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Assessing The Magnitude and Impact of Seawater/ Pore Water Exchange in Salt Marsh Systems

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ASSESSING THE MAGNITUDE AND IMPACT OF SEAWATER/PORE WATER
EXCHANGE IN SALT MARSH SYSTEMS

by

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ABSTRACT

Submarine groundwater discharge is a hydrological process that is important to study and understand as it impacts biogeochemical processes and hydrological cycles. Particularly in coastal salt marsh systems, it is an important process to analyze as these systems serve as crucial interfaces between terrestrial and marine waters and particulates. There is evidence that these systems, typically thought to have little exchange across the interface due to impermeable sediments, could actually allow for significant flow of water and particulates at shallow depths. In order to measure and quantify this flow, a method using ^{224}Ra as a tracer has been tested. The extensive, gas-filled root system present in salt marshes could be a significant factor in an increased water/particulate circulation. This root system could also allow for oxygen gas exchange between roots and sediment and lead to rapid redox oscillations. Metal binding onto iron oxide nanoparticles under ambient conditions was studied using centrifuge filtration and ICP-MS (inductively coupled plasma mass spectrometry) to better understand the potential transport of redox reactive species.

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CHAPTER 1

INTRODUCTION

Submarine groundwater discharge (SGD) is a combination of hydrological processes that control the flow of freshwater and seawater at the land/ocean interface. SGD is an important factor in understanding coastal biogeochemical processes, hydrological cycles, and the release and/or trapping of particles and is in turn affected by factors such as hydraulic gradients, tidal pumping, waves, storms, and sediment permeability. In systems with highly permeable sediments, such as sand, water can flow easily and thus there is rapid groundwater/freshwater circulation and high particle turnover (Thibodeaux and Boyle 1987; Huettel and Rusch 2000; Huettel et al. 2007; Santos et al. 2012). Conversely, systems characterized as having low permeability should have a restricted circulation of water and particulates between the sediment and the overlying water (Blair and Aller 2012; Bianchi 2011). Salt marshes, which have fine grained, muddy sediment, are therefore assumed to have a low exchange of water and particulates. Another characteristic of salt marshes is their function as a repository for heavy metals due to characteristic land use practices and unique phase change reactions that occur within these transitional zones (Breitbarth et al., 2010). These metals accumulate in the sediment as solid metal-sulfide phases and are considered stable as long as they are left undisturbed; that is, as long as redox conditions remain anoxic. However, exposure of anoxic sediments to oxygen through processes such as dredging, storm events, and groundwater flow through permeable sediments can lead to oxidation

of sulfides and potential mobilization of associated metals. The assumption that the sediment has low permeability implies that groundwater flow is not a significant factor in the mobilization of metals in salt marsh systems.

However, studies have provided evidence that there is greater advective flow in salt marsh sediments than thought and that this flow can cause redox reactions and mobilize contaminants. Despite low permeability, high hydraulic conductivities have been measured in salt marsh systems containing marsh grass, allowing for significant shallow horizontal and vertical advective flow and implying that sediment permeability does not directly correlate with hydraulic conductivity (Osgood and Zieman 1998; Osgood 2000). Another study found that particle mixing in marsh sediments can occur deeper than bioturbation alone would account for (Smoak and Patchineelam 1999). Altogether, there is potential for significant advective flow and particle transport in shallow marsh sediments. This higher than assumed circulation could be because of the high root mass and burrows that are typical of salt marsh systems (Gribsholt et al. 2003; Daleo and Iribarne 2009). Marsh grasses, like many wetland plants, have adapted to living in aquatic environments by developing aerenchyma. These spaces or channels extend throughout the plant and allow for the exchange of gasses between the top and bottom of the plant (Sundby 2005). As the tide rises and falls, the gas spaces in the roots may expand and contract as a consequence of pressure changes due to loading. This process could lead to channeling of water along roots as the marsh systems fills and drains with the tidal cycle. The roots may become conduits that could facilitate water flow and particle transport. The combination of highly compressible sediment rich in

plant debris, the extensive and highly porous root system, and the presence of burrows could provide the means for increased advective flow throughout the system.

