	30-Aug	1155	23.9	1.1	0.40	7
BD/MRO2	30-Aug	1220	24.5	4.3	0.41	
BD/MRO3	30-Aug	1910	25.8	7.9	0.60	17
BD/MRO4						
MW01S	30-Aug	1400	26.1	38.4	0.05	90
MW01N	30-Aug	1540	26.1	36.6	0.69	76
MW02	30-Aug		26.9	49.3	0.10	83
MW03	30-Aug	1645	27.9	34.9	0.83	62
MW04	31-Aug	1245	26.4	34.5	0.07	99
MW05	31-Aug	1305	24.6	27.9	0.22	123
MW06	31-Aug	1415	27.3	37	**1.32**	117
MW07	1-Sep	1131	24	27	0.07	62
MW08	1-Sep	1205	28.8	32.7	0.20	74
MW09	1-Sep	1300	26.5	29	0.11	58
MW10	30-Aug	1807	24.8	28.4	0.08	381
creek 1	30-Aug	910	23.7	0.3	0.14	9
creek 2	30-Aug	1045	23.6	0.1	0.13	11
creek 3	30-Aug	1130	23.8	0.1	0.13	12
creek 4	30-Aug	1245	24.2	0	0.12	14
creek 5	30-Aug	1415	24.7	0	0.14	13
creek 6	30-Aug	1600	25	0.5	0.15	15
creek 7	30-Aug	1710	25.3	0	0.09	14
creek 8	30-Aug	1830	25	0	0.13	14

Table A.3 Data for samples collected on August 29, 30, 31, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

October 6, 2002						
Sample	Date	Time	Temp (cst)	Salinity (psu)	Uranium [ ] ppb	Barium [ ] ppb
FW	12-Oct	1330		0	0.09	30
WMC	8-Oct	745	28.4	30.4	2.54	17
BD/MRO1	7-Oct	1645	1645	24.4	0.95	111
BD/MRO2						
BD/MRO3						
BD/MRO4						
MW01S		1430	28.1	37.2	0.06	84
MW01N		1700		31.7	0.28	72
MW02	7-Oct	1318	30.9	51.9	0.12	84
MW03		1730	27.2	35.1	0.46	75
MW04	7-Oct	840	26.1	33.2	0.05	97
MW05	7-Oct		24.6	26.6	0.22	120
MW06	6-Oct	1910	25.9	35.2	**2.04**	90
MW07	6-Oct	1815	24.9	25.8	0.07	63
MW08	6-Oct	1720	27.7	25.5	0.20	53
MW09	6-Oct	1615	28.2	28.2	0.08	62
MW10	7-Oct	1840	24.7	26.9	0.17	172
creek 1	7-Oct	945	28.4	22	1.77	21
creek 2	7-Oct	1100	29	23.5	1.92	19
creek 3	7-Oct	1150	29.2	23.7	1.87	19
creek 4	7-Oct	1250	29.8	22.8	2.07	20
creek 5	7-Oct	1410	30.2	19.5	1.67	26
creek 6	7-Oct	1430	29.9	16.6	1.32	30
creek 7	7-Oct	1500	29	11	0.77	33
creek 8	7-Oct	1513	28.4	7	0.50	33
creek 9	7-Oct	1528	27.7	3.5	0.38	28
creek 10	7-Oct	1608	26.8	0.7	0.18	21

Table A.4 Data for samples collected on October 6, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

