

EVALUATION OF THE FLUSHING RATES OF APALACHICOLA BAY, FLORIDA VIA  
NATURAL GEOCHEMICAL TRACERS

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## Abstract

We used naturally occurring radium isotopes as tracers of water exchange in Apalachicola Bay, a shallow coastal-plain estuary in northwestern Florida. The bay receives fresh water and radium from the Apalachicola River, and mixes with Gulf of Mexico waters through four inlets. We deployed moored buoys with attached Mn-fibers at several stations throughout the estuary during two summer and two winter periods. After deployment for at least one tidal cycle we measured the ratio of the two short-lived radium isotopes  $^{223}\text{Ra}$  (half-life = 11 d) and  $^{224}\text{Ra}$  (3.6 d) to estimate “radium ages” of the water in the bay.

During our four seasonal deployments the river discharge ranged from 338 to 1016 m<sup>3</sup> s<sup>-1</sup>. According to our calculations the water turnover time in the bay during these samplings ranged from 6 to 12 days. Age contours in the bay showed that winds and tides as well as river discharge influence the water movement and the residence time of freshwater in the bay. We also calculated the mean age of river water in the bay which was between 5 to 9 days during the studied periods. We suggest that this approach can be used to quantify transport processes of dissolved substances in the bay. For example, soluble nutrient or pollutant transport rates from a point source could be examined. We conclude that the radium age technique is well suited for flushing rate calculations in river dominated shallow estuaries.

## 1. Introduction and study area

Estuarine residence time and salinity variations directly influence the ecological conditions and production rates in estuaries. Circulation models that are based on monitoring of river discharge, tides, weather conditions, and salinity distribution have traditionally been used to evaluate the residence time of water within estuaries. In our study, we applied natural radium isotopes to trace the direction and speed of water movement in a shallow estuary in northwestern Florida. Radium isotopes have previously been applied as tracers to determine transport rates in estuaries, bays, and sounds (Moore, 1984; Torgersen et al., 1996; Turekian et al., 1996; Krest et al., 1999; Kelly and Moran, 2002) where the decay and dilution of radium isotopes determined across a water body based on discrete samples were compared to radium concentrations at their source, i.e., from rivers, groundwater discharge, or diffusion from sediments.

Here we address the importance of the time-scale of sample collection, since in small water bodies influenced by rivers and tides there may be significant salinity and radium concentration changes at one location on a time scale of few hours. To assess flushing rates representative of at least a full tidal cycle, one cannot rely on discrete samples which, even if one managed to sample all sites at the same time, would only represent a snap-shot of water ages across a bay or estuary. Another complicating aspect that we address in this work is the presence of submarine groundwater discharge (SGD) around the periphery of bays and sounds. With all these factors in mind, the purpose of this study was to apply a simple, geochemical alternative to numerical modeling to derive flushing rates in a small estuary.

We used Apalachicola Bay, Florida as our study site. The bay is ideal for this application because of the availability of a 3-D circulation model for comparison (Huang et al., 2002a, b) and the excellent logistics afforded by the Apalachicola National Estuarine Research Reserve

(ANERR). The bay is a sub-tropical, shallow estuary in the northeastern Gulf of Mexico (GOM), surrounded by a chain of barrier islands. The main source of fresh water to the bay is from the Apalachicola River and it exchanges water with the GOM at four inlets: St. George Sound, Sike's Cut, West Pass and Indian Pass (Fig. 1). River discharge and exchange through these inlets are important factors for determining the flushing rate and the salinity variations in the bay.

Currents in the bay are primarily tidal (Huang et al., 2002b), but are strongly affected by wind direction and speed, and the river flow (Huang et al., 2002a; Dawson, 1955; Niu, et al., 1998). Huang et al. (2002b) developed a tidal circulation model of the estuary, and Mortazavi et al. (2000, 2001) calculated the water export from the estuary to the Gulf of Mexico with a 3-dimensional numerical model based on freshwater inflow, tidal stage, temperature, salinity, and wind-stress forcing. During Mortazavi's two-year study in 1994 and 1995 they found that the water from St. George Sound (east of the bay) accounted for all the seawater input from the GOM, except in June, 1995 when Indian Pass, on the western side, contributed some seawater. Their results indicated that 69% of the water outflow from the estuary generally occurred through West Pass. However, in April and June, 1995, St. George Sound was the major outlet for the bay water. The water residence time within the estuary during their study period in 1994 and 1995 varied from 2 to 12 days, while the river discharge ranged from 300 to 2750 m<sup>3</sup> s<sup>-1</sup>.

