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Marine Chemistry 101 (2006) 248–265
MARINE CHEMISTRY
www.elsevier.com/locate/marchem

Biogeochemical transport in the Loxahatchee River estuary, Florida: The role of submarine groundwater discharge

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Accepted 10 March 2006
Available online 6 May 2006

Abstract

The distributions of dissolved organic carbon (DOC), Ba, U, and a suite of naturally occurring radionuclides in the U/Th decay series (^{222}Rn, ^{223,224,226,228}Ra) were studied during high- and low-discharge conditions in the Loxahatchee River estuary, Florida to examine the role of submarine groundwater discharge in estuarine transport. The fresh water endmember of this still relatively pristine estuary may reflect not only river-borne constituents, but also those advected during active groundwater/surface water (hyporheic) exchange. During both discharge conditions, Ba concentrations indicated slight non-conservative mixing. Such Ba excesses could be attributed either to submarine groundwater discharge or particle desorption processes. Estuarine dissolved organic carbon concentrations were highest at salinities closest to zero. Uranium distributions were lowest in the fresh water sites and mixed mostly conservatively with an increase in salinity. Suspended particulate matter (SPM) concentrations were generally lowest (<5 mg L^{-1}) close to zero salinity and increased several-fold (~18 mg L^{-1}; low discharge) toward the seaward endmember, which may be attributed to dynamic resuspension of bottom sediments within Jupiter Inlet.

Surface water-column ^{222}Rn activities were most elevated (>28 dpm L^{-1}) at the freshwater endmember of the estuary and appear to identify regions of the river most influenced by the discharge of fresh groundwater. Activities of four naturally occurring isotopes of Ra (^{223,224,226,228}Ra) in this estuary and select adjacent shallow groundwater wells yield mean estuarine water-mass transit times of less than 1 day; these values are in close agreement to those calculated by tidal prism and tidal frequency. Submarine groundwater discharge rates to the Loxahatchee River estuary were calculated using a tidal prism approach, an excess ^{226}Ra mass balance, and an electromagnetic seepage meter. Average SGD rates ranged from 1.0 to 3.8×10^5 m^3 d^{-1} (20–74 L m^{-2} d^{-1}), depending on river-discharge stage. Such calculated SGD estimates, which must include both a recirculated as well as fresh water component, are in close agreement with results obtained from a first-order watershed mass balance. Average submarine groundwater discharge rates yield NH_4^+ and PO_4^{-3} flux estimates to the Loxahatchee River estuary that range from 62.7 to 1063.1 and 69.2 to 378.5 μmol m^{-2} d^{-1}, respectively, depending on river stage. SGD-derived nutrient flux rates are compared to yearly computed riverine total N and total P load estimates.

Keywords: Submarine groundwater discharge; Estuarine transport; Nutrient fluxes; Radium isotopes; Radon; Electromagnetic seepage meter

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0304-4203/$ - see front matter
doi:10.1016/j.marchem.2006.03.007

1. Introduction

Estuaries are well-known biogeochemical reactors (Sholkovitz, 1976, 1977; Boyle et al., 1977; Sholkovitz et al., 1978; Shiller and Boyle, 1991; Millward and Turner, 1994; Swarzenski et al., 1995) wherein terrigenous material, carried downstream by rivers, eventually is mixed into seawater (Turekian, 1977; Martin and Whitfield, 1983). The reactions and processes that occur during estuarine mixing are similarly well conceptualized (Mackin and Aller, 1984; Yan et al., 1990; Chiffoleau et al., 1994; Robert et al., 2004; Turner et al., 2004), and reflect an integration of diverse biogeochemical controls across land–sea margins (Martino et al., 2004). Many estuarine systems are variably contaminated by anthropogenic inputs that may influence estuarine transport and mixing (Shank et al., 2004). In addition, the ubiquitous nature of submarine groundwater discharge along many coastlines may directly affect estuarine water and geochemical budgets alike (Bokuniewicz, 1980; Johannes, 1980; Oberdorfer et al., 1990; Valiela et al., 1990; Moore, 1996, 1997, 1999; Corbett et al., 1999; Li et al., 1999; Charette et al., 2001; Swarzenski et al., 2001, 2004a; Burnett et al., 2001, 2002, 2003; Slomp and Cappellen, 2004). To understand biogeochemical transport in the Loxahatchee River estuary better, we have employed a suite of natural tracers that can provide information on i) traditional biogeochemical scavenging reactions initiated by an increase in salinity, as well as ii) the role of groundwater/surface water exchange or submarine groundwater discharge in impacting or defining such estuarine biogeochemical transport.

In this study, we investigate the distributions of dissolved organic carbon (DOC), select trace elements (Ba, U), and a suite of naturally occurring U/Th-series isotopes (^{222}Rn, ^{223,224,228,226}Ra) during estuarine transport and mixing in the Loxahatchee River estuary. This subtropical estuary, located just east of Lake Okeechobee, FL, in a predominantly carbonate geologic environment (McPherson et al., 1982; Wanless et al., 1984; Noel et al., 1995), may consequently have a strong groundwater contribution to the surface water budget (Russell and McPherson, 1983; Russell and Goodwin, 1987). Therefore, we utilize naturally occurring isotopes of Ra and Rn as tracers of submarine groundwater flow in our investigation of biogeochemical transport in the Loxahatchee River estuary (Cable et al., 1996, 1997; Krest et al., 1999, 2000; Swarzenski et al., 2001; Scott and Moran, 2001; Kelly and Moran, 2002; Burnett and Dulaiova, 2003; Krest and Harvey, 2003; Charette and Buesseler, 2004; Purkl and Eisenhauer, 2004; Hussain et al., 1999).

2. Geographic setting

The 500-plus km^2 Loxahatchee River catchment (Fig. 1) provides water for three principal distributaries, the Northwest, North, and Southwest Forks that discharge through Jupiter Inlet to the Atlantic Ocean (Russell and McPherson, 1983). Natural and anthropogenic change in the watershed since the 1940s has resulted in increased saltwater intrusion up the Loxahatchee River estuary and consequent dramatic ecosystem change (McPherson and Sabanskas, 1980; Noel et al., 1995). Compounding the issue of saltwater intrusion is a gradual decrease in available fresh surface- and groundwater due to the regional construction of extensive canal networks for expansive urban growth centered around Jupiter, FL (McPherson and Sonntag, 1984).

The lower Loxahatchee River estuary is mostly shallow (average depth ~1.2 m), although a partially dredged and natural channel 3+ m deep extends about 14 km upstream. In the upper reaches of the river, water depths are generally less than 2–3 m. The tides in the estuary are mixed semi-diurnal and range <1 m. A typical tidal wave may propagate upstream for about 16 km (Russell and Goodwin, 1987) at a rate of 8–16 km h^{-1}.

Freshwater inflows to the Loxahatchee River estuary may include local and regional upward groundwater flow, precipitation, surface water runoff, storm drainage, and canal discharge. This composite inflow, which is seasonal in nature and can be partially regulated during wet (May–November) months, may have a strong tropical weather imprint (e.g., two hurricanes made landfall very close to the estuary in September 2004). Fig. 2 illustrates both mean monthly precipitation rates at site A (SFWMD Sta. No. C18W_R; 26°52′19″ N, 80°14′42″ W), as well as daily mean stream flow upstream of the NW Fork of the Loxahatchee River. This two plus-year record suggests a reasonably positive relation between precipitation and stream flow. Average daily discharge rates for the upper NW Fork of the Loxahatchee River (USGS site ID: 2277600; 26°56′20″ N, 80°10′31″ W) during the high- and low-discharge sampling cruises were 4.02 and 0.88 m^3 s^{-1}, respectively. A 2-year mean stream-flow rate during the two sampling efforts was 2.15 m^3 s^{-1}. For comparison, an average discharge rate of about 300 m^3 s^{-1} has been reported for Jupiter Inlet (Mehta et al., 1992).