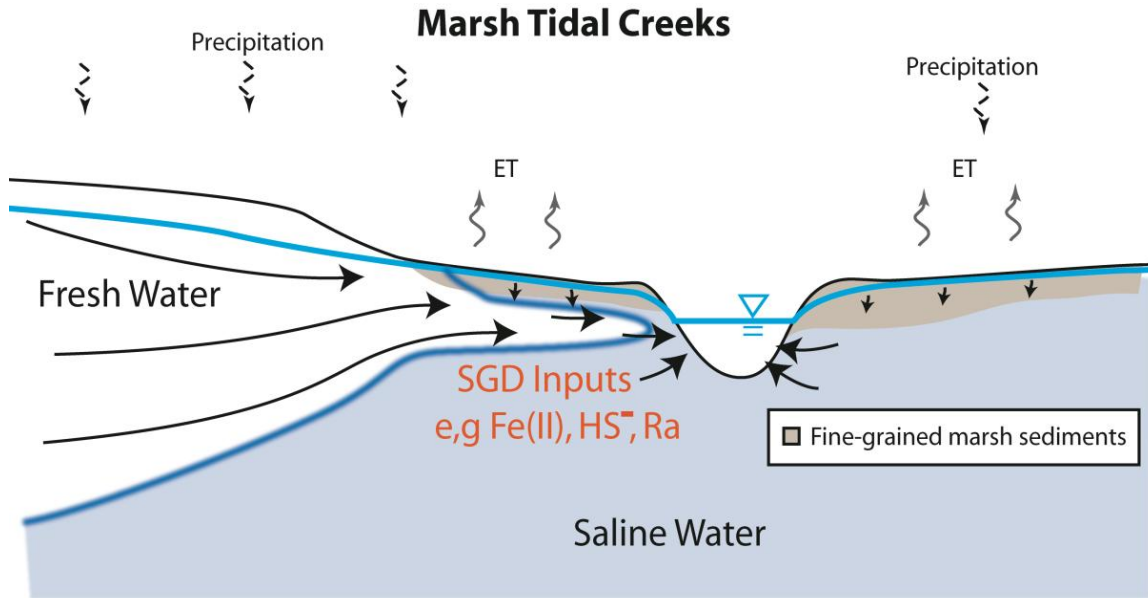


Figure 1.1. Simple schematic of hydrological processes in a marsh tidal creek. Water and particle flow through the sediment could create a batch reactor within the system. (ET stands for evapotranspiration.)

In addition to facilitating advective flow in the upper sediment column, the marsh grass root system could allow for oxygen gas exchange between the roots and the surrounding sediment (Koop-Jakobsen 2015). This gas exchange could lead to the oxidation of sedimentary sulfide and iron phases and cause rapid redox oscillations capable of mobilizing and transporting pore water species (Thursby 1984; Lee et al., 1999; Lee 2003; Koretsky et al., 2008; Winkel et al., 2011). Recent laboratory studies have demonstrated that such oscillations can cause changes in the redox speciation of a suite of redox sensitive trace elements (Couture et al., 2015). When the metals are mobilized, they are transformed into different phases including dissolved “free” ions, complexed metals, and colloid associated phases. The vast majority of the mobile phase

in coastal marsh systems has been found to be the colloid associated phases (Duncan and Shaw 2003). These colloid associated phases are a consequence of redox dependent transformations of the metal containing iron sulfide phases that predominate in salt marsh systems; rapid redox oscillations could therefore increase the significance of iron cycling.

Reduced iron sulfides in coastal sediments rapidly undergo a redox transition to Fe(III) phases upon exposure to oxygen (Burns 2011). The iron can continue to cycle between Fe(II) and Fe(III) phases or some iron can leave the cycle through the formation of solids, typically iron oxide, potentially in the nanoscale (Guo 2013; Charette 2002; Burns 2011; Rose 2003). The resultant colloidal (nano) ferric oxide phases adsorb metal cations mobilized by the phase sulfide oxidation. It has been shown that iron oxides are capable of adsorbing metals under environmentally relevant pH and ionic strength ranges and that natural organic matter (specifically, humic acid (HA) as representative of NOM) is also capable of adsorbing both metals and iron oxides (Lion 1982; Lowry 2012; Baalousha 2008; Maurer-Jones 2013; Jirsa 2013). It has even been shown that humic acid complexed with iron oxides can still bind metals (Kretzschmar 2005; Manciulea 2009). A study conducted by Plathe and colleagues (2013) concluded that approximately 80% of nanoparticles analyzed in a river system were associated with heavy metals and that iron oxides represented the largest portion of this percent. Thus, association and transport of these iron phases are critical to the mobility of heavy metals in these systems.

The importance of burrows in redox oscillations in marsh sediments has been well established (Aller and Aller 1998), but the root gas system could be an additional significant factor that needs to be investigated along with the potential formation and reactivity of iron oxides (Koop-Jakobsen 2015). It is crucial, therefore, to develop a

method to quantify the advective exchange rate of water and particulates through the system and then assess the reactivity of redox sensitive elements in the system. This study uses ^{224}Ra as a tracer to determine the volume of water that flows through shallow (20-50 cm) salt marsh sediments. Filtration and ICP-MS techniques are used to study metal binding to iron oxide nanoparticles and the potential for subsequent transport. The field site chosen for this investigation is the Folly Creek watershed in South Carolina, USA.