As described later in this paper, an additional source of water to the bay is meteorically-derived SGD which appears to be the most intense at the river mouth. There are also some minor amounts of seepage of a combination of fresh and recycled seawater discharging episodically during and after storm events from the barrier islands.

### *1.1. General approach*

We based our tracer study on a method pioneered by Moore (2000) who used natural radium isotopes to derive “ages” of continental shelf waters and large river plumes (Moore and Krest, 2004; Moore and Todd, 1993). The source of  $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  isotopes to coastal waters may include river discharge of dissolved radium, diffusion from sediments, discharge of salty and brackish groundwater, and desorption from suspended particles in the case of estuaries. As particles carrying thorium and radium from the river encounter saltwater, radium isotopes are desorbed from particles due to the increase of ionic strength of the surrounding waters. Unlike radium isotopes, the thorium parents stay attached to these particles because of thorium’s highly particle-reactive nature. The dissolved radium isotopes are therefore no longer supported by the parent nuclides and decay according to their own decay constants.

The half-lives of the four naturally occurring radium isotopes are  $^{224}\text{Ra} = 3.6$  days,  $^{223}\text{Ra} = 11.4$  days,  $^{228}\text{Ra} = 5.7$  years, and  $^{226}\text{Ra} = 1600$  years. Apparent radium ages may be calculated using a ratio of a short-lived radium isotope to a longer-lived one. The approach assumes that radium is added from a source with a fixed isotopic composition and that the change in this ratio occurs solely by radioactive decay. In Apalachicola Bay the expected range of the flushing rate is 2 to 12 days (Mortazavi et al., 2000) and we chose to use the ratio of  $^{224}\text{Ra}/^{223}\text{Ra}$  because we were able to measure both isotopes with a very good uncertainty and these isotopes should be the least influenced by offshore sources ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are non-negligible in shelf waters). As the water mass moves away from its source and ages,  $^{224}\text{Ra}$  decays faster than  $^{223}\text{Ra}$ . Assuming that the river supplies the estuary with a constant radium isotopic composition at least over a period comparable to the effective mean life of the  $^{224}\text{Ra}/^{223}\text{Ra}$  activity ratio (7.8 days), one can estimate apparent radium ages of the water (Moore, 2000):

$$\left[ \frac{{}^{224}\text{Ra}}{{}^{223}\text{Ra}} \right]_{obs} = \left[ \frac{{}^{224}\text{Ra}}{{}^{223}\text{Ra}} \right]_i \frac{e^{-\lambda_{224}t}}{e^{-\lambda_{223}t}}, \quad (1)$$

where  $[\text{}^{224}\text{Ra}/\text{}^{223}\text{Ra}]_{obs}$  and  $[\text{}^{224}\text{Ra}/\text{}^{223}\text{Ra}]_i$  represent the observed and initial activity ratios (AR) of the radium, and  $\lambda_{224}$  and  $\lambda_{223}$  are the decay constants of  ${}^{224}\text{Ra}$  and  ${}^{223}\text{Ra}$ , respectively. The equation can be rearranged to solve for  $t$  which represents the “radium age” i.e., the amount of time since radium was added to the water:

$$t = \ln \frac{\left[ \frac{{}^{224}\text{Ra}}{{}^{223}\text{Ra}} \right]_i}{\left[ \frac{{}^{224}\text{Ra}}{{}^{223}\text{Ra}} \right]_{obs}} * \frac{1}{\lambda_{224} - \lambda_{223}}. \quad (2)$$

The apparent radium age ( $t$ ) is an age of the water mass that is derived based on the  ${}^{224}\text{Ra} / {}^{223}\text{Ra}$  AR which is a result of radioactive decay and mixing of various water masses, i.e. new river inputs and low radium GOM water. Also, any apparent age derived by this model reflects an integrated history of the circulation over the past several days (residence time of the water). The basic assumptions for the age model are: (1) there is a single major source of  ${}^{224}\text{Ra}$  and  ${}^{223}\text{Ra}$  into the estuary; (2) the source supplies a constant  ${}^{224}\text{Ra} / {}^{223}\text{Ra}$  AR on the time scale of the water residence time; (3) the losses of radium after leaving the source are only by dilution by waters with no excess  ${}^{223}\text{Ra}$  or  ${}^{224}\text{Ra}$  (which does not affect the ratio) and radioactive decay; and (4) the GOM water contains negligible amounts of excess  ${}^{224}\text{Ra}$  and  ${}^{223}\text{Ra}$ . The excess  ${}^{224}\text{Ra}$  refers to radium activities unsupported by its dissolved thorium parent  ${}^{228}\text{Th}$ , which occurs in very small amounts in the water. The parent of  ${}^{223}\text{Ra}$ ,  ${}^{227}\text{Ac}$ , has an activity below the detection limit of our method and is neglected. All  ${}^{224}\text{Ra} / {}^{223}\text{Ra}$  AR hereafter refer to  ${}^{224}\text{Ra}$  and  ${}^{223}\text{Ra}$  in excess to its thorium parent. The possible radium sources to the bay are:

