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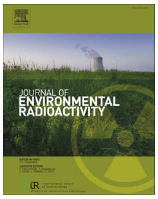

Applications of radon and radium isotopes to determine submarine groundwater discharge and flushing times in Todos os Santos Bay, Brazil

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ABSTRACT

Todos os Santos Bay (BTS) is the 2nd largest bay in Brazil and an important resource for the people of the State of Bahia. We made measurements of radon and radium in selected areas of the bay to evaluate if these tracers could provide estimates of submarine groundwater discharge (SGD) and flushing times of the Paraguaçu Estuary and BTS. We found that there were a few areas along the eastern and northeastern shorelines that displayed relatively high radon and low salinities, indicating possible sites of enhanced SGD. A time-series mooring over a tidal cycle at Marina do Bonfim showed a systematic enrichment of the short-lived radium isotopes ^{223}Ra and ^{224}Ra during the falling tide. Assuming that the elevated radium isotopes were related to SGD and using measured radium activities from a shallow well at the site, we estimated groundwater seepage at about 70 m^3/day per unit width of shoreline. Extrapolating to an estimated total shoreline length provided a first approximation of total (fresh + saline) SGD into BTS of 300 m^3/s, about 3 times the average river discharge into the bay. Just applying the shoreline lengths from areas identified with high radon and reduced salinity results in a lower SGD estimate of 20 m^3/s. Flushing times of the Paraguaçu Estuary were estimated at about 3–4 days based on changing radium isotope ratios from low to high salinities. The flushing time for the entire BTS was also attempted using the same approach and resulted in a surprisingly low value of only 6–8 days. Although physical oceanographic models have proposed flushing times on the order of months, a simple tidal prism calculation provided results in the range of 4–7 days, consistent with the radium approach. Based on these initial results, we recommend a strategy for refining both SGD and flushing time estimates.

1. Introduction

Submarine groundwater discharge (SGD) is recognized as a significant, but poorly quantified, source of nutrients and other dissolved species to coastal waters and estuaries. It may also be a pathway for land-derived chemicals (nutrients and trace elements) of anthropogenic origin (Bishop et al., 2017; Burnett et al., 2009; Rodellas et al., 2015; Slomp and Van Cappellen, 2004). Progress has been made in a number of SGD investigations in different types of coastal zones including coastal plain, karst, fractured crystalline rock, glacial and volcanic (Bone et al., 2007; Burnett et al., 2006; Slomp and Van Cappellen, 2004). These studies have shown that SGD is a significant water and chemical compounds pathway from land to sea (Bokuniewicz, 1980; Moore, 1996; Taniguchi et al., 2002). SGD may occur through surficial aquifers or through breaches in deeper semi-confined coastal aquifers. While the overall flow of fresh groundwater into the ocean is likely no more than about 6% of global runoff, it has been estimated that the total dissolved salt contributed by terrestrially-derived SGD may be as much as 50% of that contributed by rivers (Zetser and Loaiciga, 1993). In addition to inputs of terrestrially derived groundwaters,

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recirculation of seawater through sediments by tidal pumping and other processes can provide significant biogeochemical inputs and is also considered “SGD” (Burnett et al., 2003; Moore, 2010). One possible consequence of SGD is that high N:P ratios in contaminated coastal groundwater relative to surface waters may drive the coastal ocean towards P-limitation within the coming decades, perhaps changing the present N-limited nature of coastal primary productivity (Hwang et al., 2005; Slomp and Van Cappellen, 2004).

Even in coastal regions with significant riverine inputs, SGD may be important. Krest et al. (1999), Moore (1997) and Moore and Krest (2004) have identified groundwater discharge in the Mississippi and Atchafalaya Rivers (USA) and Ganges–Brahmaputra (Bangladesh, India) estuaries using radium isotopes. Dulaiova et al. (2006) assessed SGD in the Chao Phraya Estuary (Thailand) and concluded that groundwater inputs represented about 20% of the river flow during low flow in January (dry season) but only ~4% during July, the wet monsoon.

The most widely used methods of assessment of SGD are direct measurement techniques (seepage meters), hydrological modeling, and the application of geochemical tracers (Burnett et al., 2001a, 2006; Moore, 2010; Taniguchi et al., 2002). Radon (^{222}Rn) and radium isotopes are the most frequently used geochemical tracers. Because groundwater is in contact with radon-emanating aquifer material, ^{222}Rn concentrations in groundwater are often two to three orders of magnitude higher than most surface waters. This makes radon very useful in identifying areas of groundwater input into surface waters (Burnett et al., 2002; Burnett and Dulaiova, 2003; Cable et al., 1996).

Naturally occurring radium isotopes have also been shown to be good tracers of SGD (Charette et al., 2008, 2001; Kelly and Moran, 2002; Moore, 1996) and are widely applied to study estuarine and coastal mixing rates. Particles transported by rivers are one of the major sources of the four naturally occurring radium isotopes in estuaries: ^{224}Ra (half-life 3.6 d), ^{223}Ra (11.4 d), ^{228}Ra (5.7 y), and ^{226}Ra (1600 y). As river water mixes with seawater, the water's ionic strength increases and radium isotopes are released from particles by ion exchange reactions. This results in the well-documented non-conservative distribution of radium versus salinity with a maximum concentration occurring in the mixing zone (Li et al., 1977).

In August 2015, a two-week training course on “Applications of Radioisotopes in Coastal and Environmental Sciences” was organized at the Federal University of Bahia (UFBA) in Salvador (Brazil). The course was co-sponsored by the Todos os Santos Bay (BTS) Multidisciplinary Project and the Scientific Committee on Oceanic Research (SCOR). Lecture and laboratory sections and field-based studies were conducted. The field studies consisted of sampling and analysis of radon, radium isotopes and nutrients throughout the Todos os Santos system including the Paraguaçu River, the largest source of fresh water to the bay.

Our goals in presenting the analysis shown in this paper are to: (1) provide an initial assessment of the SGD potential into BTS; and (2) evaluation of the usefulness of Ra isotopes to evaluate flushing times in the Paraguaçu Estuary and BTS. Both of these objectives, combined with nutrient data, can be used to estimate the potential importance of SGD to the nutrient and other chemical budgets of BTS.