CHAPTER 2

EXPERIMENTAL

2.1 Description of field site

Studies were conducted within the Folly Creek Watershed, a salt marsh system in South Carolina, USA. The Folly Creek watershed is primarily comprised of the Folly River, the Folly Creek, and other small creeks that branch off of these waterways that have little fresh water input from nearby river systems. The watershed sits in a zone of depression causing it to receive little deep SGD. The main land formation is Folly Beach, a barrier island on the southeastern side of the watershed. The total area of Folly Creek watershed is 8162 acres. About 74% of this is comprised of water cover including bay/estuary and non-forested wetland (Carter 2010). The Folly Creek Watershed shares an inlet with the Stono River Watershed. The Stono River is a tidal channel in southeastern South Carolina, southwest of Charleston. Similar to the Folly system, the Stono system receives little to no fresh water input that is not generated by runoff in the watershed. Due to the above conditions, contributions to the Folly system from rivers or groundwater sources other than near surface circulation through permeable marsh sediments are at a minimum, making it an ideal site to study near SGD circulation. Samples were collected in one location dominated by *Spartina alterniflora* marsh grasses and in another location dominated by fiddler crab burrows.

2.2 Analytical methods

Sediment cores about 25 cm deep were collected from the field site, immediately transported to the lab, and cut into 1-cm slabs at 2-4 cm intervals. Half of the slab was transferred to Teflon large mouth bottles for $^{224}\text{Ra}/^{228}\text{Th}$ analysis. To each of these bottles, 150 mL of 18 M Ω water was added to form a slurry which was then ultrasonicated for 5 minutes. The pH was then adjusted to 8-9 by the addition of concentrated ammonium hydroxide. Next, a suspension of MnO_2 was formed by adding 1.0 mL of KMnO_4 (3.0 gL $^{-1}$) and 1.0 mL of MnCl_2 (8.0 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ L $^{-1}$); any radium present absorbs onto this surface. The slurry was then filtered onto 142 mm GF/F filters and loaded into a modified recirculation chamber (Cai et al. 2012) for the counting of ^{220}Rn and ^{219}Rn on the radium delayed coincidence counter (RaDeCC) developed by Moore and Arnold (1996). Samples were measured a second time two weeks later and a third time six weeks later in order to differentiate between supported and excess ^{224}Ra .

The other half of the sediment core slab was transferred to pre-weighed petri dishes, weighed, dried, and weighed again in order to determine porosity.

To examine the implications of redox oscillations, a metal binding experiment was conducted. Iron oxide nanoparticles were synthesized under ambient conditions using a procedure adapted from Karaagac (2012). Ten mmol of ferrous chloride and 15 mmol of ferric chloride were combined with 6.25 mL of 18 M Ω water and stirred for approximately 10 minutes. Then 6.25 mL ammonium hydroxide was added and the mixture was heated gently and stirred for an hour. A diluted sample was centrifuge filtered and analyzed by ICP-OES (inductively coupled plasma optical emission spectroscopy) to determine if there were free iron ions present. A set of 8 solutions were then prepared. Abbreviations used are as follows: FeO = iron oxide nanoparticles, HA =

Suwannee River humic acid, and M = metals. Metals used were a mixture of Al, Cr, Cu, Fe, Pb, and Zn. Where present, the concentration of FeO was 10 ppm, HA was 16 ppm, and M was 1 ppm. The eight solutions prepared were: FeO, FeO + M, FeO + HA, FeO + HA + M, HA, HA + M, M, and a blank. All solutions were 0.5 M NaCl and all were separated into 3 portions of 16 mL each and adjusted to pH 6, 8, and 10 resulting in 3 solutions for each of the 8 stock solutions. These pH adjusted solutions were then separated into 3 portions so the experiment could be conducted in triplicate resulting in a total of 72 samples. These samples were centrifuge filtered (using 30 kD filters), stored in a refrigerator, and the filtrate was later analyzed by ICP-OES.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Water flux

The advective water movement in the sediments was determined using the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium approach developed by Cai et al. (2012; 2014). ^{228}Th is the daughter of ^{228}Ra whose activity in seawater is supported by the decay of the abundant ^{232}Th parent. ^{228}Th generated in seawater and sediments remains strongly bound to sediment particulate phases and when left undisturbed, the $^{224}\text{Ra}/^{228}\text{Th}$ in the sediments will reach 1, indicating secular equilibrium (for every decay of the parent there is a decay of the daughter). However, the ^{224}Ra daughter ion is more soluble than the parent in saline waters and can be mobilized from the sediment if seawater flows through the sediments at rates comparable to the decay rate of the daughter (3.6 days). Thus, advective flow can result in a disequilibrium as a change in the $^{224}\text{Ra}/^{228}\text{Th}$ ratio. This disequilibrium indicates the extent of the sediment permeability; at a depth where there is no longer water flowing through, the isotopes will be in secular equilibrium.

