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**RADIUM ISOTOPES AS SEDIMENT-WATER INTERFACE  
TRACERS: INDIAN RIVER LAGOON, FLORIDA**

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by

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# **RADIUM ISOTOPES AS SEDIMENT-WATER INTERFACE TRACERS: INDIAN RIVER LAGOON, FLORIDA**

## **Introduction**

Isotopic disequilibria can readily occur in ground water and coastal waters between pairs of isotopes in the  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  decay series. For example, disequilibria between  $^{238}\text{U}$  and  $^{234}\text{U}$  (i.e.,  $^{234}\text{U}/^{238}\text{U}$  ratios) have been observed to range from 0.5 to over 20 in varied ground waters (Osmond and Cowart, 1982; Asikainen, 1981; Dickson et al., 1983). Laboratory experiments confirm that uranium isotopes are fractionated by alpha recoil effects (Fleischer, 1982; Sun and Semkow, 1998), as well as by physico-chemical differences in oxidation states and bonding energies (Beneš et al., 1982). Similar processes also effect the fractionation of other isotopes in the U-Th decay series (Fig. 1), such as Th, Ra, Pb or Po (Ivanovich and Harmon, 1982). However, it is often easier to explain such disequilibria by the chemical properties and long half-lives of the intermediate radionuclides. Decay of  $^{232}\text{Th}$  to  $^{228}\text{Th}$ , for example, occurs via the decay of  $^{228}\text{Ra}$ , and in this decay sequence each parent-daughter radionuclide exhibits unique geochemical behaviors that facilitate isotopic disequilibria (Kadko et al., 1987). Coastal bottom sediments older than ~10 years will therefore likely have thorium activity ratio

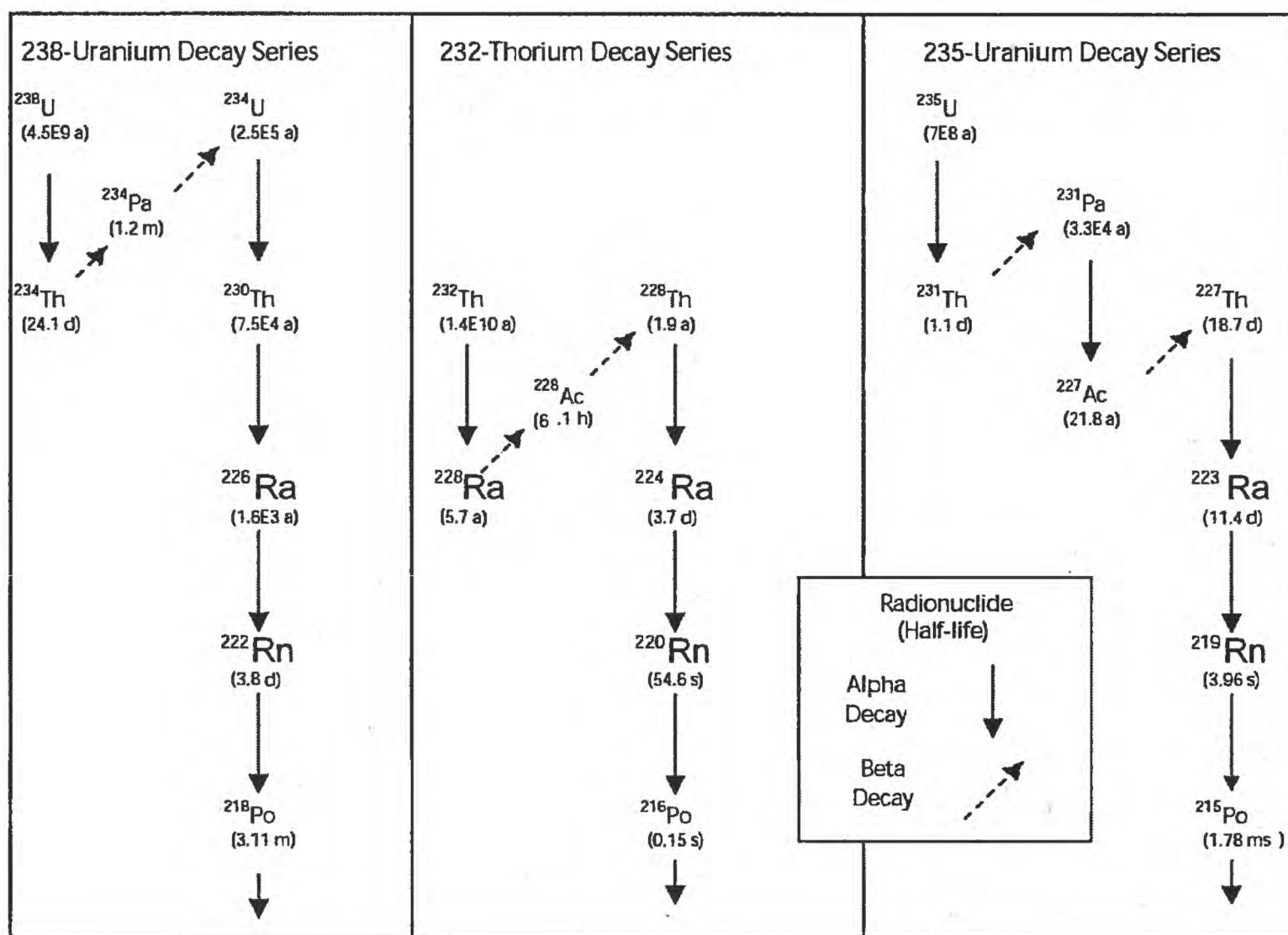


Figure 1. Decay chains of the U and Th series isotopes and the half life of each isotope. The vertical arrows represent alpha decay and the diagonal arrows represent beta decay.

( $^{228}\text{Th}/^{232}\text{Th}$ ) much less than one (Ivanovich and Harmon, 1982), while the overlying water column activity ratios can become quite large (5-30).

In the past, only two of the four naturally occurring isotopes of radium were considered to be useful in environmental disequilibrium studies (Cochran, 1980; Rama and Moore, 1996). As the daughter of  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$  ( $t_{1/2} = 1600$  yr) is usually present in excess of its parent in natural waters, and the greater solubility of Ra over Th facilitates the upward diffusion of radium across the sediment-water interface (Li et al., 1977; Webster et al., 1994, 1995; Boynton et al., 1995; Hancock and Murray, 1996). Current

estimates suggest that about 25% of  $^{226}\text{Ra}$  in seawater originates from coastal sediments via such diffusion/advection (Ivanovich and Harmon, 1982). Radium-228 ( $t_{1/2} = 5.75$  yr), is the direct daughter of  $^{232}\text{Th}$ , and like  $^{226}\text{Ra}$ , is also found in excess of its parent in natural waters due to diffusion/advection (Hammond et al., 1990; Ghose et al., 2000). The remaining two radium isotopes,  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ , have much shorter half-lives of 11.4 days and 3.7 days, respectively. Due to recent advances in our detection capabilities (Moore and Arnold, 1996) can we now begin to utilize these 'new found' isotopes as short-lived water mass or sediment-water interface tracers (Swarzenski, 1999; Hancock et al., in press). Collectively, radium isotopes can thus provide a powerful suite of naturally occurring tracers that span a time window from days to 1000's of years.

