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Radium Sampling Methods and Residence Times in St. Andrew Bay, Florida

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Abstract Activity ratios (AR) of radium isotopes have been used with success to constrain estimates of water ages and to approximate residence times in coastal waters. We compared two common radium sampling methods (grab sampling and stationary moorings) to estimate water ages and the residence time of St. Andrew Bay waters in northwest Florida, USA. Both sampling methods utilize manganese dioxide fibers ("Mn fibers") to adsorb dissolved radium from the water column. Grab samples capture radium activities at a discrete time while moorings integrate radium activities over longer deployments. The two methods yielded similar results in this study and thus both approaches are useful for water age comparisons and residence time approximations. However, since radium often varies as a function of tidal stage, deploying moorings over a complete tidal cycle is the preferred approach. An estimated residence time for North Bay and West Bay of 8–11 days was approximated using ARs for both ex^{224}Ra/^{223}Ra and ex^{224}Ra/^{228}Ra. Some complications were introduced as St. Andrew Bay is a tidally dominated, rather than a river-dominated bay system where this method has previously been applied. The largest freshwater source to this bay system is from a man-made reservoir, with an average freshwater flow of only 20 m^3 s^{-1}. The activity concentrations and ARs measured by both sampling methods suggest that while the reservoir is the prominent radium source, it is not the only radium source. Nonetheless, a tidal mixing model applied to the western half of the system yielded an approximate flushing time of 10–12 days, similar to that derived from our radium-based water age approach.

Keywords Residence time · Water ages · St. Andrew Bay · Florida · Radium isotopes · Geochemical tracers

Introduction

The residence time of a system is an important parameter for defining the environmental sensitivity of a water body to land use, pollution, and development (Brooks et al. 2003; Huang 2007; Murphy and Valle-Levinson 2008; Wolanski 2007; Knee et al. 2011). We follow the definition of residence time based on Monsen et al. (2002), i.e., "the time it takes for any water parcel of the sample to leave the lagoon through its outlet to the sea." Residence times are controlled by many factors including tides, basin size and geometry, prevailing winds, and inputs from terrestrial and subsurface waters. Naturally occurring radium isotopes were evaluated as potential tracers of water movement in this study of a northwestern Florida bay system. One may evaluate "water or radium ages," i.e., "the time a water parcel has spent since entering the estuary through one of its boundaries" from radium isotopic data as described by Moore (2000a; Monsen et al. 2002). This radium water age approach was shown to be a useful method for estimating residence times in other estuaries such as Apalachicola Bay in Florida (Dulaiova and Burnett 2008), the Chao Phraya estuary in Thailand (Dulaiova et al. 2006), as well as other coastal systems (Moore 2000a; Kelly and Moran 2002). While a system's residence time can be calculated via hydraulic (water volume) models, the benefit of the radium isotope approach is it provides "age" information for different portions of the water body, i.e., the amount of time since the radium has been

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added to the system. One can thus evaluate relative mixing rates of differing portions of an estuarine system rather than evaluating the entire water body as a whole. If one focuses on the water age at the incoming and outgoing boundaries of a system, than the water age should approximate residence time.

There has been some confusion in the literature concerning the terminology used for residence time, flushing time, water age, etc. As mentioned above, we use the term "residence time" here to describe the time it takes for a parcel of water to leave the water body through its outlet to the sea. On the other hand, "flushing time" is seen as an integrative parameter describing the general exchange characteristics of a water body without identifying the underlying physical processes (Monsen et al. 2002). "Radium water ages" reflect the time elapsed since the water sample became enriched in Ra and was isolated from the source (Moore 2000a). The radium isotopic data presented are used to calculate water ages which we will use to assess the residence time by evaluating the water age when it leaves the study area. Although radium water ages and residence times are disparate, we can use the radium ages as a tool for evaluating residence time if we trace the radium from its source to where it exits the system in question (Monsen et al. 2002). For comparison, we will also calculate a flushing time based on a tidal prism model.

Radium has four naturally occurring radioactive isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) with varying half-lives (11.4 days, 3.66 days, 1,600 years, and 5.75 years, respectively). These isotopes are all radiogenic daughters of different thorium isotopes, a particle reactive element under almost all normal environmental conditions. In freshwater, radium tends to attach to particle surfaces rather than remain in solution (Li et al. 1977; Krest et al. 1999). As long as the radium remains on the particle with the thorium parent, it is considered to be "supported" because thorium will continually decay producing radium at the same rate radium decays. Upon entering a saline water body, radium becomes more soluble due to the increased ionic strength of the saline water, which promotes ion exchange processes. It readily desorbs from particle surfaces into solution and thus becomes "unsupported." A continual flux of radium from one source results in a unique and constant isotopic composition providing a fingerprint of the source term (Moore 2000a; Moore 2000b). Unsupported radium isotopes in solution will mix at the same rate but decay at their respective rates governed by their half-lives, and thus, provide a time scale for estuarine and coastal mixing.