The method validation included a loading experiment to determine an upper limit of how much sediment could be placed in the RaDeCC sample holders without blocking air flow and depressing the number of counts detected. The goal was to find the greatest sample size that could be measured in order to yield the highest number of counts while remaining within the linear response of the instrument. The detector response remained linear up to a sample loading of about 30 g wet sediment.

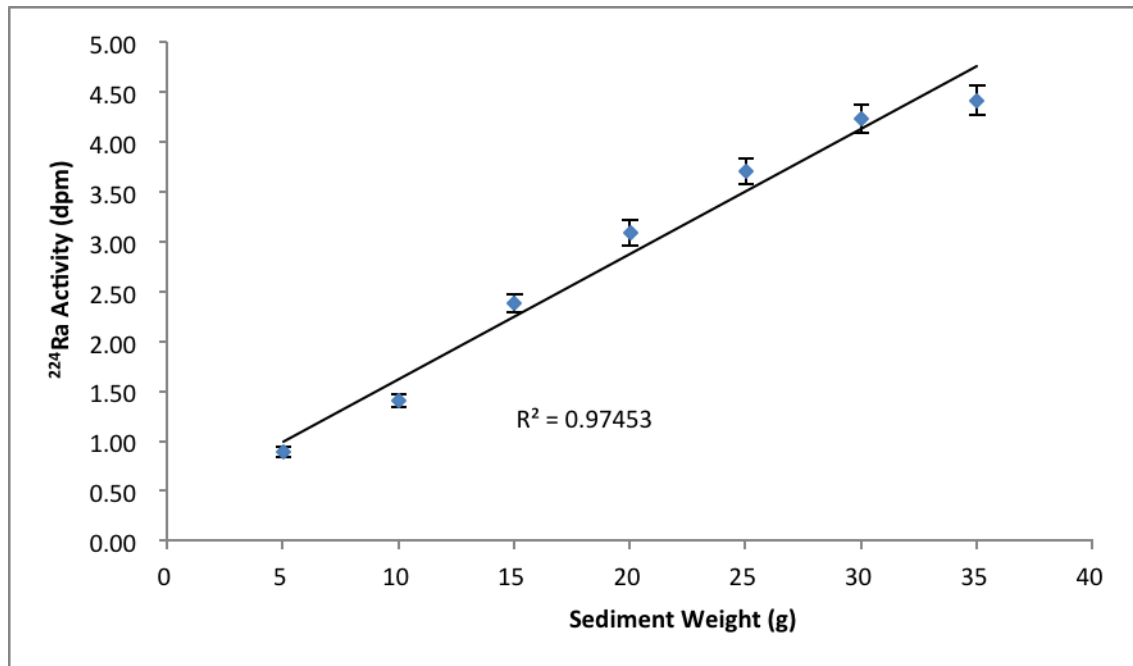


Figure 3.1. Sediment loading results.

Two sediment cores were collected in December 2014; one core was taken from a location dominated by marsh grasses and the other was taken from a location with many burrows and no grass. In the grass dominated core, a distinct ²²⁴Ra deficit can be seen throughout the length of the core representing disequilibrium between parent and daughter and suggesting advective flow of water out of the sediment. However, in the burrow dominated core, this deficit is not as extensive, with narrow zones of deficiency at points throughout, near the surface, and at the bottom of the core. The zones may indicate exchange around burrows. In April 2015 another two cores were collected from a location next to the grassy area the December core was taken from. Both of these cores show distinct deficits in the top and, more importantly, the bottom layers. There is, however, little evidence of water flux through the middle 10-20 cm.