November 25, 26, 2002 (past spring Tide)						
Sample	Date	Time	Temp (cst)	Salinity (psu)	Cond (mS)	Barium [ ] ppb
FW	25-Nov	1435	13.8	0	0.315	35
WMC	25-Nov	1615	16.4	28.3	44.3	16
BD/MRO1						
BD/MRO2						
BD/MRO3						
BD/MRO4						
MW01S	26-Nov	1100	20.1	36.8	55.7	76
MW01N	26-Nov	1224	20.8	26.3	41.2	50
MW02	26-Nov	DNM	20.3	46.6	67	48
MW03	26-Nov	1400	21.7	37	55.5	67
MW04	25-Nov	1350	21.3	33.3	50.9	85
MW05	25-Nov	1315	22.7	27	42.1	117
MW06	25-Nov	1230	20.8	35.7	54.2	99
MW07	25-Nov	1115	22.2	26	40.8	63
MW08	25-Nov	1030	21.3	27	42.2	51
MW09	25-Nov	900	20.8	28.1	43.7	60
MW10	26-Nov	850	21.7	27.1	42.3	184
creek 1	26-Nov	815	11.1	0.1	0.752	27
creek 2	26-Nov	1005	11.5	0.9	2.09	26
creek 3	26-Nov	1028	11.6	2	3.92	26
creek 4	26-Nov	1043	11.7	3	5.65	25
creek 5	26-Nov	1103	12.1	4.5	8.24	24
creek 6	26-Nov	1133	13.4	6.2	11.05	23
creek 7	26-Nov	1155	13.7	7.9	13.81	23
creek 8	26-Nov	1220	13.9	10.3	17.55	22
creek 9	26-Nov	1250	14.7	12.4	20.8	22
creek 10	26-Nov	1345	15.6	14.4	24	20

Table A.5 Data for samples collected on November 25 and 26, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

January 5, 2003 (Past Spring tide by 2 days)

Sample	Date	Time	Temp (cst)	Salinity (psu)	Cond (mS)	Temp (pH)	pH	Uranium [ ] ppb	Barium [ ] ppb
FW								DNM	
WMC	6-Jan	830	10.4	29.2	46.2	10.5	7.9	2.55	12
BD/MRO1								DNM	
BD/MRO2								DNM	
BD/MRO3								DNM	
BD/MRO4								DNM	
MW01S	5-Jan	900	13.2	37	56.6	13.4	6.1	0.03	64
MW01N	5-Jan	940	12.2	27.4	43.4	12.4	6.5	0.40	42
MW02	5-Jan	1100	14.6	52.8	76.6	14.6	6.0	0.20	62
MW03	5-Jan	1015	12.4	38.2	58.2	12.8	7.1	0.40	63
MW04	5-Jan	1620	15.3	33.5	51.6	15.5	6.4	0.03	84
MW05	5-Jan	1630	18.3	27.7	43.3	18.2	6.7	0.09	110
MW06	6-Jan	1130	16.1	35.7	54.5	16.3	6.8	1.71	91
MW07	6-Jan	1045	17.2	26.4	41.4	-	6.7	0.77	55
MW08	6-Jan	1000	17.5	29.5	45.9	17.7	6.7	0.14	53
MW09	6-Jan	915	16.6	28.9	45	16.7	6.6	0.05	62
MW10	5-Jan	1330	18.1	27.2	42.6	18.4	6.8	0.07	161
creek 1	5-Jan	856	5.6	17.1	29.2		7.5	1.48	18
creek 2	5-Jan	DNM	8.7	21.7	35.6		7.6	2.00	17
creek 3	5-Jan	1145	9.4	22.2	36.4		7.7	1.97	17
creek 4	5-Jan	1420	11	13.5	22.8		7.3	1.17	22
creek 5	5-Jan	1430	9.6	10.5	18.17		7.2	0.89	23
creek 6	5-Jan	1445	9	7.9	14.05		7.1	0.67	24
creek 7	5-Jan	1456	9.2	5.3	9.64		7.0	0.46	23
creek 8	5-Jan	1505	8.5	3.43	6.38		7.0	0.32	22
creek 9	5-Jan	1513	8.3	2.2	4.38		6.9	0.23	21
creek 10	5-Jan	1523	8.2	1.2	2.72		6.8	0.17	20
Creek 11	5-Jan	1535	8.1	0.5	1.401		6.7	0.12	19

Table A.6 Data for samples collected on January 5, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