Sediments: In the case of shallow estuaries like Apalachicola Bay, there are several reasons why assumptions (1) and (2) have to be verified. The average depth of Apalachicola Bay is only about 2 meters. The muddy sediments in this shallow bay may be disturbed by wind events allowing additional radium input into the water by sediment resuspension and make the apparent radium ages appear younger. Additionally, the river itself carries sediments that are slowly settling as they are transported through the estuary. As these suspended particles are subjected to water of increasing salinity the change in ionic strength makes more radium to desorb over time. Particles can give off as much as 30-50 % of the originally desorbed  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  when transitioning from salinity 5 to salinity 25 water (M. Gonnee, personal communication).

Apalachicola River: The historical river discharge records investigated back to 1978 show an annual long-term average of  $710 \pm 200 \text{ m}^3 \text{ s}^{-1}$  (data from USGS; Fig. 2, Table 1). The river discharge is usually highest from January to April, and lowest in the summer months. Since the discharge over the past 27 years ranged from 180 to  $2750 \text{ m}^3 \text{ s}^{-1}$  we also needed to check whether the radium input is constant for the period of the water residence time at different river stages.

Submarine groundwater discharge: Another source of radium into the bay could be groundwater discharge that occurs along the coastline of the land and barrier islands. To locate areas influenced by submarine groundwater discharge and estimate its magnitude we made a survey along the entire coastline during which we monitored the radon concentration and radium isotope ratios in the water. In order to estimate how much radium brackish and salty SGD can bring to the bay, we also investigated groundwater discharge in more detail in a study site located on the bay side of St. George Island (Fig. 1) using automated seepage meters (Taniguchi

and Fukuo, 1993) and time-series radon experiments (Burnett et al., 2001; Burnett and Dulaiova, 2003).

## **2. Methods**

### *2.1. Sampling plan*

In order to calculate the apparent radium ages in the bay we arranged sampling at 17 stations in Apalachicola Bay as indicated on Fig. 1. Because of large salinity and water compositional changes over short periods at many of these stations due to tidal circulation, we felt that grab samples would not be a good representation of the daily state of the bay. Instead, we wished to obtain radium AR that would integrate a signal over a period of at least one tidal cycle to capture a representative state including low and high tides.

Although some areas of the bay are stratified year-round (Supplementary Table 1), to confirm whether inputs from bottom sediments are important we also monitored the radium isotopes in bottom water layers. We also sampled near-zero salinity river water in a time series to determine if the river supplies a constant  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR.

#### *2.1.1. Dissolved radium isotope ratios measured in the river and bay*

We sampled radium isotopes in the bay on four occasions, July 30 - August 4, 2003; March 3 - 4, 2004; August 30 - 31, 2004; and January 25 - 26, 2005. We distributed passive radium collectors called “Mn fibers” (Moore, 1976) at the same 17 locations within the estuary during each sampling trip. Two stations were in the river, one at the river mouth, one in East Bay, and 13 were positioned systematically across Apalachicola Bay (Fig. 1). Each station consisted of a float attached by a line to a cinder block that served as an anchor. We attached a mesh bag filled with ~ 50 g of MnO<sub>2</sub>-coated acrylic fiber to the line about 0.3 m from the float so



when it was deployed it collected radium from 0.3 m below the water surface. We also attached several of these passive collectors 0.3 m above the bottom of the block to sample the deeper layers. These passive collectors were deployed for 4 days in August 2003 but they collected very high levels of radium. Therefore the collectors were deployed only one day during the other seasons. At each deployment we measured the water salinity at the surface and bottom of the station with a YSI 85 conductivity probe.

To measure absolute radium concentrations in the river and the bay and to confirm our assumption that the river  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR is constant over at least a period of several days, we collected several grab samples during our study between September 2003 and August 2004, including a time series sampling over 8 days in August 2004. Although elevated radium concentrations originating from submarine groundwater discharge were found in nearby coastal regions outside of the bay (Burnett and Dulaiova, 2003; Moore, 2003), for logistic reasons we did not sample outside the bay area and we do not have information about the radium isotopes immediately outside of the inlets of the bay. According to the measurements of Moore (2003) 28 km offshore in Apalachee Bay, short-lived radium isotope activities in the Gulf of Mexico are equal to their radioactive parents without excess radium activities.