Radium isotopes are introduced into estuarine waters either in solution or through desorption from particles transported via rivers and groundwater inputs. As the nuclides move through an estuary, both decay and mixing will influence their activity. Under certain conditions, the radium age of the water may be calculated based on the activity ratio (AR) of short-lived to longer-lived radium isotopes, the initial AR at the point of entry to the system, and the AR at the location of sampling. The objectives of this study were to compare two radium isotope field sampling methods, define the freshwater sources to the St. Andrew Bay system, and to estimate the water ages and extrapolate these to residence times of waters within St. Andrew Bay. We also compared our Ra-derived age determinations to a tidal mixing model.

Study Area and Methods

St. Andrew Bay, FL

This research investigated St. Andrew Bay, near Panama City in Bay County, Florida (Fig. 1). St. Andrew Bay spans approximately 230 km^2 and is comprised of four inter-

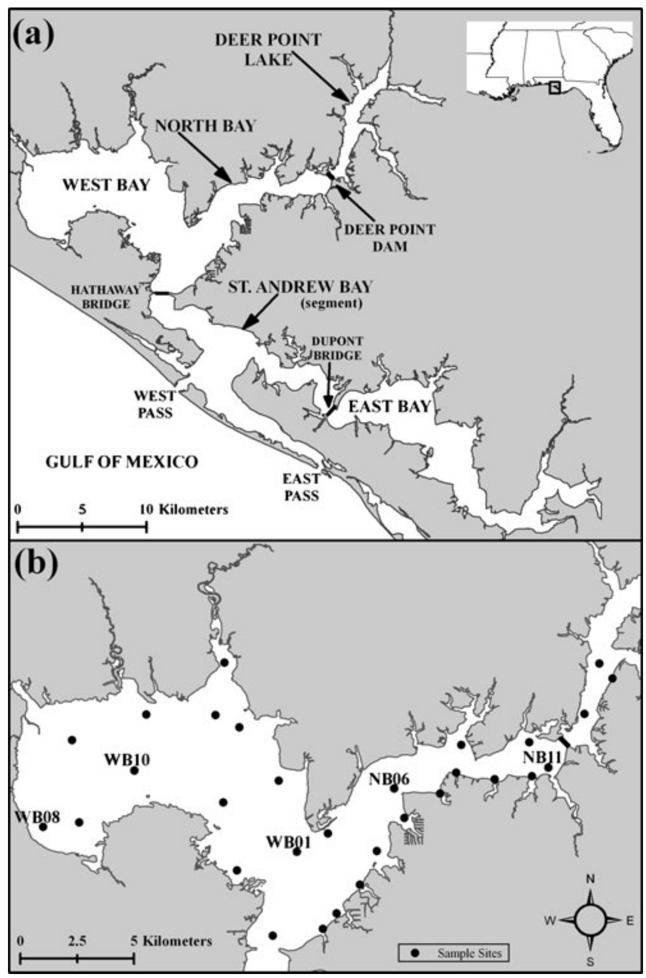

Fig. 1 (**a**) Map of St. Andrew Bay, Florida, in Bay County. (**b**) This study concentrated in Deer Point Lake, North Bay, and West Bay. All sampling sites are noted here, but the *labeled sites* represent site locations for the methods comparison portion of this project

connected water bodies: East Bay, West Bay, North Bay, and St. Andrew Bay (segment). The entire system has an average depth of 5 m with depths ranging from less than a meter in the shallow regions to around 20 m in the deepest areas (Rodriguez and Wu 1990). This study was concentrated in West Bay, North Bay, and Deer Point Lake. North Bay and West Bay combined have an approximate volume of 240×10^6 m^3 with an area of 100 km^2. In 1961, Deer Point Dam was built creating Deer Point Lake which has an area of 22 km^2 and a volume of about 45×10^6 m^3 (Ichiye and Jones 1961; Brim and Handley 2007; Huang 2007; Crowe et al. 2008). The bay system is influenced by diurnal tides with an average tidal range of less than a meter. The highest recorded tide during our study period was 1.15 m above mean sea level and the lowest was 0.58 m below.

Ra Collection Methods

Two different techniques were used to extract radium isotopes from bay waters. Both methods used negatively charged manganese-oxide fibers ("Mn fibers") which act as adsorbers extracting radium from the saline waters and concentrating it onto the fiber surfaces (Moore and Reid 1973; Moore 1976). The two methods tested in this study were grab sampling and stationary moorings. For grab sampling, the target water was pumped rapidly into large collection barrels. A flow meter recorded the volume of water (~70 L) collected for each sample. After collection, a peristaltic pump transferred the sampled water from the barrel through a cartridge containing Mn fibers at approximately 1 L min^{-1} for near quantitative adsorption of radium (Moore and Reid 1973; Dulaiova and Burnett 2004; Swarzenski et al. 2007). The sample fibers were then rinsed with radium-free water either in the field or back at the laboratory. This process removes any salt and dislodges any imbedded sediment from the fibers. Sediment can alter the radium concentrations skewing the final activity calculations and salt can interfere with radon emanation from the fibers (Dulaiova et al. 2006).

