14   The Behavior of U- and Th-series Nuclides in the Estuarine Environment

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1. INTRODUCTION

Rivers carry the products of continental weathering, and continuously supply the oceans with a broad range of chemical constituents. This erosional signature is, however, uniquely moderated by biogeochemical processing within estuaries. Estuaries are commonly described as complex filters at land-sea margins, where significant transformations can occur due to strong physico-chemical gradients. These changes differ for different classes of elements, and can vary widely depending on the geographic location. U- and Th-series nuclides include a range of elements with vastly different characteristics and behaviors within such environments, and the isotopic systematics provide methods for investigating the transport of these nuclides and other analog species across estuaries and into the coastal ocean.

There are numerous types and definitions of estuaries (see Dyer 1973). In this paper, it is simply considered to be a region where freshwater and seawater mix, to emphasize the chemical focus of the issues involved here. This region can either be contained within a river channel or extend onto the shelf, with effects often extending well into an adjoining ocean basin (Fairbridge 1980). These are complex ecological, biogeochemical, and hydrodynamic systems, with strong gradients in the concentrations and composition of micro- and macro particulate matter as well as dissolved organic and inorganic species. Particle-reactive radionuclides and trace elements being transported across estuaries are subject to partitioning between the dissolved, colloidal and particulate phases. The variable chemical nature of the U- and Th-series radionuclides is evident in their

distributions in an estuarine environment. Such radionuclides can effectively serve as tracers to identify the sources, fate and transport of particles and colloids as well as other pollutants that behave similarly to these nuclides. These nuclides also have a wide range of half-lives that can be used to examine processes over various time scales. For example, Th and Ra daughter isotopes have half lives of 3.6 days to 75,200 years. Although most of the U- and Th-series radionuclides with half-lives less than ~100 yrs are commonly measured with standard counting techniques, recent advances in mass spectrometry have greatly improved the measurement of the long-lived nuclides, leading to smaller sample size as well as much higher precision. Studies involving high precision determinations of uranium isotopic compositions are now possible using mass spectrometric techniques (Goldstein and Stirling 2003), such as thermal ionization mass spectrometry, TIMS, (Chen et al. 1992) and more recently also multiple collector inductively coupled plasma mass spectrometry, MC-ICP-MS (Halliday et al. 1998; Henderson 2002) and Sector ICP-MS (Shiller and Mao 2000).

Understanding the behavior of radionuclides in estuaries, as the dynamic interface between the continental hydrochemical systems and the ocean basins, requires consideration of broader chemical cycling in the hydrosphere. In this volume, the behavior of U- and Th-series isotopes in rivers is discussed by Chabaux et al. (2003), that in groundwaters by Porcelli and Swarzenski (2003), and that in oceans by Cochran and Masque (2003). General background information is provided by Bourdon et al. (2003).

1.1. Estuarine mixing

When riverine dissolved species (metals, radionuclides, and other organic and inorganic contaminants) are discharged into an estuary, they can behave *conservatively* or *non-conservatively* during mixing. During conservative mixing, there is no net loss or gain of a particular constituent as a function of salinity, so that variations in concentrations are due only to dilution of river water (with ~0 salinity) and ocean water (~35 salinity). However, some elements show non-conservative behavior; that is, they are removed or added in an estuarine system during mixing. When the concentration of a chemical species is plotted against salinity, mixing between two components falls on a straight line if the species is conservative as a function of salinity, with the endmembers defined by river and seawater concentrations (Fig. 1). Where data fall below a line connecting these endmember components, removal occurs, and where data fall above the ideal dilution line, there must be additional inputs, presumably either from underlying sediments, from lateral mixing, or from submarine groundwater discharge. Boyle et al. (1977) pointed out that it is only where curvature in this line occurs that losses or gains take place, while elsewhere mixing is likely to be conservative. Unfortunately, in practice there are sometimes regions where such a distinction cannot be clearly made, due either to limited data coverage or multi-component mixing. Clearly, identification of the regions where inputs or removal occur requires good coverage across the salinity gradients to unambiguously define salinity-concentration relationships. Note that salinity is not exactly defined as it becomes more dilute, as the mixture of major elements is not likely to be the same as in seawater (see discussion in Millero and Sohn 1992). Strictly, conductivity or total dissolved solids (TDS) should be used. However, on the scale of effects seen in the species of interest here, such accurate specification of salinities is unnecessary.

An important issue that influences estuarine behavior is the determination of the riverine component. Variations in the riverine endmember may occur over timescales that are short compared to the residence times of water in the estuary, which result in nonlinear relationships between salinity and trace elements across the estuary as different riverine compositions progress through the estuary (Loder and Reichard 1981; Officer
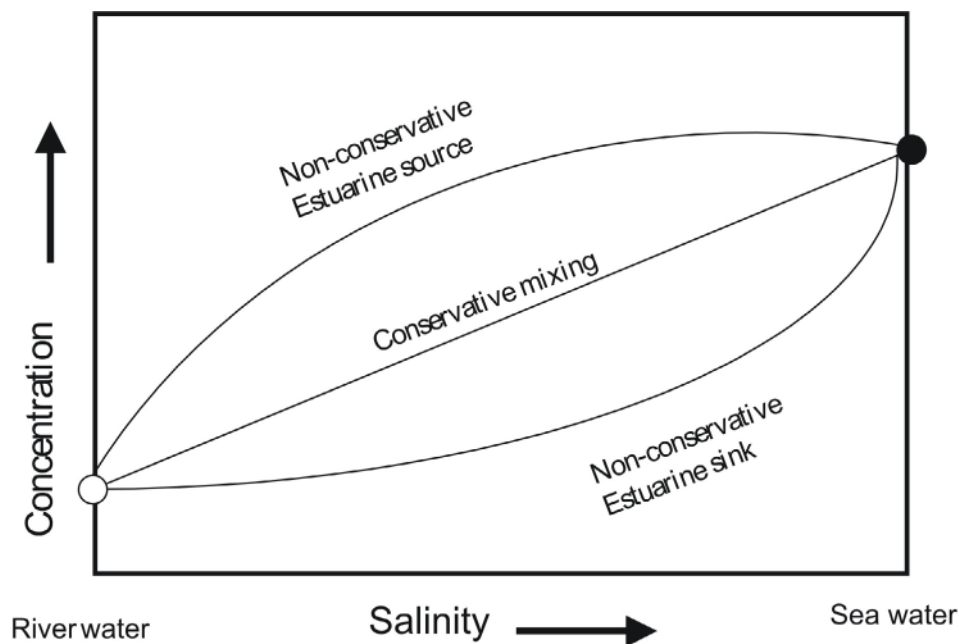
Figure 1. Schematic cartoon for idealized estuarine mixing of a dissolved component versus salinity, which serves as a conservative measure of the degree of mixing between freshwater and seawater. Redrawn after Berner and Berner (1987).

and Lynch 1981). Also, comparison of estuarine profiles with a river sample that was collected at another time may incorrectly define the conservative mixing benchmark. Note that this is a one-dimensional representation and assumes that concentrations normalized to salinity always remain constant, and so the plotted data follow the pattern across the estuary. This therefore does not take into account lateral differences across the estuary. Vertical redistributions of components can occur as well, as discussed in detail by Shiller (1996). This may be due to such mechanisms as the gravitational settling of biogenic particulates that have adsorbed solutes and are then oxidized and at least partially re-dissolved. Such a process can effectively redistribute nutrients and particle-reactive species, and may be overlooked in studies relying on suites of surface samples. Unfortunately, there is limited data available regarding the impact of these reservoirs on some of the U- and Th-series nuclides.

An important element for the cycling of trace elements, and so for considering the background to radionuclide behavior, is Fe. Fe is highly insoluble in oxidized waters, and is generally present in river water either on particles or in colloids (e.g., Kennedy et al. 1974). When discharge into an estuary occurs, Fe flocculates at very low salinities to form rapidly removed particulates (Sholkovitz 1977; Boyle et al. 1977). The result is that Fe concentrations drop off precipitously within the lowest salinity regime of an estuary. Since ferrous oxyhydroxides have highly reactive surfaces, this removal of Fe provides a vehicle for the associated removal of surface-reactive trace elements.

1.2. Estuary fluxes

Estuaries are clearly open systems, and several radionuclide fluxes must be considered to balance an estuarine mass budget (Fig. 2):

- Seawater inflow. The seawater endmember is relatively uniform, although coastal processes and upwelling can generate local variations. This is
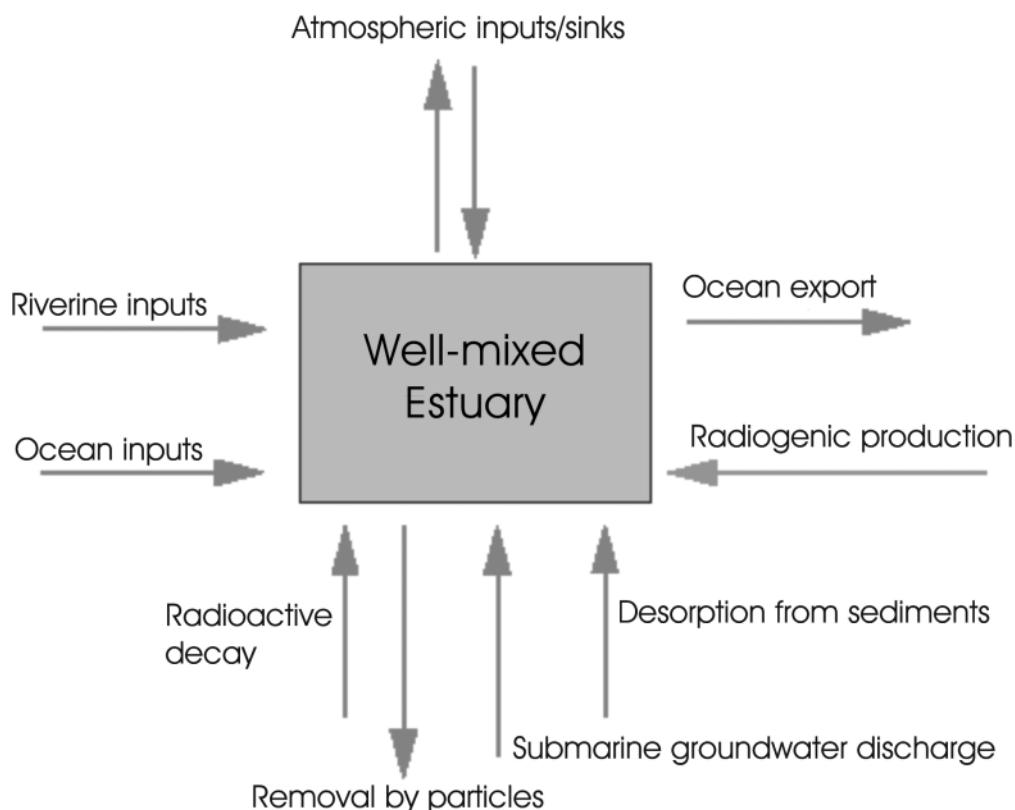
Figure 2. Simplified box model depicting the dominant input and removal functions for a particle reactive radionuclide such as ^{210}Pb in a well-mixed estuarine system.

particularly true of trace elements with short residence times in the ocean, such as Th, that have wide variations in concentration, as opposed to less reactive uranium.