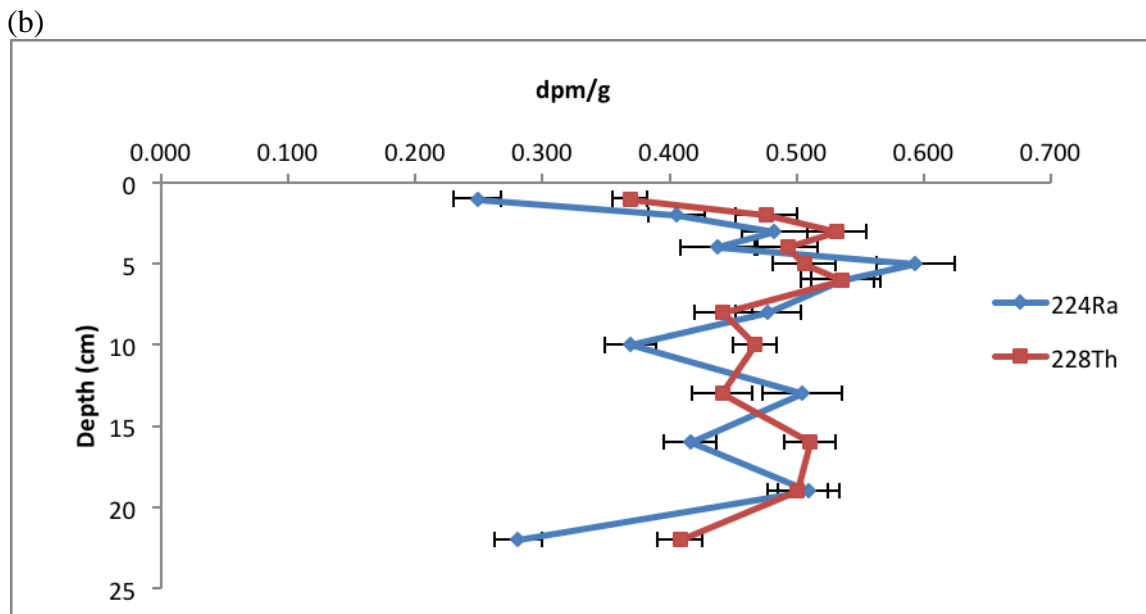
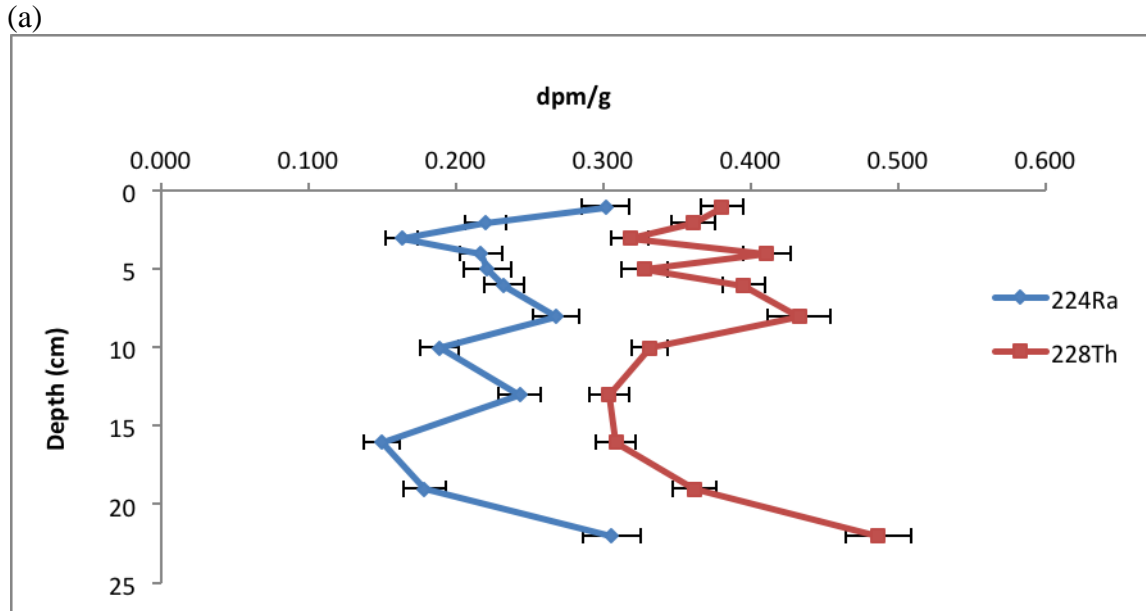


Figure 3.2. December cores. (a) Core collected from a marsh grass dominated area. (b) Core collected from area dominated by burrows.