Grab sampling provides a snap-shot of the radium activities at the time of sampling representing the activity conditions at the particular time and location of collection and will not reflect any short-term changes in radium activities at the site. On the other hand, stationary moorings are deployed for an extended period of time and will be influenced by changes in the radium conditions over the deployment period thus providing an integrated view of the AR over that period.

The moorings were based on a design used in Dulaiova and Burnett (2008) where an anchor placed on the seabed is attached to a buoy on the surface. Approximately 1 m below the buoy two to three mesh bags are attached to the line. Mn fibers are placed in these bags allowing passive filtration and adsorption to concentrate the Ra in solution onto the fibers. Duplicate or triplicate mesh bags were deployed on each mooring to evaluate precision. Multiple bags yield replicate results for a single mooring without adding considerable effort or time yet providing additional confidence in the results. The moorings were deployed for approximately one full tidal cycle (~24 h). Deployments occurred during both neap and spring tides in order to represent all conditions; however, this area on the northern Gulf of Mexico is known to have a very small tidal range. As the natural radium activity concentrations and ARs may vary during such deployments, the Mn fibers will integrate these changes over the deployment period since the fibers will continually adsorb Ra from the bay waters while deployed. The Ra isotopes will begin to decay as soon as they attach to the Mn fibers, so the individual isotopes will have undergone different amounts of decay. To take this into account, the mid-point during the deployment is used as the collection time and the respective radium isotopes are decay corrected back to that time. The amount of water passing through the fibers throughout the deployment is unknown and likely variable between moorings preventing absolute activities from being calculated. However, ARs may be calculated from the total measured activities as the uptake of the individual radium isotopes should be consistent. Any volume differences between the moorings are thus eliminated by using ratios allowing for direct comparisons of ARs between moorings and grab samples.

Samples were collected during seven sampling trips beginning in February 2009 and ending in April 2010. Both sampling methods were used through the duration of this study although both methods were not always used during each sampling trip.

Counting Methods

To determine the activities of the radium isotopes adsorbed on the fibers, different approaches are taken for the short-lived and long-lived isotopes. The short-lived isotopes were counted immediately after sampling using a Radium Delayed Coincidence Counter or RaDeCC system (Moore and Arnold 1996). Ra-223 and the unsupported or excess ^{224}Ra (ex^{224}Ra) activities were determined with this counting method (Moore and Todd 1993; Moore and Krest 2004; Dulaiova and Burnett 2008). The long-lived isotopes do not require immediate counting given their much slower decay rates. Gamma-spectrometry is the most common method for determining ^{226}Ra and ^{228}Ra activities which requires the Mn fibers to be destroyed. The fibers were ashed in custom-designed steel crucibles at 600 °C for 6 h, crushed and then sealed to allow for ingrowth of radon and daughters before counting on the γ-spectrometer (Michel et al. 1981; Dulaiova and Burnett 2004). We also used a non-destructive method to determine ^{226}Ra via the ingrowth and emanation of its daughter ^{222}Rn using a radon-extraction line and Lucas cells (Peterson et al. 2009). All samples were processed by both methods yielding ^{228}Ra activities measured via γ-

spectrometry and duplicate results for ^{226}Ra from both counting methods. Most ^{226}Ra analyses agreed within the analytical uncertainty between the γ-spectrometric and Lucas cell approaches.

Estimating Radium Water Ages

We estimated water ages using radium ARs via Eq. (1) originally published by Moore (2000a):

$$\left[\frac{^{X}\mathrm{Ra}}{^{Y}\mathrm{Ra}}\right]_{\mathrm{obs}} = \left[\frac{^{X}\mathrm{Ra}}{^{Y}\mathrm{Ra}}\right]_{i} \frac{e^{(-\lambda_X)t}}{e^{(-\lambda_Y)t}} \qquad (1)$$

where $(^{X}Ra/^{Y}Ra)_{obs}$ represents the observed AR of a short-lived (x) to a longer-lived (y) isotope measured at the sampling locations, and the $(^{X}Ra/^{Y}Ra)_{i}$ is the initial AR of the same isotope pair in the source water. The t refers to the time passed since radium was added to the bay waters and disconnected from its source. The λ defines the decay constant for the individual isotopes. Equation (1) may be applied within certain parameters and assumptions, which include:

(a) Only one dominant source of radium exists and that source is characterized by a constant isotopic composition
(b) Offshore waters contain insignificant amounts of the short-lived radium isotopes
(c) Radium isotopes are only added from one source and only removed from the bay through mixing and radioactive decay

Stratification of the water column is important for the successful application of this technique because it isolates the bottom water from the surface waters preventing sediment from acting as an additional radium source and thus affecting the results. We collected temperature and salinity measurements from both surface and near-bottom layers to evaluate this parameter and found there was stratification in nearly all cases. Should any of the above mentioned assumptions not hold, this approach may not provide an accurate age and therefore not useful for estimating residence time for the system in question. In the cases where the assumptions appear to hold, one can solve Eq. (1) for t:

$$t = \ln \frac{\left[\frac{^{X}\mathrm{Ra}}{^{Y}\mathrm{Ra}}\right]_{i}}{\left[\frac{^{X}\mathrm{Ra}}{^{Y}\mathrm{Ra}}\right]_{\mathrm{obs}}} \times \frac{1}{\lambda_X - \lambda_Y} \qquad (2)$$

We will show here that while the situation in St. Andrew Bay apparently violates some of these assumptions, mainly because it does not have a single source of radium, the data trends provide reasonably good estimates of the overall age progression and residence time for this system based on the one dominant source.