Groundwater/surface water interactions are often enhanced in carbonate-dominated coastal rivers and wetlands of Florida (Parker et al., 1955; Krest and Harvey, 2003). Biogeochemical transport in the Loxahatchee River estuary was thus investigated from the perspective that submarine groundwater discharge could play an important role in geochemical and water budgets

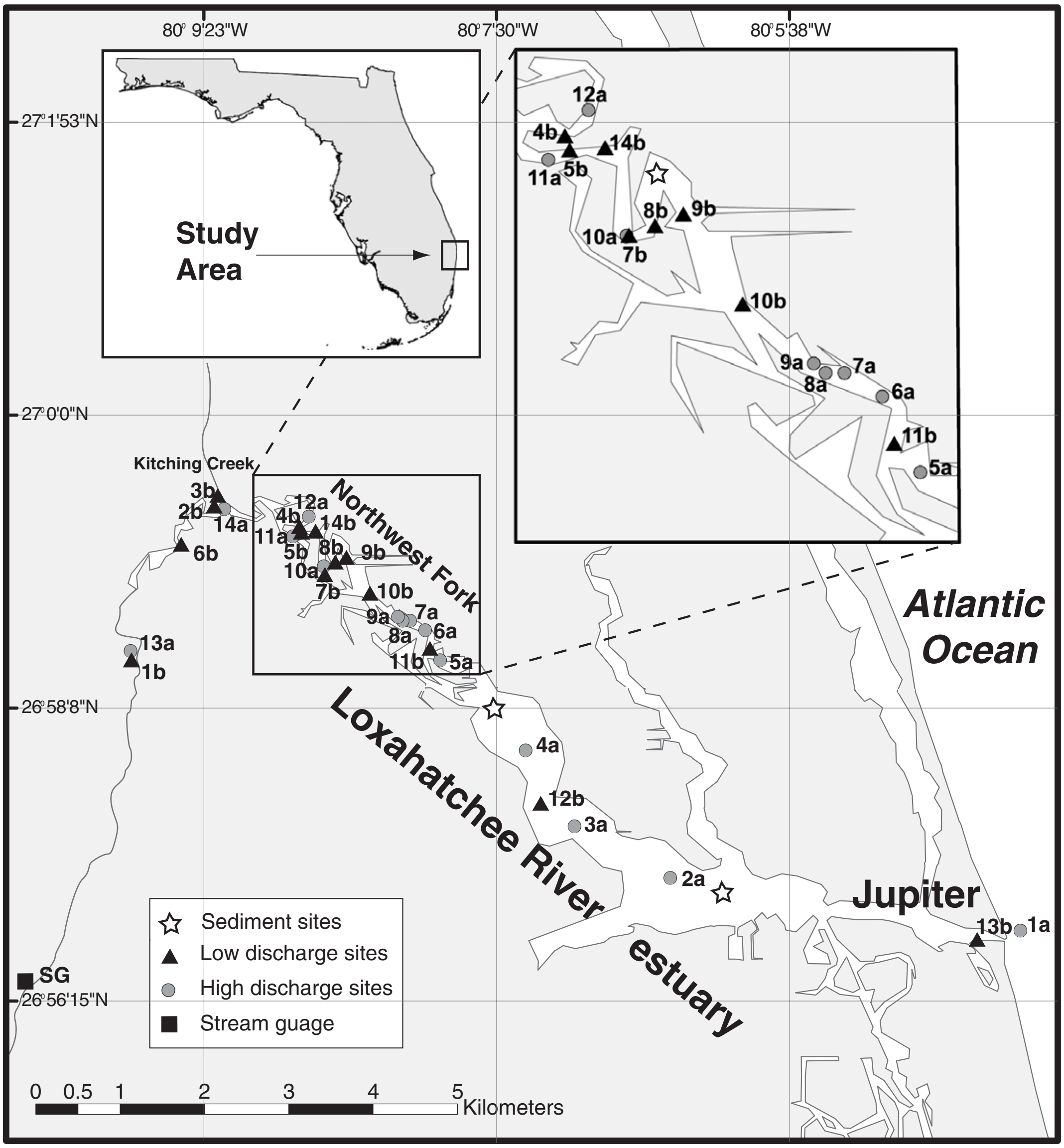

Fig. 1. Station location map for high (September 2003) and low (March 2004) discharge sampling efforts. Piezometer (nutrient samples) and well (Ra + nutrient samples) locations and associated hydrogeologic descriptions from a series of six shore-perpendicular transects adjacent to the Loxahatchee River estuary are described in Orem et al. (in review).

of this estuarine system. Consequently, the following discussion will develop in two directions, i) traditional biogeochemical transformations across salinity gradients, and ii) the potential role of submarine groundwater discharge in impacting such estuarine transport.

3. Methods

3.1. Field

Estuarine water samples (Fig. 1) were collected during two river-discharge regimes (September 2003 and March 2004) for dissolved constituents from a small boat, using 'trace metal clean' procedures (Swarzenski et al., 2004c). Briefly, uncontaminated estuarine water was collected using a gimbaled collection port from ~0.5 m below the water surface and away from the boat's hull using a small-volume peristaltic pump and acid-rinsed tubing. Pre-rinsed, large surface-area filter cartridges (0.45 μm cutoff; GEOTECH dispose-a-filter™, 700 cm^2) were used to filter dissolved trace metals in situ. Trace-metal sub-samples were acidified to pH < 2 in the field using SeaStar ultra-pure HNO_3, and stored chilled. Samples for dissolved organic carbon

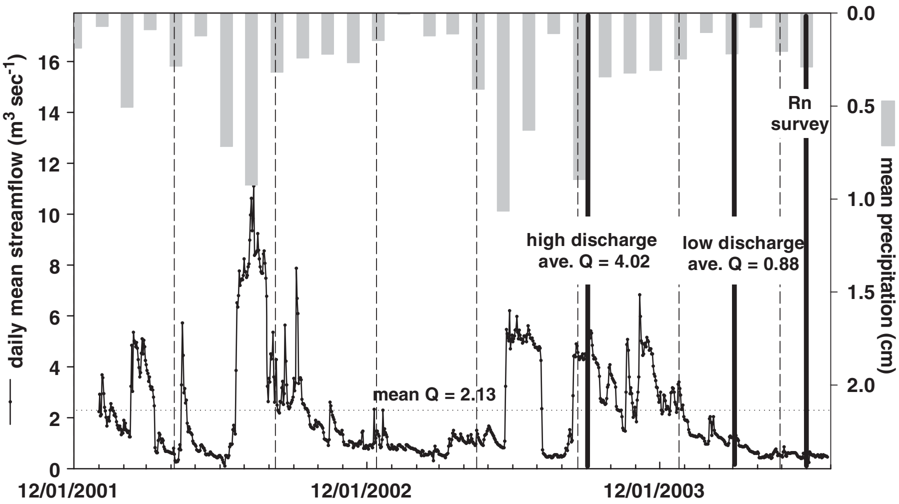

Fig. 2. Mean daily stream flow ($m^3\ s^{-1}$) and monthly precipitation (cm) for the Loxahatchee River estuary. Individual sampling intervals are denoted by the vertical gray (Ra, elements) and black (Rn) bars.

(DOC) were collected separately using a metal bucket, triple Milli-Q rinsed glassware, a portable glass filtration system, and pre-combusted 47 mm Whatman GF/F filters. Each DOC sample was preserved in a brown glass bottle with 1.1 M high purity HCl, and stored frozen until subsequent analyses. Shallow, unfiltered groundwater samples were collected for Ra isotopes at three well sites along transects perpendicular to the estuary during both sampling efforts. These transects were established to reflect upstream, middle and down stream hydrogeologic characteristics. Well water was extracted by peristaltic pump after allowing sufficient flushing. Geographic locations and associated hydrogeologic information of these well sites are described in detail in Orem et al. (in review). To complement these well samples, roughly ~50 additional porewater samples were collected along each transect using a high resolution Teflon micro-piezometer system for groundwater-nutrient analyses (Orem et al., in review). These 0.45 μm-filtered and total nutrient samples were collected and prepared using ‘clean’ USGS water sampling procedures.

Estuarine samples for all four radium isotopes (^{223,224,226,228}Ra) were collected using the same gimbaled arm and a 12 v submersible pump by passing a known volume of estuarine water through either 1 or 2 MnO_2-impregnated acrylic-fiber cartridges. Flow rates were maintained at ~1 L per minute. Two serial cartridges were used sporadically to evaluate the Ra extraction efficiency onto the MnO_2 fiber (typically >96%). Target salinities and water characteristics (e.g., temperature, pH, dissolved oxygen, specific conductivity, and salinity) were continuously monitored during pumping operations with a multi-parameter YSI probe. The suspended particulate-matter (SPM) concentration per sample was determined gravimetrically in the lab, using pre-weighed 0.4-μm Nuclepore 47 mm filters.

Near-continuous excess radon-222 activities were measured in the Loxahatchee River estuary in June 2004 using six commercial air radon detectors (RAD7 — Durridge, Co., INC), routed simultaneously through a single air–water exchanger (Burnett et al., 2001). By applying a temperature and solubility coefficient correction, one can calculate the activity of ^{222}Rn in water, as the Rn in air will attain equilibrium with estuarine water flowing through the exchanger after about 20 min. Utilizing six RAD7 detectors simultaneously permits almost real-time (once every 5-min) Rn data acquisition. During this survey, water-column characteristics were again monitored both at the exchanger site and within the water column using an IN SITU multi-parameter sensor array, as well as WTW multi-probes.

To validate the Ra-derived submarine groundwater discharge rate for the estuary physically, direct seepage across the sediment/water interface was measured during the high-discharge sampling cruise in September, 2003, at Kitching Creek (Fig. 1), using an autonomous electromagnetic seepage meter (Rosenberry and Morin, 2004; Swarzenski et al., 2004b). A streaming-resistivity-profiling survey (Manheim et al., 2002; Belaval et al., 2003; Swarzenski et al., 2004c) was also conducted in this estuary during the June 2004 field effort to provide detailed information on the dynamic subsurface freshwater/saltwater interface of this estuary.