If we assume a constant rate of supply from a parent nuclide, then the activity of a particular daughter isotope in solution can be expressed by the first order decay equation:

$$A_t = A_\infty(1 - e^{-\lambda t}), \quad (3-1)$$

where  $t$  is the contact time between a solid and solution,  $A_t$  is the activity at time  $t$ ,  $A_\infty$  is the activity at secular equilibrium, and  $\lambda$  is the decay constant ( $\lambda = \ln 2/t_{1/2}$ ). For either  $^{223}\text{Ra}$  or  $^{224}\text{Ra}$ ,  $\lambda t$  is considerably larger than 1; even in relatively 'young' waters the expression  $(1 - e^{-\lambda t})$  rapidly approaches 1 (equilibrium) as  $t$  exceeds  $\sim 50$  days. In contrast, for long-lived  $^{226}\text{Ra}$ ,  $\lambda_{226}t$  is much less than 1, and thus  $(1 - e^{-\lambda t})$  remains close to the value of  $\lambda_{226}t$ . Therefore, where ground-water residence times are small, one will likely obtain high values of  $^{223}\text{Ra}/^{226}\text{Ra}$  ratios relative to equilibrium ( $^{223}\text{Ra}/^{226}\text{Ra} = 0.046$ ) values, i.e.,  $(^{223}\text{Ra}/^{226}\text{Ra})_t$  will approach  $(^{223}\text{Ra}/^{226}\text{Ra})_\infty/\lambda_{226}t$ . One objective of this

paper is thus to determine the utility of radium as a sediment-water interface tracer in the northern section Indian River Lagoon, where it is hydrogeologically feasible that 'recycled' ground water can discharge into lagoon bottom waters.

## **2 Sampling and Analytical Methods**

The field effort for this project was divided into two sampling trips that were timed to correspond to dry (May, 1999) and wet (August, 1999) precipitation seasons. During a third trip (December, 1999), several previously deployed interstitial water samplers (multi-samplers/peepers) were sampled and retrieved. An unusually large number of energetic tropical weather systems (Floyd: 09/99, Harvey: 09/99 and Irene: 10/99) directly affected our study area by increased precipitation and wind-driven storm surge.

A series of ground water samples was collected during the dry and rainy season sampling trips from several private and monitoring wells around the perimeter of our field site. Each well was first purged and then sampled using either peristaltic or rotary vane pumps. To ensure adequate purge volumes, hydrologic parameters such as pH, dissolved oxygen, conductivity, salinity and temperature were simultaneously measured.

Twenty one-liter samples of ground water were collected for radium isotopes. Water samples from the lagoon proper were collected from a series of shore-perpendicular transects, from several end-member sources (Turnbull Creek, Haulover Canal), as well as from numerous mid-lagoon sites. For radium, large volume (50 - 150 L) lagoon samples were collected approximately 20-cm off the sediment water interface

with a rotary vane pump. Interstitial waters were also collected for radium analyses using three unique methods; conventional-type (diameter = 60 cm) seep meters (Lee, 1977), multi-samplers consisting of an array of finely screened tubing, and 60.75-L benthic flux chambers. Radium was quantitatively removed from all water samples onto pre-weighed  $\text{MnO}_2$  impregnated acrylic fiber packets. The efficiency of Ra adsorption was periodically monitored by a second Mn column placed in series below the first column. Uncertainties in Ra isotope activities correspond to  $1\sigma$  counting errors.

Ground water and lagoon surface/interstitial water samples were analyzed for the two short-lived radium isotopes and  $^{228}\text{Th}$  by delayed coincidence alpha scintillation counting. Mn fibers were transferred to the laboratory as soon as possible to minimize the loss of radium due to radioactive decay. The fibers were rinsed in distilled and de-ionized water to remove sea salts, partially air dried, and then placed into a He gas recirculating line linked to a 1.1-L scintillation cell directly connected to 5" photo-multiplier tubes (PMT). Scintillation signals were routed via a Ortec PMT base to a delayed coincidence computer program that time discriminated alpha decays of  $^{219}\text{Rn}$  and  $^{220}\text{Rn}$  produced by the radioactive decay of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  (Moore and Arnold, 1996). The Mn fibers were subsequently re-analyzed after about 4 – 6 weeks to allow for the initial excess  $^{224}\text{Ra}$  to equilibrate with  $^{228}\text{Th}$ , which also quantifiably adsorbed to the fiber. Background activities in each of the two delayed coincidence systems were monitored after every sample run. Isotopic standards derived from  $^{227}\text{Ac}$  and  $^{232}\text{Th}$  were analyzed periodically, as well as after each batch sample run (approximately every twelfth sample). Activities of  $^{226}\text{Ra}$  were measured on a separate water sample either by Rn emanation or by  $\gamma$ -ray spectrometry.

### 3.3 Results and Discussion

#### 3.3.1 Hydrography

Indian River Lagoon (IRL) is subtropical in climate, and precipitation generally follows a seasonal pattern. A typical dry season period extends from January through May. During both sampling trips in 1999, monthly precipitation values were considerably greater (~130 - 160%) than the 30-yr accumulated rainfall averages. Nonetheless, during the dry season (May 1999) sampling trip, salinity in the lagoon was typically in excess of seawater (35‰), averaging 38.1‰. Water column temperatures fluctuated daily from a low of 23 - 27 °C. The ~ 9% enrichment in lagoon salinities relative to open ocean seawater values reflect heightened rates of evaporation of lagoon water relative to water mass renewal rates. The salinity of Turnbull Creek, which traverses a large wetland north of IRL, was only slightly below 35‰, and further suggests minimal fresh water exchange and long water residence times in the lower reaches of this distributary wetland system. Haulover Canal forms the only conduit between IRL and Mosquito Lagoon, which is another shore-parallel coastal lagoon system that does have limited exchange with the Atlantic Ocean. Small-scale baroclinic forces facilitate water exchange through Haulover Canal. The salinity of Haulover Canal (36.1‰) indicates an integration of water mass mixing and transport processes water within these two lagoon systems.

During August 1999 average water column salinities (36.2‰) and water temperatures were consistently lower than during the May cruise. In contrast, ground

water samples from the same well sites reflect little change in either temperature or conductivity from wet to dry season.

### **3.3.2 Ground Water**

Sources for ground water on the east coast of Florida can consist of several discrete components that originate from the Surficial, Intermediate or Floridan Aquifers. The Surficial Aquifer is contained within highly permeable Plio-Pleistocene strata and usually responds rapidly to local precipitation/evaporation events. There is evidence of discontinuous confining layers within the Surficial Aquifer (Toth, 1988), which could facilitate vertical ground water mixing. A deeper Eocene (~ 40 million year old) Ocala Limestone forms one of the most productive formations of the Floridan Aquifer system. Above the Ocala Formation, the clay-rich confining Hawthorn Group generally thins out in the vicinity of the study site, and discontinuous, inter-bedded limestone deposits may contain ground water of various sources (Surficial to Floridan) (Bermes, 1958).

Regional-scale potentiometric surface maps of the Upper Floridan suggest a positive hydrostatic head differential relative to sea level in upper Indian River Lagoon (Figures 3-2 and 3-3). Based on such maps that rely on a network of variable well data, the potentiometric surface of the upper Floridan does not appear to fluctuate by more than +/- 2 m seasonally.