Results and Discussion

Grab Samples Versus Stationary Moorings

The methods comparison portion of this study included ten mooring deployments with accompanying grab samples. The grab samples were taken before and/or after deployment. In the cases where two grab samples were taken for one mooring sample, the average of the two results is reported. All mooring results are an average of the duplicate or triplicate samples attached to each mooring. The reported results also include a tidal cycle experiment where grab samples were collected every 2 h during a 22-h mooring deployment at site location NB06 (Fig. 1b).

Not unexpectedly, we observed changes in the radium activities and ARs in St. Andrew Bay during the tidal experiment. Figure 2 illustrates the fluctuation of two ARs ($ex^{224}Ra/^{223}Ra$ and $^{223}Ra/^{228}Ra$) over the course of this experiment. The horizontal shaded fields represent the average AR measured in the mooring samples including the ratio's standard deviation. The grab samples ranged from 2.24±0.20 to 4.82±0.77 for the $ex^{224}Ra/^{223}Ra$ AR with an overall average of 3.03±0.13 compared to the average mooring AR of 3.52±0.13. The $^{223}Ra/^{228}Ra$ ARs of the grab samples ranged from 0.22±0.04 to 0.75±0.46 with an overall average of 0.36±0.16 compared to the mooring result of 0.26±0.02.

Radium activity variations over the course of a tidal cycle are not surprising. An ebbing tide will impart more of a "land or river signal," usually consisting of higher short-lived

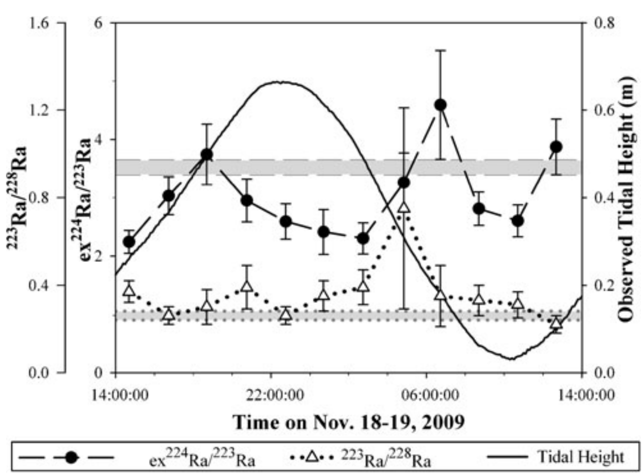

Fig. 2 AR results from a 22-h tidal experiment. The *horizontal lines* represent the average mooring ARs measured in the study area including the associated standard deviation. The *uncertainty bars* for the grab samples are ±1σ

activities and ARs (Peterson et al. 2008). This can be due to a more recent addition of radium from a river source or an increase in the hydraulic gradient during the falling tide causing enhanced groundwater flow into the estuary. Shifts in the hydraulic gradient and corresponding changes in groundwater flow over a tidal cycle with consequent variations in Ra activity ratios have been observed at other locations (Li et al. 1999; Hancock et al. 2000; Burnett et al. 2006; Paytan et al. 2006).

This trend was observed in both ARs throughout the experiment. When the results are pooled, the mooring results are within one standard deviation of the average grab sample AR thus confirming that this approach provides a good integrated view of the ARs over a tidal cycle. This agreement between the two methods was observed with the other deployments as well. Figure 3 contains the ARs measured from the grab samples and moorings for five deployments which are representative of the entire data set. More variation was measured in the ex^{224}Ra/^{228}Ra than the ^{224}Ra/^{223}Ra AR