March 4 & 5, 2003

Sample	Date	Time	Temp (cst)	Salinity (psu)	Cond (mS)	Temp (pH)	pH	Uranium [ ] ppb	Total Fe (uM)	PO_4^{3-} (uM)	Barium [ ] ppb
FW	5-Mar	1100	14.9	0	0.121	15.9	6.5	0.11			33
WMC	5-Mar	1200	14.8	28.8	45.4	15.3	7.7	2.38			12
BD/MRO1											
BD/MRO2											
BD/MRO3											
BD/MRO4											
MW01S	4-Mar	1200	15	36	55.3		6.1	0.12	127.21	2.7	59
MW01N	4-Mar	1230	15	24.4	39	15.1	6.4	0.17	0.20	0.1	38
MW02	4-Mar	1030	14.4	50.5	74.3	14.5	6.0	0.10	18.40	0.7	60
MW03	4-Mar	1400	13.9	39	59.5	14.2	6.7	0.41	2.14	0.1	66
MW04	5-Mar	946	15.3	31.4	48.9	16.6	6.4	0.09	0.33	23.7	81
MW05	5-Mar	1025	17.2	27.3	43.1	19.6	6.6	0.12	0.29	74.2	105
MW06	5-Mar	1400	17	34.5	53.1	18.1	6.7	2.72	84.08	10.7	85
MW07	5-Mar	1430	18.9	26	41.1	21	6.6	0.44	0.24	34.1	52
MW08	5-Mar	1500	20.5	29.9	46.3	20.6	6.6	0.12	0.24	35.0	56
MW09	5-Mar	1600	19.1	28.3	44.3	19.4	6.7	0.07	0.29	52.2	63
MW10	5-Mar	1300	18.5	26.4	41.6	25.5	5.6	0.09	0.24	69.0	144
creek 1	4-Mar	1137	14	13.3	22.4	14.6	7.1	0.93			18
creek 2	4-Mar	1230	13.7	5.4	9.79	13.9	6.9	0.37			21
creek 3	4-Mar	1245	13.8	3.7	6.89	14	6.8	0.29			20
creek 4	4-Mar	1255	13.6	2.4	4.66	13.7	6.8	0.22			20

Table A.7 Data for samples collected on March 4 and 5, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

April 16 and 17, 2003

Sample	Date	Time	Temp (cst)	Salinity (psu)	Cond (mS)	Temp (pH)	pH	Uranium [ ] ppb	Total Fe (uM)	PO_4^{3-} (uM)	Barium [ ] ppb
FW											
WMC	16-Apr	930	19.1	26.3	41.5	19.1	8.0	2.059			13
BD/MRO1	17-Apr	1300	26	15.7	25.6	26.3	7.4	1.30			23
BD/MRO2											
BD/MRO3											
BD/MRO4											
MW01S	16-Apr	1555	20	34.9	53.3	20.1	6.1	0.037	103.55	2.9	64
MW01N	16-Apr	1630	21.6	22.4	35.7	21.8	6.54	0.807	0.23	0.1	55
MW02	16-Apr	1445	22.3	46.8	68.6	21.8	6.1	0.140	42.62	1.1	65
MW03	Not Sampled										
MW04	17-Apr	1755	19.2	32.2	49.7	19.3	6.3	0.035	0.28	20.9	87
MW05	17-Apr	1830	18.7	27.8	43.6	18.8	6.6	0.100	0.32	68.0	117
MW06	17-Apr	1250	22.5	35	53.3	22.6	6.7	2.966	167.68	45.4	85
MW07	17-Apr	1415	22	26.4	41.5	22.1	6.6	0.268	0.59	32.0	60
MW08	17-Apr	1500	23.2	28	43.5	23.3	6.5	0.159	0.37	31.1	62
MW09	17-Apr	1630	22.4	28.8	44.8	22.5	6.7	0.054	0.59	52.5	65
MW10	16-Apr	1800	21.4	26.6	41.7	21.3	6.8	0.075	0.28	72.1	165
creek 1	16-Apr	1040	21.6	15.5	25.5	21.8	7.5	1.126			19
creek 2	16-Apr	1150	21.3	13.5	22.5	21.1	7.2	0.965			23
creek 3	16-Apr	1215	21.4	12	20.1	21.4	7.1	0.840			24
creek 4	16-Apr	1230	21.4	10.4	17.66	21.2	7.1	0.726			28
creek 5	16-Apr	1244		8.9				0.578			29
creek 6	16-Apr	1255	20.8	6.6	11.6	20.9	6.9	0.474			28
creek 7	16-Apr	1307	20.4	5	8.91	20.3	6.8	0.340			34
creek 8	16-Apr	1315	20.1	3.6	6.6	20.4	6.7	0.264			29
creek 9	16-Apr	1328	19.8	2.2		20	6.6	0.204			26
creek 10	16-Apr	1338	19.6	1.4	2.87	19.9	6.6	0.148			26
Creek 11	16-Apr	1400	19.4	0.2	0.951	19.5	6.4	0.106			27

Table A.8 Data for samples collected on April 16 and 17, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples.