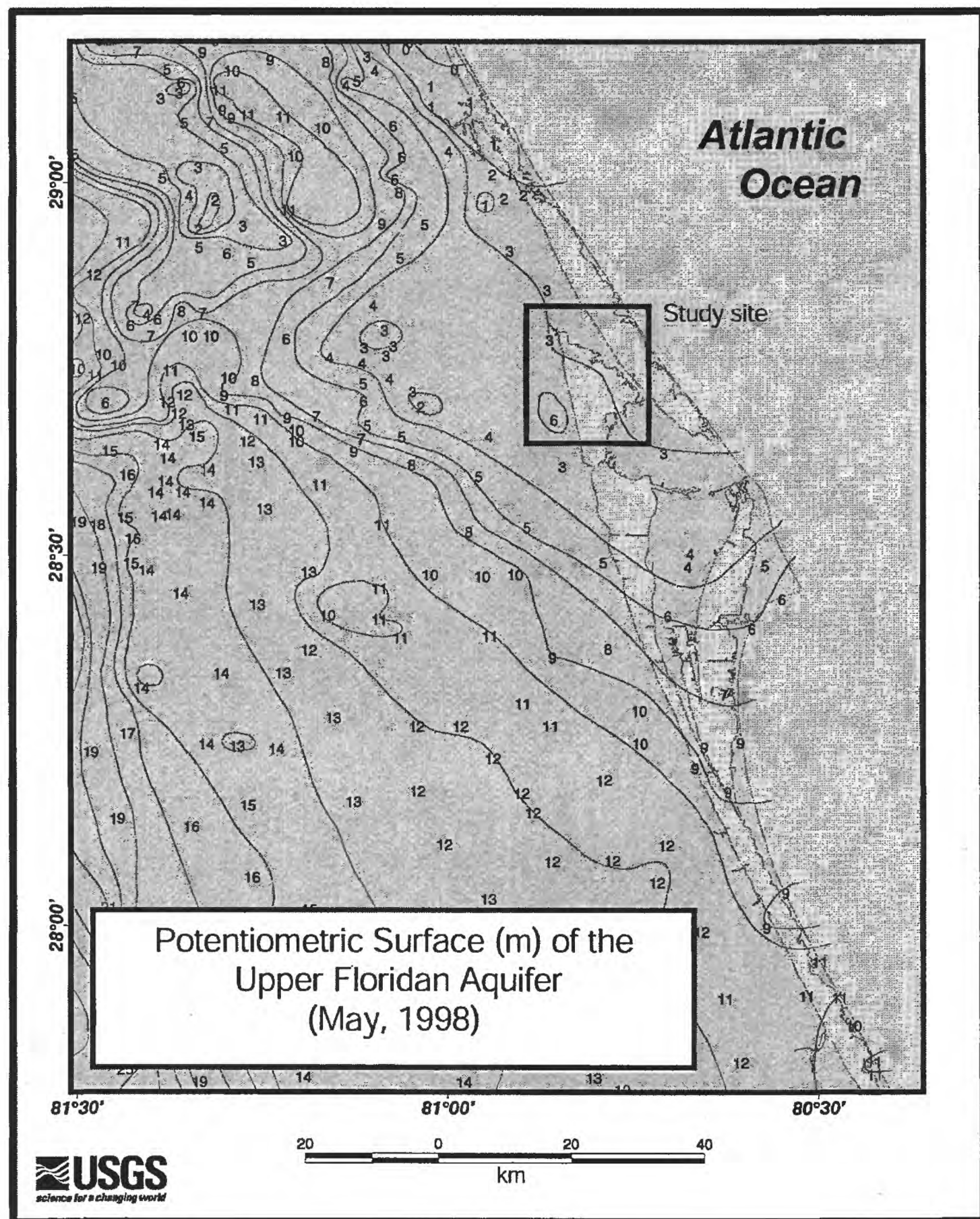


Figure 3-2. Potentiometric surface map of the Upper Floridan Aquifer in the vicinity of upper Indian River Lagoon for May, 1998. (After Bradner, 1998)

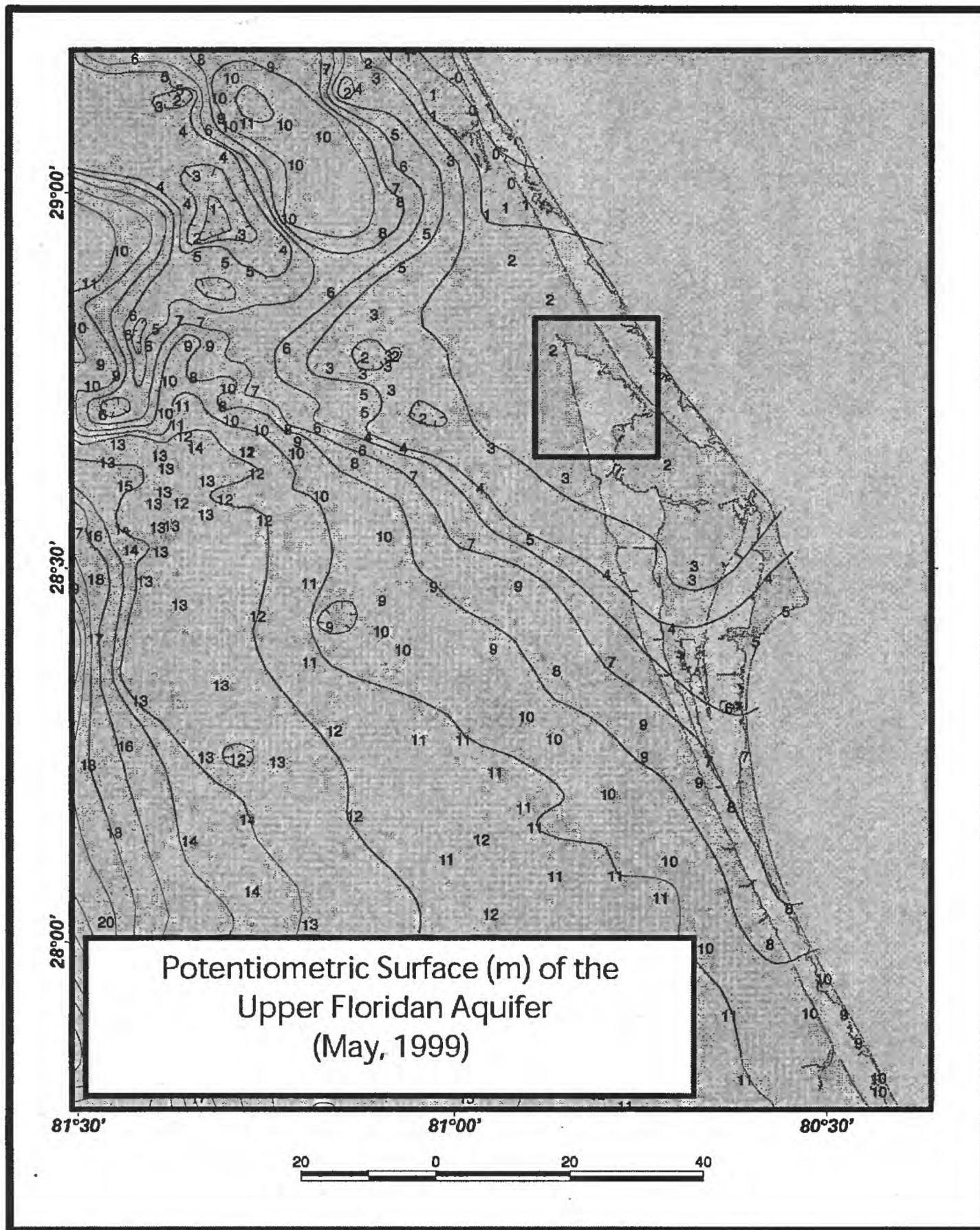


Figure 3-3. Potentiometric surface map of the upper Floridan Aquifer in the vicinity of upper Indian River Lagoon for May, 1999. (After Bradner and Knowles, 1999)

### 3.3.3 Radium Isotopes

The lagoon and ground water radium isotope activities for May and August 1999 are compiled in Appendices B and C. This discussion will describe and interpret the behavior of Ra from the following sample sets: 1) overall trends, 2) endmembers (ground water samples, Turnbull Creek and Haulover Canal), 3) shore-perpendicular transects (Stations IRL-1 - 8, 17 - 20 and 21 - 24), 4) mid-lagoon stations (Stations IRL-11, 16, 25, 26, 28) and 5) interstitial waters (IRL-4).