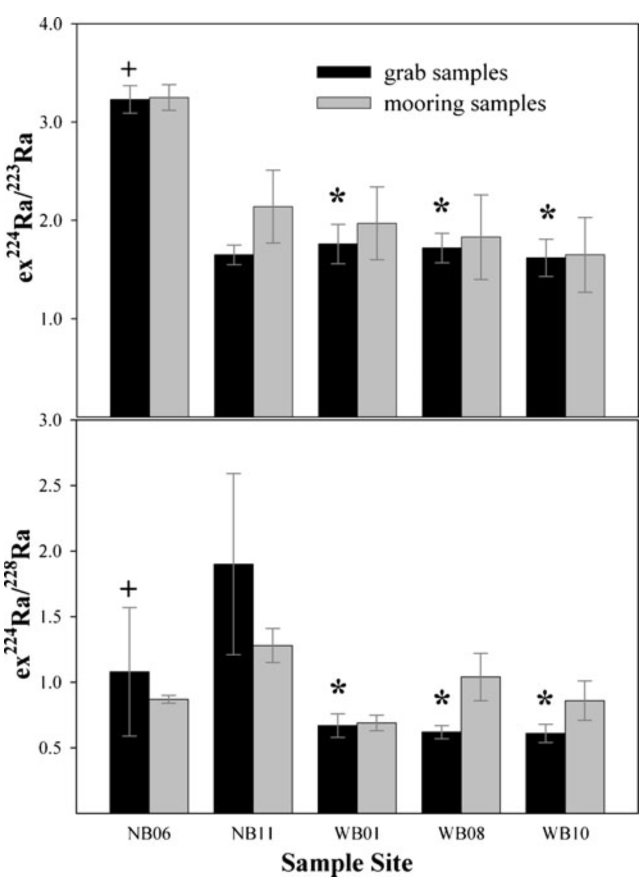

Fig. 3 Comparisons between ARs measured from grab samples and mooring samples at the same location. There is considerable overlap in the results from both methods. The *asterisk* indicates the grab sample results are an average of two grab samples taken both before and after mooring deployment. The *plus sign* indicates the results are from the tidal experiment with the grab sample result, an average of 12 different samples

because of the larger difference between the half-lives of ^{224}Ra and ^{228}Ra (a factor of ~600) in the first ratio compared to ^{224}Ra versus ^{223}Ra (approximately 3 times faster decay of ^{224}Ra than ^{223}Ra) in the latter AR. ^{223}Ra has a half-life on the same time scale as ^{224}Ra decreasing the influence the decay of ^{224}Ra will have on the ex^{224}Ra/^{223}Ra AR since both isotopes are decaying rather quickly. On the other hand, ^{228}Ra decays much slower than ^{224}Ra allowing the decay of ^{224}Ra to dominate the ex^{224}Ra/^{228}Ra AR. Therefore, the decay of ^{224}Ra will disproportionately have a larger impact in the ex^{224}Ra/^{228}Ra ratio (compared to the initial) than the ex^{224}Ra/^{223}Ra AR because ^{228}Ra is decaying so much slower than ex^{224}Ra.

Overall, the two methods yielded similar results with overlapping uncertainties in 80 % of the grab sample and mooring comparisons. Of course, the two methods are not designed to capture the same activity conditions. The grab samples represent a snapshot of the radium activities present at the exact time of sampling and are able to encompass a larger spatial area due to the sampling procedures. This method can be more variable than the mooring approach due to natural variability in the environmental conditions in the bays during the tidal cycle. Our results indicate the mooring approach represents a reasonable time-integrated view of the radium ARs over the deployment period reducing temporal variability. Depending upon the extent of the variation in ARs as a function of the tidal cycle, either grab samples or stationary moorings may produce comparable results when applied for water age calculations. In estuaries which are tidally dominated, and thus may experience more tidally mediated effects, moorings should be the preferred approach.

Radium Sources in St. Andrew Bay

Significant salinity gradients from North to West Bay indicate a separation of end members within the St. Andrew Bay system: the freshwater reservoir, Deer Point Lake (salinity=0), and the Gulf of Mexico with an average salinity of 35 (Fig. 1). Deer Point Lake is the largest single source of freshwater to the bay with an estimated average discharge of 20 m^3 s^{-1} over the dam (Musgrove et al. 1968; Hydroqual, Inc. and B.A. Vittor and Associates, Inc. 1993; Handley et al. 2007; Email communication, Bay County Official, 2010). Even with this relatively low discharge, the northern portion of North Bay is dominated by its influence given the significantly lower salinity waters in this area compared to the main sections of the bay system especially during periods after heavy rainfall. The remaining portions of North Bay and West Bay typically have intermediate salinities in the range of 20–30.

The radium activities or ARs do not show signs of the separation observed between the low and higher salinity waters. For example, almost all of the ^{226}Ra activities measured in North Bay and West Bay are higher than the freshwater end member, Deer Point Lake (Fig. 4). The activities measured inside of Deer Point Lake were barely higher than the ^{226}Ra activities typically measured in the Gulf of Mexico (Reid et al. 1979). The bay activities range from about 10 to 40 dpm 100 L^{-1}, with the highest activities in the intermediate salinities. This suggests multiple minor radium sources, in addition to Deer Point Lake. For example, springs and bayous are known to exist along the St. Andrew Bay boundaries and these may contribute to higher activities and ARs in the southern portion of the bay system. This trend was observed for all radium isotopes.

The highest ex$^{224}Ra/^{223}Ra$ ARs were measured inside of the freshwater reservoir, Deer Point Lake (Fig. 5). However, this was not the case with the ex$^{224}Ra/^{228}Ra$ AR. The radium isotopes had very low activities inside Deer Point Lake due to radium's particle reactivity in freshwater and the ex$^{224}Ra/^{228}Ra$ ARs were also very low. Nonetheless, consistently higher activities and ARs were measured in North Bay in close proximity to the dam in the low salinity waters, including the highest ex$^{224}Ra/^{228}Ra$ AR. After passing over the dam and entering the saline waters of North Bay, the radium isotopes, some attached to particles, readily entered solution increasing the ARs at this particular location. These low salinity waters with high associated ARs may thus be considered source waters.