3.2. Analytical

River and estuarine water samples were analyzed for dissolved trace elements with a Perkin Elmer SCIEX ELAN 6100 inductively-coupled plasma mass spectrometer (ICP/MS). International certified reference materials USGS GXR-1, GXR-2, GXR-4, and GXR-6 were analyzed at the beginning and end of each sample run. Internal control standards as well as duplicates were analyzed every 10 samples. Reported detection limits (in nM) of the quadrupole ICP/MS for uranium and barium are 0.004 and 0.73, respectively. Dissolved organic carbon (DOC) concentrations were quantified by high-temperature catalytic oxidation, using a Shimadzu TOC 5000A analyzer in the Univ. of South Florida laboratory of Dr. Paul Coble. Duplicates and standards were routinely analyzed before and after each sample run, and reported analytical uncertainty was less than 5%. Radium-223 and ^{224}Ra ($t_{1/2}$ = 11.4 and 3.7 d, respectively) activities were determined using delayed-coincidence alpha counting techniques (Moore and Arnold, 1996; Swarzenski et al., 2001; Charette and Buesseler, 2004). The short-lived Ra isotopes were recounted after ~3 weeks to correct for supported ^{224}Ra activities (^{228}Th), and decay-corrected to the sampling time. Propagated errors for the delayed coincidence counters are typically <10%. The two longer-lived Ra isotopes (^{228,226}Ra — $t_{1/2}$ = 5.7 and 1620 years, respectively) were quantitatively extracted from the MnO_2 fiber and analyzed by high-resolution well-type gamma spectroscopy, using the 352 and 609 keV gamma energies for ^{226}Ra, and 338 and 911 keV peak energies for ^{228}Ra. The estimated error for these measurements is <7%. Aqueous ^{222}Rn activities were quantified using multiple RAD7 detectors routed through a single air–water exchanger (Burnett et al., 2001; Burnett and Dulaiova, 2003).

4. Results and discussion

The Loxahatchee River estuary was sampled during high- and low-discharge conditions along a ~14 km transect that extended from just seaward of Jupiter Inlet, where salinities were >30, to the upper reaches of the Northwest Fork, where salinities approach <0.1 (Table 1). The estuarine freshwater/saltwater mixing zone exhibited an expected strong dependency on river-discharge stage. In general, the entire salinity regime was pushed upstream several kilometers during low-flow conditions (Russell and McPherson, 1983). During low discharge sampling, an Atlantic Ocean endmember sample was obtained just seaward of Jupiter Inlet with a salinity of 34.42.

During both river-discharge regimes, pH and specific conductance values of the two most freshwater end-member samples (13a, 1b) remained consistent at ~7.7 and 0.5 mS cm^{-1}, respectively. In contrast, suspended particulate matter (SPM) concentrations in the headwater samples were noticeably lower during low-flow conditions, and both profiles uncharacteristically increased in concentration with an increase in salinity. Average SPM concentrations for each set of estuarine samples were just slightly higher during low-flow conditions (6.9 versus 5.5 mg L^{-1}), but both SPM datasets indicate a general paucity of organic/inorganic particulates retained on a 0.4 μm filter. The concentration profile of suspended particulate matter in the estuary indicates that resuspension of particles is greatest within the tidally flushed waters of Jupiter Inlet (Noel et al., 1995).

4.1. Biogeochemical estuarine trace-element transport

The material transport through estuaries is variably controlled by terrestrial processes such as river discharge and groundwater flow (Eyre, 1988). Select trace-element (U, Ba) and dissolved organic carbon (DOC) concentrations in estuarine surface water samples are presented in Table 2 and illustrated in Fig. 3a,b,c. DOC concentrations decreased ten-fold from values just over 1200 μM in freshwater samples to those observed in the most saline surface waters at Jupiter Inlet. Of the studied trace elements, the estuarine distribution of Ba exhibited a similar decreasing trend with an increase in salinity. In contrast, U exhibited a positive trend with salinity; that is, its concentration increased conservatively as salinity also increased. During both discharge conditions, the estuarine distributions of DOC, Ba and U indicate that physical mixing processes in the Loxahatchee River estuary, where an estuarine water parcel is transported very quickly seaward, strongly influence any biogeochemical removal and supply processes. In spite of this generalization, there exists some evidence for non-conservative estuarine behavior.

As an alkaline earth metal, dissolved Ba has been shown to be enriched across a salinity regime of some estuaries (Coffey et al., 1997) due either to ionic strength-initiated desorption reactions of particulate-bound Ba or due to SGD-redox processes (Charette and Sholkovitz, in press). For example, such non-conservative estuarine Ba behavior has been reported in the Fly River (Swarzenski et al., 2004c) as well as the Ganges (Moore, 1997). In the Loxahatchee River estuary during high discharge, Ba concentrations remained reasonably constant to a salinity of 25. Similarly, during low discharge conditions one can

Table 1
Station locations and water column hydrographic characteristics (pH, specific conductivity, salinity, temperature, dissolved oxygen, and suspended particulate matter (SPM) concentrations) per river discharge (season)

	ID	Latitude (N)	Longitude (W)	pH	Conductivity (mS cm^{-1})	Salinity	Temp. (°C)	DO (mg L^{-1})	SPM (mg L^{-1})
High discharge									
9/15/2003	1a	26.9451	−80.0692	7.82	46.80	30.60	28.80	4.51	8.13
9/15/2003	2a	26.9507	−80.1065	8.13	38.20	24.40	29.30	3.66	9.40
9/15/2003	3a	26.9562	−80.1167	8.00	29.30	18.20	29.80	3.64	8.20
9/15/2003	4a	26.9643	−80.1219	7.91	23.40	14.30	30.10	3.56	4.60
9/15/2003	5a	26.9739	−80.1310	7.78	20.30	12.30	30.60	3.04	4.60
9/15/2003	6a	26.9771	−80.1326	7.70	17.60	10.50	30.90	3.09	5.00
9/15/2003	7a	26.9781	−80.1342	7.62	14.42	8.00	31.50	3.04	4.00
9/15/2003	8a	26.9781	−80.1350	7.74	9.59	5.50	31.30	3.16	4.60
9/15/2003	9a	26.9785	−80.1355	7.62	7.35	4.10	31.40	2.89	4.40
9/15/2003	10a	26.9839	−80.1434	7.49	4.79	2.50	30.20	2.55	3.80
9/15/2003	11a	26.9871	−80.1467	7.51	2.25	1.00	29.80	2.44	5.20
9/15/2003	12a	26.9892	−80.1450	7.59	0.54	0.00	29.40	2.66	5.60
9/16/2003	13a	26.9749	−80.1640	7.67	0.42	0.00	28.50	2.75	4.60
9/16/2003	14a	26.9814	−80.1548	7.97	0.41	0.00	28.80	3.30	4.80
Low discharge									
3/10/2004	1b	26.9739	−80.1639	7.69	0.64	0.31	21.50	5.94	1.50
3/10/2004	2b	26.9914	−80.1547	7.66	1.01	0.92	21.40	6.10	3.50
3/10/2004	3b	26.9903	−80.1651	7.65	4.60	2.48	21.87	6.02	3.00
3/10/2004	4b	26.9881	−80.1460	7.65	6.74	3.69	22.05	5.91	6.20
3/10/2004	5b	26.9875	−80.1458	7.68	8.27	4.60	22.11	5.96	3.40
3/10/2004	6b	26.9862	−80.1586	7.68	11.16	6.37	22.20	5.80	3.40
3/11/2004	7b	26.9839	−80.1433	7.65	13.90	8.05	20.25	6.03	5.20
3/11/2004	14b	26.9876	−80.1443	7.77	15.74	9.28	21.51	6.62	6.40
3/11/2004	8b	26.9843	−80.1422	7.72	22.06	13.30	20.83	6.02	4.80
3/11/2004	9b	26.9848	−80.1410	7.78	23.35	14.14	20.81	6.29	5.80
3/11/2004	10b	26.9810	−80.1385	7.87	30.81	19.34	20.86	6.35	6.40
3/11/2004	11b	26.9751	−80.1321	8.04	38.73	24.72	21.25	6.75	13.40
3/11/2004	12b	26.9586	−80.1203	8.10	45.41	29.48	21.33	7.12	15.00
3/11/2004	13b	26.9441	−80.0738	8.17	52.20	34.42	21.60	7.58	18.60

(Note that the two sampling efforts are sequentially arranged by ID, not salinity).

also interpret non-conservative Ba behavior if one simply extends an ideal mixing line across the two endmember concentrations. Such non-conservative Ba distributions suggest that riverine Ba is not simply diluted during estuarine transport, and one can argue for a slight Ba excess. This excess may be attributed to either particle desorption processes or a groundwater source. The general scarcity of terrigenous, suspended particles in the upper river weakens the first option. Subsurface reductive dissolution of Fe- and Mn oxides may contribute to the enrichment of Ba in surface waters.