### *2.1.2. Radium isotopes measured on suspended and bottom sediments*

In August 2004, we collected water samples from three different locations in the river. At each location we pumped about 160 liters of water into a barrel and also collected about 140 liters into several 20-liter collapsible plastic containers. A one liter aliquot of the river water from each station was set aside to determine the concentration of suspended particulate matter by filtering the water through pre-weighed 0.2  $\mu\text{m}$  Nucleopore filters. The water from the barrels was pumped through a Mn-fiber column with raw acrylic fiber used as prefilter. We saved both the Mn-fibers and the prefilters with the collected particles for radium analysis.

The plastic containers were moved to the ANERR laboratory in Eastpoint where we passed the water through a continuous-flow centrifuge system (Contifuge Stratos, manufactured by Kendro Laboratory Products) to separate river particles from the water. We used a relative centrifugal force of 20,000 g and passed the water continuously through the system at a flow-rate of 0.4 l min<sup>-1</sup>. Under these conditions the centrifuge separates and retains particles larger than 2  $\mu\text{m}$ . We collected particles from all three samples and saved them wet for later processing.

We also collected sediment from the river bottom at two stations. We took one grab sample of sandy sediment at 8 km upstream from the river mouth and we collected one silty sample at 2.6 km upstream. These bottom sediments were dried at 60°C, homogenized and packed into 100 ml containers that were counted on a germanium detector for determination of radium isotopes.

### *2.1.3. Radon and radium isotope survey as indicator of submarine groundwater discharge into Apalachicola Bay*

We performed a spatial radon and towed Mn-fiber survey on the periphery of Apalachicola Bay over two days in July 2003 to assess if any areas showed evidence of

significant groundwater discharge. The survey was done aboard the R/V C-Hawk of Apalachicola NERR at a relatively slow speed (5-7 km/hr) to ensure good spatial resolution for our automated radon measurements. We used a multi-detector continuous radon measurement system for radon mapping (Burnett et al., 2001; Dulaiova et al., 2005). The radon results were matched to the GPS locations and a radon map was created along the shoreline of Apalachicola Bay.

## *2.2. Radioanalytical measurement techniques*

The short-lived radium isotopes  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  collected on Mn fibers were measured on a delayed coincidence counting system (Moore and Arnold, 1996) which was calibrated using  $^{232}\text{Th}$  and  $^{227}\text{Ac}$  standards that are known to have their daughters in radioactive equilibrium and are adsorbed onto similar  $\text{MnO}_2$ -coated fiber. After the first counting immediately after collection, the fibers from all deployments were re-measured on the counting system again within 7 to 10 days when the initial high  $^{224}\text{Ra}$  activity partially decayed and we were able to obtain a more precise  $^{223}\text{Ra}$  value. The fibers were recounted again after about one month to assess the  $^{228}\text{Th}$  collected on the fiber. The  $^{228}\text{Th}$  activity was subtracted from the measured  $^{224}\text{Ra}$  to estimate the excess  $^{224}\text{Ra}$  activity. The  $^{227}\text{Ac}$  activity in the water column is below our detection limit therefore all  $^{223}\text{Ra}$  activities reported here are also considered excess.

Because of the large sorption capacity of the fibers we assumed linear radium uptake on the fibers over the time of deployment in the bay for all four samplings. The radium sorption capacity of the Mn-fibers might have come close to maximum or reached an equilibrium state during the 4-day deployment but this would not be important for the 1-day deployments. The large difference in measured activities between the one-day and four-day deployments indicates

that there was still considerable capacity remaining on the fibers after remaining in the water for a single day.

Assuming a linear radium uptake model, the measured  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  were decay corrected to the beginning of sampling. In the case of the passive collection we applied a combined decay correction term to consider differences in decay rates while the deployed Mn-fiber collected radium from the water:

$$A_{224i} = A_{224m} \times \frac{1}{e^{-\lambda_{224}t_1}} \times \frac{\lambda_{224}t_2}{1 - e^{-\lambda_{224}t_2}}, \quad (3)$$

$$A_{223i} = A_{223m} \times \frac{1}{e^{-\lambda_{223}t_1}} \times \frac{\lambda_{223}t_2}{1 - e^{-\lambda_{223}t_2}}, \quad (4)$$

where,

$A_{224i}$  and  $A_{223i}$  are the  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  activities at the start of deployment;

$A_{224m}$  and  $A_{223m}$  are the  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  activities at the time of measurement;

$\lambda_{224}$  and  $\lambda_{223}$  are the  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  decay constants;

$t_1$  is the time between the end of sampling and the mid-point of measurement; and

$t_2$  is the duration of deployment of the Mn fiber in the water.