The two short-lived radium isotopes ( $^{223,224}\text{Ra}$ ) exhibit slight spatial and temporal variability in upper Indian River Lagoon (Table 3-1), and Ra activities were generally higher during the rainy season (August). Although mean lagoon-wide  $^{223}\text{Ra}$  activities remained constant (0.10 dpm/L),  $^{224}\text{Ra}$  activities increased by a factor of 1.2 from May to August. As expected, dissolved  $^{228}\text{Th}$  activities were low ( $\sim 3$  dpm/100L) in the water column, and can be largely discounted as an *in situ* source for dissolved Ra. The  $^{223,224}\text{Ra}$  activities in two sources of surface water to the lagoon (Haulover Canal and Turnbull Creek) were comparable to lagoon water Ra activities. In these inlets, mean  $^{223}\text{Ra}$  activities increased slightly from May to August, while  $^{224}\text{Ra}$  remained constant.

During the time of sampling, radium isotope mass balance estimates do not suggest significant water exchange through either inlet. This does not imply zero net water exchange per se (Smith, 1992), but rather indicates that surface water radium activities in the inlets and lagoon waters are insensitive to surface water mass movements.

**Table 3-1. Mean radium and  $^{228}\text{Th}$  activities for lagoon, ground water and creek/inlet water (May, August 1999).**

Sample type	Depth (m)	$^{223}\text{Ra}$ (dpm/L)	ex $^{224}\text{Ra}$ (dpm/L)	$^{228}\text{Th}$ (dpm/100L)	$^{226}\text{Ra}$ (dpm/L)	223/226 AR*	224/223 AR
<i>May, 1999</i>							
<i>Lagoon waters</i>							
Mean	1.21	0.10	0.09	3.86	2.05	0.05	0.98
STDEV	n/a	0.03	0.02	1.29	0.23	0.01	0.36
<i>Ground waters</i>							
Mean	29.70	1.38	6.86	23.77	3.59	0.46	9.97
STDEV	n/a	1.54	3.49	0.41	2.06	0.41	7.41
<i>Creek and inlet waters</i>							
Mean	n/a	0.08	0.14	3.14	2.42	0.03	1.70
STDEV	n/a	0.05	0.11	0.18	0.60	0.01	0.29
<i>August, 1999</i>							
<i>Lagoon waters</i>							
Mean	1.07	0.10	0.11	3.39	2.63	0.04	1.16
STDEV	n/a	0.02	0.02	0.82	0.26	0.01	0.32
<i>Ground waters</i>							
Mean	29.70	0.87	5.28	23.87	n/a	n/a	6.88
STDEV	n/a	0.31	2.70	0.38	n/a	n/a	4.54
<i>Creek and inlet waters</i>							
Mean	n/a	0.10	0.14	2.56	3.01	0.03	1.35
STDEV	n/a	0.05	0.09	0.31	0.73	0.01	0.26

\*AR =activity ratio (unitless)

Ground water  $^{223,224}\text{Ra}$  activities from wells surrounding upper Indian River

Lagoon were typically an order of magnitude greater than lagoon water activities. The highest  $^{224}\text{Ra}$  activities (~ 10 dpm/L) were observed at wells GW2,4, which are among the deepest wells (~ 37 m) in our field site and likely tap the Upper Floridan. The shallower wells (GW3,6) access the Surficial Aquifer and exhibit widely fluctuating radium activities ( $^{223}\text{Ra}$ : 0.39 – 4.61 dpm/L and  $^{224}\text{Ra}$ : 1.34- 7.96 dpm/L). At GW4, the  $^{224}\text{Ra}/^{223}\text{Ra}$  ratio exceeded a value of 14 during August 1999. Such elevated ratios reflect

variations in U/Th isotopic compositions of the source strata (Osmond and Cowart, 1982; Rama and Moore, 1996).

There is no apparent correlation between well depth and radium activities for either field season. The variable radium activities and activity ratios suggest abundant lateral and vertical transport between the Upper Floridan and Surficial Aquifers. Well GW-3 extends only into the Surficial Aquifer (open depth = 1.5 – 4.6 m), yet it has an isotopic signature that implies a mixture of several ground water sources. The mobility of ground water can be considerably enhanced through karst conduits or through fractures. Due to rapid sorption reactions, the mobility of radium once released to solution by alpha recoil or by decay of Th is likely to be very limited. Thus the source for radium in ground water is usually close to the well structure itself (Asikainen, 1981; Dickson et al., 1983; Rama and Moore, 1996).

Shore-perpendicular transects (Big Flounder and Duck Roost Cove) within the lagoon have highest excess  $^{224}\text{Ra}$  activities closest to shore. In contrast,  $^{223}\text{Ra}$  activities generally increase along these transects toward the middle of the lagoon. A plot of  $^{223}\text{Ra}$  from samples with water depths less than 1.5 m (removing the mid-lagoon samples) suggests a potential correlation with depth (Fig. 3-4). However, such a bottom effect is clearly not evident using  $^{223}\text{Ra}/^{226}\text{Ra}$  ratios, although most values suggest a lowered (i.e., depleted)  $^{223}\text{Ra}$  activity relative to the secular equilibrium isotopic ratio ( $^{223}\text{Ra}/^{226}\text{Ra} = 0.046$ ). It is possible that this bottom effect may indicate a time-dependent dilution of water being exchanged across the sediment-water interface. Because of the short half-life of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$ , exchange processes at the sediment-water interface may be examined with much greater resolution than using only long-lived radium isotopes ( $^{228,226}\text{Ra}$ ).