1.1. Study site

The Todos os Santos Bay (BTS, Fig. 1) is the second largest bay of Brazil, with an area of 1112 km^2 and approximate maximum width and length of 32 km and 50 km, respectively. The bay is relatively shallow (average depth of 9.8 m) and has an intertidal area of 327 km^2. The bay is part of the sedimentary Recôncavo-Tucano-Jatobá Rift in the northeast of Brazil that was formed during the South Atlantic rifting (Magnavita, 1994). The geomorphology of the bay is determined by tectonic alignments and these could also influence the groundwater flow. Deep drainage channels, reaching depths up to 70 m, branch inside the bay following an old drainage network going towards the Paraguaçu River, Subaé River and Aratu Bay (Cirano and Lessa, 2007).

The salinity distribution in BTS demonstrates that the circulation is dominated by tidal flushing. Estuarine conditions occur only within the channel of the Paraguaçu River (Wolgemuth et al., 1981). During summer, the waters inside the bay have oceanic characteristics, while during winter there is a significant increase in freshwater fluxes. There is a gradual decrease in salinity and an increase in temperature in surface waters from the BTS main entrance towards inland. This trend is observed in summer and winter in both neap and spring tides. Maximum vertical gradient in temperature is less than 1 °C, whereas the highest instantaneous salinity gradient during spring tide is 2.27, at the Aratu bay channel (25 m depth) (Lessa et al., 2009). Tides are characteristically semi-diurnal, with a maximum range of 3.5 m during spring tides at Iguape Bay, and 1.2 m during neap tides at the main entrance to the BTS. Siliciclastic sand can be found in the channels at the entrance to the bay and close to the river mouths, whereas mud occurs predominantly in the northern areas of the bay (Dias, 2004).

The Paraguaçu, Subaé and Jaguaripe rivers are the three main tributaries of the BTS. The Paraguaçu River, which was dammed in 1985, drains a large semi-arid watershed (56,300 km^2) and the river has a daily mean discharge of 93 m^3 s^{-1} (1946–2003; Genz, 2006). The flow regime of the Paraguaçu is intense, and a typical flood hydrograph is 7 days long (Genz and Lessa, 2015). Maximum flows are observed during the southern summer, especially in December and January. The other two main tributaries of the BTS are the Jaguaripe (2200 km^2) and Subaé rivers (600 km^2). The maximum discharge of the Jaguaripe and Subaé rivers occurs in June (winter), where mean monthly discharges are observed of 28 m^3/s and 9 m^3/s, respectively (Cirano and Lessa, 2007).

As a result of the large metropolitan area that surrounds the BTS, which includes, industrial complexes, ports, shrimp farming, fisheries and inputs of untreated sewage make BTS an example of a coastal environment that is largely affected by anthropogenic activities (Hatje and de Andrade, 2009; Hatje and Barros, 2012 and references therein).

2. Methods

2.1. General approach

We performed surveys parallel to the shoreline of BTS (Fig. 1) with continuous radon and salinity measurements. This was done to see if we could locate any discernible areas where SGD may be particularly active based on positive radon and/or negative salinity anomalies. We also collected groundwater from wells and natural springs around BTS (W1-W9; Fig. 1) to evaluate the range of radon concentrations. Samples W1, W2 and W3 are all located in the extreme northern area of BTS while W4 is in the northwest. Both W5 and W6 are on Itaparica Island while W7 and W8 are on the west shore. In order to evaluate temporal variations, we set up a mooring at the end of a 140 m long pier at Marina do Bonfim and collected hourly radon and radium isotope measurements over a tidal cycle (T1-T13 in Fig. 1).

Large volume (100 L) samples were collected for radium isotopes throughout BTS and the Paraguaçu Estuary. All samples in the estuary (P1-P9) were collected August 10 and all the BTS samples (B1-B13) were collected August 25 during an incoming tide. All radium samples were collected by quickly pumping near surface