Inside of West Bay and the southern reaches of North Bay, higher salinities were measured with lower radium ARs. The

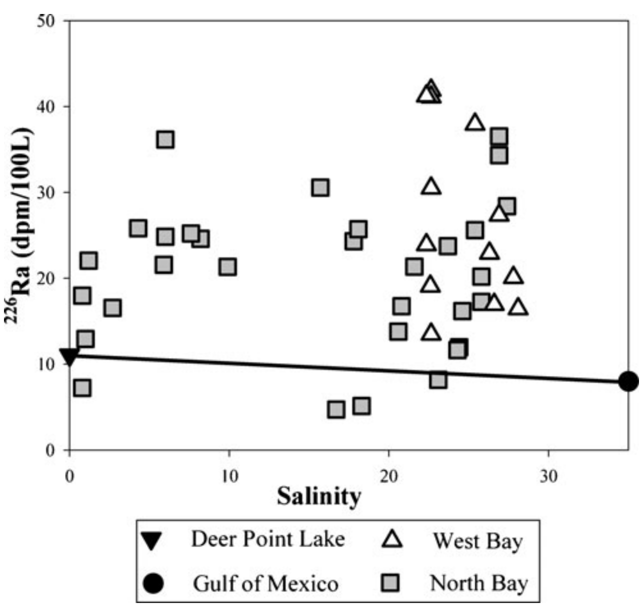

Fig. 4 Ra-226 activities plotted as a function of salinity indicate additional radium sources are present in St. Andrew Bay. The activities measured in the end members, Deer Point Lake and the Gulf of Mexico (Reid et al. 1979), are both lower than what was observed in the majority of the bay samples. This suggests multiple minor sources exist in St. Andrew Bay contributing to higher activities and AR in the bay system

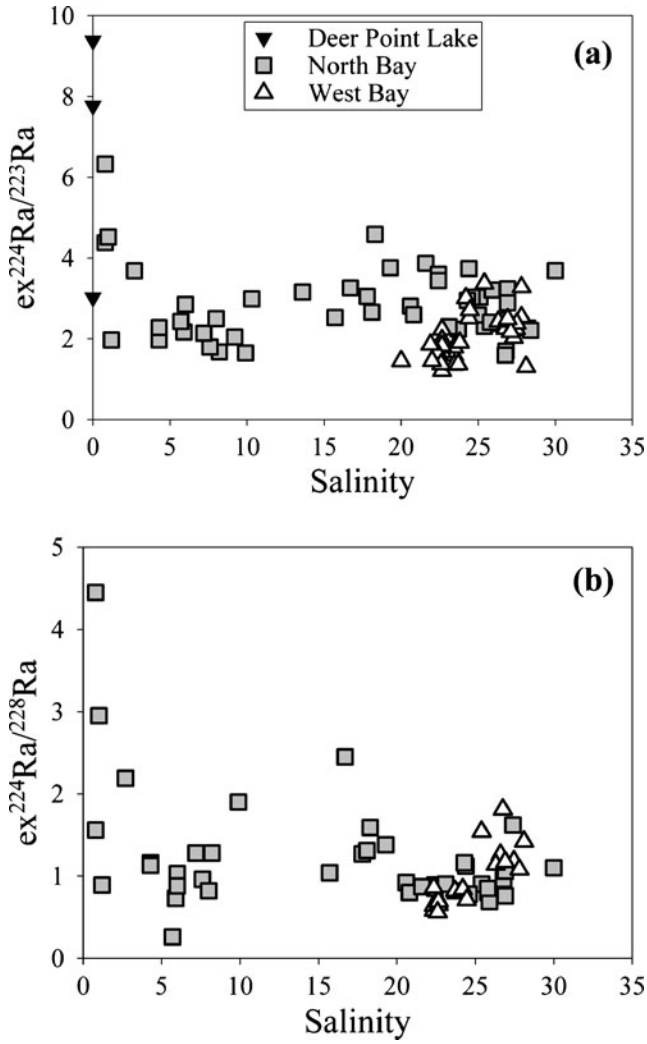

Fig. 5 Plots of (**a**) ex$^{224}Ra/^{223}Ra$ and (**b**) ex$^{224}Ra/^{228}Ra$ versus salinity. The highest ARs were measured inside of Deer Point Lake and just south of the Deer Point Dam. The most upstream and highest AR were used as initial AR for the residence time calculations (ex$^{224}Ra/^{223}Ra_i$=9.38, ex$^{224}Ra/^{228}Ra_i$=4.45). The data indicate Deer Point Lake as a radium source to St. Andrew Bay. These data were collected using both grab samples and stationary moorings

ARs decreased from the high ARs measured near the dam to a point where they became relatively constant between the salinities of 20 to 30. Within this salinity range, the ex$^{224}Ra/^{223}Ra$ and ex$^{224}Ra/^{228}Ra$ ARs remained relatively invariable at about 2 and 1, respectively. The North Bay waters are moving south and mix with West Bay waters creating this relatively constant AR throughout a large section of the bay.