The raw acrylic fibers that served as prefilters were also kept and we measured them for  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  on the delayed coincidence counter. The prefilters were packed into the measurement columns and measured in the same manner as the Mn-fibers. We re-measured the prefilters several times over a one-month period to see if the  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  were supported. The three samples of river suspended particles collected using the continuous centrifuge were kept wet and we packed them into a measurement flask that consisted of an Erlenmeyer flask, a rubber stopper with two copper tubes, and Tygon tubing attached to the copper tubes. About 2 grams of wet sediments were spread in a thin layer on the bottom of each flask. We connected the Erlenmeyer

flasks to the delayed coincidence counter and allowed the helium to circulate through the flask and sweep the radon isotopes into the scintillation cell. For these measurements we applied the same calibration as used for the Mn-fibers with the assumption that radon emanation from sediments is not as efficient as from the wet fibers. Therefore we adjusted the humidity of the prefilters and sediments to allow the recoiling radons to dissolve in water and diffuse into the air (Sun and Torgersen, 1998). We assume that  $^{220}\text{Rn}$  and  $^{219}\text{Rn}$  have the same emanation efficiency from the surface of the particles and once these radon isotopes get in the helium stream the counting conditions are the same as for the Mn-fibers. Radium measured on the particles on the delayed coincidence counting system only represents surface-bound radium on the particles that may be available for desorption. This measurement does not account for total radium because radon does not escape from the lattice bound radium and is not measured by these counters. Our results, therefore, do not include radium that may be released by slow dissolution of the particles. Since we do not have an absolute calibration for these types of samples, we report only  $^{224}\text{Ra} / ^{223}\text{Ra}$  ARs, not absolute activities, of the particle-bound radium.

### **3. Results**

#### *3.1. Initial tracer survey*

The results of the radon survey revealed that the highest radon activity ( $14,000 \text{ dpm m}^{-3}$ ) occurs near the river mouth. It is possible that there is enhanced groundwater seepage either immediately in this area or farther upstream. The survey showed low radon concentration ( $2,000 \text{ dpm m}^{-3}$ ) in all the other parts of the bay. The radium isotope ratio survey showed low AR without any higher values along the coastline except near the river mouth. The  $^{224}\text{Ra} / ^{223}\text{Ra}$  ARs ranged from 4 in St. George Sound,  $\sim 6$  along the coastlines in the east part of the Bay, and up to

9 along the coastline in the western part of the bay. The ratios in the river mouth area and in East Bay were 16 and 17, respectively. Seepage meter studies indicated that water advection rates from the barrier islands to the bay were 0.5 -10 cm day<sup>-1</sup>, which when recalculated to the whole length of the barrier island totaled to about 2 m<sup>3</sup> s<sup>-1</sup>, increasing to 15 m<sup>3</sup> s<sup>-1</sup> after extreme rain events (Fig. 3). These water fluxes represent 1 to 10 % of the river flow. Based on groundwater radium activities measured in wells on the barrier island (15-56 dpm m<sup>-3</sup> <sup>223</sup>Ra and 153-746 dpm m<sup>-3</sup> <sup>224</sup>Ra), SGD flux accounts for about 4-10 % of the total river radium input. The <sup>224</sup>Ra / <sup>223</sup>Ra ARs in groundwaters were 10-30.

### 3.2. Environmental parameters and radium isotopes measured in Apalachicola Bay

River discharge values measured at a gauging station near Sumatra, FL at about 30 km from the river mouth (USGS 02359170) were obtained from a website maintained by the USGS ([http://nwis.waterdata.usgs.gov/fl/nwis/dv?format=html&period=730&site\\_no=02359170](http://nwis.waterdata.usgs.gov/fl/nwis/dv?format=html&period=730&site_no=02359170)). The river discharge during our four main samplings ranged from 338 to 1016 m<sup>3</sup> s<sup>-1</sup> (Fig. 2). Wind and water level data (Table 1) were gathered from a station (#8728690) operated under NOAA's Center for Operational Oceanographic Products and Services (CO-OPS) in Apalachicola, FL ([www.tidesonline.nos.noaa.gov/geographic.html](http://www.tidesonline.nos.noaa.gov/geographic.html)).