The transport of dissolved uranium in south Florida surface water is enhanced by the formation of stable, hexavalent uranyl–carbonate and humic complexes. It is unlikely that the presence of abundant peat deposits should significantly affect the stability of these complexes (Zielinski et al., 2000). As a consequence, surface waters of the northern Everglades contain very low concentrations of natural uranium. Under reducing conditions, U should exist as the more particle reactive, tetra-valent complex. Since the U concentration within quartz and limestone deposits is typically low, most of the uranium is likely incorporated in the organic rather than the mineral fraction (Zielinski et al., 2000). The freshwater endmember site (13a: 1.0 nM) of the Loxahatchee River estuary contains the lowest observed U concentration in this system, a value just slightly lower than the global U average (1.3 nM; Palmer and Edmond, 1993; Windom et al., 2000). The size and nature of the Loxahatchee River watershed, as well as the pronounced role of groundwater/surface water exchange in the upper river, suggests that the observed lower U concentrations in the Loxahatchee could stem from the subsurface mixing and discharge of reducing groundwater. Removal of U due to SGD and redox processes has recently been shown to occur in Waquoit

Table 2
Dissolved organic carbon (DOC), uranium and barium concentrations per river discharge (season)

	ID	DOC (μM)	U (nM)	Ba (nM)
High discharge				
9/15/2003	1a	300	10.6	76.5
9/15/2003	2a	482	7.7	91.8
9/15/2003	3a	518	7.1	96.1
9/15/2003	4a	473	6.1	93.9
9/15/2003	5a	669	4.6	95.4
9/15/2003	6a	774	4.1	94.7
9/15/2003	7a	730	3.3	101.9
9/15/2003	8a	699	2.6	100.5
9/15/2003	9a	1162	2.0	98.3
9/15/2003	10a	832	1.7	101.2
9/15/2003	11a	973	1.3	96.9
9/15/2003	12a	1248	1.1	96.9
9/16/2003	13a	1229	1.0	102.7
9/16/2003	14a	1249	1.1	100.5
Low discharge				
3/10/2004	1b	1004	1.6	142.7
3/10/2004	2b	942	2.6	152.9
3/10/2004	3b	802	2.8	145.6
3/10/2004	4b	620	3.3	149.3
3/10/2004	5b	996	3.5	145.6
3/10/2004	6b	900	4.1	144.2
3/11/2004	7b	697	4.3	139.8
3/11/2004	14b	645	5.0	131.1
3/11/2004	8b	780	5.4	130.3
3/11/2004	9b	553	6.1	126.7
3/11/2004	10b	436	7.9	106.3
3/11/2004	11b	232	9.5	92.5
3/11/2004	12b	289	11.3	80.1
3/11/2004	13b	122	13.0	63.1

Bay (Charette and Sholkovitz, in press). Within the estuary, the behavior of U across either salinity gradient (Fig. 3b) suggests that U is mostly mixed conservatively in this system and approaches the open ocean U concentration (13.6 nM; Chen et al., 1986) at the highest salinities.

Concentrations of dissolved organic carbon (DOC), like uranium, are influenced by the reversible exchange of groundwater and organic-rich surface water. Surface water and groundwater DOC concentrations are typically high in south Florida (McPherson et al., 2000) and may thus enhance the transport of particle-reactive constituents. DOC concentrations (Fig. 3c) decreased roughly an order of magnitude from ~1200 μM (high discharge) to just above 100 μM at the high-salinity endmember (low discharge). This decrease in DOC, although erratic during both sampling efforts, was most pronounced at salinities below 15. Above a salinity of 15, DOC concentrations appeared to be less scattered, and reflects physical mixing processes in the lower estuary more so than biogeochemical reactions. Observed scatter in DOC at low salinities may suggest either a difference in the reactivity of groundwater- versus surface water DOC or local heterogeneities in DOC source terms within the upper estuary. In spite of the general paucity of suspended particulate matter and the rapid flushing times of this estuary, the observed decrease in DOC concentrations with an increase in salinity may also be influenced by organic matter removal processes (i.e., flocculation) initiated during estuarine transport (Sholkovitz, 1976; Sholkovitz et al., 1978).

The studied element–salinity plots suggest that physical mixing processes strongly influence removal and/or release processes in the Loxahatchee River estuary. Such trends set this estuary apart from many other estuaries, where biological and inorganic processes control the estuarine distribution of many constituents. To evaluate the physical controls of this system, water-mass transit times (i.e., flushing times) and the potential contribution of submarine groundwater discharge in the Loxahatchee River estuary were investigated using multiple tracer techniques.

4.2. Surface water Ra and Rn isotopes

Radium-223,224,228,226 isotope activities in estuarine surface water and shallow groundwater are presented in Tables 3 and 4. The highest Ra activities in estuarine surface water were generally observed in the freshwater endmember samples (Figs. 4a,b and 5a,b). Radium-226 ($t_{1/2}$ = 1600 year) activities during both high- and low-discharge conditions ranged from 70 dpm 100 L^{-1} in the headwater fresh water samples to about 15 dpm 100 L^{-1} in the seawater endmember sample (salinity = 34.42). Radium-228 similarly ranged from about 6–15 dpm 100 L^{-1} (seawater endmember samples) to more than 18 dpm 100 L^{-1} (freshwater endmember samples) during both river-discharge regimes. The two short-lived Ra isotopes, ^{223}Ra, ^{224}Ra, ranged from < 14 to 10–35 dpm 100 L^{-1}, respectively. A simple mixing line drawn through the respective endmember concentrations suggests non-conservative mixing for all four Ra isotopes. Excluding the thermal spring-derived discharge off west-central Florida (Fanning et al., 1981), and the phosphate-enhanced Ra isotopes observed in Tampa Bay, such Ra activities are typical for Florida coastal waters and estuaries (Burnett et al., 1990; Swarzenski et al., 2001; Cable et al., 2004).

Rn-222 ($t_{1/2}$ = 3.8 d) activities were measured almost real-time from the seaward endmember close to the Jupiter Inlet at a salinity ~34 upstream to the confluence of Kitching Creek and the Loxahatchee River, where

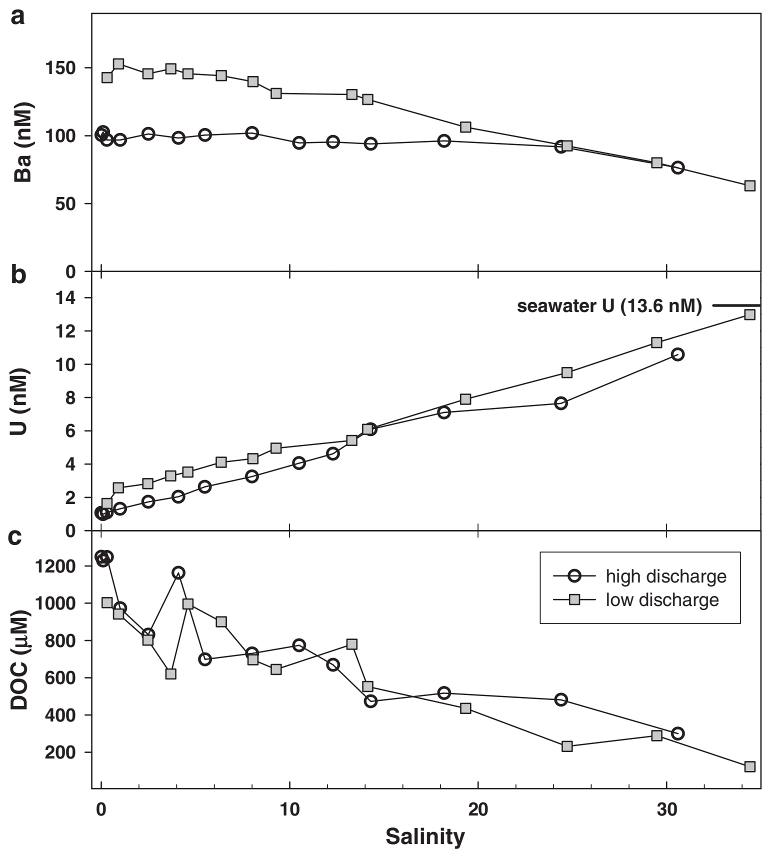

Fig. 3. (a) Salinity versus barium, (b) uranium and (c) dissolved organic carbon (DOC) concentrations for the two sampling periods. Note that the open ocean U value of 13.6 nM (Chen et al., 1986) is shown for comparison.

salinities approach zero. During this Rn survey, activities were inversely related to salinity (Fig. 6) and ranged from a background value of ~2.5 dpm L^{-1} at Jupiter Inlet to more than 28 dpm L^{-1} at Kitching Creek.

4.3. Ra-derived estuarine transit times

The construction of a Ra-derived submarine groundwater discharge model, which builds upon a mass

Table 3
Dissolved ^{226,228,223,224}Ra activities and salinity in shallow groundwater wells adjacent to the Loxahatchee River estuary per river discharge (season)

	ID	^{226}Ra (dpm 100 L^{-1})	Error	^{228}Ra (dpm 100 L^{-1})	Error	^{223}Ra (dpm 100 L^{-1})	^{224}Ra	Salinity
High discharge								
9/15/2003	WELL1	108.5	13.7	59.6	16.6	78.5	161.8	0.3
9/16/2003	WELL3	88.1	14.4	58.2	19.6	54.2	146.0	0.1
9/15/2003	WELL7	47.4	12.4	bd	bd	34.4	82.2	0
ave.		81.4		58.9		55.7	130.0	
Low discharge								
3/8/2004	WELL1	88.5	12.6	42.4	17.6	57.4	121.8	0.2
3/9/2004	WELL3	520.7	21.8	152.4	25.4	106.8	269.4	0.1
3/8/2004	WELL7	34.1	11.0	42.4	19.4	46.4	131.1	0
ave.		214.5		79.1		70.2	174.1	

A comprehensive description of the well locations can be found in Orem et al. (in review).
bd = below detection.