- Atmospheric inputs. The atmosphere can be either a source or sink for select coastal radionuclides; for example, for ^{210}Pb the atmosphere can be a sizeable source, yet for ^{222}Rn the atmosphere is a sink.

- River inputs. The riverine endmember is most often highly variable. Fluctuations of the chemical signature of river water discharging into an estuary are clearly critical to determine the effects of estuarine mixing. The characteristics of U- and Th-series nuclides in rivers are reviewed most recently by Chabaux et al. (2003). Important factors include the major element composition, the characteristics and concentrations of particular constituents that can complex or adsorb U- and Th-series nuclides, such as organic ligands, particles or colloids. River flow rates clearly will also have an effect on the rates and patterns of mixing in the estuary (Ponter et al. 1990; Shiller and Boyle 1991).

- Removal to sediments. Removal of surface-reactive trace elements from the oceans readily occurs by adsorption onto settling particles, and this process is most pronounced in the typically high-energy, particle-rich estuarine environment. Particles are supplied by rivers, augmented by additions of organic material generated within the estuary. Also, flocs are created in estuaries from such components as humic acids and Fe. The interaction between dissolved and colloidal species is enhanced by the continuous resuspension of sediments in

turbulent zones. Outputs to sediments by sediment-water interactions are also important. Marshes through which large proportions of river and estuarine water can filter through, and which are rich in organics and particles, provide local environments for trace element complexing and retention.

- Input from sediments. Sediments can release constituents that are produced within sediments, those that were bound onto surfaces during sedimentation, or those within phases that are mobilized by breakdown or transformation of the sediments. Therefore, the evolution of underlying sediments due to changes in such factors as redox conditions, which can redistribute Fe and Mn from phases that may have held radionuclides, must also be considered. Radionuclides can be transported into the overlying water through diffusion from interstitial waters, flushing of sediments, and resuspension of sediments. This includes turbidity maxima that can occur at intermediate salinities, and fluid muds with very high suspended particle concentrations.

- Submarine groundwater inputs to the coastal zone. In some areas, submarine groundwater discharge (SDG) is an important source of nutrients and other dissolved constituents. However, precise estimates of the magnitude and geographic location of submarine groundwater flow are still scarce, as SGD sites are difficult to identify and quantify. The contributions of SGD-derived species are important to an estuarine mass budget if either the discharge rates or the ratio of constituents in groundwater relative to coastal bottom waters is sufficiently large (Moore 1996, 1999).

Due to the complexities involved with identifying and quantifying these fluxes, defining the behavior of elements in an estuary has required more extensive and continuing studies at many locations. Note that the 20 largest world rivers account for only 30% of the global water discharge into the oceans. This makes a comprehensive accounting difficult, and the transfer or extrapolation of knowledge from one river-estuarine system to another, unstudied system uncertain and tenuous.

1.3. Colloids

Many of the earlier studies that were summarized by Moore (1992) did not include a discussion of the role of colloids in the removal and cycling of U- and Th-series radionuclides. Colloids are defined as particles or macromolecules with an equivalent spherical diameter in the size range of 1 nm to 1 μm (Buffle and van Leeuwen 1992). Colloids play a major role in the behavior and cycling of aquatic trace elements and radionuclides. Past studies generally defined all constituents passing through a 0.2 or 0.45 μm filter membrane as "dissolved" while the filter-retained phase was defined as "particulate" and comprised a size class that can effectively undergo gravitational settling. However, the "dissolved" constituents clearly contain not only dissolved ions and small inorganic as well as organic complexes that are traditionally considered in speciation calculations, but also larger constituents such as macromolecules and mineral phases (see discussion by Buffle and van Leeuwen 1992). The mass concentration of colloidal material in the coastal ocean and the open ocean has been found to be significantly higher than in the filter-retained particulate matter. Colloids have been shown to mediate the distribution of Th isotopes between dissolved species and settling particles in the oceans (Honeyman and Santschi 1989; Baskaran et al. 1992), and much of the colloidal materials undergo coagulation and are removed from the water column by settling particles. Once a particle-reactive radionuclide (or trace metal) is introduced to the water column, such as ^{234}Th produced from its dissolved parent, ^{238}U, it is taken up by colloids and removed by coagulation to form sinking particles and sedimentation

(Honeyman and Santschi 1989). Therefore, flocculation of colloids to form settling particles in estuaries is an important mechanism for trace element removal (Sholkovitz 1977). This is particularly true of Fe, which is a ubiquitous colloidal species and is removed at low salinities. Additional removal may occur by adsorption onto flocs, as demonstrated by mixing of organic-rich waters with seawater in the laboratory (Sholkovitz 1977).

Improvements in filtration techniques now allow separation of particles and colloids found in aqueous environments for studies of phase partitioning of U- and Th isotopes (Quigley et al. 2001). This has been crucial for studying the importance of particles and colloids for estuarine geochemistry. Previous studies isolated colloidal material using methods that were dependent upon the nature of the colloidal material, such as by adsorption on XAD resins. Isolation of colloidal material based on the molecular sizes from large volume water samples was developed using cross-flow ultrafiltration cartridges to investigate the size distribution of dissolved organic carbon and of trace metal carriers in coastal water (e.g., Moran and Moore 1989; Whitehouse et al. 1990; Baskaran et al. 1992; Swarzenski et al. 1995; Guo and Santschi 1996; Guo et al. 2000, 2001; Wen et al. 1997). Application of different ultrafiltration techniques that separate particles and colloids from dissolved species have been applied in a variety of hydrological and geochemical settings such as the Amazon and the sub-arctic boreal Kalix River system (Swarzenski et al. 1995; Porcelli et al. 1997; Andersson et al. 2001).

A comprehensive discussion of ultrafiltration methods is given by Buffle and van Leeuwen (1992). Generally, materials >0.45 μm are first separated using conventional filtration techniques and are considered "particles." A commonly used and effective method to further separate the filtrate has been cross-flow ultrafiltration, which uses high flow rates perpendicular to the filter surfaces to minimize buildup of excluded material on membrane surfaces. A portion of the sample passes through the membrane and this ultrafiltrate containing <1 kD or <10 kD material (here nominally referred to as "solutes") is collected separately. The remainder of the sample, along with colloids excluded from passage through the membrane, is recirculated until the ultrafiltered water that has passed through the walls of the fibers is ~90% of the initial sample volume. The remaining circulating sample, the colloid concentrate, contains colloids often enriched in concentration by ~10. After each sample is filtered, acid (and sometimes base) washes are circulated through the system to remove material trapped on the filter. These are retained separately for analysis and are sometimes assumed to contain only colloidal material. An experimental set-up for seawater Th is shown by Baskaran et al. (1992).

Several caveats should be considered in evaluating ultrafiltration data.

- The separation of colloids is set by operational criteria only. Filters are generally rated by the size exclusion of some globular macromolecule that may have a size of 1 kD to 10 kD. However, other molecules with different shapes may not be separated as predicted by their size alone, and this effect may vary between filtering systems and filter materials. A comparison between ultrafiltration systems for seawater analyses (Buesseler et al. 1996) found that there might be significant differences in the fraction of trace constituents that pass through the filters, depending upon the composition of the filter material. Therefore, while qualitative characteristics can be more readily considered, quantitative values for the association with colloids must be considered to be somewhat dependent upon operational conditions.

- The operational separation of colloids does not directly identify the nature of the colloid fraction, which may consist of clays, Fe and Mn oxyhydroxides, or

organic compounds such as humic and fulvic acids. Colloids may directly bind to trace elements, or, due to the very large specific surface area, adsorb constituents. The likelihood that the colloid fraction is often a complex mixture of components hampers relating ultrafiltration data to experimental data or thermodynamic calculations (see Gustafsson and Gschwend 1996). For example, Fe not only forms colloids but also combines with humic acids, so that it is often difficult to separate the association of these components with trace elements from field studies.

- The operational distinction between colloids and particles may not accurately describe inherent physico-chemical differences in surface sites and scavenging capabilities. Continuous aggregation/dissaggregation processes produce a particle size continuum (Baskaran et al. 1992; Gustafsson and Gschwend 1996; Gustafsson et al. 2000a,b). For example, settling characteristics will vary considerably; dense mineral phases, such as Fe-Mn oxyhydroxides, will have higher settling velocities while more loosely associated organic aggregates that might be considered part of the colloid pool may remain as non-settling material.

- Comparison between the inventories in the collected fractions (the colloidal and ultrafiltered fractions) and in the starting sample often indicate that there are losses of nuclides on to the ultrafiltration cartridge. These are largely recovered by subsequent acid rinses of the ultrafilters and filtration system. It is not clear whether the recovered abundances should be considered part of the colloids retained by the filter, or solutes that have adsorbed in the system (Gustafsson et al. 1996; Andersson et al. 2001), even though test experiments with colloidally-bound ^{234}Th showed significant losses in the ultrafiltration system (Baskaran et al. 1992.)

Overall, colloids appear to play a fundamental role in the behavior of radionuclides and trace elements, and while ultrafiltration data must be treated with some caution, it provides valuable information. Other methods may soon be developed to directly address some of these difficulties, although for species such as Th, processing sufficient volumes of material for analysis will continue to remain a major challenge.