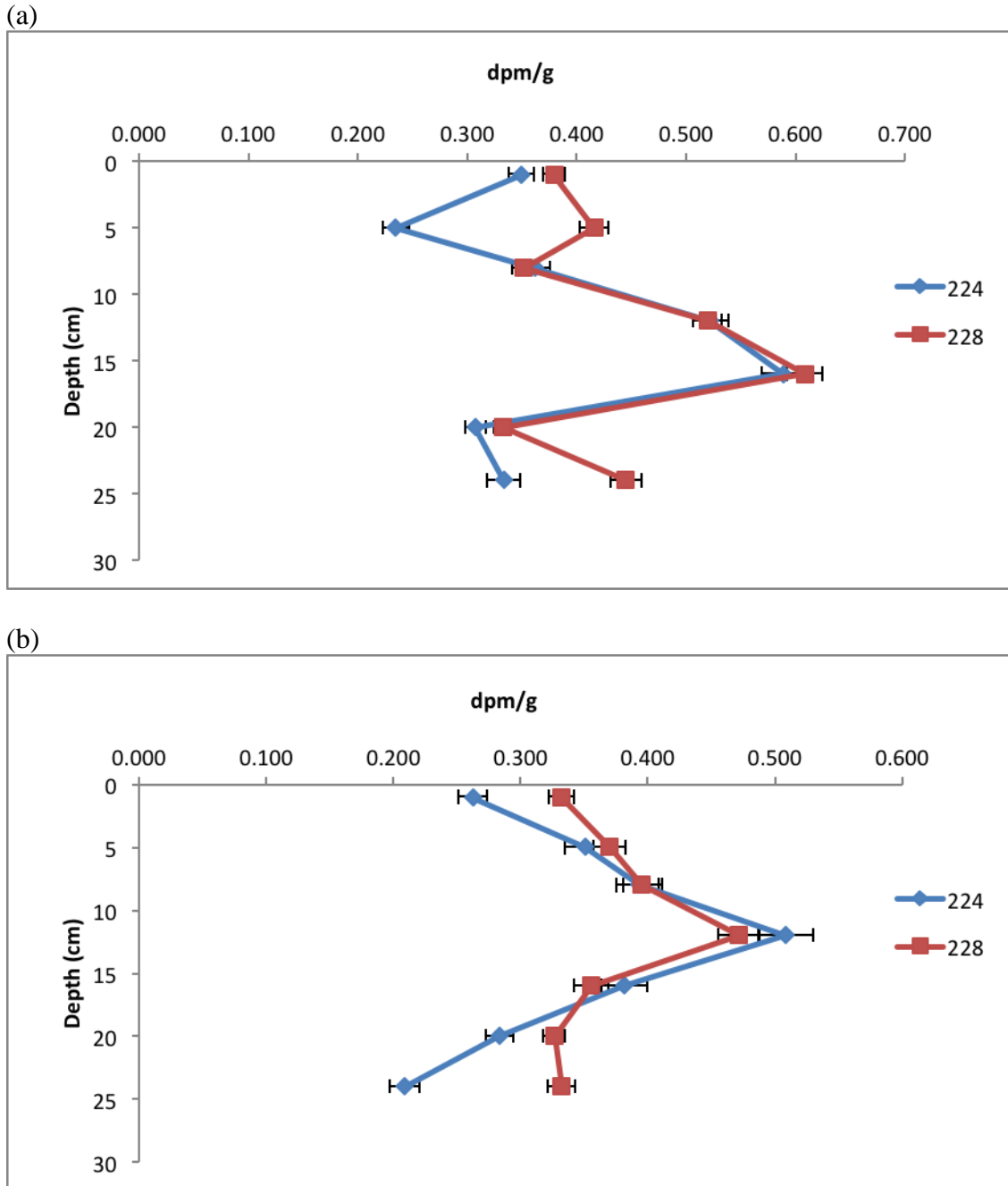


Figure 3.3. April cores. Both cores (a) and (b) were collected from a site adjacent to marsh grasses.

These results provide evidence of advective water flow through the fine grained, muddy sediment at depths up to 25 cm when marsh grass is present. The net export can be calculated using the steady-state equation: $F_{Ra} = \lambda_{224Ra}(A_{228Th} - A_{224Ra})$, where F_{Ra} is the

pore water export of ^{224}Ra in disintegrations per minute (dpm) $\text{gram}^{-1}\text{day}^{-1}$, $\lambda_{224\text{Ra}}$ is the decay constant for ^{224}Ra (0.189 day^{-1}), and $A_{228\text{Th}}$ and $A_{224\text{Ra}}$ are the activities of ^{228}Th and ^{224}Ra in dpm $\text{gram sediment}^{-1}$. To convert this flux to units of $\text{Lm}^{-2}\text{day}^{-1}$, a pore water ^{224}Ra activity estimate of 10 dpmL^{-1} was used along with a particle density of 2.6 gcm^{-3} and the known sediment porosity at each depth. This resulted in a pore water flux of approximately $10\text{-}40\text{ Lm}^{-2}\text{day}^{-1}$, depending on the specific core and depth.

3.2 Modeling root volume changes

One possible mechanism for the higher than expected advective flow in these sediments may be related to the overall compressibility of the sediments due to changes in root volume. For comparison, clay sediments typically have a compressibility of no greater than 1% so a maximum change in volume associated with the fine sediments can be easily calculated. Given a measured porosity of about 70% by mass for the non-root containing muds collected from the marsh, the sediments account for about 30% of the total mass. Corrected for a density of approximately 2.6 gcm^{-3} , they only account for about 14% of the volume for these muds when saturated. Compression of these sediments by 1% would only account for a 0.1 percent change in volume or about 0.5 Lm^{-2} in the upper 50 cm of the sediment column per tidal cycle, a small fraction of the calculated flow. Some draining of the non-vegetated sediments has been observed at low tide as cracks in the surface mud, but these do not represent a large volume.