Table 4
Dissolved ^{226,228,223,224}Ra activities and salinity in the Loxahatchee River estuary, per river discharge (season)

	ID	^{226}Ra	Error	^{228}Ra	Error	^{223}Ra	^{224}Ra	Salinity
	(dpm 100 L^{-1})							
High discharge								
9/15/2003	1a	28.0	0.5	14.7	2.0	3.8	21.2	30.6
9/15/2003	2a	43.9	0.5	18.3	1.8	7.0	26.1	24.4
9/15/2003	3a	63.8	0.8	24.0	1.8	3.7	34.7	18.2
9/15/2003	4a	57.4	0.7	19.9	1.4	4.3	26.7	14.3
9/15/2003	5a	58.3	0.7	22.6	1.5	7.3	30.1	12.3
9/15/2003	6a	59.5	0.7	17.7	1.5	7.3	23.6	10.5
9/15/2003	7a	47.7	0.6	18.0	1.6	6.1	25.0	8.0
9/15/2003	8a	59.9	0.7	17.0	1.3	4.3	23.5	5.5
9/15/2003	9a	59.5	0.7	16.7	1.7	3.0	24.3	4.1
9/15/2003	10a	64.2	0.8	17.5	2.0	3.0	25.0	2.5
9/15/2003	11a	63.3	0.7	19.5	1.6	2.1	29.2	1.0
9/15/2003	12a	67.9	0.7	16.3	2.1	2.3	24.5	0.3
9/16/2003	14a	69.8	0.7	16.3	1.8	2.2	23.6	0.1
9/16/2003	13a	67.5	0.7	18.3	1.7	4.5	28.3	0.0
Low discharge								
3/10/2004	1b	67.0	3.5	16.1	4.5	3.2	23.1	0.3
3/10/2004	2b	–	–	–	–	2.6	15.2	0.9
3/10/2004	3b	27.6	1.7	8.4	2.6	2.1	12.2	2.5
3/10/2004	4b	26.5	1.7	4.6	2.2	9.7	35.7	3.7
3/10/2004	5b	59.0	2.4	16.1	2.8	13.4	23.4	4.6
3/10/2004	6b	72.5	2.6	18.1	3.1	10.1	26.0	6.4
3/11/2004	7b	75.4	2.5	21.4	3.1	10.6	30.1	8.1
3/11/2004	14b	73.8	2.7	21.4	2.9	8.4	30.7	9.3
3/11/2004	8b	63.9	2.4	18.3	2.9	3.6	26.2	13.3
3/11/2004	9b	73.3	2.5	19.5	2.9	6.2	27.6	14.1
3/11/2004	10b	48.2	2.1	18.9	2.8	6.3	26.0	19.3
3/11/2004	11b	43.6	2.1	17.1	2.8	7.3	23.0	24.7
3/11/2004	12b	47.2	1.6	14.4	1.9	6.1	19.0	29.5
3/11/2004	13b	14.9	1.0	6.7	1.7	4.3	9.2	34.4

balance of source and removal terms, relies on the derivation of an accurate estuarine transit time. The transit time of a water parcel transported through an estuary, T_r, can be affected by various physical parameters, such as the hydraulic gradient, the rate and seasonality of stream flow, the tidal range and amplitude, as well as anthropogenic demand on coastal freshwater resources. Such a transit time can be calculated using either physical (Pilson, 1985) volume and area estimates (i.e., tidal prism) or isotopic tracers (Moore, 1999; Charette et al., 2001). In the Loxahatchee River estuary, the transit time of water calculated using a best estimate for the tidal prism volume ($tp_{vol} = 4.0 \times 10^6$ m^3; McPherson et al., 1982), the surface volume (6.3×10^6 m^3), and the tidal frequency ($f_{tidal} = 1.9$ d^{-1}) is less than one day, ~0.8 d. Such a short transit time confirms the energetic exchange that occurs through Jupiter Inlet and implies rapid estuarine-flushing rates into the Atlantic Ocean.

Alternatively, to calculate T_r values using Ra isotopes, an approach that compares excess isotopic ratios (^{224}Ra/$^{228}_{xs}$Ra) in surface waters to such ratios in groundwater can be expressed as (after Moore, 1999; Charette et al., 2001):

$$\left(\frac{^{224}\mathrm{Ra}}{\mathrm{xs}^{228}\mathrm{Ra}}\right)_{\mathrm{estu}} = \left(\frac{^{224}\mathrm{Ra}}{^{228}\mathrm{Ra}}\right)_{\mathrm{gw}} e^{-\lambda_{224} T_r} \quad (1)$$

Where $[^{224}\mathrm{Ra}/^{228}_{xs}\mathrm{Ra}]_{estu}$ represents the observed activity ratio of the estuarine sample, $[^{224}\mathrm{Ra}/^{228}\mathrm{Ra}]_{gw}$ the average activity ratio in groundwater, and λ_{224} is the decay constant for ^{224}Ra, 0.1894 d^{-1}. Excess Ra ($^{228}_{xs}\mathrm{Ra} = {}^{228}\mathrm{Ra}_{sample} - {}^{228}\mathrm{Ra}_{seawater}$) activities are calculated here by simply subtracting the adjacent seawater endmember activity (e.g., ^{228}Ra = 6.71 dpm 100 L^{-1}; Table 4) from the observed activities. Re-arranging Eq. (1) allows one to solve for T_r:

$$T_r = \frac{\ln\left(\frac{^{224}\mathrm{Ra}}{^{228}\mathrm{Ra}}\right)_{\mathrm{gw}} - \ln\left(\frac{^{224}\mathrm{Ra}}{\mathrm{xs}^{228}\mathrm{Ra}}\right)_{\mathrm{estu}}}{\lambda_{224}} \text{ (days)} \quad (2)$$

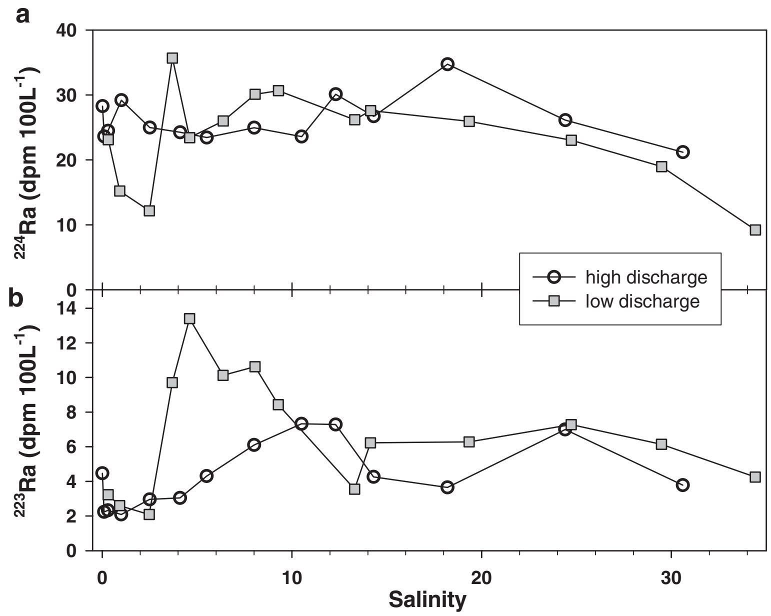

Fig. 4. (a) Salinity versus dissolved ^{224}Ra and (b) ^{223}Ra.

Necessary assumptions for Eqs. (1) and (2) are that the endmember activity ratios remain constant, and that the ratios change only in response to SGD fluxes. For each station, a transit time was calculated based on Eq. (2) using average $(^{224}\mathrm{Ra}/^{228}\mathrm{Ra})_{gw}$ values of 2.63 (high discharge) and 2.58 (low discharge). The range in calculated transit-time estimates spans from $\sim$0.4 to 1.4 d for both sampling efforts. Individual transit-time estimates were averaged to yield composite estuarine T_r rates of 1.0 and 0.8 d for high- and low-flow conditions, respectively, which are in close agreement with those calculated via the tidal prism method. Calculated transit times are shorter for the high-salinity samples for both sampling efforts and suggest that this Ra-based technique might be sensitive enough to resolve seasonal fluctuations in estuarine transit times on a per site basis.

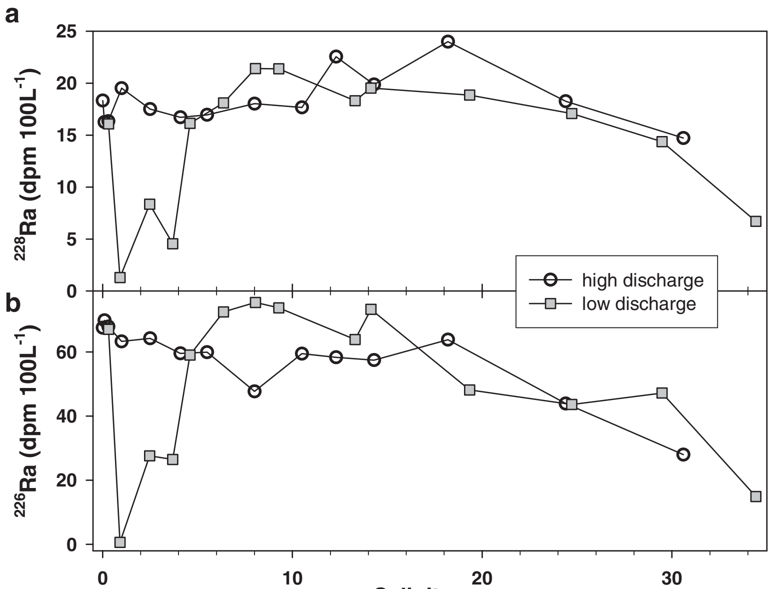

Fig. 5. (a) Salinity versus dissolved ^{228}Ra and (b) ^{226}Ra.