2. URANIUM

The marine geochemistry of uranium has been studied for several decades, although more recently progress has been made in understanding geochemical reactions in the estuarine environment that greatly impact the terrestrial flux of uranium to the ocean. Some of the first determinations of uranium in the marine environment dates back to the 1930's (Hernegger and Karlik 1935; Föyn et al. 1939). Although the uranium data for the open ocean displayed a large range in concentration it was suggested that "coastal seawater," with lower salinity, showed lower concentration of uranium compared to seawater from the open ocean (Föyn et al. 1939). Holland and Kulp (1954) reviewed the status of the knowledge of uranium in the marine environment and suggested that there was a need for improvement in the determination of uranium concentration in river and ocean water to be able to obtain a quantitative understanding of the geochemical cycling of uranium. However, it was not until the 1960's that an "oceanic average" for the uranium concentration became generally accepted (Burton 1965). In contrast to uranium concentrations, reported (^{234}U/^{238}U) activity ratios for open ocean waters showed less variation and with a value of about 1.15 (Koide and Goldberg 1964), a value earlier suggested from the study of marine carbonates (Thurber 1962). Determination of uranium in river and brackish water from the Baltic Sea showed a general correlation between

salinity and U and it was also suggested that U was being removed when uranium (VI) is reduced to uranium (IV) in anoxic waters (Koczy et al. 1957). It was not until the late 1970's that studies of uranium estuarine chemistry continued (Martin et al. 1978a,b).

2.1. U in seawater

Uranium appears to behave conservatively in oxygenated seawater because of the formation of a variety of stable and soluble uranyl (U^{6+}) carbonate complexes (Langmuir 1978; Djogic and Branica 1991), and so there are no strong associations with particles or colloids. The uranium concentration in seawater, normalized to a salinity of 35, is 13.60 nmol/kg (Chen et al. 1986) and the residence time is estimated to be in the range of 0.2 to 0.4×10^6 years (Ku et al. 1977). The activity ratio ($^{234}U/^{238}U$) is higher than secular equilibrium and appears to be constant, with a value of 1.144 (Chen et al. 1986; Cheng et al. 2000). This reflects the process of α-recoil during weathering and preferential release of ^{234}U into continental waters, which keep seawater above secular equilibrium. When examining uranium behavior during estuarine mixing, the seawater component can be considered well defined in uranium concentration as well as ($^{234}U/^{238}U$) ratio.

2.2. River water U inputs

The characteristics of riverine U are reviewed in Chabaux et al. (2003). Continental weathering releases the naturally occurring U isotopes ^{238}U, ^{235}U and ^{234}U to solution in oxidizing environments. Uranium is transported to the ocean by rivers and the riverine uranium concentrations vary considerably between different river systems, with an average value of about 1.3 nmol/L (Bertine et al. 1970). This value was later confirmed by a study of more than 250 rivers (Palmer and Edmond 1993). However, it was concluded that the world average river concentration was biased by very high levels observed in the Ganges-Brahmaputra and Yellow Rivers. In a recent study another 29 rivers were added, but these new data do not significantly change the world average river value of about 1.3 nmol/L (Windom et al. 2000). The ($^{234}U/^{238}U$) activity ratios in river waters also show large variations, mainly related to weathering intensity, with values close to equilibrium when intense weathering prevails (Osmond and Ivanovich 1992). Overall, due to large differences both in U concentration and ($^{234}U/^{238}U$) activity ratio between different rivers, the freshwater component can vary substantially between different estuaries.

A study of the Kalix River in northern Sweden monitored seasonal chemical changes. During times of increased discharge, many inorganic constituents are diluted by factors of up to 4 (Ingri 1996). However, U concentrations fall in a much more restricted range, probably due to buffering of U-bearing organic deposits in the watershed (Porcelli et al. 1997). In contrast, the isotopic composition to U varies significantly (Andersson et al. 1995). It is clear that the river and estuary must be sampled simultaneously in order to define the relevant estuarine river inputs (see Swarzenski and McKee 1998).

2.3. U behavior in estuaries

Thorough reviews of U data from the estuarine and coastal zone by Cochran (1992) and Moore (1992) established that different estuarine systems behave differently and that chemical reactions in the estuary may affect the flux of uranium through the system. Early studies of U behavior from the Zaire (Martin et al. 1978a), Gironde, France (Martin et al. 1978b), the Narbada, Tapti and Godavari estuaries, India (Borole et al. 1977; Borole et al. 1982), and estuaries in the UK (Toole et al. 1987) suggest that U behaves conservatively at these locations. In contrast, examples of substantial removal were found in the Ogeechee and Savannah Rivers in Georgia (USA) (Maeda and Windom 1982), and were attributed to precipitation of iron and manganese and/or flocculation of organic matter during low river discharge. In the low-salinity zone of the Narbada estuary in

India (Borole et al. 1982) and the Forth estuary in the UK (Toole et al. 1987), non-conservative behavior of uranium was also demonstrated. In the Amazon estuary, uranium showed elevated concentrations compared to simple mixing (McKee et al. 1987). Release of uranium from bottom sediments on the shelf was suggested to be a source of dissolved (<0.4 μm) uranium. However, subsequent studies in the Amazon also demonstrated that U removal (Fig. 3) occurred at salinities <12 (Swarzenski et al. 1995, Swarzenski et al. 2003). Overall, it was established that the behavior of U is highly variable; examples have been found of conservative behavior as well as both additions and removal of U by interaction with sediments.

The extensive review by Moore (1992) concluded that a better understanding of U estuarine behavior was central to establishing a quantitative budget for the ocean. It was also stressed that the transport of U on colloids and particles and on authigenic coatings on larger particles might be of importance for the estuarine behavior of U. Improved analytical techniques to measure low uranium concentrations and high precision
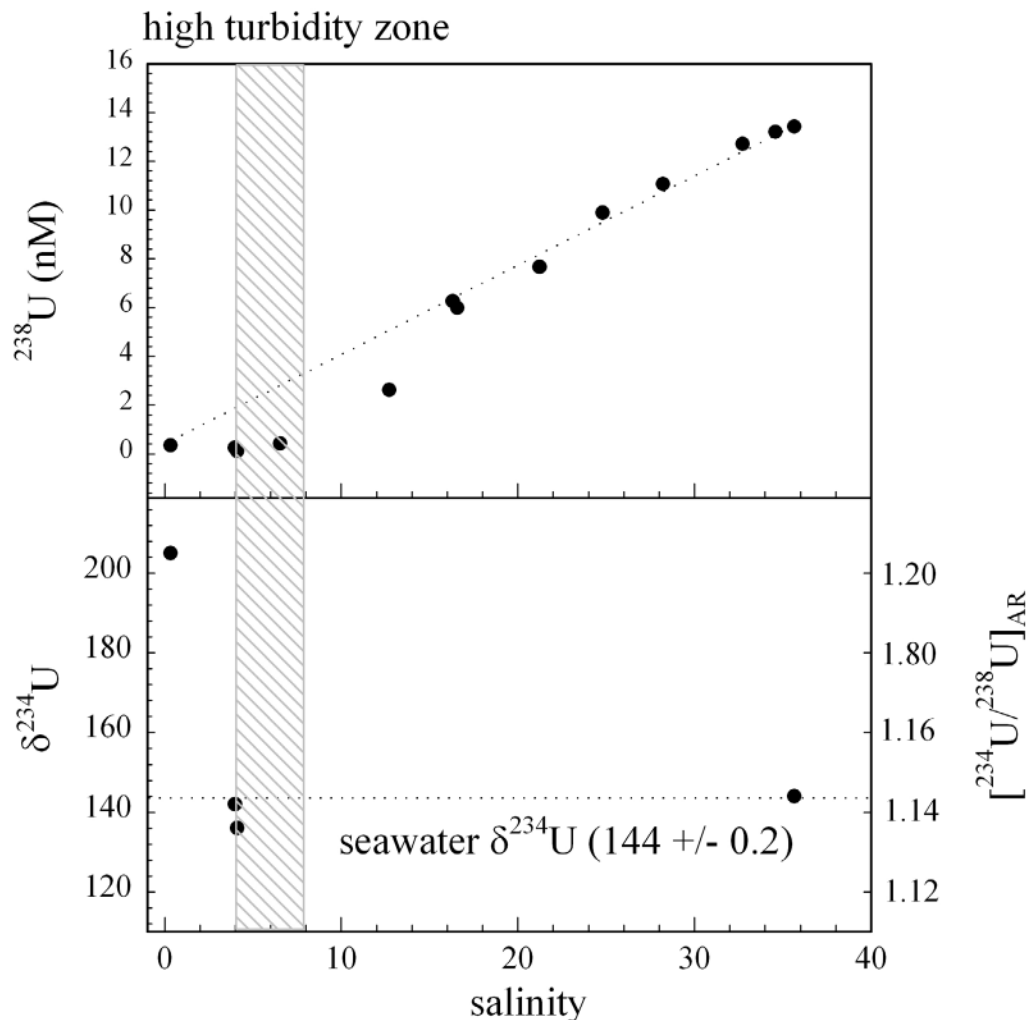

Figure 3. The concentration of uranium (nM) versus salinity on the Amazon Shelf with an ideal dilution line drawn through the riverine and seawater end members. Removal of dissolved U is evident at salinities that range from 0 to 16. The bottom illustration shows $\delta^{234}U$ as a function of salinity for the same waters on the Amazon Shelf. A seawater value (144 ± 0.2) is rapidly reached at a salinity of 4 during estuarine mixing. The high turbidity zone of the water column is defined by the greatest suspended particulate concentrations. Data from Swarzenski et al. (2003).

determination of $(^{234}U/^{238}U)$ activity ratios were suggested to be essential for a better understanding of the U estuarine behavior. During the 1990's, studies of uranium during estuarine mixing continued. In the Mahanadi River-estuarine system in India, (Ray et al. 1996) and from the sediment-rich Fly River estuary of Papua New Guinea, uranium appears to exhibit reasonably conservative behavior (Swarzenski et al. 2003).

The Ganges-Brahmaputra River system supplies about 10% of the estimated global river flux of dissolved U. Non-conservative behavior, with removal of U during low discharge, was reported in the low salinity region, with <12 salinity, of the Ganges-Brahmaputra mixing zone (Carroll and Moore 1994) as well as in the nearby Hooghly estuary (Somayajulu 1994). It was suggested that U removal occurs in the organic-rich sediments of the mangrove forest due to redox processes but no detailed removal mechanism was presented (Carroll and Moore 1994).