While the sediment compressibility alone is only a small fraction of the volume change, the compressibility of roots within the sediment could add a significant amount. An estimate of the total root volume in a typical marsh system can be made from measurements of root biomass. Roots of marsh grasses contain gas vacuoles that can

account for 40% to 60% of their volume (Winkel 2011) so an estimate of root density while gas filled of 0.5 gcm^{-3} is reasonable (half of the root being air). If the roots are considered as gas filled balloons and are at 1 atm due to gas transport across exposed leaves in the air being at 1 atm, then compressibility under different tidal heights is likely to result in significant volume changes. Sundby found in a separate but similar environment that root biomass accounts for up to 25% dry weight of the total mass 20 cm deep in the summer and about 1% in the winter (2005). Taking the root mass to be 25% of the sediment mass and the density ratio of the sediments versus the roots yields a relative volume estimate for the roots of about 15%. A compression of the roots by 10% would then result in an overall change in volume of 1.5%, or 7 Lm^{-2} in the upper 50 cm (the typical root depth in this system). Assuming two tidal cycles per day, this would then be $14 \text{ Lm}^{-2}\text{day}^{-1}$. This conservative estimate is on the order of the low end of the disequilibrium based estimates from the field study and support the hypothesis that the root system could allow for advective flow of water in the sediment due to root volume changes.

A related study by Winkel measured root oxygen levels in *Spartina anglica* and found oxygen pressure changes of 20-65% depending on the time of day (2011). So there is a fluctuation of oxygen levels in the total gas within the roots, with less oxygen being present at night. In a preliminary study conducted by our lab group, a correlation was found between ^{224}Ra flux and Fe (II).

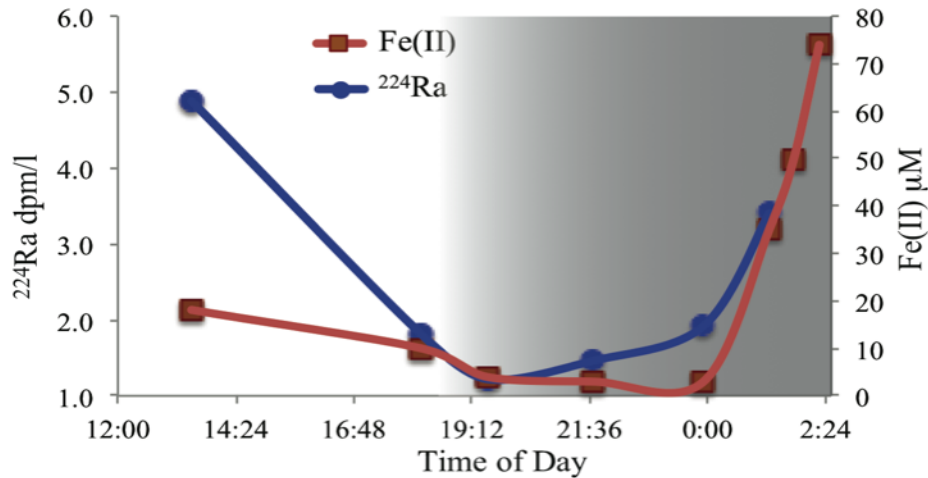


Figure 3.4. Fe (II) and ^{224}Ra levels over an extended time period.

While the flux of ^{224}Ra is high at low tide stands during both the day and night, the nighttime flux of Fe(II) corresponds with lower oxygen levels in the root system and reduction of solid Fe(III) phases surrounding the roots. This is consistent with observations of orange, presumably Fe(III) rich, zones around the roots of the cores collected for this study. The oxygen exchange would lead to redox cycles between reduced and oxidized phases in the sediments. This conceptual model of redox mediated iron mobility is supported by the correlation between ^{224}Ra flux and Fe (II) concentrations at night. As it appears the root volume changes can create channels deep into the sediment and that oxygen can be exchanged, sulfides deeper in the sediment can be oxidized and the mobilized metals can be transported out of the sediments. These redox sensitive species may continue to react within a redox cycle or they may precipitate out of the cycle as solids capable of binding and transporting reservoirs of other metals.

3.3 Implications of redox oscillations

Initial characterization of the synthesized iron oxide nanoparticles found that the particles were in the range of 600-900 nm over a pH range of 2-12 with a polydispersity of approximately 0.5. The addition of humic acid helped to decrease the aggregation at higher pHs; however, the particles are still largely aggregated. This was expected since the particles were synthesized in a manner to imitate a natural formation and as such were not treated with any sort of capping agent. No imaging techniques were used; however, the particles appeared to be a reddish brown color indicative of the maghemite form of FeO (Fe_2O_3). After centrifuge filtration of a diluted portion there was no Fe detectable by ICP-OES in the filtrate indicating that all of the iron present in the particle solution was in the form of particles and not dissolved Fe ions. This measurement was conducted one month after synthesis signifying good stability of the particles. Table 3.1 shows the result of the metal binding experiment using these particles.