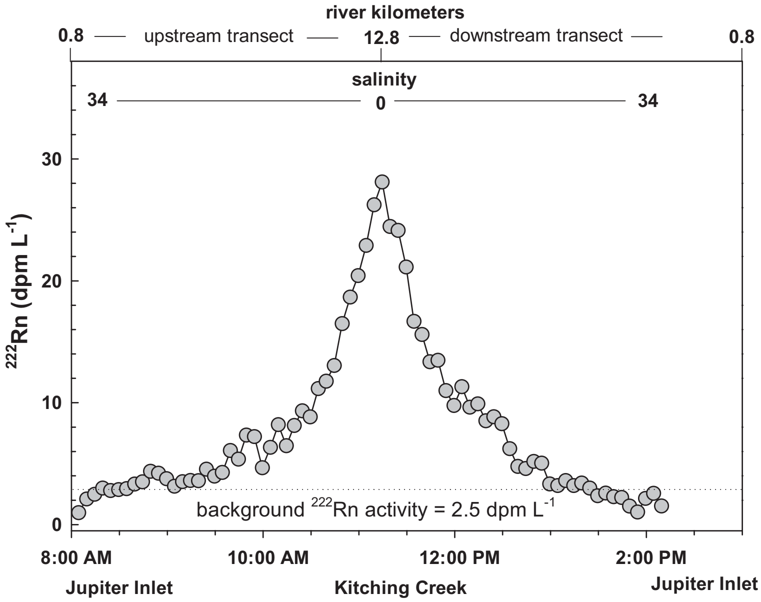

Fig. 6. Dissolved ^{222}Rn activities (dpm L^{-1}) in the Loxahatchee River estuary.

Such an approach has been developed in the Elizabeth River estuary of the Chesapeake Bay system by Charette and Buesseler (2004).

Although one could also calculate an estuarine transit time using ^{223}Ra/^{228}Ra activity ratios, the mean life ($\tau = \lambda^{-1}$) of ^{223}Ra (16.5 d) is somewhat longer than the timescales of processes that we are investigating in the Loxahatchee river estuary. In turn, ^{224}Ra has a mean life of just 5.3 d and is thus better suited to study estuarine transport within this system. In addition, both ^{224}Ra and ^{228}Ra are derived from the same ^{232}Th series while ^{223}Ra is derived from the ^{235}U series, and thus any variations in the activities of parent U and Th could affect the ^{223}Ra/^{228}Ra ratios.

4.4. Ra-derived submarine groundwater discharge models

To quantify the role of submarine groundwater discharge, an equation can be written that identifies known source terms of Ra in an estuary. The calculated activity of Ra_c may thus be defined as the sum of the fractional contribution of Ra present in seawater (Ra_s), river water (Ra_r), as well as the fractional contribution of Ra desorbed from riverine particulates (Ra_{des}) (Krest et al., 1999; Kelly and Moran, 2002):

$$Ra_c = f(Ra_s) + (1-f)(Ra_r) + ((1-f)Ra_{des}) \times \left(1 - e^{\left[\frac{-S_{estu}}{\xi}\right]}\right) \ (\text{dpm } 100 \text{ L}^{-1}) \tag{3}$$

Here, S_{estu} denotes the sample salinity, and ξ represents the salinity at which the particulate-bound Ra activity is thought to be reduced to e^{-1} of its initial activity due to a change in ionic strength (Krest et al., 1999; Kelly and Moran, 2002). In Eq. (3), the term f represents the fractional contribution of a sample's salinity derived by the seawater and freshwater end-members (Krest et al., 1999) as follows:

$$f = \frac{(S_{estu} - S_r)}{(S_{sea} - S_r)} \tag{4}$$

where S_{sea} and S_r represent seawater and freshwater endmember salinities, respectively.

Applying Eq. (4), one can quantitatively evaluate the relative contribution of each of the Ra source terms against observed Ra distributions. In general, such calculated activities are consistently less than observed activities present in the estuary for all four Ra isotopes, which suggest that either Ra is being actively advected into the estuarine water column by submarine groundwater discharge, and/or Ra production via the decay of parent Th ubiquitously present in bottom sediment contributes substantially to the estuarine Ra mass balance.

To demonstrate that the production or regeneration rate of Ra within Loxahatchee River estuary bottom sediments is a minor contributor to the overall Ra mass balance, we collected six bottom-sediment samples (3 sites per cruise) from sites within the entire estuary (salinity 0 to 34) that represent the spectrum of geologic strata present in this estuary. An average production rate of ^{226}Ra, derived from the disequilibrium between ^{226}Ra and its immediate parent, ^{230}Th ($t_{1/2}=1.4\times10^{10}$ year), and integrated over the entire Loxahatchee River estuary area was calculated to be 1.5×10^{4} dpm d^{-1} — two orders of magnitude lower than corresponding water column Ra activities. We have used the upper 5-cm sediment layer to estimate the ^{226}Ra flux, as sediments below the surface layer are expected to be as deficient in desorbable ^{226}Ra as are surface sediments. Therefore, no significant contribution is expected from bottom sediments below 5 cm. Such a calculation assumes that ~75% of the sediment-bound Ra is available for desorption and subsequent transport into estuarine waters (Rama and Moore, 1996). By deriving estimates for Ra_c, T_r, and Ra_{des}, one can then establish an equation that describes that mass balance of excess ^{226}Ra in the estuary (Charette et al., 2001; Kelly and Moran, 2002) as follows:

$$^{226}\mathrm{Ra}_{\mathrm{xs}} = \left[\frac{(^{226}\mathrm{Ra}_{\mathrm{ave}} - {}^{226}\mathrm{Ra}_{\mathrm{sea}})^{*}V_{\mathrm{estu}}}{T_r}\right] - \left[^{226}\mathrm{Ra}_r{}^{*}Q_r\right] - \left[^{226}\mathrm{Ra}_{\mathrm{des}}{}^{*}A_{\mathrm{estu}}\right]\ \left(\mathrm{dpm\ d^{-1}}\right) \quad (5)$$

where $^{226}Ra_{ave}$ is the average measured activity in the estuary, $^{226}Ra_{sea}$ is the activity in the adjacent Atlantic Ocean that can be tidally exchanged through Jupiter Inlet, T_r is the Ra-derived estuarine transit time calculated from Eq. (2), V_{estu} and A_{estu} are volume and area estimates for the estuary, respectively (Russell and McPherson, 1983), Q_r is the river-discharge rate (see Fig. 2), and $^{226}Ra_{des}$ is the calculated estuarine-wide regeneration rate of ^{226}Ra from bottom sediments.

The calculated estuarine $^{226}Ra_{xs}$ activity using Eq. (5) ranged from 2.9×10^{8} to 6.4×10^{8} dpm d^{-1}, during high- and low-river discharge conditions, respectively. To confirm these estimates, one can also calculate such excess Ra estimates using tidal prism characteristics for the Loxahatchee River estuary and calculated Ra_{xs} values (Krest et al., 2000; Kelly and Moran, 2002), such that:

$$\mathrm{Ra}_{\mathrm{xs}} = \mathrm{Ra}_{\mathrm{obs}} - \mathrm{Ra}_{\mathrm{c}}\ \left(\mathrm{dpm\ 100\ L^{-1}}\right) \quad (6)$$

where Ra_{obs} represents the observed estuarine Ra activities and Ra_c the calculated activities, after Eq. (3), and,

$$^{226}\mathrm{Ra}_{\mathrm{xs}} = [\mathrm{Ra}_{\mathrm{xs}}{}^{*}f_{\mathrm{tidal}}{}^{*}\mathrm{tp}_{\mathrm{vol}}{}^{*}10].\ \left(\mathrm{dpm\ d^{-1}}\right) \quad (7)$$

In Eq. (7), $^{226}Ra_{xs}$ (dpm d^{-1}) is expressed as a function of the tidal prism volume (tp_{vol}), the tidal frequency (f_{tidal}), and the calculated excess Ra present in the estuarine water column, and ranged from 0.1 to 3.0×10^{8} dpm d^{-1}, during both low and high discharge, respectively. During high-flow conditions, the two independent methods provide estimates that are in close agreement. Differences in the two calculated estimates during low discharge are likely influenced by the lower ^{226}Ra activities observed at salinities between 0.92 and 3.69. Such results validate some of the inherent assumptions in these submarine groundwater discharge techniques, which imply, for example, that the Ra-derived transit times are truly representative of the entire estuary, or that the endmember Ra activities (including groundwater activities) are held constant for the entire duration of the sampling effort.