In the Delaware and Chesapeake estuaries (USA), uranium shows distinctly non-conservative behavior at salinities <5 (Sarin and Church 1994; Church et al. 1996). This was suggested to be due to sedimentary redox processes in the extensive salt marshes in the Delaware and Chesapeake bays. From mass balance calculations it was concluded that almost two-thirds of the uranium in the tidal waters were retained in the sediments. It was also suggested that, extrapolated globally, uranium removal in salt marshes and marine wetlands, including mangroves, are important sinks for U that may responsible for up to 50% of the total marine removal (Church et al. 1996). Removal of U is also observed within the Baltic Sea, related to the association of U with colloids (see Section 2.5).

In contrast, U within surface waters of the Mississippi shelf-break region predominantly displays conservative behavior. U behavior therefore is not foremost controlled by traditional sorption and/or desorption reactions involving metal oxides or colloids. Mixing of the thin freshwater lens into ambient seawater is largely defined by wind-driven rather than physical processes. As a consequence, in the Mississippi outflow region uranium removal is evident only during anomalous river discharge regimes (Swarzenski and McKee 1998).

2.4. Uranium removal to anoxic sediments

There are a few estuarine environments where seasonal anoxia exists and it is important to review the behavior of U in those environments (Cochran et al. 1986; Barnes and Cochran 1990, 1993). Reduction of U(VI) to insoluble U(IV) during diffusion across the sediment-water interface in organic-rich reducing sediments has been suggested to be a major sink of uranium in the ocean (Klinkhammer and Palmer 1991). Accumulation of uranium in organic rich anoxic sediments has been documented from anoxic basins around the world (Cochran 1992). U oxidation/reduction processes are also possible in a water column. Examination of the behavior of uranium isotopes in estuarine waters of the Baltic Sea showed that in the periodically anoxic deep water from a depression in the central Baltic Sea has dissolved uranium concentrations that are depleted by up to 48% compared to those calculated assuming a linear relationship between salinity and U concentration (Löfvendahl 1987; Andersson et al. 1995). This removal is attributed to reduction of U(VI) to insoluble U(IV). Work done in Framvaren Fjord in southern Norway found that U in the water column was depleted in the anoxic waters below the oxic surface layer, but this depletion is initiated not at the redox boundary but at a maximum in microbial activity (McKee and Todd 1993) due to redox cycling of Fe and Mn carriers (Swarzenski et al. 1999a,b). However, direct measurements of U oxidation states (Anderson 1987; Anderson et al. 1989; Swarzenski et al. 1999b) indicated that U remains mostly in the U(VI) form, implying that U reduction likely requires catalysis on sedimentary surfaces.

2.5. Importance of particles and colloids for controlling estuarine uranium

Several studies have examined the partitioning of U on particles and colloids. Results from detailed sampling and particle separation in the Amazon estuary shows that most of the uranium at the Amazon River mouth is associated with particles (>0.4 μm) and that >90% of the uranium in filtered water (<0.4 μm) is transported in a colloidal phases (from a nominal molecular weight of 10 000 MW up to 0.4 μm) (Swarzenski et al. 1995; Moore et al. 1996). Mixing diagrams for uranium in different size fractions in the Amazon estuary reveal that uranium in all size fractions clearly display both removal and substantial input during mixing.

Concentrations of colloidal U comprise up to 92% of the dissolved U fraction at the river mouth and attain highest values in the productive, biogenic region of the Amazon shelf (salinities above approximately 20). Both colloidal and dissolved (i.e., passing through ultrafilters) phases are highly nonconservative relative to ideal dilution of river water and seawater, indicating extensive removal at salinities below approximately 10. Saltwater-induced precipitation and aggregation of riverine colloidal material is most likely the dominant mechanism of U removal in the low salinity region of the Amazon shelf. There is evidence of a substantial colloidal U input (approximately 245% of the riverine colloidal U flux) into surface waters above a salinity of 5. Such enrichment of colloidal U most likely is the result of colloidal U-rich porewater advection, or U diffusion within the porewaters, from the seabed and fluid muds or shelf-wide particle disaggregation. The colloidal fraction rapidly becomes less significant and at salinities approaching 35 only about 15% of the uranium is in the colloidal phase.

The Kalix River drains into the Baltic Sea, which is a broad, shallow estuarine environment, with relatively gradual and stable salinity gradients. The Kalix River estuary and the Baltic Sea have been subject to a comprehensive research program on a variety of uranium series radionuclides (Andersson et al. 1995, 1998, 2001; Porcelli et al. 1997, 2001). At the river mouth the uranium transport is also found to be dominated by particles (>0.45 μm) and >90% of the uranium in the filtered water is also associated with a colloidal phase (3 kD – 0.2 μm) (Porcelli et al. 1997; Andersson et al. 1998; Andersson et al. 2001). Upon entering the estuary, the colloidal fraction still dominates at low salinities, with >80% at about a salinity of 1, but rapidly becomes less significant and at salinities of about 3 the colloid-bound uranium is insignificant (Fig. 4). A closer examination of the uranium concentration in unfiltered water, along with 0.2 μm- and 3 kD- filtered waters from the Kalix River estuary low salinity zone (0 to 3) all show linear trends that seem to reflect simple conservative mixing (Fig. 4), and this is confirmed using U isotope variations (see Section 2.6 below). The uranium concentrations in the filtered water are lower than those in the corresponding unfiltered waters and the uranium concentration increases with salinity but the difference between the different size fractions is less than 5% at a salinity of 3. The rapid decrease of colloid-bound U indicates that U desorbs rapidly from the colloidal carriers due to decreasing colloid concentration and the stabilization of dissolved uranyl carbonate complexes in the estuary (Andersson et al. 2001). The observation that the U concentration in the Kalix River water is above the extrapolated freshwater input to the estuary, implied by the conservative mixing relationships, suggest that there must be removal at very low salinities so that the freshwater input falls upon the mixing lines for low salinity waters. It is likely that during initial estuarine mixing, riverine uranium associated with Fe-organic rich colloids, is removed. This removal is due to colloidal aggregation into larger particles that can sink on a short time-scale. Note that U removal is not likely to occur due to adsorption onto inorganic colloids, as adsorption is diminished in higher ionic strength waters. Rather, U is likely removed as U-humate complexes discharged from the
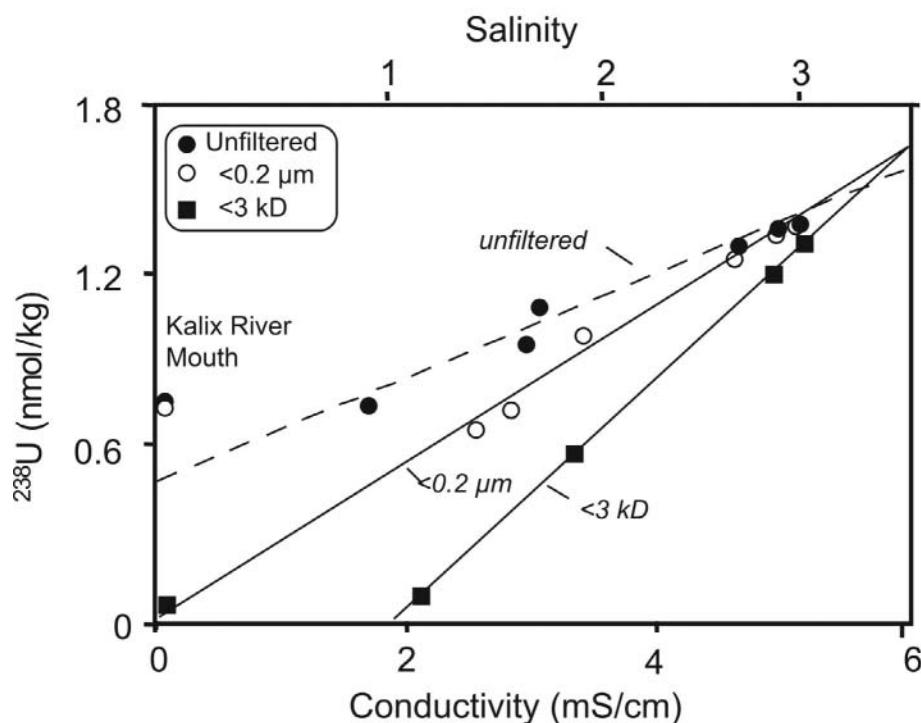
Figure 4. The uranium concentration in unfiltered water, 0.2 µm and 3 kD filtered water in river water from the Kalix River mouth and samples from the low salinity estuarine zone (0-3). Data plotted against conductivity (although the salinity scale is not defined below 2, a tentative scale is indicated). The lines represent the best fit for each fraction in the estuary. The data from the Kalix river mouth represent the river water component, which show <10% annual variation in concentration. The analytical errors are smaller than the symbols. Data from Andersson et al. (2001). Copyright 2001 Elsevier Science.

Kalix. This is consistent with the suggestion of Mann and Wong (1993) that the speciation of U may be important for estuarine behavior, based upon evidence that a significant fraction of U in coastal waters with relatively high concentrations of DOC were associated with organic matter. Concurrently, there is also desorption and re-association to other colloidal carrier phases, probably other organic phases such as humic substances (Andersson et al. 2001), but which do not cause further U removal. The results from the Kalix River estuary show that uranium adsorbs and desorbs from a variety of colloidal carrier substances that alternately dominate at different stages during river – estuarine mixing.

Evidence for the association of U with humic acids has been documented elsewhere. Dearlove et al. (1991) showed that U concentrated by ultrafiltration techniques from organic-rich groundwater samples were associated with humic colloids. Humic and fulvic acids have been shown to strongly complex U. Lienert et al. (1994) modeled the distribution of U species in the Glatt River and concluded that U-humate complexes become important at pH < 6.8. These results reinforce the conclusions in the estuarine studies that U humate and fulvate complexes may account for the association of U with colloids.

2.6. The (^{234}U/^{238}U) activity ratios in estuaries

Measuring the isotopic composition of U in estuaries has the potential for further constraining the interpretations of uranium behavior. However, this has been hampered by large uncertainties in conventional methods using counting techniques. While rivers often display (^{234}U/^{238}U) activity ratios above equilibrium, the ratios generally do not

represent a strong contrast to the value for the ocean, and due to the high oceanic U concentration, the isotopic composition of U in the estuaries rapidly approaches the value for the ocean. The development of mass spectrometric methods to obtain highly precise isotopic compositions has made it possible to document more subtle variations, and on smaller samples, than previously possible (Goldstein and Stirling 2003), and so examine U mixing, at least at low salinities. Mass spectromentric data are generally reported as per mil deviations from equilibrium, such that $\delta^{234}U=[((^{234}U/^{238}U_s)/(^{234}U/^{238}U_{eq}))-1]\times10^3$, where $(^{234}U/^{238}U_{eq})$ is the secular equilibrium ratio of 1 and $(^{234}U/^{238}U)_s$ represents the measured ratio in the sample.