June 2 and 3, 2003

Sample	Date	Time	Temp (cst)	Salinity (psu)	Cond (mS)	Uranium [ ] ppb	U UF [ ] ppb	Total Fe (uM)	PO_4^{3-} (uM)	Barium [ ] ppb	Ba UF [ ] ppb
FW	4-Jun	1000	23.2	0	0.106	0.07	0.086			34	36
WMC	4-Jun	900	24.8	25.2	39.6	1.86	2.02			13	13
BD/MRO1	3-Jun		27.6	14.3	23.4	0.86	0.95	39.06	1.43	21	23
BD/MRO2											
BD/MRO3											
BD/MRO4											
MW01S	3-Jun	1615	23.6	34.9	53.1	0.03		149.86	6.2	69	
MW01N	3-Jun	1315	26	21.3	33.9	0.43		0.19	0.3	37	
MW02	3-Jun	1635	24.9	41.1	61.2	0.14		40.84	1.1	62	
MW03	NS										
MW04	3-Jun	1030	23.3	32.4	49.6	0.05		0.41	22.7	94	
MW05	3-Jun	1045	23.8	27.9	43.4	0.12		0.37	74.3	109	
MW06	2-Jun	2000	22.7	34.9	53.1	2.76		159.66	43.3	88	
MW07	2-Jun	1930	20.7	26.5	41.6	0.25		0.32	34.9	57	
MW08	2-Jun	1856	23.6	29.1	45.1	0.33		0.37	33.8	54	
MW09	2-Jun	1815	23.1	28.8	44.7	0.04		0.32	52.8	63	
MW10	10-Jun		22.1	26.9	42.2	0.16		0.55	79.4	172	
creek 1	3-Jun	1300	27.1	16.5	26.8	1.17	1.254			22	22
creek 2	3-Jun	1310	27	14.9	24.4	1.02	1.109			22	22
creek 3	3-Jun	1351	26.5	13.6	22.5	0.89	0.947			23	24
creek 4	3-Jun	1415	26	11.1	18.58	0.73	0.723			25	25
creek 5	3-Jun	1425	25.8	9.5	16.03	0.57	0.648			30	30
creek 6	3-Jun	1440	25.3	6.8	11.88	0.42	0.467			29	29
creek 7	3-Jun	1450	25.2	4.9	8.78	0.34	0.386			24	38
creek 8	3-Jun	1501	24.9	3	5.65	0.23	0.282			23	34
creek 9	3-Jun	1520	24.3	0.9	2.02	0.12	0.188			20	30
creek 10	3-Jun	1540	24.6	0.2	0.915	0.11	0.182			20	31

Table A.9 Data for samples collected on June 2 and 3, 2002. FW=Fresh water samples; WMC=Surface water samples collected at the Waddell Mariculture Center; BD/MRO=Bank Discharge/Marsh Runoff Samples; creek=Okatee tidal creek samples; UF=unfiltered.

LIST OF REFERENCES

Abdelouas, A., Lutze, W., Gong, W., Nuttall, W.H., Strietelmeier, B.A., Travis, B.J. (2000) Biological reduction of uranium in groundwater and subsurface soil. *Sci. Total Environ.*, **250,** 21-35.

Andersson, P.S., Porcelli, D., Gustafsson, O., Ingri, J., Wasserburg, G.J. (2001) The Importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. *Geochim. Cosmochim. Acta*, **65**, 13-25.

Barnes C.E. and Cochran J.K. (1993) Uranium geochemistry in estuarine sediments-controls on removal and release processes. *Geochim. Cosmochim. Acta,* 55, 555-569.