To quantify the rate of submarine groundwater discharge for the Loxahatchee River estuary, the calculated $^{226}Ra_{xs}$ value using either Eqs. (5) or (7) is assumed to be in steady-state with respect to the groundwater input. Therefore, one can calculate an estuarine-wide submarine groundwater discharge rate, as follows,

$$\mathrm{SGD} = \frac{^{226}\mathrm{Ra}_{\mathrm{xs}}}{^{226}\mathrm{Ra}_{\mathrm{GW}}}\ \left(\mathrm{m^3\ d^{-1}}\right) \quad (8)$$

where $^{226}Ra_{GW}$ represents an average groundwater ^{226}Ra activity (dpm 100 L^{-1}) per sampling cruise. Based on the tidal prism approach, the Ra-derived input of groundwater to the estuary (Table 5) ranged from 6.0×10^{3} to 4.3×10^{5} m^{3} d^{-1}, while the Ra-derived residence-time method (Eq. (7)) produced a rate of submarine groundwater discharge that varied from 6.1×10^{3} to 3.7×10^{5} m^{3} d^{-1}, depending on flow conditions. In comparison, by applying a simple mass-balance approach to derive a $^{226}Ra_{xs}$ estimate (i.e., Eq. (5)), the calculated submarine groundwater discharge varied little with a change in discharge stage: 3.6×10^{5} and 3.0×10^{5} m^{3} d^{-1}, during high- and low-flow conditions, respectively. While such estimates are difficult to compare to other studies without normalizing the data to a specific geographic area, Kelly and Moran (2002) and Kim and Swarzenski (in press) compiled such estimates. Average Loxahatchee River estuarine SGD rates calculated here (20–74 L m^{-2} d^{-1}) fall well within the reported range (6–500 L m^{-2} d^{-1}) observed in other coastal systems.

4.5. Groundwater recharge estimates

One can independently evaluate the accuracy of such Ra-derived submarine groundwater discharge rates

Table 5
Tidal prism-, radium-, and electromagnetic (EM) seepage meter-derived submarine groundwater discharge rate estimates for the Loxahatchee River estuary, per river discharge (season)

Season	Ra-derived				
	Tidal prism (m^3 d^{-1})	Transit time[a] (m^3 d^{-1})	Transit time[b] (m^3 d^{-1})	EM seepage meter (m^3 d^{-1})	Ave. (m^3 d^{-1})
High discharge	4.0E+05	3.7E+05	3.6E+05	8.9E+04	3.8E+05
Low discharge[c]	6.0E+03	6.1E+03	3.0E+05	n/a	1.0E+05

[a] Based on Eq. (7).
[b] Based on Eq. (5).
[c] The geometric mean of the three low discharge values is 22,000 m^3 d^{-1}.

using simple surficial-aquifer parameters to estimate groundwater recharge for the entire Loxahatchee River watershed. The assumption for such a comparison is that the total volume of precipitation (P_R) per unit time interval in the watershed available for recharge is a function of:

$$P_R = \left[\sum P^* \phi^* A_w\right] / d \ (\mathrm{m}^3\ \mathrm{d}^{-1}) \quad (9)$$

where $\sum P$ is the cumulative precipitation to the watershed (0.5207 m), ϕ is a dimensionless term that incorporates evapotranspiration and surface water runoff (0.60 to 0.85; B. McPherson, pers. communication), A_w defines the watershed area (5.44×10^8 m^2), and d represents the defined time interval (in this case 212 d). By applying the range in ϕ values, an average P_R value or groundwater-recharge rate to the Loxahatchee River estuary is estimated to be 1×10^6 m^3 d^{-1}. In spite of the inherent simplicity in such calculations and if one also acknowledges that some component of this recharged water may be discharged as offshore SGD, it is encouraging that this recharge estimate is slightly greater than the average Ra-derived submarine groundwater discharge rate. The difference in these two flux estimates may be due to some small component of groundwater that discharges either directly into the Loxahatchee River estuary from a deeper aquifer or discharges offshore as SGD. Alternatively, inherent physico-chemical properties of Ra may bias submarine groundwater discharge somewhat by preferentially tracing brackish or saline, rather than fresh groundwater.

4.6. Electromagnetic seepage-meter measurements

In order to validate the calculated Ra-derived submarine groundwater discharge rates for this estuary, we also deployed an autonomous electromagnetic (EM) seepage meter (Rosenberry and Morin, 2004; Swarzenski et al., 2004b) at the confluence of Kitching Creek and the Loxahatchee River estuary, close to 12 km upstream from Jupiter Inlet (Fig. 1). An advantage of such an automatic instrument is that the wide range of bi-directional sediment/water interface exchange rates that can be measured rapidly and precisely can provide a precise, although very point-specific, groundwater/surface water exchange rate. There are well-known limitations in the accuracy and interpretation of some manual seepage-meter results (Lee, 1977; Taniguchi and Fukuo, 1993), and these can potentially be identified and minimized using autonomous instruments such as the EM seepage meters. Nonetheless, such seepage-meter results should be interpreted cautiously, because here in this system they record groundwater/surface water exchange conditions at only one site. For a 2-day deployment in September 2003, a 10-min averaged SGD rate of 1.71 cm d^{-1} yielded an estuarine-wide upward submarine groundwater discharge rate of $\sim 0.9 \times 10^5$ m^3 d^{-1}; a value very close in magnitude to the Ra-derived estimate. Thus, it appears that three independent techniques provide at least a first-order, reliable estimate of submarine groundwater discharge for this estuary. Observed variations in the calculated estimates of submarine groundwater discharge from these two very different techniques may result from the EM seepage work being only from one site in the estuary, while the Ra-derived estimates incorporate data that were derived from samples collected across the entire salinity gradient. The particular strength of each SGD technique (e.g., Ra, Rn and physical seepage measurements) in recording slight nuances in fluid exchange across the sediment/water interface cannot be overemphasized.

4.7. Surface water Rn-222 activities

It has been repeatedly shown that ^{222}Rn ($t_{1/2}$ = 3.8 d) activities, when measured in surface waters, may provide useful insight into rates and magnitudes of groundwater/surface water exchange (Cable et al., 1996; Corbett et al., 1999; Burnett et al., 2001; Burnett and Dulaiova, 2003; Oliviera et al., 2003; Lambert and Burnett, 2003; Purkl and Eisenhauer, 2004). To evaluate the contribution of groundwater discharge to the Loxahatchee River estuary using ^{222}Rn as a tracer, we surveyed the surface water column using six commercial radon detectors, plumbed in parallel through one air/water exchanger (Burnett et al., 2001, 2003; Swarzenski et al., 2004d). These new techniques have greatly simplified the collection and subsequent detection of Rn, such that one now can obtain almost real-time excess ^{222}Rn activities in situ.

From a river survey initiated close to the Atlantic Ocean at Jupiter Inlet, ^{222}Rn activities increased rapidly from near-background activities (~2.5 dpm L^{-1}) to values in excess of 28 dpm L^{-1} in the Loxahatchee River close to the Kitching Creek confluence (Fig. 6). The near-symmetrical shape of the Rn profile as a function of salinity or distance from Jupiter Inlet suggests that submarine groundwater discharge occurs prevalently in the headwaters of the river system, and that the short transit time within the estuary (<one day) and the ubiquitous nature of SGD upstream seem to offset any expected tidal control on SGD rates. The ^{222}Rn profile in the Loxahatchee River estuary very clearly demonstrates the utility of this tracer to identify specific regions of a river/estuary that are active sites of submarine groundwater discharge. Such results also provide evidence that Rn appears to preferentially trace the exchange of fresh water rather than more saline water, which Ra isotopes appear to trace more effectively.

4.8. Subsurface streaming-resistivity-profiling measurements

Streaming-resistivity-profiling techniques were used in the Loxahatchee River estuary to investigate subsurface freshwater/saltwater interface dynamics in light of the enriched ^{222}Rn activities in the source waters of the Loxahatchee River. Fig. 7 shows one example of an inverse modeled streaming-resistivity profile from the June 2004 survey; line a) depicts an east–west transect line close to Jupiter Inlet (salinity = 33), while b) illustrates a transect line upstream in the vicinity of the Kitching Creek/Loxahatchee River confluence (salinity = 0). Sediments that are saturated in freshened interstitial water masses generally have higher resistivity ranges (up to 20 Ω m), while more saline interstitial waters would correspond to lower resistivity values. If one assumes that the sediments underlying the Loxahatchee River estuary are homogenous in composition

