

# Examining Freshwater-Saltwater Interface Processes with Four Radium Isotopes

Tracking the cycling of nutrient-laden ground water in upper Florida Bay with a suite of radium isotopes yields information on the rate and quantity of water exchange.

## Introduction

The complex exchange of fluvial, subsurface, and marine material within an estuary directly affects global biogeochemical cycles. Environmental scientists have few tools to accurately quantify such processes directly and must therefore rely on various tracer techniques. Satellite imagery, for example, provides an invaluable means for tracking some freshened river plumes into the open ocean, often for many hundreds of kilometers. However, the mixing of fresh water into seawater cannot always be tracked remotely and generally cannot yield information on the movement and rate of water mixing. Fortunately, natural and artificially produced radioactive tracers can be used to determine recent chronologies of such processes as: recently deposited sediments, water mass mixing, and exchange processes across the sediment-water interface.

In order for a chemical constituent to be implemented successfully as an environmental tracer, its source and sink functions, as well as all processes that regulate them, must be known and quantifiable. For example, methane ( $\text{CH}_4$ ) and radon-222 ( $^{222}\text{Rn}$ ) are two natural tracers that have been utilized successfully in coastal ground-water studies because their respective concentrations in ground water are usually much higher than in surrounding seawater. There are some known caveats in using these two tracers successfully.  $\text{CH}_4$  is a product of organic matter decomposition and therefore has a strong microbial component that can complicate its environmental behavior. Radon-222, while being chemically inert, has an additional atmospheric source that can be difficult to constrain from what is being produced within the sediments or the water column. The naturally occurring isotopes of radium are an additional suite of tracers ideal for freshwater-saltwater interface processes.

## Radium Isotopes as Tracers

There are four radium isotopes (fig. 1) in the uranium-238, thorium-232, and uranium-235 decay series; and their wide range in half-lives ( $t_{1/2}$ ) corresponds well with the duration of many coastal processes. These four radium isotopes are  $^{223}\text{Ra}$  ( $t_{1/2} = 11.4$  d),  $^{224}\text{Ra}$  ( $t_{1/2} = 3.7$  d),  $^{226}\text{Ra}$  ( $t_{1/2} = 5.7$  yr), and  $^{228}\text{Ra}$  ( $t_{1/2} = 1600$  yr). Their wide range in half-lives corresponds well with the duration of many coastal processes. A suite of highly particle-reactive thorium isotopes decays to form the four radium isotopes. In fresh water, radium is chemically bound onto particle surfaces. As these particles become exposed to higher salinity water during estuarine mixing, radium will undergo a phase transformation and will

eventually reside exclusively in the dissolved phase in the open ocean. In contrast, thorium will continue to remain bound to particles, regardless of salinity. Consequently, estuarine sediments provide a continuous source for radium isotopes to coastal waters, and the production rate is defined directly by their individual isotopic decay constants (fig. 2). The combined source functions for radium in an estuary thus include a) riverine particulates and dissolved, b) oceanic dissolved, c) estuarine sediments, and d) ground water. The relative significance of each of these sources is usually a function of the site-specific hydrogeology and where the samples are taken relative to the salinity gradient (extent of freshwater-saltwater mixing).