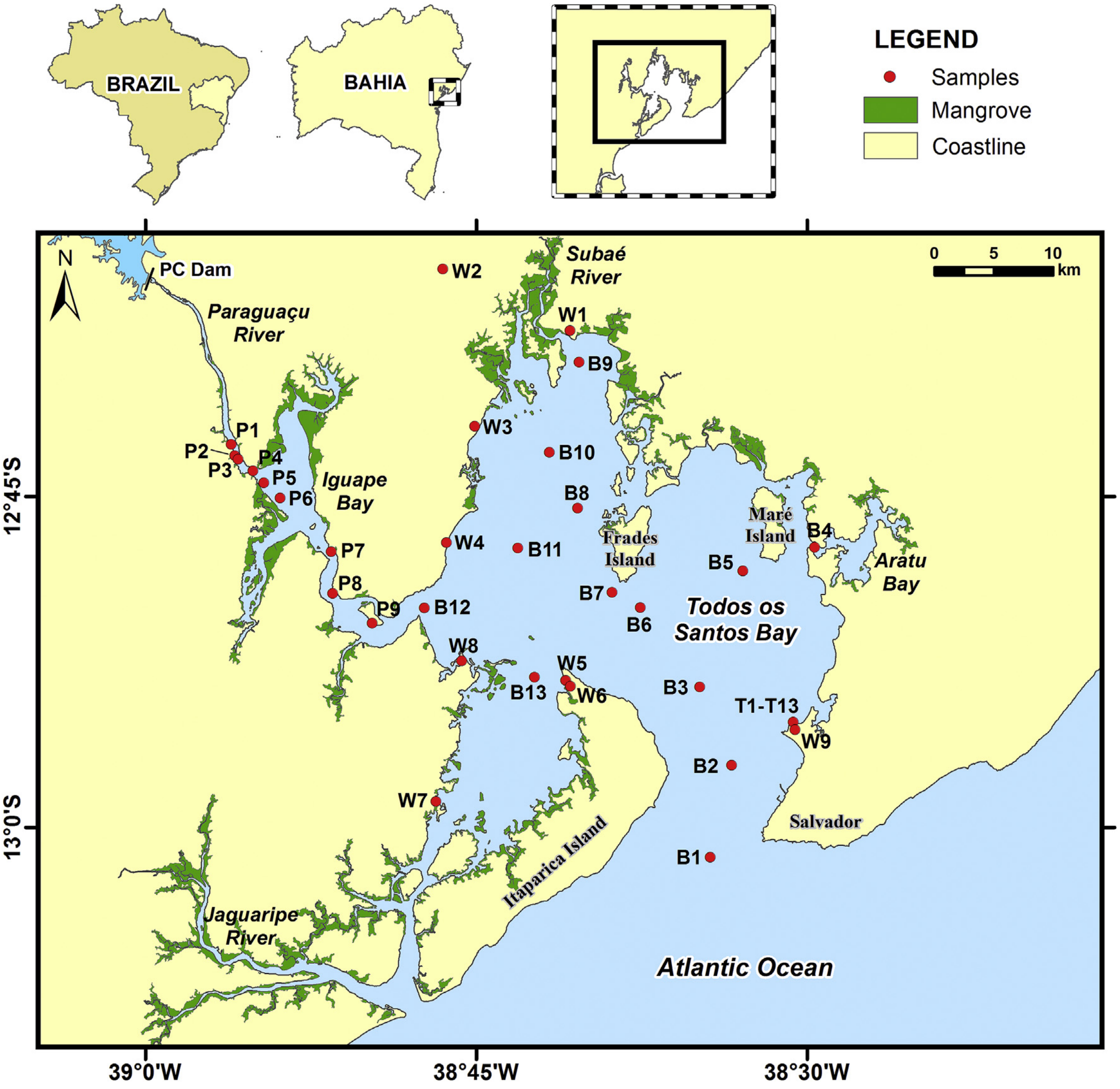

Fig. 1. Index map of BTS showing station locations. B = Todos os Santos Bay; P = Paraguaçu Estuary; T = time-series at Marina do Bonfim; and W = groundwater wells.

water into large barrels. The water from each station was then pumped slowly (1–2 L/min) through "Mn-fiber" (manganese impregnated acrylic fiber) to adsorb the radium. These fibers were then processed for both short-lived (^{223}Ra, ^{224}Ra) and long-lived (^{226}Ra, ^{228}Ra) isotopes of radium (see analytical method descriptions below).

We did not have an opportunity to collect sediment samples to evaluate diffusional or bioturbational inputs of ^{222}Rn and ^{224}Ra into the water column. Since the average depth of BTS is 9.8 m and much of its seafloor consists of siliciclastic sands, which are generally low in natural radioactivity, such fluxes are likely low.

2.2. Radioisotope measurements

Dissolved radon was analyzed using the automated systems described in Burnett et al. (2001b) and Dulaiova et al. (2005). Surveys were conducted from a boat with underway speeds of less than 5 km/h to optimize spatial resolution. The multi-detector system used measures ^{222}Rn from a constant stream of water passing through an air-water exchanger ('RAD-AQUA') that distributes radon between the water and a closed air loop. The radon-enriched air is fed to three commercial radon-in-air monitors (RAD-7, Durridge Co.) arranged in parallel that evaluate the activity of ^{222}Rn via measurement of the short-lived ($T_{1/2} = 3$ min) α-emitting daughter, ^{218}Po. Radon activity in water is then calculated from the temperature- and salinity-dependent solubility coefficients (Schubert et al., 2012). Radon counts were integrated over 10-min cycles with resulting measurement uncertainties of 10–15%. Continuous temperature and electrical conductivity (salinity) measurements were recorded with a Van Essen Instruments CTD Diver attached to the submersible pump used to deliver water to the air-water exchanger. In order to match the salinity measurements, which are instantaneous, to the radon measurements a 20-min delay was put into the radon readings. This delay accounts for the time required for radon to establish a chemical equilibrium between the water and air phases and for ^{218}Po to reach radioactive equilibrium with ^{222}Rn (Burnett et al., 2001a,b). Samples for radon in groundwater were collected in discrete 250-mL bottles and analyzed using the RAD-H2O accessory to the RAD7. Uncertainties of these measurements are estimated at 15–20%.

The ^{223}Ra and ^{224}Ra measurements were made within a few days of sampling using a specially designed system known as a

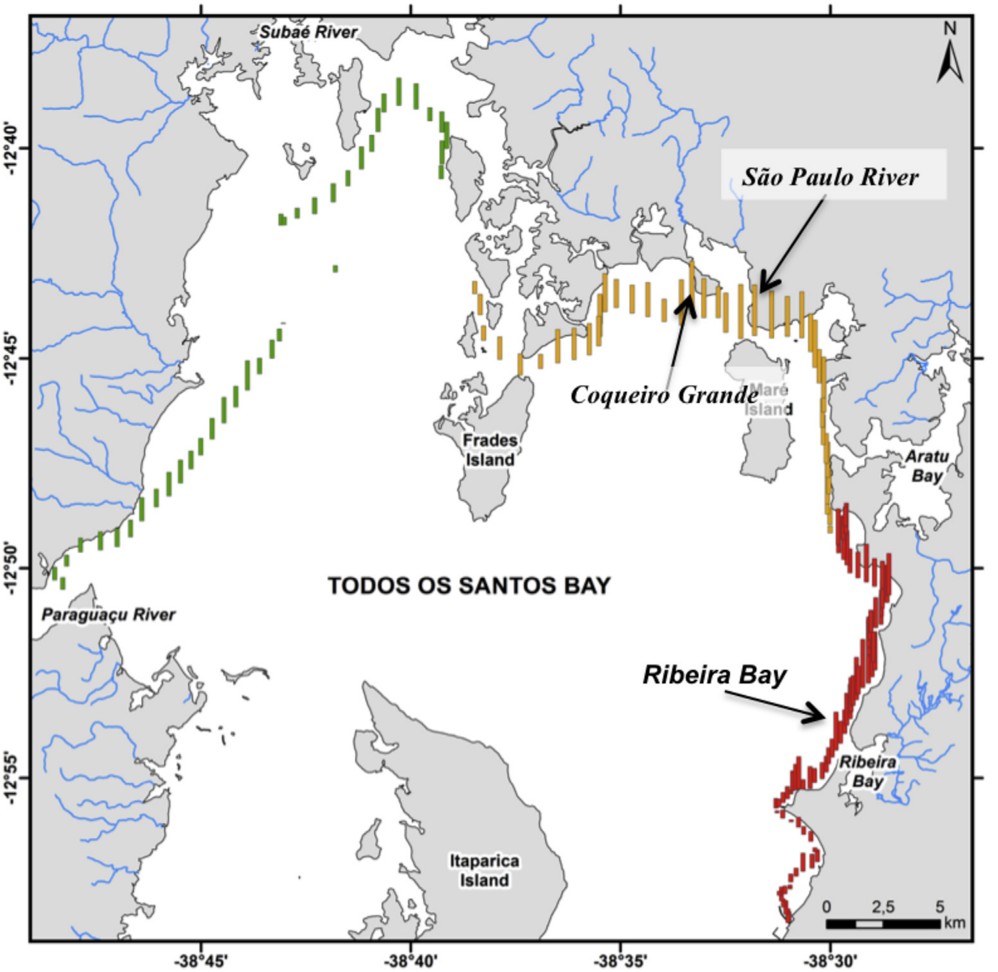

Fig. 2. Map of BTS with alongshore radon survey results shown for August 4 (east shore; red), 5 (northeast shore; orange) and 6 (western coast; green), 2015. The height of all bars is proportional to the measured ^{222}Rn activity in the near surface waters. The highest ^{222}Rn measured in these surveys was 3.2 dpm/L. Arrows indicate areas with radon and salinity anomalies that may indicate enhanced SGD inputs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Radium Delayed Coincidence Counter (RaDeCC; Moore and Arnold, 1996). We measured ^{228}Th on the same system to correct for supported ^{224}Ra so all values reported here are excess ^{224}Ra activities. The estimated uncertainties are 15% for ^{223}Ra and 10% for ^{224}Ra.