The distribution of radium isotopes throughout the bay lacked any discernible seasonal trend. While samples were collected at various times of the year, the radium activity concentrations and patterns did not appear to respond to seasonal variations (Fig. 6). The April 2009 and November 2009 sampling consisted of only North Bay sites while only

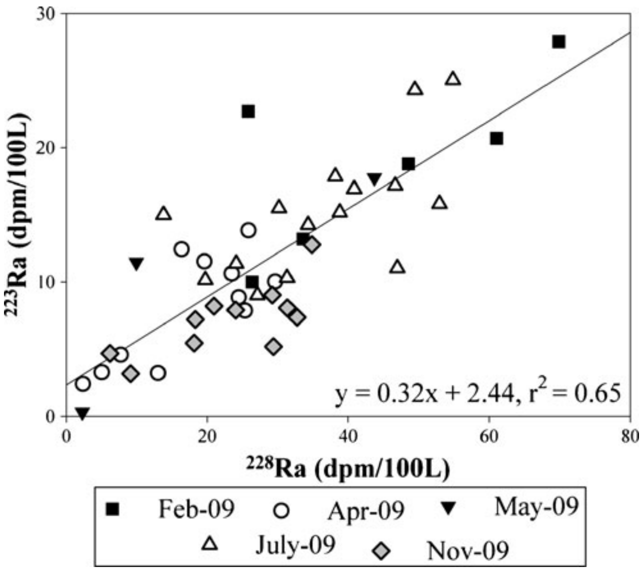

Fig. 6 A plot of ^{223}Ra versus ^{228}Ra show basically the same trend existed throughout several different sampling periods. The seasonal changes do not appear to have an influence on the radium conditions in St. Andrew Bay. In February 2009, only West Bay samples were collected while only North Bay was sampled during April and November 2009. The remaining sampling periods included both North Bay and West Bay sites

West Bay sites were collected during February 2009. The small differences observed are thought to be influenced more by site location than seasonal change. We noticed, for example, that the ^{223}Ra and ^{228}Ra activities overlapped during the May 2009 and July 2009 samplings. During these two periods both North Bay and West Bay were sampled relatively uniformly.

Water Age and Residence Time Calculations

Calculation of Radium Water Ages

The radium isotopic data from St. Andrew Bay indicates multiple radium sources may exist within the system which violates one of the prime assumptions for "age" dating as previously outlined. The water ages calculated via the Moore (2000a) equation (Eq. 1) can be used to estimate a residence time by evaluating the water ages as it leaves the bay waters relative to an initial AR. Multiple sources make it difficult to identify this initial AR because other sources could vary in size, flux, and Ra isotopic composition. A river-dominated estuary, on the other hand, would likely represent a case where there is one dominant radium source. However, St. Andrew Bay is a tidally dominated system with a relatively small freshwater contribution from Deer Point Lake. In spite of this relatively small signal, the influence from Deer Point Lake can be traced as it moves into the southern extent of our study area suggesting that it is the prominent radium source to the bay system. This source helps to negate influences from minor sources allowing us to make age estimations.

To evaluate residence time, we utilized the relatively stable AR previously observed in the 20–30 salinity range (Fig. 5) since they are indicative of the Ra signatures observed as the waters leave our study area rather than the whole bay system. The observed AR utilized for the equation is an average of 28 samples measured in this range using both sampling methods. The initial ARs were the most upstream and consequently highest ARs. These were taken from Deer Point Lake (ex^{224}Ra/^{223}Ra) and from the northern tip of North Bay, just south of Deer Point Dam (ex^{224}Ra/^{228}Ra). For the ex^{224}Ra/^{223}Ra age calculation, the initial AR applied was 9.38±2.75 while the average observed AR was 2.21±0.25 (range=1.21±0.11- 3.37±0.24) yielding an estimate of St. Andrew Bay's residence time of just over 11 days. Using the range of ex^{224}Ra/^{223}Ra ARs observed, the range in water ages would be 7.1 to 15.8 days. The ex^{224}Ra/^{228}Ra AR calculation had a similar, but slightly lower result of approximately 8 days based on an initial AR value of 4.45±3.47 and an observed AR of 0.93±0.12 (range=0.48±0.03–1.81±0.16, which would indicate a range in radium ages from 4.7 to 11.6 days). Substantial error can be associated with these calculations, but it has been determined the ratios utilized have lower degrees of uncertainty than other radium ratio combinations. Additionally, the highest uncertainty is found with calculated water ages less than 5 days and with individual Ra activity errors greater than 10 % (Knee et al. 2011). The activity uncertainties measured during this project were on average less than 10 % and therefore the calculated ages should be a reliable representation of the flushing throughout this area.