Bollinger, M.S., Moore, W.S. (1993) Evaluation of salt marsh hydrology using radium as a tracer. *Geochim. Cosmochim. Acta*, **57**, 2203-2212.

Blanton, J., Skidaway Institute of Oceanography (2003) Approximate residence time of Okatee River system determined using hydrographic methods and usage of hypsometric relationships for determining system volumes. *Personal communication.*

Cable, J.E., Burnett, W.C., Chanton, J.P. (1997) Magnitude of variations of groundwater seepage along a Florida marine shoreline. *Biogeochemistry*, **38**, 189-205.

Carroll, J.L., Moore, W.S. (1993) Uranium removal during low discharge in the Ganga-Brahmaputra mixing zone. *Geochimica et Cosmochimica Acta*, **57**, 4987-4995.

Chaillou G., Anschutz P., Lavaux G., Schafer J., Blanc G. (2002) The distribution of Mo, U, and Cd in relation to major redox species in muddy sediments of the Bay of Biscay. *Marine Chemistr*y, **80**, 41-59.

Chen, J.H., Edwards, R.L, Wasserburg, G.L., (1986) ^{238}U, ^{234}U and ^{232}Th in seawater. *Earth Planet. Sci. Lett.*, **80**, 241-251.

Church, T.M., Sarin, M.M., Fleisher, M.Q., Ferdelman, T.G. (1996) Salt marshes: An important coastal sink for dissolved uranium. *Geochim. Cosmochim. Acta,* **60**, 3879-3887.

Clewell, A.F. (1997) Vegetation. In: *Ecology and management of tidal marshes*. Edited by Coultas, C.L. and Hsieh, Y. Delray Beach, FL, St. Lucie Press.

Coffey, M., Dehairs, F., Collette, O., Luther, G., Church, T., Jickells, T. (1997) The behavior of dissolved barium in estuaries. *Estuarine Coastal and Shelf Science,* **45**, 113-121.

Connors, K. (1990) *Chemical Kinetics: The study of reaction rates in solution*, John Wiley & Sons.

Drewes, P., USGS Water Resources, South Carolina District. (2003) Methods for determining freshwater discharge component of tidally influenced tidal creek discharge data. *Personal Communication.*

Dunk, R.M., Mills, R.A., Jenkins, W.J. (2002) A reevaluation of the oceanic uranium budget for the Holocene. *Chemical Geolog,y* **190**, 45-67.

Fredrickson JK, Zachara JM, Kennedy DW, Duff MC, Gorby YA, Li SMW, Krupka KM. (2000) Reduction of U(VI) in goethite (alpha-FeOOH) suspensions by a dissimilatory metal-reducing bacterium. *Geochim. Cosmochim. Acta,* **64** 3085-3098.

Grasshoff, K., (Editor) Kremling, K. (Editor), and Ehrhardt, M. (Editor) (1999) *Methods of Seawater Analysis (3rd ed.)*, VCH Publishing.

Howarth, R.W., Teal, J.M. (1979) Sulfate reduction in a New England salt marsh. *Limnol. Oceanogr,.* **24**, 999-1013.

Hughes, C.E., Binning, P., Willgoose, G.R. (1998) Characterization of the hydrology of an estuarine wetland. *Journal of Hydrology*, **211**, 34-49.

Jahnke, R.A., Alexander, C.R., Kostka, J.E. (2003) Advective pore water input of nutrients to the Satilla River Estuary, Georgia, USA. *Estuarine Coastal and Shelf Science,* **56**, 641-653.

Klinkhammer, G.P. and Chan, L.H. (1990) Determination of barium in marine waters by isotope dilution inductively coupled plasma mass spectrometry. *Analytica Chemica Acta*, **232**, 323-329.

Klinkhammer, G.P. and Palmer, M.R. (1991) Uranium in the ocean: Where it goes and why. *Geochim. Cosmochim. Acta*, **55**, 1799-1806.

Krest, J.M., Moore, W.S., Gardner, L.R., and Morris, J.T. (2000) Marsh nutrient export supplied by groundwater discharge: Evidence from radium measurements. *Global Biogeochemistry,* **14**, 167-176.