The long-lived radium isotopes were analyzed by a radiochemical method that required dissolution of the MnO_2-impregnated acrylic fiber (de Oliveira et al., 2006; Moore and de Oliveira, 2008). Each fiber was leached with 300 mL of concentrated HCl and 10 mL of a 40% solution of hydroxylamine hydrochloride that was added to ensure reduction of the Mn. The solution was then raised to 600 mL with concentrated HCl. Activity concentrations of ^{226}Ra and ^{228}Ra were determined by co-precipitation with $Ba(Ra)SO_4$ after separation of ^{210}Pb, followed by counting of gross alpha and gross beta activity in the precipitate on a low background gas flow proportional counter. The paper filter containing the precipitate was measured after 21 days to ensure equilibrium between ^{226}Ra and its daughters and to eliminate contribution from ^{224}Ra and ^{223}Ra. The uncertainties by this technique are estimated at 5% for ^{226}Ra and 8% for ^{228}Ra.

2.3. Nutrients and ancillary variables

Samples were collected with a surface pump system that included a peristaltic pump (Masterflex–Cole Parmer Instrument Company) and PFA Teflon tubing. The sample inlet, mounted on a telescopic rod, was lowered to around 1 m below the water surface at each sample station, and samples were filtered through polysulfone capsule filters and stored frozen until analysis. Phosphate, ammoniacal nitrogen ($NH_4^+ + NH_3$), nitrite, nitrate and dissolved silicate (DSi) were analyzed according to Grasshoff et al. (1989). Dissolved inorganic nitrogen (DIN) is defined as the sum of nitrate, nitrite and ammoniacal nitrogen. Precisions were 3% for phosphate, 9% for NH_4^+, 4.2% for nitrite, 0.7% for nitrate and 3.8% for DSi. Salinity, pH, and dissolved oxygen were measured, at each station, with a calibrated water quality analyzer (Datasonda Hydrolab 4 A).

3. Results and discussion

3.1. Radon surveys

The alongshore radon/salinity surveys on August 4, 5 and 6 showed mostly relatively low radon values (Fig. 2) on the eastern shoreline (most measurements < 2.0 dpm/L) and especially low activities along the northern and western shoreline (most < 1.0 dpm/L). Salinities were almost all in the range from 29 to 34.5 with the lowest readings near the outflow from the Paraguaçu River. The low radon readings may have been a consequence of high winds

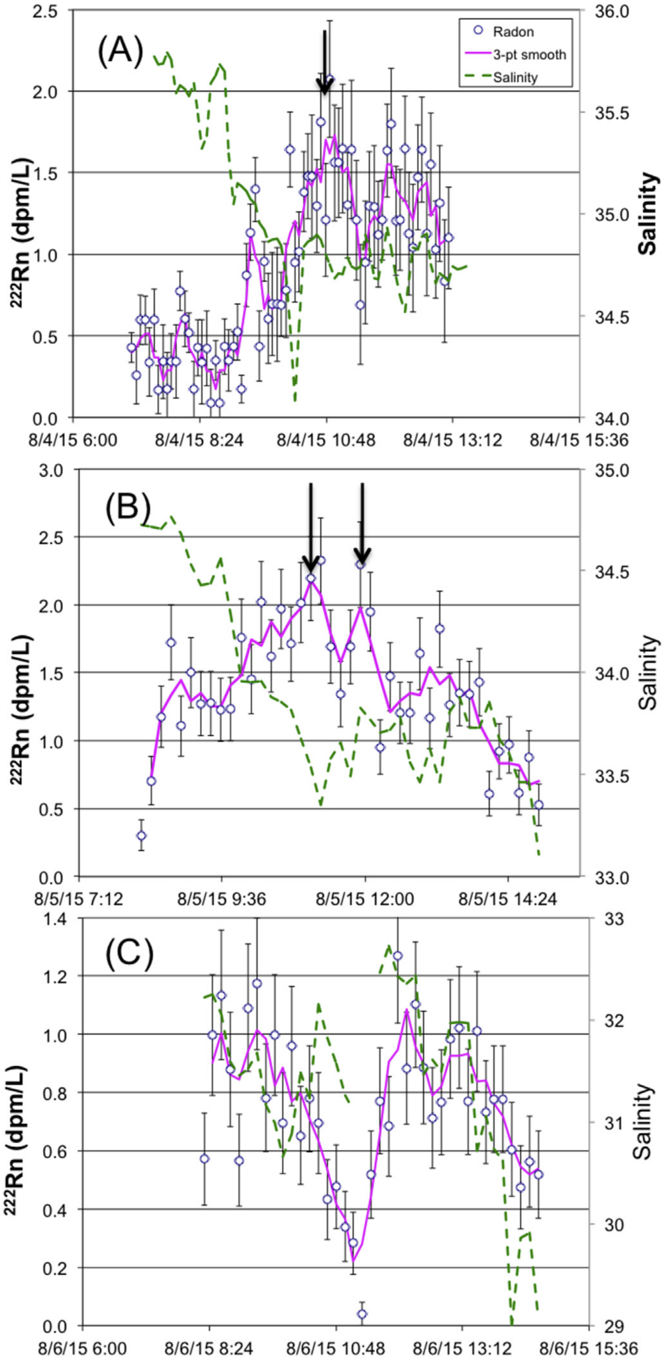

Fig. 3. Plot of salinity (dashed green line) and ^{222}Rn activities (open circles and 3-pt smooth in solid line) during the surveys of Aug. 4 (A), 5 (B) and 6 (C), 2015. Areas with radon spikes (arrows) may indicate elevated SGD inputs at those locations. Radon spikes that match significant salinity reductions may be of particular interest. A few possibilities are indicated by the down facing arrows shown here and in Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

during this period (5–8 m/s) and not being able to survey too close to shore due to shallow depths (i.e., 0.5 m).