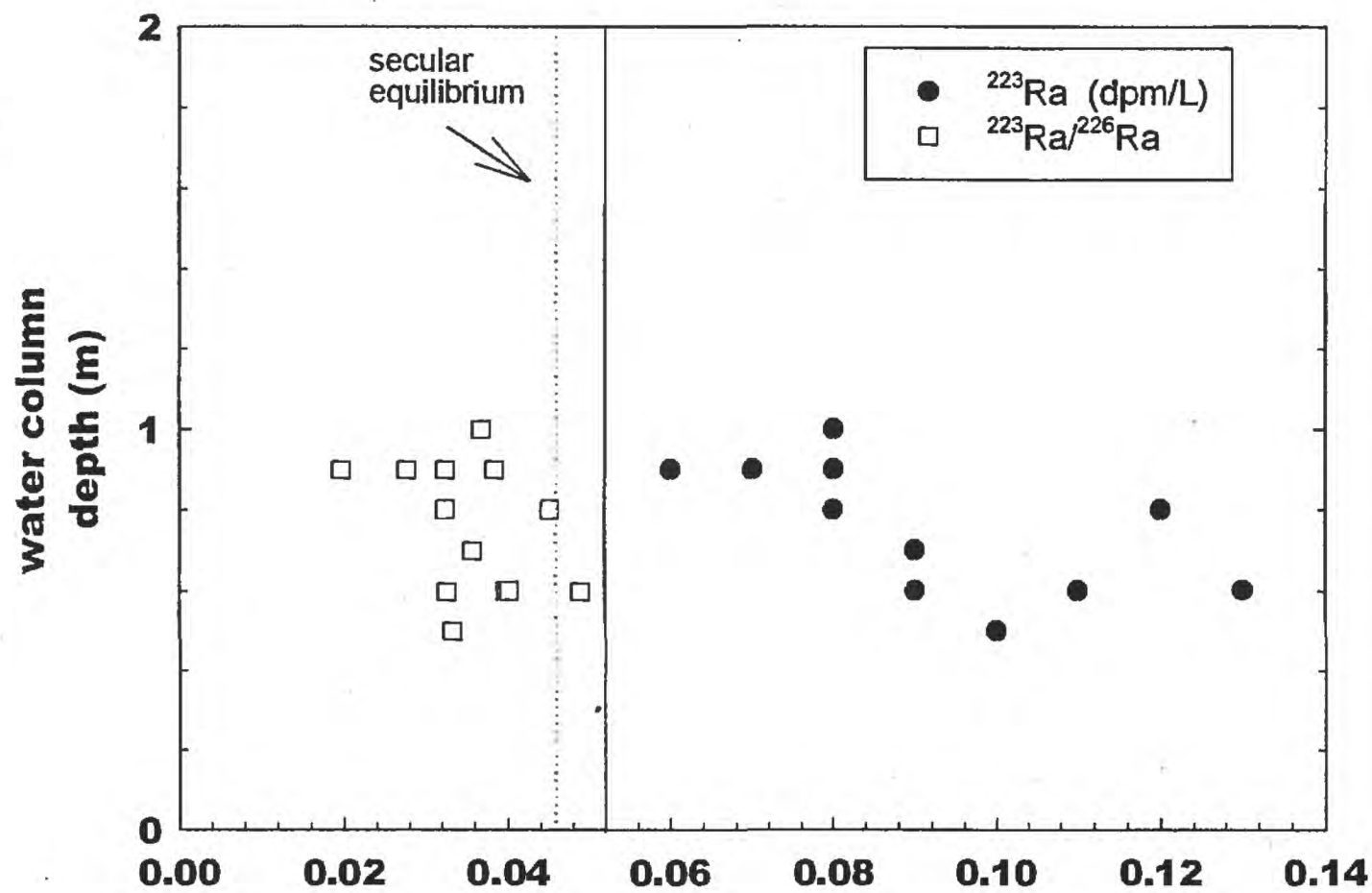


Figure 3-4. Water column ( $z < 1.5$  m) profile of  $^{223}\text{Ra}$  activities (dpm/L) and  $^{223}\text{Ra}/^{226}\text{Ra}$  activity ratios (August, 1999). The deep water stations have been excluded here to look only at sediment effects and dilution.

To quantify exchange across the sediment-water interface in upper Indian River Lagoon, two methods will be presented that provide an indirect measure of flux, albeit on very different spatial scales. These results will then be compared to a simple diffusion model (Berner, 1980; Santschi et al., 1990; Hammond et al., 1999) using interstitial radium profiles.

### 3.3.4 Flux measurements

To estimate flux across the sediment-water interface in upper Indian River Lagoon, input and removal functions for water and radium must be well constrained. The field site at upper Indian River Lagoon is effectively isolated from adjacent surface water bodies except at Haulover Canal, which connects Mosquito River Lagoon to Indian River Lagoon. By comparing salinities, Turnbull Creek in essence forms a northward extension of Indian River Lagoon. It is expected that only during high precipitation events will Turnbull Creek discharge freshened waters to upper Indian River Lagoon. At the southern boundary of the study site, dredged materials from the Intercoastal Waterway form a 'quasi' sill that limits water exchange with Indian River Lagoon proper. Generalized flow in upper Indian River Lagoon can therefore be expressed simply as a function of the lagoon area,  $A$  and the time-dependent mean water depth,  $h(t)$ :

$$Q = A \frac{dh}{dt}. \quad (3-2)$$

Water levels in this confined region of the lagoon are controlled seasonally by winds, precipitation/evaporation and tidal oscillations (Smith, 1992; 1993). Due to the small tidal amplitude of upper Indian River Lagoon, water transport through Haulover Canal is largely a wind-driven process (Smith, 1992). As suggested, this is a potential source and/or sink for lagoon water radium isotopes. Although the mean inlet  $^{223}\text{Ra}$  activities are comparable to lagoon values for both field seasons (Table 3-1),  $^{224}\text{Ra}$  activities were consistently higher in Turnbull Creek, suggesting a possible marine source (via thorium).

The flux of radium in upper Indian River Lagoon is calculated first by simple mass balance ('lagoon budget method'). In doing so, the time-dependant mass of Ra in the lagoon ( $VRa_L$ ) can be modeled as function of the area-integrated flux of Ra across the sediment-water interface ( $AJ$ ) plus the mass of Ra being transported through Haulover Canal ( $QRa_{inlet}$ ), minus the mass of Ra lost due to radioactive decay ( $\lambda VRa_L$ ):

$$\frac{d}{dt}(VRa_L) = AJ + QRa_{inlet} - \lambda VRa_L, \quad (3-3)$$

where  $V$  is the volume ( $m^3$ ),  $Ra_L$  is the radium activity in the lagoon (dpm/L),  $J$  is the flux (dpm/ $m^2$ /d) of radium from the lagoon sediment into the water column, and  $Ra_{inlet}$  is the Ra activity at Haulover Canal. The term  $J$  is estimated by adjusting its value until it matches the observed lagoon activities,  $Ra_L$ .

### 3.3.5 Benthic Flux Chambers

Exchange across the sediment-water interface may also be constrained on a very localized scale by the use of benthic flux chambers (Fig. 3-5). The flux of radium into such chambers can be evaluated by assessing the change in Ra activity over the deployment duration. We positioned two benthic flux chambers (Boxes 1 and 2) about 3 cm into the seabed at IRL-6, in about 1 m of water. The two benthic chambers were placed about 2 m apart (see Chapter 4). The 45 x 45 x 30 cm boxes were periodically hand-stirred to maintain a well-mixed chamber water column. The initial ( $t = 0$ ) activity of radium was measured in a water parcel adjacent to the chamber (Table 3-2).

