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Uranium distribution in the coastal waters and pore waters of Tampa Bay, Florida

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Abstract

The geochemical reactivity of uranium (^{238}U) and dissolved organic carbon (DOC), Fe, Mn, Ba, and V was investigated in the water column, pore waters, and across a river/estuarine mixing zone in Tampa Bay, Florida. This large estuary is impacted both by diverse anthropogenic activity and by extensive U-rich phosphatic deposits. Thus, the estuarine behavior of uranium may be examined relative to such known U enrichments and anthropogenic perturbations.

Dissolved (<0.45 m) uranium exhibited both removal and enrichment processes across the Alafia River/estuarine mixing zone relative to conservative mixing. Such non-conservative U behavior may be attributed to: *i)* physical mixing processes within the river; *ii)* U carrier phase reactivity; and/or *iii)* fluid exchange processes across sediment/water interface. In the bay proper, U concentrations were ~ 2 to 3 times greater than those reported for other estuarine systems and are likely a result of erosional inputs from the extensive, underlying U-rich phosphatic deposits. Whereas dissolved U concentrations generally did not approach seawater values (13.6 nM) along the Alafia River salinity transect, water column U concentrations exceeded 16 nM in select regions of the bay. Within the hydrogeological framework of the bay, such enriched U may also be derived from advective fluid transport processes across the sediment/water interface, such as submarine groundwater discharge (SGD) or hyporheic exchange within coastal rivers. Pore water profiles of U in Tampa Bay show both a flux into and out of bottom sediments, and average, diffusive U pore water fluxes (J_{diff}) ranged from −82.0 to 116.6 mol d^{-1}. It is likely that negative U fluxes imply seawater entrainment or infiltration (i.e., submarine groundwater *recharge*), which may contribute to the removal of water column uranium. For comparison, a bay-wide, Ra-derived submarine groundwater discharge estimate for Tampa Bay (8 L m^{-2} d^{-1}) yielded an average, advective (J_{SGD}) U flux of 112.9 mol d^{-1}. In Tampa Bay, the estuarine distribution of U indicates a strong natural, geologic control that may also be influenced by enhanced fluid transport processes across the sediment/water interface.

Keywords: Uranium; Pore water; Estuary; River water; Seawater; Non-conservative; Submarine groundwater discharge

1. Introduction

Estuaries function as efficient biogeochemical reactors, wherein a broad spectrum of geochemical reactions and processes are initiated in response to fundamental changes in water chemistry as rivers and groundwater mix into seawater (Sholkovitz, 1976; Boyle et al., 1977; Borole et al., 1982; Carroll and Moore, 1994). Knowledge of these estuarine biogeochemical transformations is essential to understand fully the fate of elements as they are transported toward the sea (Millward and Turner, 1994; Swarzenski et al., 1995; Moore et al., 1996). Furthermore, the validity

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of estuarine trace-element/radionuclide mass-balance calculations is directly bound by our understanding of these processes (McKee et al., 1987; Klinkhammer and Palmer, 1991; Shiller and Boyle, 1991; Swarzenski et al., 1995; Andersson et al., 2001). While riverine-flux estimates are usually readily quantifiable, the material contribution derived from submarine groundwater discharge (SGD) is inherently more diffuse and thus much harder to constrain (Porcelli and Swarzenski, 2003; Swarzenski et al., 2003). A study of the uranium geochemistry in Tampa Bay provides an ideal opportunity to evaluate estuarine biogeochemical processes in a coastal system influenced by complex surface-water/groundwater interactions and U-rich deposits. Rivers are generally the largest source term for continentally derived weathering products to the sea, and on average contain about 1.3 nM dissolved (traditionally defined as <0.4 μm) and 12.6 nM g^{-1} particulate U (Moore, 1967; Sackett and Cook, 1969; Mangini et al., 1979; Cochran, 1982; Scott, 1982; Palmer and Edmond, 1993). Such global estimates are most useful for large-scale mass-balance derivations and inherently cannot reflect unique seasonal and geographical variations in the distribution of uranium (Scott, 1982; Palmer and Edmond,1993; Snow and Spalding, 1994). In Tampa Bay, the combined riverine influx of fresh water is only about 63 m^3 s^{-1} (Weisberg and Zheng, 2006), and this value includes a large contribution (~ 30%) derived from non-diffusive transport through sediments, including hyporheic exchange and SGD. Such dynamic groundwater/surface-water exchange may impact the delivery and estuarine fate of diagenetically sensitive trace elements like uranium (Lienert et al., 1995).