There are a few indications of relatively high radon occurrences together with reduced salinities that may indicate areas of enhanced SGD (Fig. 3). These areas, highlighted in both Figs. 2 and 3, include an area off Ribeira Bay on the eastern shore, and the mouth of São Paulo River and Coqueiro Grande in the northern portion of BTS. We did not observe any clear evidence of SGD along the western shore.

The groundwaters collected fell into three main groups based on the radon activities (Table 1): (1) samples W1-W4 were all in the range of 1000–1300 dpm/L; (2) W5-W8 samples were all much higher at 3700–6100 dpm/L; and (3) the open well at Marina (W9) was lowest at 420 dpm/L. We could discern no difference between groundwater sampled from wells compared to samples collected from natural springs.

3.2. *Radium and nutrients in the Paraguaçu Estuary and BTS*

Samples collected for radium isotopes in the Paraguaçu Estuary ranged in salinity from 1.4 to 29 (Table 2). When plotted against salinity, radium isotopes in the Paraguaçu Estuary show a classic concave downward non-conservative trend indicating additional inputs of radium at mid-salinities (Fig. 4). The BTS samples generally fall at or near the high salinity end of these trends. While most of this additional radium likely originates from desorption of particle-bound radium, there is some indication that an addition source, possibly SGD, may be present as well. For example, the short-lived radium isotopes are clearly above the general trend at station P8.

Samples from the BTS show a relatively narrow range in salinity (~29–33) and generally fall on the same trend as the samples from the Paraguaçu Estuary. Interestingly, the 3 highest activities of all 4 radium isotopes are all from the same stations, B4 in the eastern area near the entrance to Aratu Bay and B9 and B10, both in the northern most section of BTS. These activities are higher than the most enriched activities in the estuary and suggest additional sources are present.

Nutrients throughout BTS are low in nitrogen species and particularly in phosphate, with very low N/P ratios, perhaps suggesting a potential P-limited situation (Table 3). The N/P ratios are also very low in the estuary (most ratios <4). The low levels of nutrients we observed here are in good agreement with previous studies that defined the BTS as an oligotrophic system (CRA, 2004; Hatje et al., 2016). There is an interesting pattern observed in samples from the Paraguaçu, showing that DIN and ^{224}Ra spike at the same point (P8) that PO_4^{3-} decreases (Fig. 5). While not definitive, this pattern is very suggestive of SGD input. Groundwaters are often enriched in radium and nitrogen species while depleted in phosphate because of PO_4^{3-} adsorption onto aquifer surfaces. Most of this DIN is ammoniacal nitrogen. An anomalous result was observed at stations P7 and P6 (adjacent and sampled during incoming tide), nitrite as the main dissolved inorganic nitrogen specie (Table 3). The extent of the DIN enrichment at station P8 is impressive with a greater than 50-fold enrichment from station P5 to P8. Groundwater from the Marina site has an N/P ratio of 1670. Nitrate was the prevailing nitrogen form, as expected in open wells.

3.3. *Flushing of the Paraguaçu Estuary and BTS*

Based on the activity ratios (ARs) of short-lived to long-lived radium isotopes, one can estimate "apparent radium ages" considering on how the ratios change moving away from a source. Basically, the calculation intends to show how much time has passed since the radium has entered the system. The calculation assumes that there is just one source of radium, even if the nature of that source is unknown, and that it has a known and constant isotopic composition (Moore, 2000). The appropriate equation using the ^{224}Ra/^{223}Ra activity ratios is as follows:

Table 1
Groundwater sampling stations around Todos os Santos Bay.

Sample	Site Description	Sampling Day/Time	Type	Temp °C	^{222}Rn dpm/L	2σ Uncert. dpm/L
W1	Fonte do Mato	04-Aug-15/12:20	spring	25	1160	92
W2	Timbo	04-Aug-15/14:45	spring	25	1010	86
W3	Ecoresort Enseada dos Caieros	04-Aug-15/16:13	well	28	1150	92
W4	Poço Residencial	04-Aug-15/17:25	well	29	1270	96
W5	Fonte da Bica	05-Aug-15/10:30	spring	28	6120	184
W6	Poco Residencial	05-Aug-15/10:16	well	29	4200	153
W7	Hotel Fazenda Recanto	05-Aug-15/12:09	well	29	4530	159
W8	Maricultura Valença	05-Aug-15/14:54	well	26	3670	141
W9	Marina do Bonfim (AP)	13-Aug-15/14:20	well	nd	417	112

Notes: well depths were estimated in a few cases (W3 = 50 m; W6 = 6 m; and W7 = 7 m). Salinities were measured in 4 cases (W4 = 2; W5 = 3; W7 = 0; and W9 = 0.2).

Table 2
Salinity, pH, DO and radium isotopes from the Paraguaçu Estuary, Todos os Santos Bay, and Marina Bonfim.