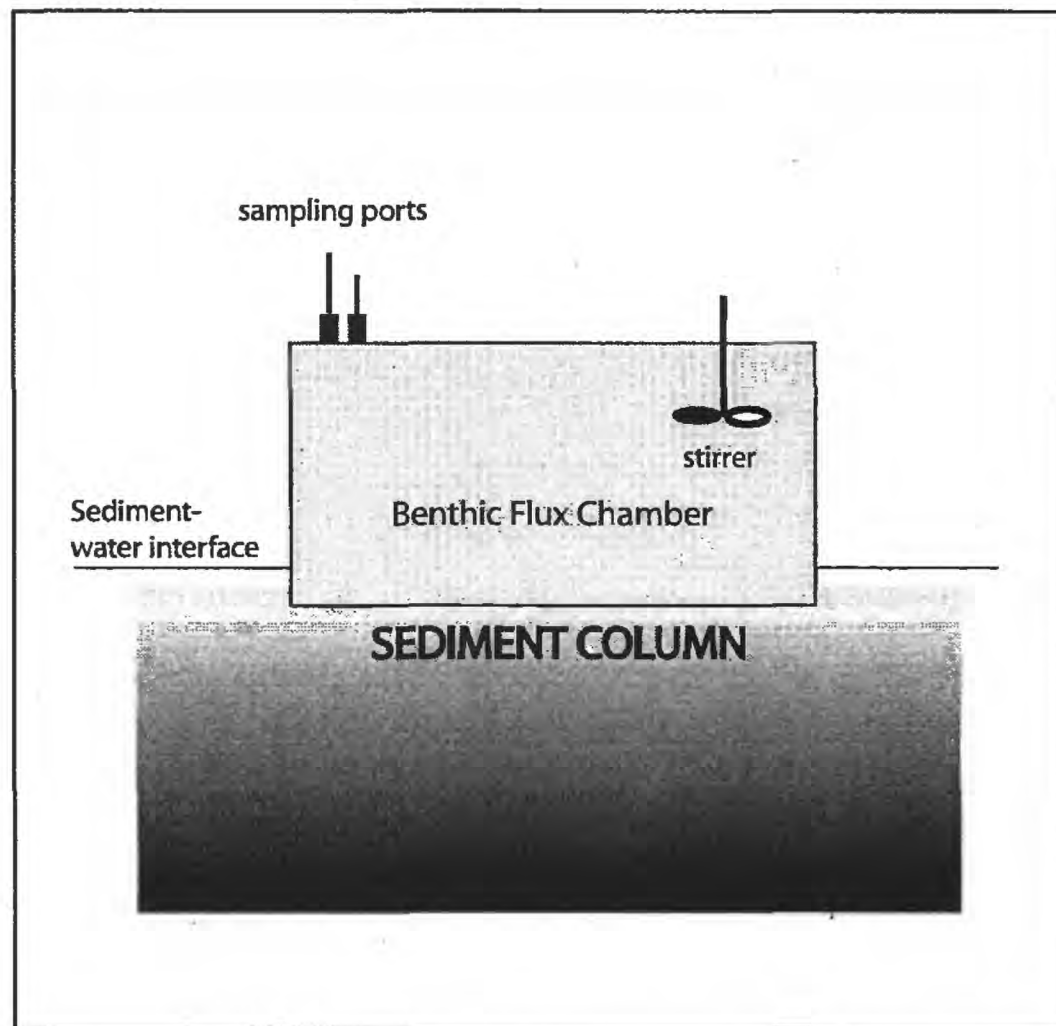


Figure 3-5. Placement of a benthic flux chamber into bottom sediments.

Because an unknown amount of ambient lagoon or subsurface water may be hydraulically drawn into a benthic chamber during time-series ( $t = 4, 8$  hr) sampling, the following corrections were applied to  $Ra_{ch}$  (after Hancock et al., in press), assuming that the chambers were reasonably well-mixed for the duration of the experiment:

$$Ra_{ch} = (Ra_{t8} - Ra_L)b \frac{1}{(1 - e^{-b})} + Ra_L, \quad (3-4)$$

**Table 3-2. Time series radium activities in two benthic flux chambers.**

Station	Date	Time (hours)	<sup>223</sup> Ra (dpm/L)	ex <sup>224</sup> Ra (dpm/L)	<sup>228</sup> Th (dpm/100L)	<sup>226</sup> Ra (dpm/L)
<i>Big Flounder Transect</i>						
IRL 6	8/17/99	initial @ $t = 0$	$0.12 \pm 0.01$	$0.11 \pm 0.01$	$3.42 \pm 0.34$	$2.34 \pm 0.43$
Box 1		$t = 4$				$2.69 \pm 0.11$
		$t = 8$	$0.14 \pm 0.01$	$0.13 \pm 0.01$	$3.38 \pm 0.34$	$2.93 \pm 0.17$
		initial @ $t = 0$	$0.12 \pm 0.01$	$0.11 \pm 0.01$	$3.61 \pm 0.36$	$2.46 \pm 0.10$
Box 2		$t = 4$	$0.11 \pm 0.01$	$0.10 \pm 0.01$	$3.34 \pm 0.33$	$2.50 \pm 0.14$
		$t = 8$	$0.13 \pm 0.01$	$0.12 \pm 0.01$	$3.76 \pm 0.38$	$2.65 \pm 0.31$

where  $Ra_{ch}$  is the radium activity within the chamber,  $Ra_{lg}$  is the radium activity measured at the conclusion of the experiment ( $t = 8$ ) and  $b$  is the sample-to-chamber volume ratio. Short-lived radium isotope activities increased by about 15% over the 8-hr deployment period. Similarly, <sup>226</sup>Ra activities increased about 7 – 20% in the two chambers during the 8-hr experiment.

For a chamber of height  $h_c$ , the change in radium activity ( $Ra_{ch}$ ) can be expressed as a function of the sediment-water interface flux ( $J$ ):

$$\frac{dRa_{ch}}{dt} = \frac{J}{h_c} - \lambda Ra_{ch} \quad (3-5)$$

Setting the initial chamber activity equal to the corresponding lagoon activity ( $Ra_{ch} = Ra_L, t = 0$ ) as a boundary condition and assuming a constant value for  $J$  (integrated over the surface area beneath the chamber) provides the following solution to Eq. 3.5:

$$\frac{J - h_c \lambda Ra_{ch}}{J - h_c \lambda Ra_L} = e^{-\lambda t}, \quad (3-6)$$

which can be rearranged for  $J$ , as follows:

$$J = \frac{h_c \lambda (Ra_{ch} - Ra_L e^{-\lambda t})}{1 - e^{-\lambda t}} \quad (3-7)$$

The calculated fluxes will be compared with results from other techniques in section 3.5.7 (e.g. Table 3.5). Minimum propagated errors for  $J$  are based on  $\pm 1 \sigma$ .

### 3.3.6 Pore Water Profiles

The exchange of radium across the sediment-water interface as well as the shape of the interstitial Ra profile depend on the rate of Ra production from sediment-bound Th isotopes, and on physico-chemical processes that can remove radium; i.e., decay and diffusion/advection (Cochran, 1980; Kadko et al., 1987; Hammond et al., 1990). Chapter 4 summarizes some of the principal processes that can affect the distribution of radium in coastal settings (excluding the atmospheric evasion term, which only affects gaseous radionuclides such as radon).

It has been shown that horizontal transport from adjacent water bodies is not a major input function for radium to our study site. Radioactive decay is an important mass balance term for any short-lived radioisotope, and is of course quantifiable. The more difficult two terms are diffusion along reasonably static geochemical gradients (diagenetically controlled diffusion) and physically-enhanced advection/diffusion that

responds to water level fluctuations (tidal pumping, ground water upwelling) and/or water mixing. Separating these two processes is important but often a daunting task.

Pore water profiles provide an integrated summary of the subsurface biogeochemical reactions. Such profiles, when used in conjunction with other sediment-water interface techniques (i.e., lagoon budget method and benthic chambers), can sometimes provide the necessary information to distinguish water flow across the sediment water interface from diffusive fluxes. Pore waters were collected using a mini-piezometer ('multi-sampler'), which enables *in situ* interstitial water to be drawn from various sediment depths. Chloride concentrations and other hydrographic parameters of these pore waters are described in Chapter 2. Table 3-3 lists the pore water radium activities for station IRL-4.