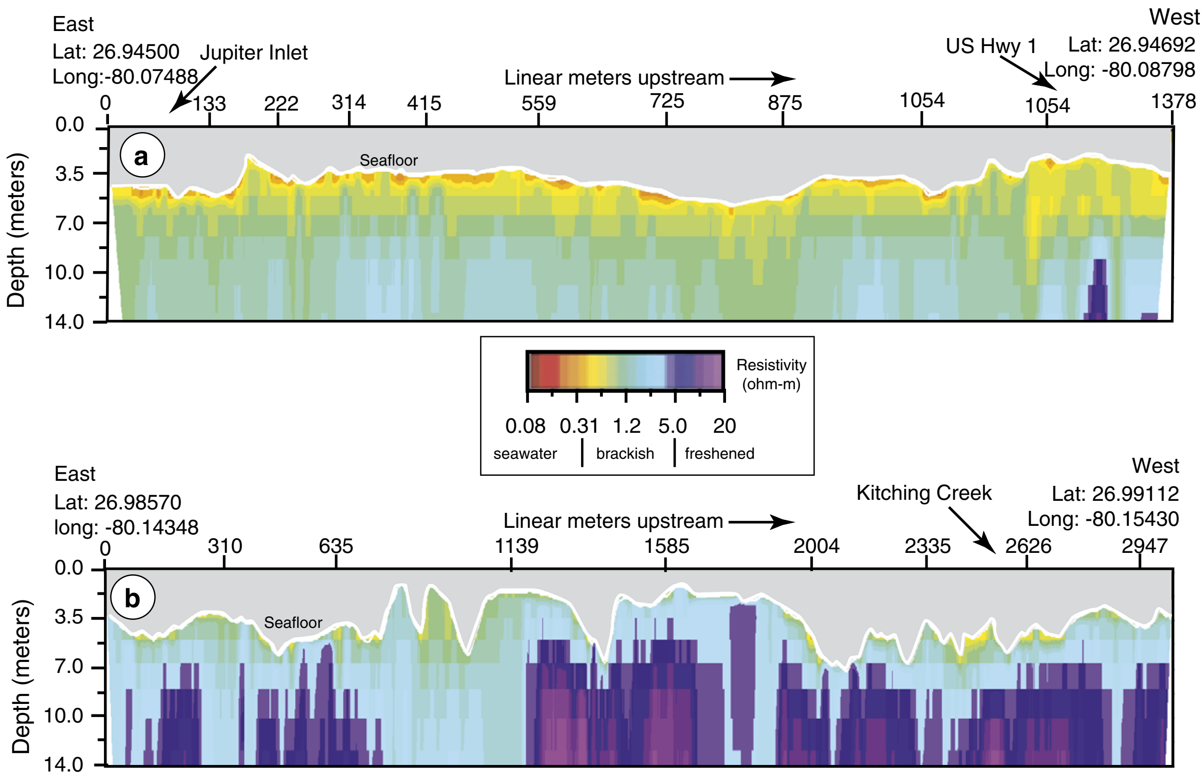

Fig. 7. A comparison of two modeled streaming resistivity profiles, (a) one proximal to Jupiter Inlet in a saline (salinity ~ 33) environment, and (2) one upstream (salinity ~ 0), close to the confluence of Kitching Creek and the Loxahatchee River.

Table 6
Radium-derived nutrient (NH_4^+, PO_4^{-3}) fluxes to the Loxahatchee River estuary, per river discharge (season)

Season	Ave. [NH_4^+] (mmol m^{-3})	Ave. [PO_4^{-3}] (mmol m^{-3})	Ave. SGD rate[a] (m^3 d^{-1})	Flux NH_4^+ (mmol d^{-1})	Flux PO_4^{-3} (mmol d^{-1})	Flux NH_4^+ (μmol m^{-2} d^{-1})	Flux PO_4^{-3} (μmol m^{-2} d^{-1})
High discharge	14.3	5.1	3.8E+05	5.5E+06	2.0E+06	1063.1	378.5
Low discharge	3.2	3.5	1.0E+05	3.2E+05	3.5E+05	62.7	69.2

Pore water nutrient concentrations from which average values have been computed are reported in Orem et al. (in review).
[a] From Table 5.

and that down-core porosity is held constant, then an observed shift toward higher resistivity would imply freshened pore waters. Such streaming-resistivity results clearly demonstrate that the sediments underlying the Loxahatchee River estuary reflect the dynamic nature of the freshwater/saltwater interface; upstream at Kitching Creek, the sediments show little influence of saltwater intrusion, while in the vicinity of Jupiter Inlet, the sediments are largely seawater-saturated.

4.9. Groundwater-derived nutrient fluxes

The delivery and potential diagenetic transformation of select nutrients during submarine groundwater discharge may directly impact coastal ecosystems (Howes and Weiskel, 1996; Harvey and Odum, 1990; Giblin and Gaines, 1990; Krest et al., 2000; Gobler and Sanudo-Wilhelmy, 2001; Crotwell and Moore, 2003; Slomp and Cappellen, 2004). For example, N and P concentrations are often elevated in coastal groundwater relative to river water, and the stoichiometry of N:P in submarine groundwater most often diverges drastically from the Redfield ratio (16:1) (Capone and Bautista, 1985; Lapointe et al., 1990; Valiela et al., 1990; Weiskel and Howes, 1992; Gallagher et al., 1996; Corbett et al., 1999, 2000; LaRoche et al., 1997; Herrera-Silveira, 1998; Miller and Ullman, 2004). By applying our calculated Ra-derived submarine groundwater discharge rate estimates (20–74 L m^{-2} d^{-1}), one can evaluate the groundwater-derived nutrient inputs to the Loxahatchee River estuary per discharge period, using average groundwater-nutrient concentrations provided in Table 6. These NH_4^+ and PO_4^{-3} concentrations represent a composite average ($n>50$) per river-discharge stage that was collected from a series of vertical porewater sites from up to six shore-perpendicular transects (Orem et al., in review). From such porewater values, mean NH_4^+ concentrations ranged from 3.2 to 14.3 mmol m^{-3} during low and high discharge, respectively, while mean PO_4^{-3} concentrations ranged from 3.5 to 5.1 mmol m^{-3}, respectively. Multiplying these mean nutrient concentrations by seasonally averaged SGD rates yields daily NH_4^+ fluxes into the estuary that range from 0.32 to 5.5×10^6 mmol (62.7 to 1063.1 μmol m^{-2} d^{-1}), depending on the river-discharge stage. The flux of PO_4^{-3} similarly ranged from 0.35 to 2.0×10^6 mmol (69.2 to 378.5 μmol m^{-2} d^{-1}) per day, during low- and high-discharge, respectively. Such SGD-derived nutrient flux rates compare closely to yearly computed riverine total N and total P load estimates, which calculated on a daily basis, are 4.6×10^6 and 3.5×10^5 mmol TP (McPherson and Sonntag, 1984).

Estimates for SGD-derived nutrient transport into the Loxahatchee River estuary may be compared to other SGD-influenced coastal waters. For example, in Waquoit Bay, MA, Charette et al. (2001) observed a SGD-derived DIN ($NO_3^-+NH_4^+$) flux of about 550 μmol m^{-2} d^{-1}. In a recent review of SGD-enhanced nutrient transport, Slomp and Cappellen (2004) report that the range in N-flux extends from ~160 μmol m^{-2} d^{-1} off Hawaii (Garrison et al., 2003) to 72,000 μmol m^{-2} d^{-1} in a small estuary off New England (Portnoy et al., 1998). Comparable SGD-derived P-flux estimates are much more infrequent and generally range from <1.0 μmol m^{-2} d^{-1} in Florida Bay (Corbett et al., 1999) to over 900 μmol m^{-2} d^{-1} off North Inlet, NC (Krest et al., 2000). The wide range in reported nutrient-flux estimates reflects the importance of hydrogeologic controls on an ecosystem, as well as potential anthropogenic perturbations.

5. Conclusions

This study has demonstrated the utility of ^{222}Rn and four naturally occurring isotopes of radium in estimating rates and occurrence of submarine groundwater discharge to the Loxahatchee River estuary during two sampling events that target high- and low-discharge conditions. Observed variations in the estuarine ^{222}Rn and ^{223,224}Ra distributions suggest that these two tracers target slightly different water masses, based solely on their respective salinity. Observed non-conservative element:salinity distributions in this estuary suggest that the role of physical mixing, which certainly dominates in a system as rapidly flushed as this one, may also be influenced by biogeochemical uptake and release processes as well as submarine groundwater discharge. Groundwater sources to this system are most likely the surficial aquifer system, and based on measured surface water ^{222}Rn activities, most fresh submarine groundwater is discharged upstream, in the vicinity of where Kitching Creek discharges into the Loxahatchee River. The mean transit time of a water parcel in the estuary as calculated by Ra isotopes is ~ 1 d, an estimate in close agreement with a value calculated by tidal prism. Ra-derived submarine groundwater discharge estimates compare favorably to those obtained from a 2-day electromagnetic seepage-meter deployment at the confluence of Kitching Creek and Loxahatchee River, as well as simple watershed-recharge estimates. Average submarine groundwater discharge estimates ranged from 1.0 to 3.8×10^5 m^3 d^{-1} (20–74 L m^{-2} d^{-1}), depending on river discharge. Such SGD rates yield NH_4^+ and PO_4^{-3} fluxes that range from 62.7 to 1063.1 and from 69.2 to 378.5 μmol m^{-2} d^{-1}, respectively, depending on river flow conditions. These SGD-derived nutrient flux rates compare favorably to yearly computed riverine total N and total P load estimates.

Acknowledgements

PWS specially thanks Bill Burnett, Henrietta Dulaiova, and Ricky Peterson (all from FSU) for expert and fun SGD collaboration. Chris Reich (USGS) and Brian Blake Collins (ETI) ably assisted with field work and laboratory analyses. DOC analyses were graciously run in Paula Coble's laboratory (USF) by Robin Comny. This paper was greatly improved by careful comments and suggestions from Alan Shiller, Ed Sholkovitz, as well as from Kevin Kroeger (USGS). PWS acknowledges financial support from SFMWD and the USGS Coastal Marine Geology Program. The use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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