Salinities measured at our 17 stations ranged from <0.1 in the river to 31 in East Bay, with higher salinities in the bottom water layers. The water column was stratified at most stations in the bay (Supplementary Table 1). The collectors were deployed for over four days in August 2003 and some of the fibers collected more than 1000 dpm Ra/fiber <sup>224</sup>Ra. The fiber collectors in the other seasons were deployed only for 24 hours and collected significantly less activities (<sup>224</sup>Ra ranged from ~10 to a maximum of 800 with most values being <50 dpm Ra/fiber). The uncertainty of each <sup>224</sup>Ra / <sup>223</sup>Ra AR was calculated from the individual measurement

uncertainties of  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  via standard error propagation ( $1\sigma$ ) and represents approximately 10-15 % of the reported values for dissolved radium and up to 50 % in case of sediment samples. The river end-member  $^{224}\text{Ra} / ^{223}\text{Ra}$  ARs calculated as the average of stations 1, 2, and 3 were  $28\pm6$  in August, 2003;  $22\pm6$  in March, 2004;  $25\pm6$  in August, 2004; and  $25\pm9$  in January, 2005. These ARs agreed with the time series measurements from the upstream river dock ( $23\pm5$ ), and the filtered and unfiltered river samples ( $23 \pm 6$ ).

The amount of suspended sediment material in the river in August 2004 was  $12.1 \pm 0.8 \text{ mg L}^{-1}$ . The average  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR from the prefilter and suspended sediment analyses for all samplings was  $23 \pm 5$  (Tables 2 and 3).

## **4. Discussion**

### *4.1 Radium flux from the Apalachicola River*

Based on river discharge and river water radium analysis we estimated the amount of dissolved  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  transported by Apalachicola River (Table 1). These amounts do not account for radium released from the particles transported by the river. Based on the comparison of sediment samples collected at stations 3 (salinity  $< 0.1$ ) and 12 (4) in March 2004, desorption from particles adds about 30 % more dissolved radium to the water. The desorbed radium has the same AR as those measured in the river. While the radium concentrations and fluxes change seasonally with the river discharge ( $^{223}\text{Ra}$ :  $1.2\text{-}3.7 \text{ dpm m}^{-3}$ ;  $^{224}\text{Ra}$ :  $38\text{-}48 \text{ dpm m}^{-3}$ ; Table 2), the radium ARs are very similar between different seasons with an overall average of  $24 \pm 6$  ( $n = 25$ ). Based on these results we can assume that the dissolved and particulate radium of the river represents a constant  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR source to Apalachicola Bay over the time scale of the bay water residence time.

#### *4.2. Radium isotopic ratios in the bay*

In order to assess the significance of radium inputs from the bay bottom sediments into the surface water we measured radium isotopic ratios in bottom waters at a depth of 0.3 from the bottom sediments. If there was a significant new radium input from the bottom sediments by diffusion or sediment resuspension, at least where the water column was stratified we would have seen much higher radium AR in the bottom than surface waters because due to its shorter half-life  $^{224}\text{Ra}$  is regenerated in the sediments faster than  $^{223}\text{Ra}$ . Even the most stratified locations, where the surface to bottom salinities are less than 1, did not show any radium enrichment or AR elevated over the surface values (Fig. 4). Radium ratios at all stations in the surface are higher or the same as the bottom ratios. Also, the fibers deployed near the surface collected significantly more (one order of magnitude higher) radium activity than those deployed 0.3 meters from the bottom sediments. Although, this could partially be explained by larger currents on the surface that allow more water to filter through the Mn-fibers and collect more radium on the surface than bottom. We acknowledge that there is radium diffusion from the bottom sediments to the water, although in comparison with the surface water radium activities it is probably small in magnitude and we can assume that due to the vertical concentration gradient working against diffusion, the radium input from the bottom sediments to surface waters is negligible.

As described earlier, sediments are also transported by the river. The results from four repeated measurements of the suspended particles from the river on the coincidence counting system over one month show that most of the  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  present on the particles are supported by their thorium parents. The particles transported by the river lose their desorbable



radium when they encounter saline water. Although radium desorption occurs within minutes of exposure to saline water, additional radium is desorbed gradually as particles are exposed to higher salinities. Such inputs can make up to 30-50 % of the initially desorbed radium (M. Gonnee, pers. comm. Data collected from a time series of desorption experiments on sands with water with salinities of 5, 10 and 25). This happens due to two reasons: 1) the change in ionic strength at higher salinity forces more radium to dissolve from the particles; and 2) the short-lived radium isotopes are continually regenerated on the suspended particles by their thorium parents. And because  $^{224}\text{Ra}$  is regenerated on the particles faster than  $^{223}\text{Ra}$  after desorption, the newly desorbed  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR is higher than it would be at secular equilibrium as is the case when the particles first enter saline water. The magnitude of this additional input would depend on how long the particle is suspended in the water column and what salinities it is exposed to.

We can therefore assume that the new radium inputs represent 30-50 % of the originally desorbed radium which corresponds to 30 % of the river dissolved radium. That means that even if all the particles remain suspended for more than 10 days and reach waters with salinity 25, the radium addition will only be 7-10 % of the total river input. Due to the complexity of such inputs we did not quantify them and together with groundwater radium inputs we consider this additional desorption the largest source of uncertainties in our age calculation approach.