At IRL-4, pore water radium activities for each isotope increased with depth.  $^{224}\text{Ra}$  exhibited the smallest down-core increase in activity (5%), while  $^{226}\text{Ra}$  activities increased the most (~ 40%). Because radium is continuously being generated in the bottom sediments of Indian River Lagoon, the rate of production can define pore water Ra profiles. The rate of Ra production in sediments is usually defined in terms of an exchangeable component that is available for desorption by ion-exchange processes (Webster et al., 1994, 1995; Hancock et al., in press). Exchangeable Ra is produced by the decay of particle reactive Th and Ac isotopes either at particle surface sites (or coatings), or within the mineral structure itself. Alpha recoil processes may also eject Ra atoms directly into solution (Fleischer, 1982; Sun and Semkow, 1998), where they are scavenged rapidly and then partitioned between sediment surfaces and pore water.

**Table 3-3. Pore water radium isotope activities at Station IRL4.**

Station	Depth (cm)	<sup>223</sup> Ra (dpm/L)	<sup>224</sup> Ra <sub>xs</sub> (dpm/L)	<sup>228</sup> Th (dpm/100L)	<sup>226</sup> Ra (dpm/L)
<i>Big Flounder Transect</i>					
Overlying water*		0.14 ± 0.01	0.10 ± 0.01	4.70 ± 0.47	2.39 ± 0.09
Pore water (12/13/99)	39	2.79 ± 0.28	5.89 ± 0.59	10.24 ± 1.02	2.21 ± 0.19
	64	2.51 ± 0.25	4.45 ± 0.45	8.38 ± 0.84	2.53 ± 1.16
	95	3.58 ± 0.36	4.69 ± 0.47	11.92 ± 1.19	2.82 ± 0.24
	124	3.82 ± 0.38	5.13 ± 0.51	12.72 ± 1.27	3.13 ± 0.85
	156	4.21 ± 0.42	7.47 ± 0.75	13.76 ± 1.38	3.20 ± 0.16
	185	4.43 ± 0.44	6.19 ± 0.62	10.87 ± 1.09	3.92 ± 0.014

\* mean from IRL-5 dry and rainy season sampling (see Appendices B and C). This site was chosen as a water column end-member.

The production rate,  $P$ , of exchangeable Ra per unit volume of dry sediment can be expressed as a function of the sediment porosity ( $\phi$ ), the Ra decay constant ( $\lambda$ ) and the activity of exchangeable Ra ( $Ra_{exch}$ ) per unit volume of saturated sediment (Webster et al., 1994, 1995):

$$P = \frac{\lambda Ra_{exch}}{1 - \phi} \quad \text{Eq. 3-8}$$

A measure of  $Ra_{exch}$  can be derived from sediment Ra/Th ratios. In upper Indian River Lagoon the mean  $^{228}\text{Ra}/^{232}\text{Th}$  ratio for eight surface sediment samples (excluding the one potentially anomalous  $^{228}\text{Ra}$  measurement; 1.65 dpm/g) was 2.02 (Chapter 4), roughly two times above the secular equilibrium value of 1.0. Such enrichment in surficial sediment daughter isotopes is attributed mainly to the enhanced solubility of Ra relative to Th (upward diffusion of Ra), source rock heterogeneities, redox associated post-depositional mobility of Ra, or a ground-water influence. Such activity ratios observed in

Indian River Lagoon are not excessive, especially in dynamic coastal settings (Bollinger and Moore, 1993; Webster et al., 1995; Hancock and Murray, 1998).

The pore water flux across the sediment-water interface was calculated using a derivation of Fick's first law (Berner, 1980; Aller, 1980; Santschi et al., 1990):

$$J = -\phi D_s \left( \frac{dRa_p}{dz} \right)_{z=0} \quad \text{Eq. 3-9}$$

where  $\phi$  is porosity (interstitial water volume fraction),  $D_s$  is a tortuosity-corrected molecular diffusion ( $D_s \theta^2$ ) coefficient (Li and Gregory, 1974; Boudreau, 1998; Hammond et al., 1999),  $Ra_p$  is the depth dependent pore water radium activity and  $z$  is depth below the sediment-water interface. The most difficult decision in determining calculated fluxes is the choice of concentration gradients for the dissolved pore water profiles (Fig. 3-6). We used the bottom and upper most pore water sample to determine two concentration gradients that provided a range of flux estimates. The calculated flux of dissolved radium out of the seabed could thus still over-estimate the total flux due to adsorption/precipitation across the redox boundary.

A mean (May and August) water-column Ra value from a site most proximal to IRL-4 was used as the end-member value for flux calculations. A sample calculation for the diffusive flux of  $^{223}\text{Ra}$  using Eq. 3.9 is presented in Table 3-4. The concentration gradient in pore water radium activities from a depth of 185 cm to above the sediment-

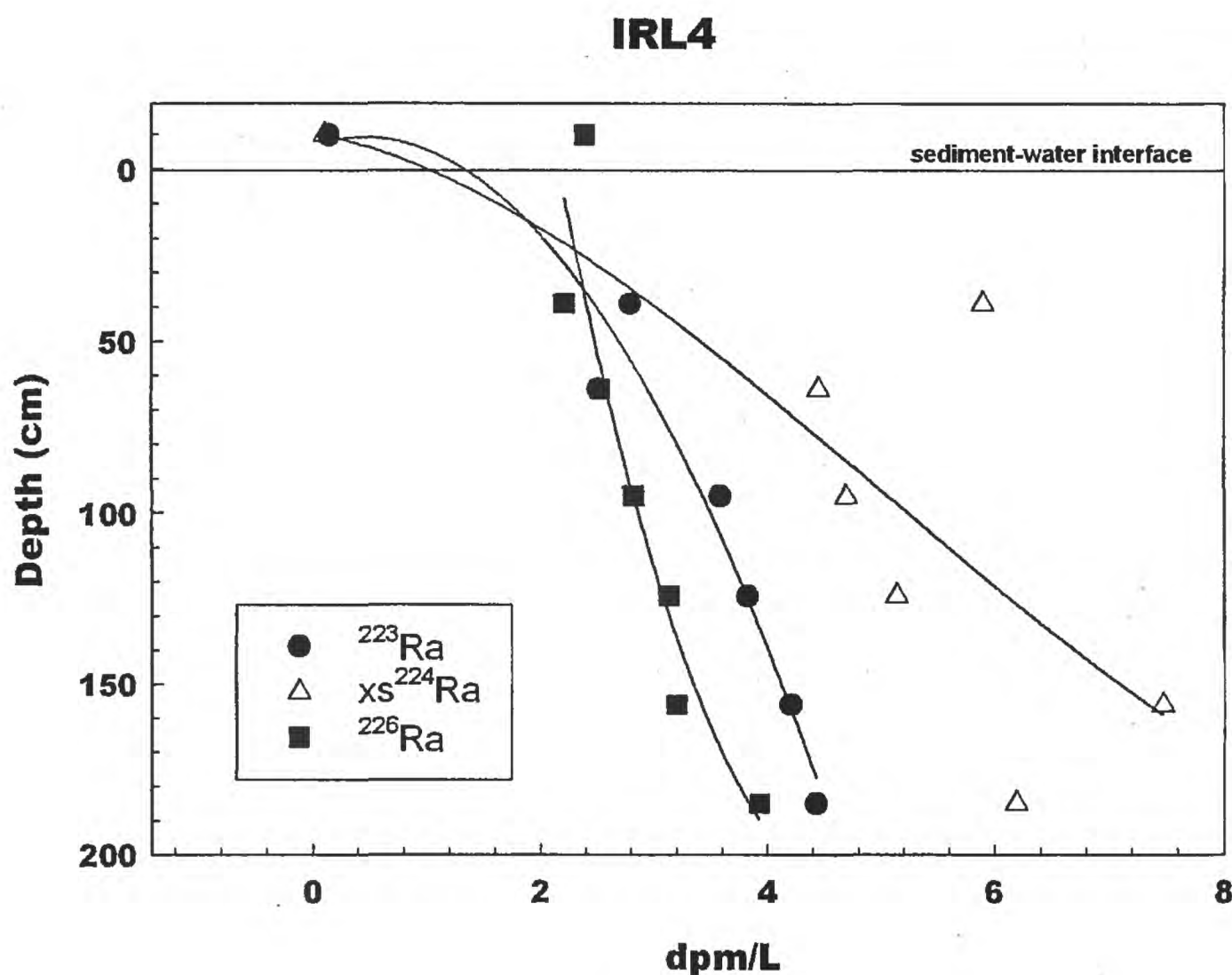


Figure 3-6. Pore water profiles for  $^{224}\text{Ra}$ ,  $^{223}\text{Ra}$  and  $^{226}\text{Ra}$  at IRL4. These interstitial waters were collected *in situ* by mini-piezometer (multi-sampler).