Riverine trace elements and radionuclides are typically particle reactive and thus largely (~ 90%) associated with the particulate load of a typical river system (Gibbs, 1977; Martin and Meybeck, 1979; Presley et al., 1980; Martin and Whitfield, 1983; Davis, 1984; Trefry et al., 1986; Zielinski and Meier, 1988; Choppin and Clark, 1991; Payne and Waite, 1991; Plater et al., 1992; Waite et al., 1994; Lienert et al., 1995; Swarzenski et al., 1995). These ionized riverine particles/colloids can be efficiently stripped of their trace elements/radionuclides during estuarine mixing in response to biogeochemical reactions initiated by an increase in ionic strength (Sholkovitz, 1976, 1977; Boyle et al., 1977; McKee et al., 1987; Swarzenski et al., 1995; Moore et al., 1996).

In addition to such fluvial-source terms, much recent evidence (Burnett et al., 2003) indicates that SGD may also contribute substantively to estuarine mass budgets, particularly along coastlines that do not have large discharging rivers. It is important to recognize that SGD need not constitute fresh groundwater, but rather a composite of recycled seawater, as well as meteoric and connate groundwater. Reactions and processes during SGD may be comparable to those that occur during hyporheic exchange. For example, diagenetic transformations within the seabed and associated pore waters (or groundwater) may impact the estuarine U behavior by serving as either a sink or potential source for U, depending on the redox state and carrier phase (Cochran et al., 1986; McKee et al., 1987; Anderson et al., 1989; Barnes and Cochran, 1990, 1993; Shaw et al., 1995; Swarzenski et al., 1995, 2004). Dissolved U in pore waters can be mobilized either by Fickian diffusion across the sediõment/water interface (Barnes and Cochran, 1993) or by advective fluid transport mechanisms, such as SGD or hyporheic exchange. The release of U from particles or colloids that have already undergone partial diagenetic alterations is thought to be an additional source for reactive U into the water column (McKee et al., 1987; Swarzenski et al., 1995). Another important source of U to Tampa Bay may be derived from the ubiquitous phosphogypsum deposits. Although the uranium-rich Miocene phosphatic deposits contained within the Bone Valley Member of the Hawthorn Group (Osmond et al., 1984) of west-central Florida are not unique globally, environments where such deposits are actively forming today are unknown (Green et al., 1995). The unique U concentration and isotopic composition of the phosphatic deposits may enable U and its natural isotopes ($^{234,238}U$) to possibly be utilized as unique groundwater mass tracers into estuarine waters under ideal conditions (Osmond and Cowart, 1976).

Lastly, it is well known that U can be highly enriched and can show extreme isotopic disequilibrium in groundwater (Osmond and Cowart, 1976; Fleischer and Raabe, 1978; Hussain and Krishnaswami, 1980; Copenhaver et al., 1993; Snow and Spalding, 1994; Porcelli and Swarzenski, 2003). In areas where coastal groundwater is actively discharged into seawater (Moore, 1996), it may also be possible to separate the isotopic U activity within such inflowing groundwater from oceanic and fluvial isotopic signatures. A comprehensive mass balance of U and its daughters in coastal waters should consequently include an evaluation of such coastal groundwater discharges. Unfortunately, quantitative assessment of submarine groundwater discharge and associated trace-element and radionuclide fluxes into coastal waters is still difficult to resolve on a regional scale.

This report addresses the seasonal variability of dissolved uranium and dissolved organic carbon (DOC), Fe, Mn, Ba, and V in the surface and pore waters of Tampa Bay. Our results indicate that the role of fluid transport across the sediment/water interface, including