#### *4.3. Apparent radium ages*

The apparent radium age of the water at each station was calculated using equation (2) based on the  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR measured in the surface water samples. Table 4 lists the initial  $[^{224}\text{Ra}/^{223}\text{Ra}]_i$  AR applied for each sampling, the observed  $[^{224}\text{Ra}/^{223}\text{Ra}]_{\text{obs}}$  AR of the surface water at each station, and the calculated radium ages. The age results are also presented as contour plots in Fig. 5. The ages represent a state of flushing over four days in August, 2004 and

one day during the other periods. The average error of the apparent radium ages calculated based on the  $^{224}\text{Ra} / ^{223}\text{Ra}$  AR uncertainties is estimated to be  $\sim 1$  day. The contours plotted in East Bay and the eastern part of St. George Sound are rough approximations, since we had a limited number of stations in these areas. Another possible source of uncertainty in the estimated radium ages in this region is the excess  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  present in the coastal waters in the Gulf of Mexico outside of Apalachicola Bay since the general flux of GOM water to the bay is from the east. Measurements in coastal waters about 20 km east of St. George Sound indicate that the near-shore  $^{224}\text{Ra}$  activity is about 200-800 dpm  $\text{m}^{-3}$  and  $^{223}\text{Ra}$  is 50-200 dpm  $\text{m}^{-3}$  which gets diluted and decays to 50 and 150 dpm  $\text{m}^{-3}$ , respective, within 5 km offshore. Therefore radium sources outside the bay would mostly influence radium ratios in St. George Sound which communicates the most with near-shore waters and less significantly (because of decay and dilution) in the bay and near the other inlets that connect the bay to GOM.

Apalachicola River discharge is governed by the amount of rainfall in the watershed and can be quite variable, especially during the summer months. Discharge can vary between individual years depending on tropical storm and hurricane frequency and intensity in the region. The unusual high discharge in August 2003 was a result of several low-pressure atmospheric systems that delivered large amounts of rain to the river drainage basin. According to the observed river discharge we would expect to see faster flushing and younger bay-water ages in August 2003 when the discharge was highest ( $1016 \text{ m}^3 \text{ s}^{-1}$ ), and the oldest ages during the August 2004 sampling with low discharge ( $338 \text{ m}^3 \text{ s}^{-1}$ ). The contour plots (Fig. 5) confirm this showing much younger ages in August 2003, and they also reveal a different circulation pattern in the bay at that time. In August 2003 the river plume is more symmetrical than in August

2004. The apparent radium ages at West Pass and St. Vincent Sound, the two major water outlets, are >10 days in August 2004 and 7 - 8 days in August 2003.

Besides river discharge, wind patterns and tides will influence water movement in the bay. If we compare August 2003 and March 2004, two seasons with similar river discharge, we still see distinct differences in the salinity and age contours (Fig. 5, 6). In March, right before our deployment, there was a steady wind blowing over a period of 24 hours from the east at 2-6 m s<sup>-1</sup> (Fig. 7). Both, the salinity and the age contours during this period reflect the influence of this wind (Fig. 5 and 6). The water is forced from St. George Sound towards the western part of the bay where the water exits through West Pass and Indian Pass. The apparent radium ages in the eastern part of the bay are over 12 days, while in St. Vincent Sound the water is only 2 days old. The same pattern is evident from the salinity contours. Despite the different sampling intervals such that the ages are representative of a tidal cycle while salinity values are spot measurements at the times of fiber deployment, we observe very good agreement between salinity and the age contours (Fig. 5 and 6).

During the deployments the tidal ranges measured in the bay were generally 0.6 m. However, on January 24, 2005 one day before our sampling, the low tide was -0.304 meters below the mean lower low water (MLLW) and the high tide only +0.13 m above the MLLW, which is 0.3 m below the predicted tide levels. We surmise that such low water levels in the bay were caused by the combined effect of the intense west winds prevailing at that time (Fig. 7) and the tides. While collecting fibers from our stations the next day at low tide we noticed a very strong eastward current in the bay. The apparent tracer ages also showed that the river plume moved eastward. The oldest apparent age within the area of our investigation was 7 days in the eastern and 6 days in the western part of the bay.

Wind-driven and tidal circulation patterns switching from eastern to western direction are not unusual in Apalachicola Bay. Huang et al. (2002a) examined the effects of surface wind on the salinity distribution in the bay. They found that steady winds can induce a very large volume flux. Mortazavi et al. (2000, 2001) also observed a change in the bay-water circulation due to the strong influence of winds and tides when instead of West Pass, St. George Sound becomes the main water outlet from the bay. This was also confirmed by our results.