Table 3.2 Metal concentrations in the presence of iron oxide nanoparticles and humic acid. The metal concentrations present in each of the seven solutions (eighth solution is blank, subtracted out) after centrifuge filtration at pH of 6, 8 and 10. The blue highlights a decrease in metal concentration from the solution of metals alone (M).

pH	Metal	Average Metal Concentrations in Solutions (ppm)						
		M	FeO+M	HA+M	FeO+HA+M	FeO	HA	FeO+HA
6	Al	0.0027	0.0064	0.0063	0.0052	0.0054	0	0
	Cr	0	0	0	0	0	0	0
	Cu	0.015	0.040	0.12	0.024	0	0	0
	Fe	0.0018	0.00094	0.00031	0.0013	0.0010	0.0011	0.00097
	Pb	0.033	0.042	0.17	0.032	0	0	0
	Zn	0.16	0.26	0.25	0.21	0	0	0
8	Al	0.041	0.015	0.0034	0.0025	0	0	0
	Cr	0.044	0.0015	0	0	0	0	0
	Cu	0.00076	0	0	0	0	0	0
	Fe	0	0.011	0.0094	0.0096	0.011	0.0097	0.0098
	Pb	0.071	0	0.027	0.0058	0	0	0
	Zn	0.087	0.0086	0.056	0.018	0	0	0
10	Al	0.17	0.16	0.14	0.14	0.00091	0.0031	0.0030
	Cr	0.013	0.0066	0	0	0	0	0
	Cu	0	0	0	0	0	0	0
	Fe	0.0054	0	0	0	0	0	0.014
	Pb	0.012	0.0034	0.0061	0.0026	0.0015	0.0064	0.010
	Zn	0	0	0	0	0	0	0

As can be seen, the concentration of metals in the solution of just metals (and 0.5 M NaCl) is more or less in the ppb range. It was expected that these metals would filter through and be detected in the filtrate with a high recovery resulting in a concentration close to the 1 ppm that was initially added. The metals may have complexed with the chloride present in the solution or may have interacted with the filter. With such small concentrations, it is difficult to make comparisons; however, some trends may be proposed. At pH 8 and 10 the blue font highlights a decrease in metal concentration in the filtrate after additions of FeO and HA. In the solution containing both FeO and HA with M, this decrease is compounded. This demonstrates that FeO and HA are capable of binding metals separately and together. It appears that FeO is capable of binding Pb and Zn better than HA while HA is more capable of binding Al and Cr. At pH 6 the metal

concentration is actually seen to increase upon addition of FeO and HA. This could simply be due to increased solubility of metal complexes at lower pHs. As the particles were largely aggregated (FeO particles alone were 600-900 nm), they are not as mobile as smaller particles would be. However, due to the rapidity of the redox oscillations that take place in the marsh sediments and the volume of water flowing through, smaller aggregates are more likely resultant in their mobility.

CHAPTER 4

CONCLUSION

Salt marshes have traditionally been thought to serve as repositories for contaminants, specifically metals, and have little shallow groundwater flow. However, previous studies have provided evidence that significant flow may occur. This flow could, in part, be due to the extensive salt marsh grass root system. These roots have developed gas-filled aerenchyma in order to survive in a wetland environment and this gas can compress and expand according to the weight of the overlying water and of the saturated sediments as a function of tidal height. These changes in the gas volume can cause channels to form throughout the sediment that allow water and particulates to flow. Experiments in this study used ^{224}Ra as a tracer to quantify water flux in sediment cores about 25 cm deep and found a flux of $10\text{-}40 \text{ Lm}^{-2}\text{day}^{-1}$ in cores that were taken from grassy areas. A rough model of gas compression in these sediments is consistent with the disequilibrium based estimates of advective flow. Another effect of the root system is that it allows for oxygen gas exchange between the roots and the surrounding sediment. The amount of oxygen fluctuates depending on factors such as light intensity and tidal height and causes rapid redox oscillations to occur. These redox reactions cause metal-containing sulfides to oxidize, releasing the metal and initiating a redox cycle. These sulfides are mainly iron sulfides and when oxidized can form iron oxides that are capable of precipitating out of the iron redox cycle and binding with natural organic matter and

metals. Due to the greater than expected groundwater flow, these particulates could be more mobile than previously thought, challenging the concept of these sediments as a stable reservoir for heavy metals.

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