Ku, T.L., Knauss, K.G., Mathieu, G.G. (1977) Uranium in the open ocean: Concentration and isotopic composition. *Deep Sea Res.,* **24**, 1005-1017.

Langmuir, D. (1997). *Aqueous Environmental Geochemistry.* Upper Saddle River, New Jersey, Prentice Hall.

Liger E, Charlet L, Van Cappellen P. (1999) Surface catalysis of uranium(VI) reduction by iron(II). *Geochim. Cosmochim. Acta,* **63,** 2939-2955.

Lovely D.L., Phillips E.J.P., Gorby Y.A. and Landa E.R. (1991) Microbial Reduction of Uranium. *Nature,* **350**, 413-416.

Lovely D.L., Phillips, E.J.P (1992) Reduction of uranium by *Desulfovibrio desulfuricans*. *Applied and Environ. Microbiol*., **58**, 850-856.

Lovely D.L., Widman, P.K., Woodward, J.C., Phillips, E.J.P. (1993) Reduction of uranium by cytochrome C3 of *Desulfovibrio vulgaris*. *Applied and Environ. Microbiol*., **59**, 3572-3576.

Maeda, M. and Windom, H.L. (1982) Behavior of Uranium in two estuaries of the South Eastern United States. *Marine Chemistry,* **11**, 427-436.

Malcolm, S.J., Sivyer, D.B. (1997) Nutrient Recycling in intertidal sediments. In. Biogeochemistry of Intertidal Sediments. T.J. Jickells and J.E. Rae. Cambridge University Press, Cambridge, UK 1997. (84-98)

Mangini A., Jung M., Laukenmann S. (2001) What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geology,* **177,** 63-78.

Moore, W.S. (1996) Large groundwater inputs to coastal water revealed by ^{226}Ra enrichment. *Nature*, **380**, 612-614.

Moore, W.S. (1999) The subterranean estuary: a reaction zone of groundwater and sea water. *Marine Chemistry*, **65**, 111-125.

Moore, W.S., University of South Carolina (2003) Approximate residence time of Okatee River system determined using Ra isotopes. *Personal communication*.

Nameroff T.J., Balistrieri L.S., Murray J.W. (2002) Suboxic trace metal geochemistry in the eastern tropical North Pacific. *Geochim. Cosmochim. Acta,* **66,** 1139-1158.

Nozaki, Y., Yamamoto, Y., Manaka, T., Amakawa, H., Snidvongs, A. (2001) Dissolved barium and radium isotopes in the Chao Phraya River estuarine mixing zone in Thailand. *Continental Shelf Research*, **21**, 1435-1448.

Pailler D., Bard E., Rostek F., Zheng Y., Mortlock R., van Geen A. (2002) Burial of redox-sensitive metals and organic matter in the equatorial Indian Ocean linked to precession. *Geochim. Cosmochim. Acta,* **66**, 849-865.

Palmer, M.R., Edmond, J.M. (1993) Uranium in river water. *Geochim. Cosmochim. Acta,* **57**, 4947-4955.

Portnoy, J.W., Nowicki, B.L., Roman, C.T., Urish, D.W. (1998) The discharge of nitrate contaminated groundwater from developed shorelines to marsh-fringed estuaries. *Water Resources Research,* **34**, 3095-3104.

Rama, Moore, W.S. (1996) Using the radium quartet for evaluating groundwater input and water exchange in salt marshes. *Geochimica et Cosmochimica Acta*, **60**, 4645-4652.

Sarin M.M. and Church T.M. (1994) Behavior of uranium during mixing in the Delaware and Chesapeake Estuaries. *Estuarine Coastal and Shelf Science,* **39**, 619-631.

Schultz, G., Ruppel C. (2002) Constraints on hydraulic parameters and implications for groundwater flux across the upland-estuary interface. *Journal of Hydrology*, **260**, 255-269.

Shaw T.J., Sholkovitz E.R., Klinkhammer G. (1994) Redox Dynamics in the Chesapeake Bay – The effects on sediment-water uranium exchange. *Geochim. Cosmochim. Acta,* **58**, 2985-2995.