The calculated radium ages represent the rate at which river water moves through the bay. This flux refers to the flushing rate with respect to the freshwater (radium input) only. We estimated the flushing rates as the age of the oldest river water present in the bay, excluding the area of St. George Sound that may be influenced by radium additions from the GOM. These estimated flushing rates were 8, 10, 12 and 6 days for August 2003, March and August 2004, and January 2005, respectively. These rates fall into the same range as the turnover times estimated by the circulation model reported in Mortazavi et al. (2000). In their model the authors estimated the residence time as a combination of fresh and salt water inputs and outputs into the bay therefore their results represent the total bay water turnover time. We plotted their turnover time data against river discharge at the time of their experiment and derived a dependency curve. We neglected wind and tide effects so the comparison is only assessing one of the important variables. Based on this relationship and our river discharge values we estimated that their model would predict residence times of about 7, 7, 12 and 8 days for the same four periods that we investigated. The calculated flushing rates based on the radium ages are plotted in Figure 8. Also plotted here are the theoretical flushing rate calculated by dividing the bay volume ( $5.7 \times 10^9 \text{ m}^3$ ) with the river discharge and total bay water turnover times from Mortazavi et al. (2000) model.

We also calculated a mean radium age of the water in the bay. From the contour plots on Fig. 5 we estimated the area represented by each age section. For example we assumed that the area of the bay that is between contours 2 and 3 days represents the fraction of the water that is 2.5 days old. We then calculated the weighted average of the ages according to the extent of the total area each age represents. These estimated mean apparent ages were 5.5 days in August 2003, 7.6 days in March 2004, 9 days in August 2004, and 5.1 days in January 2005. This approach would be more accurate if we applied volume instead of area, but because of the shallow nature of this bay the differences in depths are probably small. The differences in mean apparent ages between the winter and summer seasons are due to the variability in river discharge caused by varying precipitation, evaporation, and water withdrawals from the river, as well as by tidally and wind-driven circulation changes in the bay.

#### *4.4. Radium age sensitivity analysis*

According to our estimates, radium inputs via additional desorption from suspended particles as they are transported from the river mouth from low to high salinity waters can make 5 days old waters seem like 4.5 days old and 10 days look as only 8.5 days old. The errors are more pronounced in older water masses, however the older the waters are the less particles they would contain due to particle settling over time, so our error calculations represent a conservative estimate.

In case of submarine groundwater discharge the median  $^{224}\text{Ra}/^{223}\text{Ra}$  AR in groundwater is 10. Based on the river end-member (AR=26) the discharging groundwater has an apparent radium age of 7 days. Where submarine groundwater discharge occurs (mostly along the coastline) the bay water is mixed with water with an apparent radium age of 7 days, therefore

SGD causes the bay water age to be over- or underestimated depending on the location in the bay. SGD radium inputs along the coastline represent up to 10 % of total river radium input and the corresponding errors in bay radium ages are on the order of 1-2 days.

## **5. Conclusions**

We applied a radium tracer technique to estimate apparent ages with respect to fresh water in Apalachicola Bay. Our results confirm the findings of previous studies that the water circulation in the bay highly depends on river discharge, but is also influenced by prevailing winds and tidal patterns. However, the goal of our investigation was not to discern the relationship between flushing rate and these parameters, but to apply a simple technique to evaluate estuarine exchange that does not require discharge, wind, tide, and water current measurements. Our approach would be useful, therefore, even in remote locations where this type of information is typically not available.

Our results indicate that Apalachicola Bay flushing times range from 6 to 12 days. We found that river discharge is not necessarily the major factor determining flushing rates because winds and tides may change circulation patterns resulting in faster (January 2005) or slower (March 2004) flushing rates at comparable river flows. We also conclude that the limitations in applying the radium approach to Apalachicola Bay are radium inputs from other sources than the river: submarine groundwater discharge, diffusion from bottom sediments, regeneration and desorption from suspended particles, and seawater intrusion through the inlets. Despite these limitations the radium apparent age results were comparable to those derived by the 3-D circulation model and the theoretically calculated turnover times.

One of the significances of our results is that radium ages can be used to quantify transport processes of dissolved substances in the bay. Should soluble pollutants enter the bay

via the river, the radium tracer approach would show how such contaminants would be dispersed and flushed out of the bay. The radium tracer approach thus provides a tool for environmental managers to evaluate pollution dispersion in the estuary.

We conclude that the radium age technique is well suited for residence time calculations in river dominated shallow estuaries where the river is the major radium source to the system.

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