The first high-precision determination of $(^{234}U/^{238}U)$ ratios in estuarine waters were reported from the Baltic Sea and showed significant deviations from that of seawater detected at salinities as high as 12 (Andersson et al. 1995). Determination of $\delta^{234}U$ in filtered water, particles and colloids has revealed that particles, colloids and dissolved fraction show no isotopic differences between the different size fractions (Porcelli et al. 1997; Andersson et al. 1998; Andersson et al. 2001). The lack of significant variation in isotopic composition between different phases within samples demonstrates that substantial and rapid isotope exchange must occur between U in particles, colloids, and dissolved species in both river and estuarine waters. Note that significant isotopic differences were found by Dearlove et al. (1991) between colloid-bound and "solute" U in groundwaters, indicating that isotopic exchange between these U species was limited. A detailed examination of $\delta^{234}U$ in the Kalix River and estuary revealed that there were indeed small differences in isotopic composition between the different carrier phases, as well as in sinking material collected in sediment traps (Fig. 5). The bulk $\delta^{234}U$ decrease from high values in the river water to those approaching the seawater value at increasing

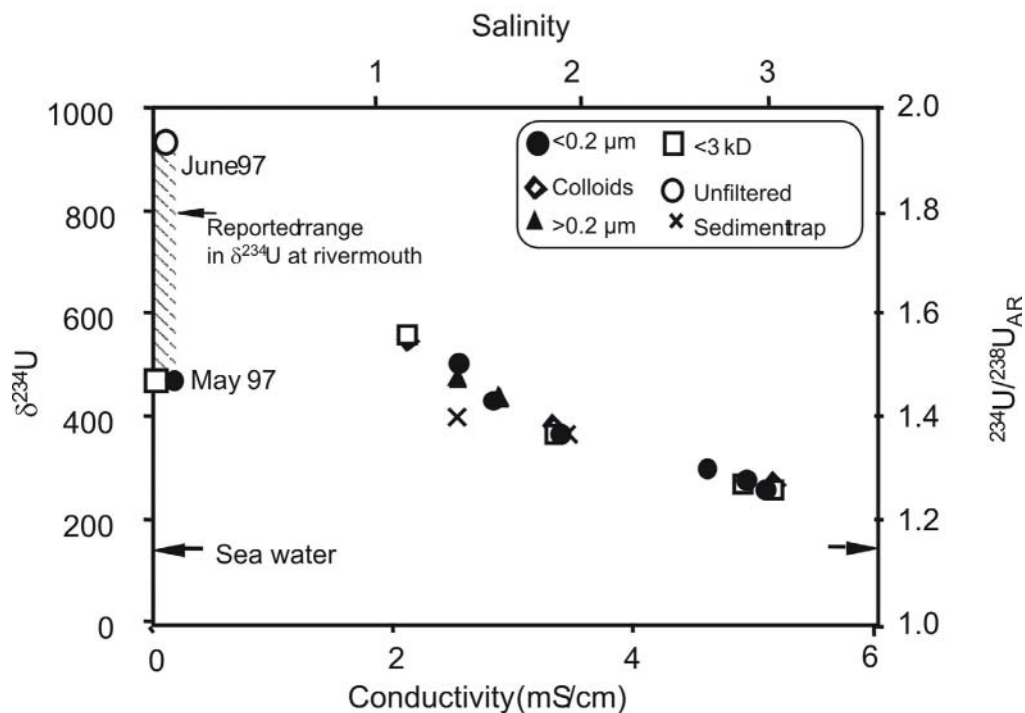**Figure 5.** The $\delta^{234}U$ in 0.2µm and 3 kD filtered water and colloids phase (3kD – 0.2µm) and particles (>0.2 µm) as well as material from sediment traps plotted versus conductivity in the low salinity zone (0-3) of the Kalix River estuary. The stippled area marks the reported annual range in $\delta^{234}U$ at the Kalix river mouth, which show a substantial variation compared to the uranium concentration. Data from Andersson et al. (2001). Copyright 2001 Elsevier Science.

salinities (Fig. 5). The δ^{234}U also indicate removal of uranium at very low salinities and was used to estimate the amount of uranium removal in the inner part of the Kalix River estuary and these data indicated a significant uranium loss of up to 50% (Andersson et al. 2001). The most important finding from the uranium isotope study is that continuous substantial and rapid isotopic exchange must occur between particles, colloids and dissolved phases in river water as well as during estuarine mixing (Andersson et al. 2001; Swarzenski et al. 2003). Such behavior cannot be readily inferred from the U concentration data alone (see Fig. 4).

3. THORIUM

Thorium is considered to be one of the most highly particle reactive radionuclides in natural waters. Therefore, it is efficiently removed from the dissolved (i.e., <0.4 μm) phase onto colloids and particulates during its residence time in aqueous systems. Thorium exhibits this affinity for particle surfaces in both fresh and marine waters. Therefore most of the thorium entering an estuary is already associated with particulates and colloids. Short-lived Th isotopes that do exist in the dissolved phase are largely produced from dissolved parents in an estuarine environment. Dissolved thorium will rapidly adsorb onto particles in the estuary and much of the thorium will be removed from the water column during estuarine mixing. In estuarine environments, thorium is of interest mainly as a tracer of sediment mixing and as a proxy for other particle-reactive species. There are six thorium isotopes in the naturally occurring uranium and thorium decay series. They are: ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ y), ^{230}Th (7.5×10^4 y), ^{228}Th (1.9 y), ^{234}Th (24.1 d), ^{227}Th (18.7 d) and ^{231}Th (1.1 d). All have been utilized in the estuarine environment with the exception ^{227}Th and ^{231}Th, which not only have relatively short half-lives but also low abundances, making measurement of these isotopes difficult. The most commonly applied estuarine tracer is ^{234}Th.

3.1. ^{234}Th

^{234}Th is produced by ^{238}U, which is present in low concentrations in river waters; therefore most of the ^{234}Th found in estuaries is supplied either in situ or from ocean water. The first ^{234}Th measurements in coastal waters revealed increased removal from dissolved to particulate phase with increasing proximity to shore (Bhat et al. 1969).

The residence time of ^{234}Th, with respect to removal by scavenging, can be calculated by assuming that the dominant source of ^{234}Th is by decay of in situ ^{238}U (Kaufman et al. 1971; Porcelli et al. 2001)

$$^{234Th}\tau_{SED} = {}^{234Th}\tau \left/ \left[\left(\frac{^{238}U}{^{234}Th} - 1 \right) \right] \right. \tag{1}$$

where $^{234Th}\tau = 1/\lambda_{234Th}$ is the mean life of ^{234}Th. Some of the first ^{234}Th estuarine measurements where made in Long Island Sound by Aller and Cochran (1982) to determine sediment mixing rates. These authors further examined the (^{234}Th/^{238}U) activity ratios in the water column of Long Island Sound to derive residence times on the order of 1-10 days.

In more recent studies, Feng et al. (1999) calculated a Th water column residence time of 2 to 12 days in the Hudson River estuary. McKee et al (1986b) determined that ^{234}Th was removed on a time scale of a day or less in the very particle-rich environment of the Yangtze River estuary. In the Amazon River estuary, another particle-rich environment, McKee et al. (1986a) determined that the residence time of dissolved ^{234}Th ranged from 2 to 4 days. McKee et al. (1986a) also calculated apparent distribution

coefficients between particulate and water in the Amazon that were much lower than expected. These low distribution coefficients implied that soluble and particulate phases of [234]Th are not in equilibrium because particle residence times are short relative to sorption times of [234]Th. McKee et al. (1986b) found locations with the shortest dissolved [234]Th residence times due to high turbidity had the longest particle residence times due to resuspension. Honeyman and Santschi (1989) suggested that the relatively slow sorption rates are due to a two-step process, sorption onto colloids coupled with colloid aggregation, in which colloid aggregation was the rate-limiting step. Moore et al. (1996) found 40-90% of the soluble phase [234]Th in the Amazon shelf waters is in the colloidal fraction. In contrast, in the Baltic, high ([234]Th/[238]U) ratios indicate that the residence time of [234]Th with respect to particle removal is long (~50 days), largely due to low particle and colloid concentrations (Porcelli et al. 1997).

Baskaran and Santschi (1993) examined [234]Th from six shallow Texas estuaries. They found dissolved residence times ranged from 0.08 to 4.9 days and the total residence time ranged from 0.9 and 7.8 days. They found the Th dissolved and total water column residence times were much shorter in the summer. This was attributed to the more energetic particle resuspension rates during the summer sampling. They also observed an inverse relation between distribution coefficients and particle concentrations, implying that kinetic factors control Th distribution. Baskaran et al. (1993) and Baskaran and Santschi (2002) showed that the residence time of colloidal and particulate [234]Th residence time in the coastal waters are considerably lower (1.4 days) than those in the surface waters in the shelf and open ocean (9.1 days) of the Western Arctic Ocean (Baskaran et al. 2003). Based on the mass concentrations of colloidal and particulate matter, it was concluded that only a small portion of the colloidal [234]Th actively participates in Arctic Th cycling (Baskaran et al. 2003).

[234]Th has been widely used to determine sediment mixing rates on a time scale of a few months. In an early study, (Aller and Cochran 1976) determined that the top 4-5 cm of sediment were mixed based on the [234]Th profile in Long Island Sound. More recently, Fuller et al. (1999) found [234]Th in sediments to a depth of up to 10 cm. Other sediment mixing rate calculations were made in the New York Bight, the Yangtze estuary (McKee et al. (1983), the Amazon estuary (McKee et al. 1986b) and Narragansett Bay (Santschi et al. 1979).

McKee et al (1983) used [234]Th to determine short-term deposition rates from the Yangtze River. The sediment [234]Th activity profiles were determined to largely reflect deposition because radiographs revealed distinct layers that would not exist if the sediment was mixed, and so could be used to calculate that deposition was on the order of 4.4 cm per month. However, this did not agree with long-time scale tracers. Therefore, it was suggested that winter storms periodically erode the sediment and transport it elsewhere reducing the long-term accumulation rates.