Sample	S	pH	DO	^{223}Ra	^{224}Ra	^{226}Ra	^{228}Ra
			mg/L	dpm/100 L			
Paraguaçu Estuary							
P1	1.4	8.18	8.22	0.31 ± 0.05	20.6 ± 2.1	6.1 ± 0.3	29.9 ± 2.4
P2	5.3	7.74	8.87	1.8 ± 0.3	34.5 ± 3.5	7.6 ± 0.4	49.5 ± 4.0
P3	9.7	8.25	9.28	2.7 ± 0.4	41.2 ± 4.1	11.1 ± 0.6	61.3 ± 4.9
P4	15.2	8.03	8.94	4.7 ± 0.7	53.7 ± 5.4	nd	nd
P5	20.6	7.98	7.90	3.2 ± 0.5	51.2 ± 5.1	14.6 ± 0.7	88.9 ± 7.1
P6	24.8	7.95	7.22	4.6 ± 0.7	44.1 ± 4.4	20.9 ± 1.0	80.7 ± 6.5
P7	27.3	7.79	6.96	3.2 ± 0.5	39.1 ± 3.9	13.6 ± 0.7	97.0 ± 7.8
P8	27.8	7.55	6.89	4.6 ± 0.7	44.8 ± 4.5	18.5 ± 0.9	70.5 ± 5.6
P9	28.9	7.85	6.82	3.8 ± 0.6	31.2 ± 3.1	28.6 ± 1.4	92.9 ± 7.4
Todos os Santos Bay							
B1	33.4	8.00	7.28	1.2 ± 0.2	21.5 ± 2.2	12.8 ± 0.6	52.0 ± 4.2
B2	32.9	8.06	6.92	1.9 ± 0.3	11.0 ± 1.1	16.2 ± 0.8	48.2 ± 3.9
B3	32.6	8.16	7.04	1.5 ± 0.2	8.30 ± 0.8	14.9 ± 0.7	52.1 ± 4.2
B4	32.5	8.21	7.35	5.6 ± 0.8	42.6 ± 4.3	14.8 ± 0.7	63.8 ± 5.1
B5	32.1	8.30	7.10	3.4 ± 0.5	20.3 ± 2.0	17.2 ± 0.9	68.2 ± 5.5
B6	30.9	8.15	7.16	2.7 ± 0.4	21.1 ± 2.1	11.3 ± 0.6	63.9 ± 5.1
B7	30.4	8.31	7.36	3.6 ± 0.5	20.7 ± 2.1	10.7 ± 0.5	59.3 ± 4.7
B8	29.7	8.36	7.42	2.7 ± 0.4	21.8 ± 2.2	10.9 ± 0.5	62.2 ± 5.0
B9	28.6	8.27	7.13	7.4 ± 1.1	87.0 ± 8.7	20.7 ± 1.0	118 ± 9.4
B10	29.7	8.34	7.14	6.3 ± 0.9	61.0 ± 6.1	18.7 ± 0.9	77.1 ± 6.2
B11	28.9	8.42	7.61	2.5 ± 0.4	27.6 ± 2.8	13.3 ± 0.7	57.9 ± 4.6
B12	29.3	8.36	7.28	2.1 ± 0.3	29.1 ± 2.9	14.2 ± 0.7	53.4 ± 4.3
B13	30.9	8.40	7.33	4.0 ± 0.6	28.7 ± 2.9	13.6 ± 0.7	67.4 ± 5.4
Marina do Bonfim							
T1	33.5	7.67	7.94	1.4 ± 0.2	20.3 ± 2.0	4.2 ± 0.2	20.6 ± 1.7
T2	33.4	8.60	7.57	0.04 ± 0.01	1.8 ± 0.2	3.8 ± 0.2	28.6 ± 2.3
T3	33.3	8.64	7.57	1.29 ± 0.02	12.9 ± 1.3	4.4 ± 0.2	28.2 ± 2.3
T4	33.3	8.65	7.53	0.72 ± 0.1	9.75 ± 1.0	4.9 ± 0.2	33.4 ± 2.7
T5	33.3	8.72	8.62	1.1 ± 0.2	12.8 ± 1.3	3.8 ± 0.2	22.0 ± 1.8
T6	33.3	8.72	8.31	1.0 ± 0.2	14.7 ± 1.5	3.7 ± 0.2	23.7 ± 1.9
T7	33.3	8.72	8.28	0.3 ± 0.05	20.5 ± 2.1	7.8 ± 0.4	37.8 ± 3.0
T8	33.5	8.71	7.92	1.8 ± 0.3	34.3 ± 3.4	8.2 ± 0.4	28.3 ± 2.3
T9	33.6	8.71	7.78	2.7 ± 0.4	41.0 ± 4.1	6.0 ± 0.3	29.2 ± 2.3
T10	33.5	8.66	7.89	4.7 ± 0.7	53.5 ± 5.4	3.5 ± 0.2	25.7 ± 2.1
T11	33.4	8.73	8.15	3.2 ± 0.5	51.0 ± 5.1	4.4 ± 0.2	28.7 ± 2.3
T12	33.5	8.72	8.22	4.6 ± 0.7	44.0 ± 4.4	6.9 ± 0.3	29.2 ± 2.3
T13	33.5	8.70	7.39	nd	nd	nd	nd

Notes: Samples at Marina Bonfim were all collected at the same site at different times from 09:00 to 21:00 on Aug. 13, 2015. Nd = not determined.

$$t = \ln\left(\frac{\left(\frac{^{224}Ra}{^{223}Ra}\right)_i}{\left(\frac{^{224}Ra}{^{223}Ra}\right)_{obs}}\right) \times \frac{1}{(\lambda_{224} - \lambda_{228})} \qquad (1)$$

Where $[^{224}\text{Ra}/^{223}\text{Ra}]_i$ represents the initial AR entering the system, and $[^{224}\text{Ra}/^{223}\text{Ra}]_{obs}$ is the observed ratio at another station thought to be receiving radium from the same source. The λ_{224} and λ_{223} represent the decay constants for the two radium isotopes. A similar equation can be written for ^{224}Ra/^{228}Ra without a need to subtract the decay constant of ^{228}Ra as it is orders of magnitude lower than that for ^{224}Ra.

Using this approach, we calculated radium ages based on initial ratios of 15.3 for ^{224}Ra/^{223}Ra and 0.70 for ^{224}Ra/^{228}Ra for samples in the Paraguaçu Estuary (Fig. 6). The initial AR for the ages based on ^{224}Ra/^{228}Ra was selected by the highest observed in the estuary (station P2) but discounting the outlier at station P8. As mentioned earlier, that station has a unique composition relative to those both upstream and downstream. An additional source of radium, as well as nitrogen, may be present in that area. The initial AR for the ^{224}Ra/^{223}Ra ages was taken as the value at upstream station P3. While the AR was higher at both stations P1 and P2, the ^{223}Ra levels were so low that they were considered unreliable.

Based on these assumptions, we estimate that it takes on the order of 3–4 days to travel the 20 + km (from P3 to P9) through the estuary. In other words, the net flushing velocity is about 5–7 km/day. While this may seem slow for a river the size of Paraguaçu, the BTS has an average tidal range of about 2 m that will inhibit fresh water flushing of the estuary.

The same approach can be applied to the entire BTS. We examined the radium ARs along a line starting from station B9 in the extreme northern part of BTS and extending through 5 of our stations to B2 at the entrance to BTS (Fig. 7). All 7 stations were collected during the same day during an incoming tide. Since we do not have end-member ARs, we select the highest ratios observed along this line. The ^{224}Ra/^{223}Ra AR is highest at station B9 and decreases systematically towards the bay entrance. The ^{224}Ra/^{228}Ra ARs have a similar trend although the highest AR was observed at the adjacent station B10. Using the highest AR at stations B9 and B10 as the initial ratio, we estimated the BTS surface water apparent age progression at about 6 days (^{224}Ra/^{223}Ra) or 8 days (^{224}Ra/^{228}Ra) from the northern interior (B10) to around 5 km to the entrance of the bay (B2). Thus, the tidal flushing time of BTS surface waters appears to be on the order of 1 week. It is important to note that the station B1, just outside the bay entrance, was not included in this analysis because of a very low, and thus imprecise measurement of radium. If one could estimate the flushing all the way to station B1, the flushing time would certainly increase.