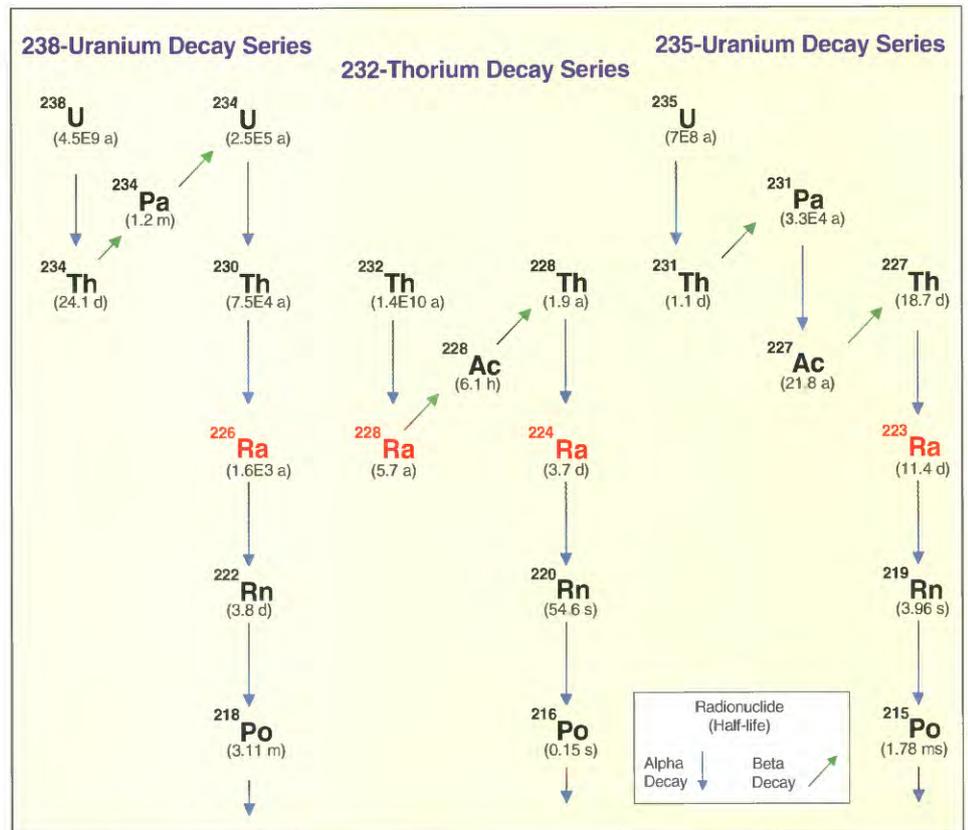
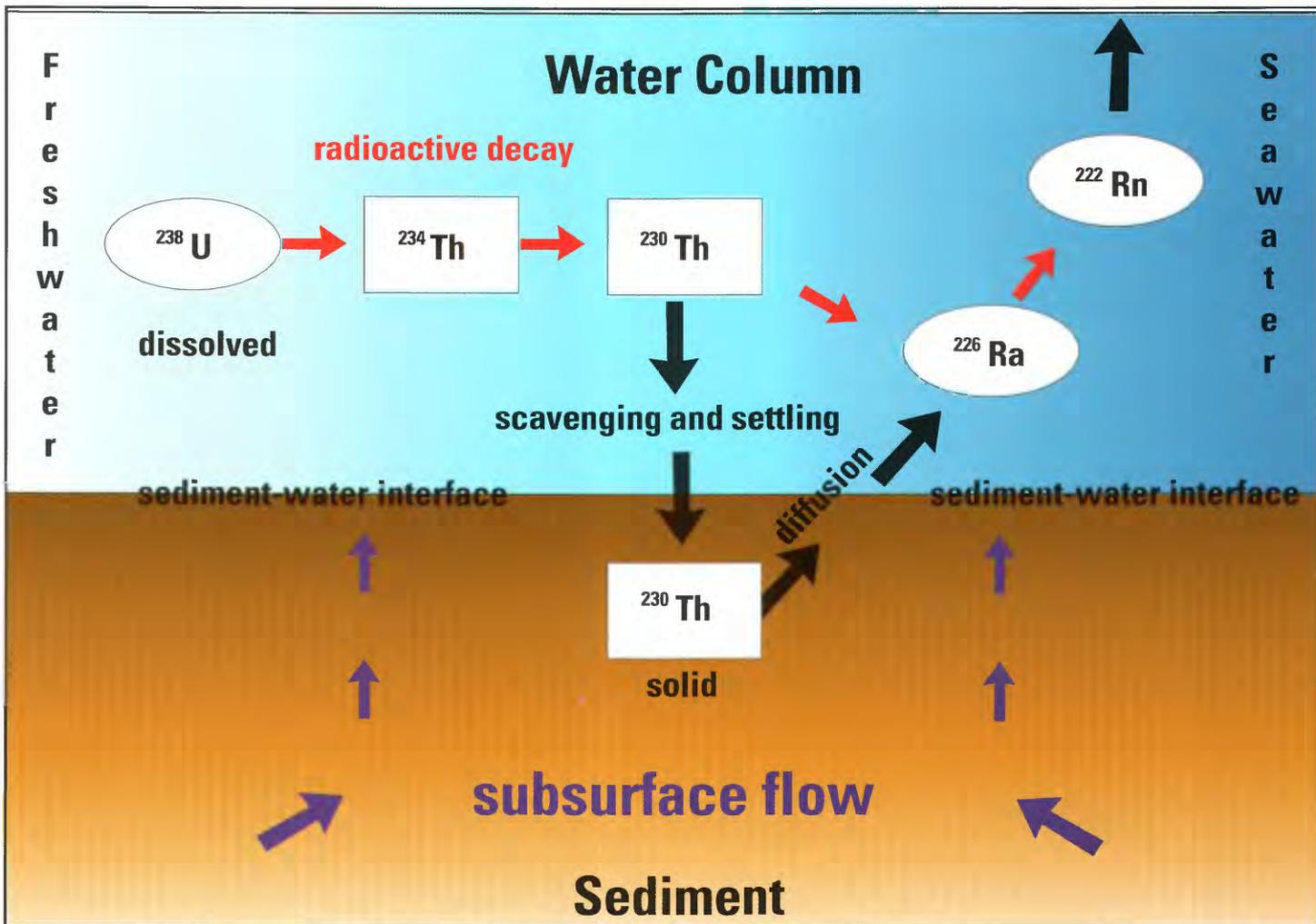