In the Amazon River estuary, DeMaster et al. (1986) determined [234]Th seabed inventories were in excess of those produced in the overlying water column. They suggest the excess [234]Th was probably supplied by lateral transport of offshore water. However, Moore et al. (1996) found that [234]Th seabed inventories were only in excess with respect to production on the outer portion of the Amazon shelf in the absence of nearbed high-concentration suspensions (i.e., fluid mud). Smoak et al. (1996) further found a large percentage of the excess inventory in the Amazon estuary is in the thick fluid mud layer and not immediately incorporated into the seabed. The distribution of [234]Th in the Amazon estuary therefore appears to be related to the formation and redistribution of the fluid-mud layer (Smoak et al. 1996), which is a function of the spring-neap tidal cycle dynamics (Kineke et al. 1996).

3.2. ^{228}Th

^{228}Th has a half-life of 1.91 years and is produced from ^{228}Ra, with ^{228}Ac as a very short-lived intermediate daughter. The first detailed investigations on the distribution of ^{228}Th in the coastal and open ocean was published by Broecker et al. (1973). They showed that the median activity ratio of (^{228}Th/^{228}Ra) was 0.5, corresponding to a mean removal time with respect to transport into sediments of 2.7 years. ^{228}Th can be used like ^{234}Th for sediment mixing studies, although on a somewhat longer time scale. However, the generation and release of ^{228}Ra ($t_{1/2}$ = 5.7 yr) in an area of sediment mixing complicates interpretations (Cochran 1992). ^{232}Th produces ^{228}Ra within the underlying sediment which in turn is readily dissolved (when recoiled into the pore water) and migrates towards the sediment-water interface where daughter ^{228}Th then accumulates. Therefore, surface sediment has a distinct (^{228}Ra/^{228}Th) ratio. Hancock (2000) used the release of Ra from the seabed to examine resuspended sediment in the Bega River estuary, Australia, where the (^{228}Th/^{232}Th) ratio was used to distinguish resuspended sediment from recent river sediment.

3.3. Long-lived Th isotopes-^{232}Th and ^{230}Th

While various studies have examined the behavior of long-lived Th isotopes in the oceans (see Cochran 1992), there is still comparatively little data for rivers and estuaries. Moore (1967) published the first values for ^{232}Th concentrations in two major rivers, the Amazon and Mississippi. The ^{232}Th concentrations were found to be an order of magnitude higher than that of Atlantic Ocean water, although it was noted that Th on particulates may not have been completely excluded in the analyses. Other data for filtered ^{232}Th in rivers are very limited (Andersson et al. 1995), and it is generally assumed that all the Th is on fine particles. Colloids and ferro-oxyhydroxides can be important for riverine U transport (Porcelli et al. 1997; Andersson et al. 1998), and are also possible carriers of Th (Viers et al. 1997). In general, non-particulate Th has been found in concentrations above the solubility of thorianite (Langmuir and Herman 1980), and so is generally dominantly present on colloids (Porcelli et al. 2001).

There is little data on the estuarine behavior of long-lived, river-supplied Th isotopes, although very little Th is likely to enter the ocean from rivers, as much is removed in the estuary. More recently, mass spectrometric methods have allowed the high precision measurements of ^{232}Th and ^{230}Th in low concentration aqueous samples (Chen et al. 1986; Guo et al. 1995). This method was employed by Andersson et al. (1995) in the Baltic Sea estuarine environment. They found ^{232}Th decreased very rapidly between salinities 0 and 5 and at a salinity of about 7 approaches the level found in seawater. A large portion of ^{232}Th transported by rivers is removed as soon as the river water enters the estuarine environment. Andersson et al. (1995) also found unusually high (^{230}Th/^{232}Th) ratios that suggested different behavior between ^{230}Th and ^{232}Th, although lower ratios were found in samples from the same locations in a later study (Porcelli et al. 1997). The reasons for the differences between these two studies is unknown. At higher salinities further into the Baltic, ^{232}Th concentrations are much lower, and the ^{232}Th budget is dominated by eolian inputs, with river-borne ^{232}Th largely lost to sediments at discharge points. Sedimentation rates calculated from the water column data are compatible with measured sedimentation rates (Porcelli et al. 1997). It was also found that a substantial fraction of the ^{232}Th was on particles. Values of (^{234}Th/^{232}Th) activity ratios in unfiltered water and on particles are similar, indicating that there is isotopic equilibrium of Th in particles and "dissolved" phases.

The association of Th with colloids may be an important precursor to incorporation in sedimenting particles (Honeyman and Santschi 1989). There is limited data available

regarding the distribution of ^{232}Th on colloids. In the Baltic, only a small fraction of the ^{232}Th appears associated with colloids at low salinities, since 85% of the ^{232}Th not on particles passed through the ultrafilter (Porcelli et al. 2001). In contrast, Baskaran et al. (1992), found that a dominant fraction of the Th in coastal waters of the Gulf of Mexico are associated with colloids. Mass balance calculations indicated that the terrigenous silicate-derived colloids (which are not expected to readily exchange Th with surrounding species) accounted for only <6% of the total colloidal mass concentration, implying that >94% is of biogenic origin that may have Th on more exchangeable surface sites. Kersten et al. (1998) used model calculations to estimate that 98% of the ^{234}Th in waters of Mecklenburg Bay in the southern Baltic is colloid-bound. Overall, it appears that the extent to which Th is associated with colloids can vary substantially.

A survey of available ^{232}Th data for the ocean basins demonstrated that the highest concentrations are found nearer to the coasts, and it was concluded that while eolian inputs likely dominated the budget in the open ocean and could account for increases near the coast, fluvial inputs may be more important in coastal regions. This implies that some a mechanism causes recycling of Th that has been removed to estuarine sediments (Huh et al. 1989). A study of an ice-covered region of the western Arctic Ocean found that significant amounts of ^{230}Th and ^{232}Th were advected into the basin (Edmonds et al. 1998). Therefore, it appears that while long-lived Th isotopes are rapidly removed into estuarine sediments, transport into the ocean basins may continue.

4. RADIUM

In the U- and Th-decay series there are four naturally occurring radium isotopes: ^{223}Ra, ^{224}Ra, ^{228}Ra and ^{226}Ra with half-lives that coincide well with the time scales of many coastal and oceanic processes (Swarzenski et al. 2001). The historic discovery of radium in 1898 by Marie Curie initiated a remarkable use of this element as an early oceanic tracer. Less than ten years after its discovery, Joly (1908) observed elevated ^{226}Ra ($t_{1/2}$ = 1600 years) activities in deep-sea sediments that he attributed to be the result of water column scavenging and accumulation of Ra in sediments. This hypothesis was later challenged with the first seawater ^{230}Th measurements, which indicated that ^{226}Ra in the sediments was due to production by scavenged parent ^{230}Th (Broecker and Peng 1982), and these new results confirmed that radium was instead actively migrating across the sediment-water interface into the overlying water. This seabed source stimulated much activity to use radium as a tracer for ocean circulation. Unfortunately, the utility of Ra as a deep ocean circulation tracer never came to full fruition, since biological cycling has been repeatedly shown to have a strong and unpredictable effect on the vertical distribution of this isotope. In addition to diffusion across the sediment – water interface into the ocean, Ra also has a riverine source, although in most marine environments the riverine flux is insignificant in the overall mass balance (Cochran, 1982). The short-lived Ra isotopes of the ^{232}Th series, which are highly depleted in the ocean basins due to their rapid decay and the strong depletion in parent Th isotopes, have been used to track advection from the coasts. Because of the 5.7 year half-live of ^{228}Ra, this isotope has been used effectively to estimate oceanic horizontal eddy diffusivities and coastal water residence times over timescales of less than 30 years. By using both ^{228}Ra and ^{224}Ra ($t_{1/2}$ = 3.7 days), timescales of less than 10 days can be investigated.

4.1. Ra behavior in estuaries

Two important geochemical characteristics make Ra isotopes potentially useful as an estuarine tracer: 1) having highly particle reactive Th isotopes residing largely in sediments as its direct radiogenic parents, which ties Ra directly to bottom sediments, and 2) exhibiting vastly different environmental behavior in fresh water and saltwater systems.

Both of these criteria control the production and input of radium in coastal systems. In coastal waters, Th is efficiently scavenged by colloids and particles, and rapidly removed to the seabed. In fresh water, radium is bound strongly onto particle surfaces; however, as the ionic strength of a water mass increases during mixing into seawater, desorption occurs and Ra is released. Therefore, Ra exhibits strongly nonconservative behavior in estuaries, with data generally falling above a mixing line between river and seawater (Li and Chan 1979; Ghose et al. 2000). This same process of ^{226}Ra release from underlying sediments permits the use of Ra as a useful water mass tracer, if one can identify and constrain water column re-distribution processes (Cochran 1982). For example, Ra behavior in estuaries can be complicated by involvement in biological cycles (Moore and Dymond 1991; Carroll et al. 1993). Estuarine sediments, enriched in Th outside crystal lattices of detrital material, provide a continuous source to coastal waters of Ra isotopes, which are supplied according to production rates that are defined directly by parent isotope decay constants (Burnett et al. 1990; Moore and Todd 1993; Webster et al. 1995; Hancock et al. 2000). Source functions for Ra in an estuary may thus include the following components: (1) riverine, (2) oceanic, (3) estuarine sediments and (4) groundwater (Miller et al. 1990; Bollinger and Moore 1993; Rama and Moore 1996; Moore 1996; Torgersen et al. 1996; Sun and Torgersen 1998). The relative significance of each of these source terms is defined by the particular environmental constraints of an estuary.

The distribution of Ra and Th isotopes in the Kalix Sea estuary and the surrounding Baltic Sea was studied by Porcelli et al. (2001). The activities of ^{226}Ra in the Baltic are generally greater than either bulk river inputs, as represented by the Kalix River, or Atlantic surface seawater. Therefore, a source of ^{226}Ra in addition to the inflow of these sources is required. Interestingly, Ba/^{226}Ra ratios are below a conservative mixing line between Kalix River water and Atlantic surface seawater; this requires that the additional source of ^{226}Ra has a relatively low Ba/^{226}Ra ratio. The (^{228}Ra/^{226}Ra) ratios in the Baltic fall within a narrow range (1.2-1.7) and are comparable to that of the Kalix (1.3) and that of average crust. This actually poses a problem, since the residence time of water (and so of conservative elements like Ra) in the Baltic (35 years) is substantially greater than the half-life of ^{228}Ra. Therefore, a supply of ^{228}Ra relative to ^{226}Ra is required to balance ^{228}Ra decay. While the absolute fluxes required for Ba and the Ra isotopes can be satisfied from sediments (or even by other rivers to the Baltic that may have higher concentrations), the fortuitous balance between Ra isotope ratios in the relatively long-lived waters of the Baltic and the surrounding continental rocks, is difficult to explain.