The flushing time of BTS has been investigated previously and estimates have been much higher than the one-week value derived here. Cirano and Lessa (2007) estimated flushing times of 38 days in winter and 62 days in summer for the innermost part of the Bay (i.e., two CTD stations, one close by B12 and one close by B8; Fig. 1) using a salt balance approach. The Regional Ocean Modeling System (ROMS) applied by Santana et al. (2015) showed that flushing times of about 68 days can be reached when river discharge is considered together with wind, heat and waters fluxes. According

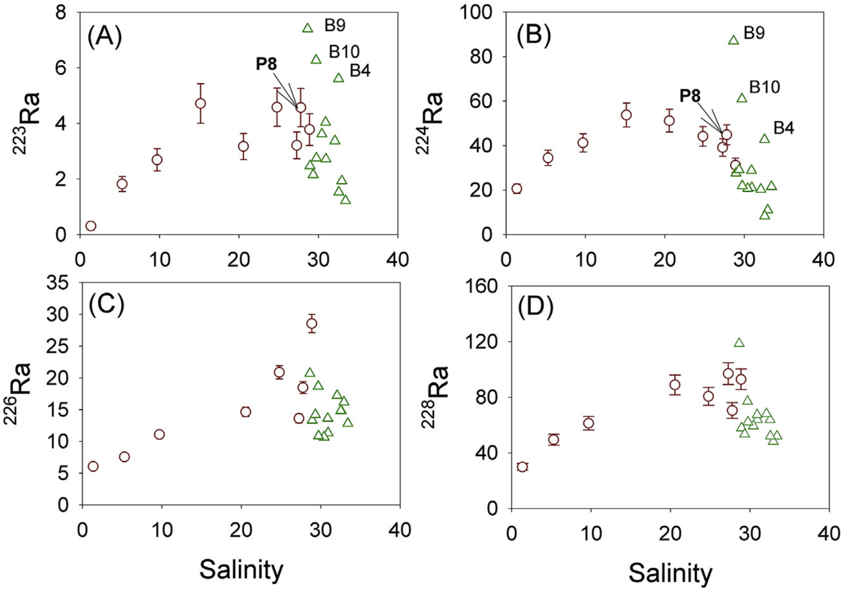

Fig. 4. Distribution of the short-lived ^{223}Ra (A), ^{224}Ra (B) and long-lived ^{226}Ra (C) and ^{228}Ra (D) radium isotopes in the Paraguaçu Estuary (circles) and BTS (triangles) plotted against salinity. All radium isotope activities are given in dpm/100 L. Station P8, from the Paraguaçu Estuary, shows some anomalous radium behavior for the short-lived isotopes as well as distinctive nutrient concentrations (see Fig. 5). Errors shown are ±1σ based on counting statistics. Uncertainty bars were excluded from the BTS data points for clarity but are similar to those shown for the Paraguaçu samples.

Table 3
Nutrients (μM) in the Paraguaçu Estuary, Todos os Santos Bay, and Marina do Bonfim.

Sample	PO_4^{3-}	NH_4^+	NO_2^-	NO_3^-	DIN	DSi
	μM					
Paraguaçu Estuary						
P1	1.05	<DL	0.17	2.30	2.48	69.1
P2	0.85	0.83	0.11	1.59	2.53	66.1
P3	0.50	<DL	0.04	0.26	0.30	18.2
P4	0.35	<DL	<DL	<DL	<DL	24.1
P5	0.50	0.15	<DL	<DL	0.15	28.9
P6	0.60	<DL	0.22	<DL	0.22	38.2
P7	0.15	<DL	0.41	0.24	0.65	24.6
P8	0.15	7.94	0.43	0.22	8.59	25.5
P9	0.50	1.13	0.46	0.28	1.87	25.1
Todos os Santos Bay						
B1	0.10	1.66	<DL	0.09	1.75	36.7
B2	<DL	1.90	<DL	1.78	3.68	3.24
B3	<DL	<DL	<DL	<DL	0.00	8.23
B4	0.15	0.16	<DL	<DL	0.16	15.5
B5	<DL	<DL	<DL	0.13	0.13	4.78
B6	<DL	<DL	<DL	0.48	0.48	5.43
B7	<DL	0.41	<DL	0.30	0.71	12.0
B8	<DL	<DL	<DL	<DL	<DL	29.9
B9	<DL	<DL	<DL	0.09	0.09	32.1
B10	<DL	0.65	<DL	<DL	0.65	14.5
B11	0.05	<DL	<DL	0.22	0.22	28.3
B12	<DL	<DL	<DL	0.04	0.04	21.8
B13	<DL	0.25	<DL	<DL	0.25	11.5
Marina do Bonfim						
T1	0.60	11.5	0.26	1.70	13.4	17.9
T2	1.15	2.90	0.26	1.43	4.60	31.9
T3	0.60	3.81	0.24	1.41	5.46	30.2
T4	1.55	3.73	0.22	1.17	5.12	44.8
T5	0.50	5.14	0.26	1.26	6.66	36.6
T6	0.80	<DL	0.13	1.04	1.17	29.7
T7	0.35	10.8	0.17	1.30	12.3	17.0
T8	0.50	4.81	0.07	0.50	5.38	22.3
T9	0.10	2.57	0.02	0.33	2.92	13.0
T10	<DL	3.57	0.09	1.13	4.79	7.45
T11	0.10	<DL	0.13	1.30	1.43	3.6
T12	0.30	0.41	0.11	0.93	1.45	32.2
T13	0.05	13.3	0.13	0.87	14.3	13.7
W9	0.10	4.87	162	<DL	167	114

Where < DL = below detection limit (phosphate = 0.01 μM; nitrite = 0.04 μM; nitrate 0.04 μM; silicate 0.01 μM; ammoniacal nitrogen = 0.80 μM); W9 = well at Marina do Bonfim.

to the authors, the model included a grid that did not allow a full representation of the bay, specifically the narrow segments and coastal boundary conditions that are very influential in some areas, such as the main entrance of the bay, at the interface ocean-bay.

For comparison, we applied a well-known tidal prism model (Monsen et al., 2002):

$$T_f = \frac{VT}{(1-b)P} \tag{2}$$

Where T_f is the flushing time parameter; V represents the bay volume (BTS = 1.18×10^{10} m^3); T is the tidal period (12.4 h); b is the return flow factor (0–1); and P is the estimated tidal volume (1.76×10^9 m^3; Lessa et al., 2001). The return flow factor represents the fraction of water that leaves the bay that is returned on the next incoming tide. We do not know this value for BTS but assume that it is in the low to mid range where it is not too sensitive to the flushing time calculation. Based on these estimates, we calculate a flushing time of 4–7 days that overlaps our estimate based on radium isotope ratios.