Shaw, T.J., Moore, W.S., Kloepfer, J., Sochaski, M.A. (1998) The flux of barium to the coastal waters of the southeastern USA: The importance of submarine groundwater discharge. *Geochimica et Cosmochimica Acta*, **62**, 3047-3054.

Spaulding, R.F. (1997) The global distribution and status of mangrove ecosystems. *Intercoast Netw. Spec. Ed,.* **1**, 20-21.

Stecher, H.A., Kogut, M.B. (1999) Rapid barium removal in the Delaware estuary. *Geochimica et Cosmochimica Acta*, **63**, 1003-1012.

Stookey, L.L. (1970) Ferrozine-A new spectrophotometer reagent for iron. *Anal. Chem.*, **42**, 779-781.

Summerton A.P. (1992) Natural Radionuclides in tidal salt-marsh soils in South Australia - An unusual distribution. *Journal of Radioanalytical and Nuclear Chemistry-Articles,* **161**, 475-482.

Swarzenski, P.W., McKee, B.A., Booth, J.G. (1995) Uranium geochemistry on the Amazon shelf-chemical phase partitioning and cycling across a salinity gradient. *Geochim. Cosmochim. Acta,* **59,** 7-18.

Swarzenski, P.W. McKee, B.A., Skei, J.M., and Todd, J.F. (1999) Uranium biogeochemistry across the redox transition zone of a permanently stratified fjord: Framvaren, Norway. *Marine Chemistry* **67**, 181-198.

Swarzenski, P.W., Reich, C.D., Spechler, R.M., Kindinger, J.L., Moore, W.S. (2001) Using multiple geochemical tracers to characterize the hydrogeology of the submarine spring off Crescent Beach, Florida. *Chemical Geology*, **179**, 187-202.

Tobias, C.R., Harvey, J.W., Anderson, I.C. (2001) Quantifying groundwater discharge through fringing wetlands to estuaries: Seasonal variability, methods comparison, and implications for wetland-estuary exchange. *Limnol. Oceanogr.*, **46**, 604-615.

Toole , J., Baxter, M.S., Thomson, J. (1987) The behavior of uranium isotopes with salinity change in 3 UK estuaries. *Estuarine Coastal and Shelf Science,* **25**, 283-297.

U.S. Geological Survey, Recent daily data for USGS 02176575 OKATEE RIVER NEAR BLUFFTON, SC. Minimum and Maximum daily gage reading for 2002. Accessed August 2003. http://waterdata.usgs.gov/sc/nwis/dv/?site_no=02176575&agency_cd=USGS

Walker, S.P., University of South Carolina (2003) Estuarine Wetland Area for Okatee River above Colleton River. *Personal Communication.*

Wersin P., Hochella M.F., Persson P., Redden G., Leckie J.O., and Harris D.W. (1994) Interaction between aqueous uranium (VI) and sulfide minerals: Spectroscopic evidence for sorption and reduction. *Geochim. Cosmochim. Acta,* **58,** 2829-2843.

Whiting, G.J. and Childers, D.L. (1989) Subtidal advective water flux as a potentially important nutrient input to southeastern U.S.A. saltmarsh estuaries. *Estuarine Coastal and Shelf Science,* **28**, 417-431.

Windom, H., Smith, R., Niencheski, F., Alexander, C. (2000) Uranium in rivers and estuaries of globally diverse, smaller watersheds. *Marine Chemistry,* **68**, 307-321.

Windom, H., Niencheski, F. (2003) Biogeochemical processes in a freshwater–seawater mixing zone in permeable sediments along the coast of Southern Brazil. *Marine Chemistry*, **83**, 121-130.

Woodwell, G.M., Rich, P.H., Hall, C.A.S. (1973) In: Woodwell, G.M., Pecan, E.V. (Eds.), Carbon in Estuaries, Brookhaven Symposium Biological Series, **24**, 221-224.

Zheng Y., Anderson R.F., Van Geen A., Fleisher M.Q. (2002) Remobilization of authigenic uranium in marine sediments by bioturbation. *Geochim. Cosmochim. Acta,* **66**, 1759-1772.