Figure 1. The radium quartet.



**Figure 2.** Examples of sources and sinks for Ra isotopes (such as  $^{226}\text{Ra}$ ) across a sediment-water interface.

Ground water, defined either as recycled marine water or freshwater, may contribute Ra to a coastal water column anywhere along this salinity gradient as long as the hydraulic gradient, hydraulic head and sediment hydraulic conductivities are favorable for ground-water discharge. Because ground water commonly is enriched in radium isotopes relative to surficial water (Ra source in the sediments), a time-dependent ground-water influence can easily be distinguished even in a dynamic water column. In surface sediments that are flushed either continuously or sporadically with ground water, a localized disequilibrium between  $^{228}\text{Th}$  and  $^{226}\text{Ra}$  will develop, because Ra is released into bottom waters by water movement, whereas thorium will remain attached to sediments. This isotopic disequilibrium can be used to assess a ground-water flux rate or an apparent water-mass age.

In the past, only the long-lived isotopes of Ra were routinely used as geochronometers because radiometric counting techniques were inadequate for many short-lived radionuclides, such as  $^{223,224}\text{Ra}$ . The U.S. Geological Survey, in partnership with the University of South

Carolina, now has acquired two delayed-coincidence alpha scintillation counters that can accurately quantify very low activities of  $^{223,224}\text{Ra}$ . This capability, in addition to standard gamma spectroscopy, allows for the rapid and precise analyses of all four radium isotopes.

#### Case Study: Florida Bay

South Florida has undergone rapid environmental change since the 1950's. In response, the hydrology of south Florida also has been significantly modified. Today, an overabundance in nutrients and saltwater encroachment often threaten to contaminate freshwater reservoirs of many south Florida municipalities. Florida Bay receives a large component of its freshwater from Taylor Slough (a freshwater wetland situated along the northeast boundary of the Everglades) and also is vulnerable to deteriorating water-quality issues in the Everglades. Heightened subsurface flow through porous strata in south Florida may further introduce anthropogenic contaminants into the bay. To address the issue of ground-water flow and ground water-surficial water exchange in upper Florida

Bay, a series of samples was collected in March, 1998, for radium isotopes. In this bay system, the radium quartet can clearly differentiate surficial- from subsurface-water masses and the ratio of  $^{223}\text{Ra}/^{224}\text{Ra}$  can provide information on the apparent age of water masses. We are currently developing models with which we hope to better constrain the exchange of ground water in upper Florida Bay and elsewhere.

—Peter W. Swarzenski

#### Collaborators:

South Florida Water Management District  
Florida Department of Environmental Protection  
University of Miami  
Florida International University  
Florida State University

#### For further information, please contact:

Peter W. Swarzenski  
Charles W. Holmes  
U.S. Geological Survey  
600 4th Street South  
St. Petersburg, FL 33701  
Telephone: (727) 803-8747 x3072  
Fax: (727) 803-2032  
E-mail: pswarzen@usgs.gov