water interface was smallest for  $^{226}\text{Ra}$ , which may be explained due to its long half-life (i.e., slow production). By contrast, both  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  exhibited pronounced increases in activity with depth relative to the overlying water column activities. The removal of Ra in the surface sediments is attributable to upward Ra diffusion.

To complement such diffusive flux calculations, we also estimated the upper limit of subsurface water exchange. This in effect utilizes benthic flux measurements to derive

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**Table 3-4. Calculating diffusive fluxes with  $^{223}\text{Ra}$ .**

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Supporting formula and data:

$$J = -\phi D_s \left( \frac{dRa_p}{dz} \right)_{z=0}$$

$$\phi = 0.90 \text{ (Trefry et al., 1992)}$$

$$D_s = 6.90 \times 10^{-5} \text{ m}^2 / \text{day}; \theta = 1.211; \text{corrected } D_s = 5.7 \times 10^{-5} \text{ m}^2 / \text{day}$$

$$\frac{dRa_p}{dz} = \frac{4.43 - 0.14 \text{ dpm/L}}{185 - 0 \text{ cm}} = 2,319 \text{ dpm/m}^4$$

$$J = 0.9(5.7 \times 10^{-5} \text{ m}^2 / \text{d})(2,319 \text{ dpm/m}^4) = 0.119 \text{ dpm/m}^2 / \text{d}$$

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a rate of upward water transport (cm/day). Based on the deepest pore water  $^{226}\text{Ra}$  activity at IRL-4 (Table 3-3; 3.93 dpm/L) and using a sediment porosity ( $\phi$ ) value of 0.90 (Trefry et al., 1992), requires an upward subsurface water flux,  $J_w$  of 6 - 17 cm/d to sustain the observed benthic flux ( $J_b$ , Table 3-2; 160 – 480 dpm/m<sup>2</sup>/d), as follows:

$$J_w = \frac{J_b}{Ra_p \phi} \quad \text{Eq. 3-10}$$

Although the flow of subsurface water is likely much less than the values derived from Eq. 3.10, the range in  $J_w$  agrees well with similar results obtained for Indian River Lagoon during this study and others (Belanger and Walker, 1990; Belanger and Montgomery, 1992).

### 3.3.7 Comparison of the Three Flux Measurements

Lagoon budget and benthic chamber calculations provide an integrated measurement of flux of Ra across the sediment-water interface during the sampling duration. Such results differ fundamentally from those derived via seepage meters ('direct' measurements) that produce a localized and at times controversial flux rate. The two radium flux methods described here provide information on  $J$  over very different spatial scales. The two benthic chambers measure flux across the sediment-water interface on a small and localized scale. In contrast, the lagoon budget method provides an integrated lagoon-wide estimate of the flux across the sediment water interface. This latter method is therefore sensitive to integrated sources and sinks for Ra in the lagoon. Due to long half-life of  $^{226}\text{Ra}$ , the uncertainties associated with the lagoon budget method using  $^{226}\text{Ra}$  can be quite large. Similar flux measurements using either  $^{223,224}\text{Ra}$  are much easier to constrain, and uncertainties are correspondingly lower (~20 %, Hancock et al., in press). Table 3-5 lists direct and modeled values for  $J$ , in units of  $\text{dpm}/\text{m}^2/\text{day}$ . All three techniques show reasonable agreement in calculated  $J$ . Lagoon budget methods produced a flux for the two short-lived Ra isotopes that ranged from ~ 7 – 22  $\text{dpm}/\text{m}^2/\text{d}$ . By contrast, the same approach using  $^{226}\text{Ra}$  produced a 'zero' flux rate, given the uncertainties of these methods. This difference may be explained by the vastly different half-lives of the three Ra isotopes. Their effectiveness in exchange derivations has to match the time frame of the processes being studied. Processes that affect and control the water budget in Indian River Lagoon are likely to occur over daily (e.g., storm event), weekly (e.g., precipitation) and monthly (e.g., seasonal weather changes) time scales. A combination of short-lived Ra isotopes, normalized to long-lived  $^{226}\text{Ra}$  may provide the

**Table 3-5. Flux measurements using various direct (lagoon budget, benthic chamber) and indirect (modeled) methods. Minimum uncertainties based on  $\pm 1\sigma$ .**

Isotope	Flux from sediment (dpm/m <sup>2</sup> /d)					
	Lagoon budget method		Benthic chamber		Pore water profile	
	May	August	August Box 1	August Box 2	December Minimum	December Maximum
<sup>223</sup> Ra	7.4	6.5	19.0	10.4	0.1	0.4
<sup>224</sup> Ra	20.4	22.1	23.0	14.2	0.2	0.8
<sup>226</sup> Ra	0.0	0.0	480.2	160.2	0.0	0

best tracer suite. Benthic flux chamber results show strong agreement between <sup>223,224</sup>Ra isotopes, and these results also agree well with the lagoon budget methods using the same Ra isotopes. Benthic chamber measurements using <sup>226</sup>Ra produced results that are considerably greater than those generated with <sup>223,224</sup>Ra, yet these differences may be reconciled with more detailed solid phase and pore water sediment work.

### 3.4 Summary and Recommendations

Sediments are often the dominant source for radium as well as nutrients in coastal waters. This chapter examined the utility of Ra as an effective sediment-water interface tracer in upper Indian River Lagoon, where the exchange of water and chemical constituents can have an important effect on water column processes. Benthic fluxes are estimated using three unique methods, lagoon budget, benthic chamber and pore water modeling. The first two yield integrated measurements of flux while the third technique generates an indirect flux estimate based on pore water profiles of radium isotopes.

Flux estimates showed a wide range that extended up to 480 dpm/m<sup>2</sup>/d. Interestingly, the lowest (lagoon budget method) and highest values (benthic flux chamber) were observed using <sup>226</sup>Ra as a tracer. Using <sup>226</sup>Ra, a maximum upward subsurface water flow of about 5 - 17 cm/day would be required to sustain observed benthic fluxes. These calculated values appear to corroborate our direct and calculated seepage results and also compare favorably to existing seepage values (Belanger and Mikutel, 1985). This work illustrates that the determination of benthic fluxes using multiple Ra isotopes with widely variable half-lives provides a useful, complementary technique to study exchange processes across the sediment water interface over many time scales.

Future work will extend the modeling efforts to include bioturbation and advection by collecting solid-phase samples down core. Such efforts will also provide crucial information on Ra adsorption-desorption and ion exchange. Subsurface temperature profiling in the lagoon will provide a means to link subsurface water to tidal oscillations and seasonal variations.

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