4.2. Ra as submarine groundwater tracer

The estuarine behavior of Ra has recently received much attention as coastal scientists begin to include a submarine groundwater discharge component in their mass balance models and estuarine studies. Much of this work has been pioneered by Moore (1996), who suggested that as much as 40% of the ^{226}Ra in the coastal waters of the South Atlantic Bight might be derived from exchange processes across the sediment-water interface, including submarine groundwater discharge. In a recent series of conceptual papers, Moore (1996, 1999) emphasized that it is necessary to extend the estuarine reaction zone to include "subterranean estuaries," a region at the land-sea margin where interstitial fluids, regardless of origin, are readily exchanged by a suite of physico-chemical processes with coastal bottom water. Moore and others concluded that many of the well-known reactions and processes are quite similar for surface and subterranean estuaries, and that a vigorous subsurface flux could introduce significant amounts of nutrients and other reactive constituents into the coastal ocean (Bokuniewicz 1980; Johannes 1980; Giblin and Gaines 1990; Lapointe et al. 1990; Valiela et al. 1990; Reay et al. 1992; Simmons 1992; Bugna et al. 1996; Cable et al. 1996a,b; Shaw et al. 1998;

Corbett et al. 1999; Krest et al. 2000; Swarzenski et al. 2001). By omitting such a subterranean component, the overall delivery of radionuclides during their transport out to sea might be significantly underestimated.

There is concern that nutrient-laden submarine groundwater discharge, whether from natural or anthropogenic sources, may contribute to coastal eutrophication (Burnett et al. 2002). Large-scale submarine groundwater discharge (SGD) is generally a widespread coastal phenomenon that can occur wherever hydrogeologic gradients enable lateral and upward groundwater transport to coastal bottom waters (Johannes 1980). There is an abundance of historic and recent evidence for global submarine groundwater discharge (Zektzer et al. 1973). "Leaky" land-sea margins where the discharge of submarine groundwater is likely to be enhanced include: karstic terrain (Back et al. 1979; Paull et al. 1990; Spechler 1994; Swarzenski et al. 2001), buried river channels (Chapelle 1997), geopressured and/or geothermal aquifers (Kohout 1967), and lagoons (Simms 1984; Martin et al. 2000).

Ra isotopes have proven to be one of the most effective tracers of large-scale groundwater flow into estuaries (Moore 1996; Moore and Shaw 1998; Yang et al. 2002). In natural groundwaters, the isotopic composition of Ra by various processes, including weathering and recoil from U- and Th-bearing phases, and adsorption (see Porcelli and Swarzenski 2003). Due to continuous inputs, the inventories of even very short-lived nuclides are maintained. Therefore, groundwaters may develop Ra isotopic compositions that are distinct from surface waters, and so provide a convenient tracer of groundwater supply into estuaries.

Submarine groundwater discharge, which can consist of recycled marine water or fresh water or a mixture thereof, may enhance the diffusive/advective flux of dissolved Ra from the seabed to a coastal water column wherever the hydraulic gradients and sediment transmissivities are favorable (Moore 1996). In coastal systems where groundwater is discharged to coastal waters either continuously or ephemerally due to tidal forcing, distinctive ^{228}Ra, ^{228}Th and ^{224}Ra activities can develop. This disequilibrium occurs because dissolved radium will be rapidly advected into the water column while thorium remains attached to bottom sediments (Webster et al. 1995). In surficial sediments that are flushed by the upward movement of groundwater, (^{224}Ra/^{228}Ra) activity ratios can become quite large as a result of this process and can be used to model the flux across the sediment/water interface (Rama and Moore 1996). Below this diagenetically active surface sediment layer, secular equilibrium is expected to develop from ^{232}Th down to ^{224}Ra. Such radioactive equilibrium in the ^{232}Th decay series requires approximately 20 years of sediment storage. Resuspension, bioturbation, and chemical dissolution, as well as groundwater flow, will allow these two sediment layers to interact. Moore and his colleagues have used such disequilibria to derive a ground-water flux rate in a South Carolina salt marsh (Bollinger and Moore 1993; Rama and Moore 1996).

To use the activity of excess ^{224}Ra in a water sample as a geochronometer for water movement or transport (i.e., residence times), one would write a mass balance equation as follows:

$$^{224}Ra_{obs} = {}^{224}Ra_i f_{EM} e^{-\lambda_{224}t} \tag{2}$$

and solving for time, *t:*

$$t = -\frac{\ln\left[\dfrac{{}^{224}Ra_{obs}}{{}^{224}Ra_i f_{EM}}\right]}{\lambda_{224}} \tag{3}$$

where λ_{224} is the decay constant for ^{224}Ra, 0.189 days^{-1}, ^{224}Ra$_i$ is the initial activity of ^{224}Ra in the water sample and f_{EM} is the fraction of the endmember remaining in the sample. Age determinations calculated in such a manner reflect the time elapsed since the water sample became enriched in Ra by the discharge of groundwater. ^{224}Ra is regenerated on the order of days. The fraction f_{EM} can be estimated either from salinity signal or from the distribution of ^{228,226}Ra isotopes, but this term can be difficult to constrain in non-two endmember systems. There are three basic assumptions that must be upheld to correctly apply this Ra model: 1) we can define a single value for the ^{224}Ra activity over the time of interest; 2) the endmembers can not change over the time period of interest; 3) there can be no inputs/sinks for Ra except for mixing and radioactive decay.

One can similarly write an equation to describe the change in activity ratios as a result of mixing and decay for ^{223}Ra and ^{224}Ra which yields (f_{EM} drops out):

$$\left[\frac{^{223}Ra}{^{224}Ra} \right]_{obs} = \left[\frac{^{223}Ra}{^{224}Ra} \right]_i \frac{e^{-\lambda_{223}t}}{e^{-\lambda_{224}t}} \tag{4}$$

This equation is particularly useful to derive apparent estuarine water mass ages (Fig. 6) because the term f_{EM} is removed. Using (^{223}Ra/^{224}Ra) isotope ratios in this manner is based on the assumption that the initial (^{223}Ra/^{224}Ra) activity ratio must remain constant. This conclusion is reasonable as the long-lived parent isotopes (^{231}Pa and ^{232}Th) have relatively constant activity ratios in sediments, and the intermediate Th isotopes (^{227}Th and ^{228}Th) are scavenged efficiently in the near-shore water column. The utility of Ra as
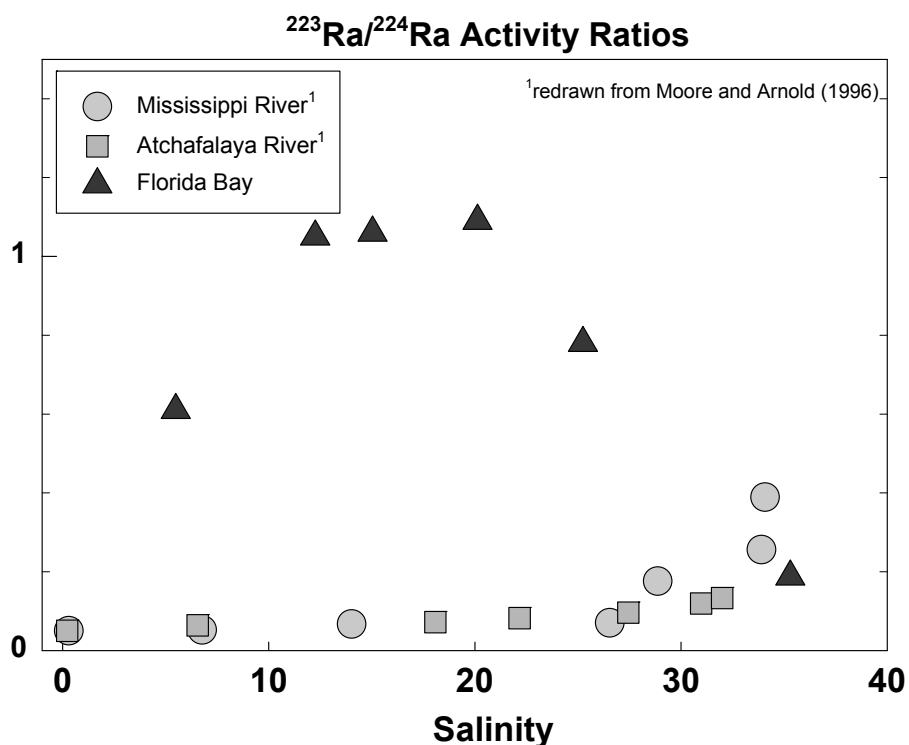

Figure 6. (^{223}Ra/^{224}Ra) activity ratios in three vastly contrasting estuarine systems: Florida Bay, and the Atchafalaya and Mississippi Rivers. Florida Bay waters, which overlie U-rich sediments, contain much higher (^{223}Ra/^{224}Ra) activity ratios than other estuaries. The increased (^{223}Ra/^{224}Ra) values observed at high salinities in the Mississippi/Atchafalaya systems indicate preferential decay of the shorter-lived ^{224}Ra over ^{223}Ra during estuarine mixing.

an accurate coastal groundwater discharge tracer has to be carefully evaluated to assure realistic flux estimates (see Porcelli and Swarzenski 2003). This validation is best accomplished by incorporating a suite of complementary tracers (e.g., [222]Rn, CH$_4$) and other techniques (e.g., streaming resistivity surveys) into coastal Ra mass balance studies.

5. RADON-222

Although there are three Rn isotopes in the U- and Th-decay series, only [222]Rn is sufficiently long lived ($t_{1/2}$= 3.8 days) to be a useful estuarine tracer. Radioactive decay of [226]Ra continuously produces [222]Rn, which because of its short half-life is generally in secular equilibrium in seawater. Being chemically non-reactive except for very weak Van der Waals bonding makes this isotope a unique marine tracer in that it is not directly involved in biogeochemical cycles.