The calculated results provide estimates of the transit time from the Deer Point Lake source to the North and West Bay portions of the St. Andrew Bay system. After leaving North Bay, we assume it takes only a short time to exit the bay through the passes and thus our estimates of water age approximate residence time. Our estimates are lower than a previous study completed by Solis and Powell (1999) although not inconsistent with their results as they considered the entire St. Andrew Bay system while we are only considering North Bay and West Bay. They applied a freshwater fraction method resulting in an overall residence time of approximately 20–25 days for the entire bay system.

Flushing Time Calculation via a Tidal Prism Approach

For an additional comparison, we employed a flushing time calculation based on a tidal mixing model. Since North Bay and West Bay do not have a direct connection to the Gulf of Mexico, we had to extend our evaluated area for these calculations and spilt the entire bay system into two sections. The passes open into the middle of St. Andrew Bay segment with its boundaries defined by the western Hathaway Bridge and the eastern DuPont Bridge (Fig. 1). Geographically this is the mid-point of the bay system and we will assume that half of the incoming tide will move east into East Bay and the other half northwest into our study area leaving us with an east and west section of St. Andrew Bay. Since our Ra approach was limited to North and West Bay, we applied our tidal model to the western section only which included the west half of St. Andrew Bay segment. The Monsen et al. (2002) tidal model was applied accordingly:

$$T_{\mathrm{f}} = \frac{VT}{(1-b)P} \tag{3}$$

where T_{f} is the flushing time parameter, and V is the water volume. T represents the tidal period of 24.8 h, b is a return flow factor estimated at 0.1–0.2 and P is an estimated tidal volume of 55×10^6 m^3 for the western section (Table 1). These latter two parameters were estimated using historic tidal data for this area (Hemming et al. 2011). The total water volume (V) is 490×10^6 m^3 which includes 170×10^6 m^3 from West Bay, 68×10^6 m^3 from North Bay and 250×10^6 m^3 from the western half of St. Andrew Bay segment. The return flow factor describes the fraction of bay water returning to the system with each flood tide. A value of 0.1 to 0.2 assumes the incoming tide is comprised of 10 % to 20 % bay waters and 80 % to 90 % Gulf of Mexico water. This estimation was based on the average salinities outside of West Pass (~31) from a multi-year sampling project by the St. Andrew Bay Resource Management Association (Hemming et al. 2011). Given this information the residence time was determined to be between 10 and 12 days. The assumptions inherent to this calculation are:

(a) Estuarine waters are well-mixed
(b) River input must be small and not dominate over the tidal pulse
(c) Gulf water outside the bay system must have a consistent salinity
(d) The water body is in steady state with a sinusoidal tidal signal

Table 1 Definition of the variables used for the tidal prism model and the values used to calculate the flushing of the western portion of St. Andrew Bay

Variable	Value	Definition
T_{f}	–	Flushing time parameter
V	490×10^6 m^3	Water volume (North Bay+West Bay+1/2 of St. Andrew Bay segment)
T	24.8 h	Tidal period
b	0.1–0.2	Return flow factor (fraction of bay water returning with the flood tide)
P	55×10^6 m^3	Estimated tidal volume

Monsen et al. (2002) states this flushing time calculation will, in general, yield a lower-limit estimate since most water bodies are stratified and not completely well-mixed as is the case for St. Andrew Bay.

Overall, the ARs appear to be relatively constant throughout the majority of North Bay and West Bay especially in the salinity range of 20–30. Repeated sampling over several seasons indicates these areas are close to a steady-state condition with respect to salinity and radium isotopes. Data indicated Deer Point Lake is the dominant freshwater source to the area with the main flushing influences from the tides. In the western portion of St. Andrew Bay, our radium approach estimated the residence time between 8–11 days. The tidal mixing model flushing time estimate of 10–12 days was slightly longer, but encompassed a larger area and is therefore consistent with this estimate.

Conclusions

This study compared two radium sampling methods and determined radium ages and residence times for St. Andrew Bay, Florida. The two sampling methods tested are both established methods for sampling radium isotopes (Moore 1990; Huh and Ku 1998; Moore 2000b; Hwang et al. 2005; Burnett et al. 2008; Dulaiova and Burnett 2008; Kim et al. 2008). We compared grab sampling and stationary mooring methods with similar results between them. The grab sampling technique is able to capture the radium activities present in the water column at the exact time and place of sampling and is more sensitive to the immediate environmental conditions. Activity concentrations and ARs can be calculated using this method, while moorings are only able to calculate ARs. However, since mooring samples requiring less equipment and on-site time provide an integrated view of the radium ARs over the entire deployment period (e.g., a tidal cycle), it is preferred for residence time evaluations, especially in tidally dominated water bodies where more temporal variation would be expected. This was also the preferred method for a similar comparison study preformed off shore in the Indian Ocean (Bourquin et al. 2008). Combining both methods allows researchers to capture different aspects of the flow conditions in a dynamic system.

Evaluating radium ages, we estimated the residence time of the North and West Bay portions of St. Andrew Bay at 8 to 11 days. This estimate is similar to a tidal mixing model that predicted a flushing time of 10–12 days for the western half of the bay system. The consistency of these results suggests that at least in this area the radium approach can successfully be applied to a water body not dominated by a river source.

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