There are two main sources of [222]Rn to the ocean, (1) the decay of sediment-bound [226]Ra and (2) decay of dissolved [226]Ra in the water column. Radon can enter the sediment pore water through alpha recoil during decay events (see discussion in Porcelli and Swarzenski 2003). Since radon is chemically inert, it readily diffuses from bottom sediments into overlying waters. The diffusion of radon from sediments to the water column gives rise to disequilibrium between [222]Rn and [226]Ra, with ratios of ([222]Rn/[226]Ra) >1 due to the addition of excess [222]Rn. This excess [222]Rn is unsupported and so is rapidly diminished by decay. Therefore, the excess [222]Rn signal is only resolvable where significant transport of [222]Rn away from the sediment can occur over timescales that do not significantly exceed the half-life of [222]Rn.

Loss of radon in the ocean occurs typically through radioactive decay (producing 4 short-lived daughters before decaying to ^{210}Pb) or loss to the atmosphere at the air-sea interface. Loss of radon due to turbulence or diffusion at the air-sea interface leads to a depletion of radon activity with respect to that of [226]Ra, allowing for studies on gas exchange at this interface (Broecker and Peng 1982). Radon can also be used as a tracer for studying the movement of other inert gaseous tracers.

Based upon these considerations, Rn has been used extensively for determining gaseous exchange rates across the air-sea interface as well as for studying exchange of pore waters into coastal bottom waters (Berelson et al. 1987). The observed depletion of [222]Rn in porewaters relative to the sedimentary production rate from its parent, [226]Rn has been widely used to examine exchange processes at the sediment/water interface (Broecker and Peng 1982). In addition, [222]Rn has also been used as a tracer for evaluating coefficients of isopycnal and diapycnal mixing in the deep sea (Broecker and Peng 1982; Sarmiento and Rooth 1980), and more recently, for tracing submarine groundwater discharge into the coastal zone (Cable et al. 1996a; Corbett et al. 1999; see Porcelli and Swarzenski 2003).

6. LEAD AND POLONIUM

The majority of ^{210}Pb studies address the utility of ^{210}Pb as a recent geochronological tool (e.g., Paulsen et al. 1999; Santschi et al. 2001) rather than as an element that is involved in complex biogeochemical cycles. Nonetheless, some of these studies do provide insight into the geochemical behavior of [210]Pb. The distribution of stable Pb to the coastal and estuarine waters also provides information regarding behavior of ^{210}Pb in this environment. Nearly all of the lead in the world's surface oceans is believed to be of anthropogenic origin—derived from combustion of leaded gasoline and a major portion of this has already been removed from the surface waters (Broecker and Peng 1982). Even the most remote areas of the world—the polar caps—show a very clear effect of

lead pollution. Recent measurements of polar ice cores show that man's activities have caused a 300-fold increase in Pb since the beginning of the industrial revolution. ^{210}Pb and its indirect daughter ^{210}Po are both important radionuclides used in geochemical research. ^{210}Pb is delivered to the water column by three sources: 1) atmospheric fallout from the decay of gaseous ^{222}Rn that has been released mainly from the continents, 2) the *in-situ* decay of ^{226}Ra (via ^{222}Rn) in the water column, 3) river inputs, which are supplied by interactions with rocks and soils during weathering (see Chabaux et al. 2003; Porcelli and Swarzenski 2003) as well from the leaching of atmospherically-delivered ^{210}Pb-laden soils (Gascoyne 1982), and 4) lateral transport (boundary scavenging) from continental margins, which could also contribute to coastal waters (Olsen et al. 1989) but which is often a minor source. ^{210}Po is a decay product of ^{210}Pb and is produced mainly by this source in the water column, but this isotope may also have an atmospheric source term within surface waters due to dust deposition. In broad terms, the marine cycle of ^{210}Pb is characterized by supply or production of dissolved ^{210}Pb, which is then scavenged on to solid surfaces and eventually removed from the water column (Santschi et al. 1983). Therefore, ^{210}Pb has been used extensively as a tracer for particle-reactive elements (Benninger 1978), as well as for geochronological studies of lake, estuarine and coastal sediments (Fuller et al. 1999). ^{210}Po appears to be somewhat more reactive than ^{210}Pb in seawater (Kadko 1993).

Like Th isotopes, ^{210}Pb is rapidly removed in estuaries by various processes in the water column (Ravichandran et al. 1995) and deposited onto the seafloor during particle deposition and accumulation (Fuller et al. 1999). The first study by Rama and Goldberg (1961) identified deficiencies of ^{210}Pb with respect to its grandparent, ^{226}Ra and the residence time of ^{210}Pb in the water column in coastal and estuarine regions was calculated to be <1 year, in contrast to the deep ocean where it is 30-100 years (Rama and Goldberg 1961; Li et al. 1981; Baskaran and Santschi 1993; Baskaran et al. 1997). In shallow sediments, the profiles of organic carbon and ^{210}Pb are often well correlated (Paulsen et al. 1999). In the coastal ocean, sinking particles are adsorption sites for ^{210}Pb and even here iron and manganese oxides are important removal phases. In the Baltic Sea near the mouth of the Kalix River and at a salinity of ~3, activities were found to be substantially depleted compared to a bulk river water value (Porcelli et al. 2001). This indicates that ^{210}Pb is rapidly removed at low salinities, with a considerable fraction of the remaining ^{210}Pb on particles. Even lower concentrations were found further into the Baltic. In anoxic environments, ^{210}Pb may be readily removed as a lead sulfide precipitate, causing this mineral component to be of importance in sulfide-rich sediments (Swarzenski et al. 1999a). In organic-rich estuaries, the residence time of dissolved ^{210}Pb could be considerably longer and where the hydraulic residence time is comparable to the residence time of ^{210}Pb, a major portion of the dissolved ^{210}Pb could be directly exported to the coastal zone, without significant removal in the estuarine zone (Baskaran et al. 1997; Baskaran and Santschi 2002). Note that in shallow environments, the atmospheric flux of ^{210}Pb may be the dominant input, rather than production within the water column (e.g., Gustafsson et al. 1998). In rivers with large watershed, the erosional input of ^{210}Pb could be significant and could be compared to the direct atmospheric fallout (Fig. 7), such as in the estuarine systems of the Texas-Louisiana border (Baskaran and Santschi 1993; Baskaran et al. 1996, 1997).

Involvement in biological cycles may affect the distribution of both ^{210}Pb and ^{210}Po. Santschi et al. (1979) noticed large seasonal variations of ^{210}Pb and ^{210}Po in Narragansett Bay. This seasonal trend was ascribed to two factors: remobilization out of the sediments during the spring and early summer, or formation of organic complexes. In a summary paper, Nozaki (1991) suggested that the removal of ^{234}Th, ^{210}Pb and ^{210}Po from marine waters may be accelerated by biological activity. One consequence of this is that
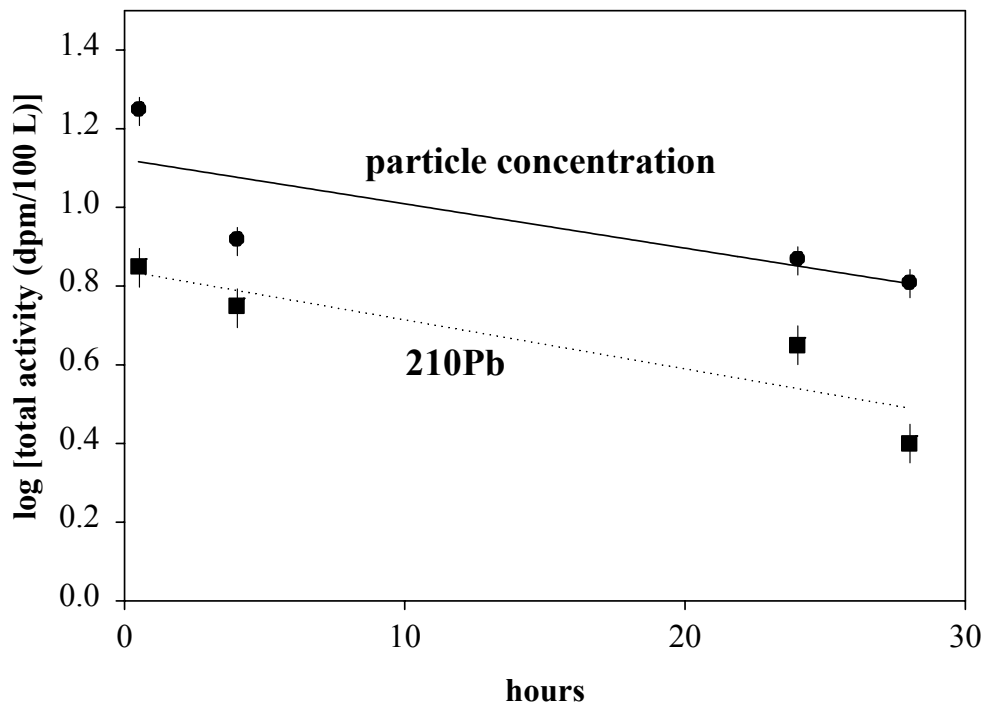
Figure 7. Log of the excess ^{210}Pb and particle concentrations plotted as a function of time after a prolonged rain event in Galveston Bay. Data from Baskaran and Santschi (1993).

preferential biological uptake of ^{210}Po relative to ^{210}Pb in some sediments may cause local disequilibria, which can affect the interpretation of ^{210}Pb-derived geochronologies. Hodge et al. (1979) demonstrated that Po, U and Pu have different uptake kinetics onto solid phases. They exposed different solid phases to seawater to determine if Po, U or Pu could be removed by inorganic material. Their results suggest that organic surface coatings may collect particles, with their associated elements, at differing rates. Such variable uptake rates led to the inference that the particulate Pu, Po, and U may be associated with different particulate phases.

7. CONCLUSIONS

Studies of U- and Th-series nuclides have discovered a range of interactions, fluxes, and removal mechanisms that can affect relatively soluble elements such as U and Ra, and particle-reactive elements such as Th and Pb. However, because of the great complexity within individual estuaries, and the tremendous differences between them, considerable work is still required. Now that the broad outline of mechanisms has been identified, more detailed, integrated studies are required to document the time-dependence of estuarine processes, as well as that of river input characteristics. This includes focusing on the composition and reactive properties of particles in rivers and estuaries, biogeochemistry of compounds that serve as ligands or surface-reactive flocs, and the hydrodynamics of sediment transport and resuspension. There is limited data regarding the role of colloids in different environments, and understanding colloid behavior will require advances in separating and characterizing a wide range of possible compositions. An important goal will be to predict transport properties to locations where less data is available, both in order to make broad calculations regarding global fluxes, and to make inferences about estuarine transport in the past.

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