The assumptions inherent to the flushing time calculation are: (a) bay waters are well-mixed; (b) river input must be small and not dominate over the tidal pulse; (c) ocean water outside the bay system must have a consistent salinity; and (d) the water body is in steady state with a sinusoidal tidal signal (Eller et al., 2014). The oceanographic characteristics of the bay (Cirano and Lessa, 2007; Lessa et al., 2009) indicate that the BTS meets these conditions. While the calculation does not include river flow, the total river flow into BTS (120 m^3/s; 4.5×10^4 m^3 per tidal cycle) is about 5 orders of magnitude lower than the tidal prism and thus would not change the result significantly.

3.4. Marina time-series results and SGD estimate

At the time-series mooring at Marina do Bonfim, radon was measured continuously over a 12-h period and nutrients and

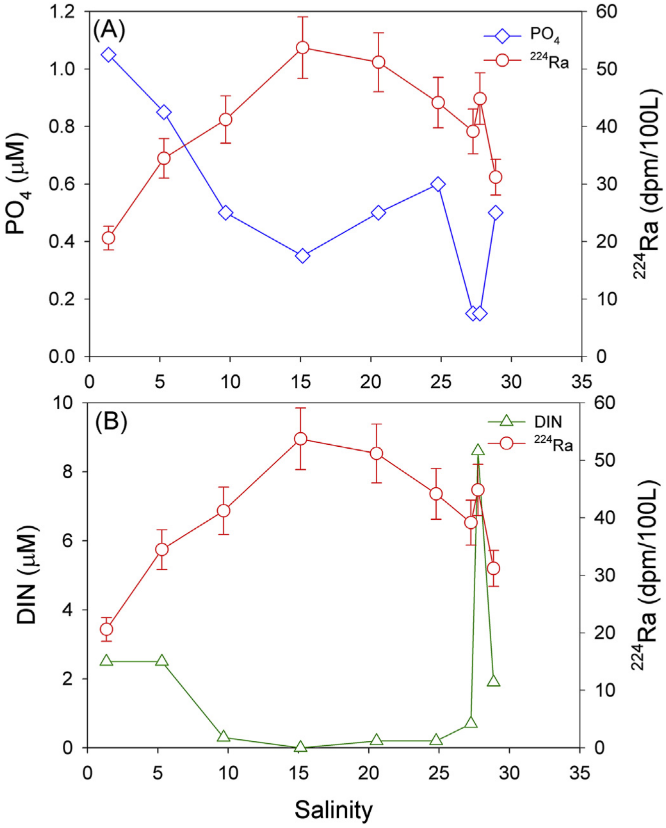

Fig. 5. PO_4^{3-}, DIN and ^{224}Ra in the Paraguaçu Estuary. Note that the PO_4^{3-} (diamonds) drops at the same location (P8) where the ^{224}Ra (circles) and DIN (triangles) both spike. This indicates a site with a different nutrient and radium composition; possibly a result of SGD influence. Errors shown are ±1σ based on counting statistics.

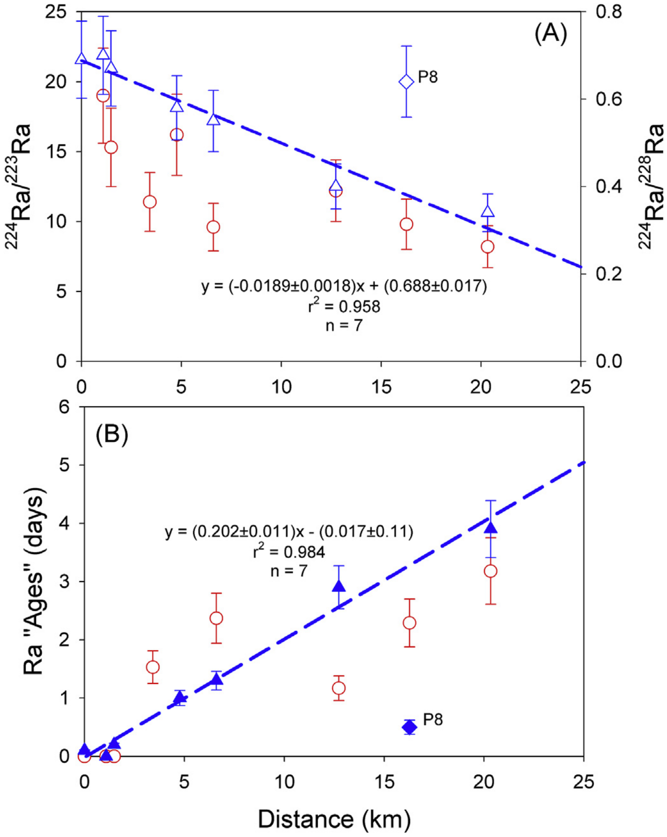

Fig. 6. (A) Activity ratios (AR) ^{224}Ra/^{223}Ra (circles) and ^{224}Ra/^{228}Ra (triangles) versus distance from station P1 in the Paraguaçu Estuary. The regression line ignores the outlier at station P8 (diamond) and is based on the ^{224}Ra/^{228}Ra AR. (B) Apparent radium ages along the same transect based on ^{224}Ra/^{223}Ra (circles; initial ratio = 15.3) and ^{224}Ra/^{228}Ra (closed triangles; initial ratio = 0.70). The regression line is based on the ^{224}Ra/^{228}Ra ages.

radium samples were collected hourly from 09:00 to 21:00 on August 13, 2015. The nutrient results were generally all low (PO_4^{3-}: 0.51 ± 0.45 μM; NH_4^+: 4.80 ± 4.37 μM; NO_2^-: 0.16 ± 0.08 μM; NO_3^-: 1.11 ± 0.38 μM; DSi: 23.1 ± 12.2 μM) and scattered with no clear trends. Radon was also low (Fig. 8A) and stayed within 95% uncertainties the entire period (1.03 ± 0.51 dpm/L). The long-lived radium isotopes fluctuated without clear trends around mean values of 5.1 ± 1.7 dpm/100 L for ^{226}Ra and a much higher mean of 27.9 ± 4.7 dpm/100 L for ^{228}Ra. Only the short-lived radium isotopes displayed a time or tidal dependent pattern. Both ^{223}Ra (not shown) and ^{224}Ra (Fig. 8B) displayed significant enrichment from about 14:00 to 18:00 as the tide was turning. Both the ^{223}Ra and ^{224}Ra increased by a factor of ~4-fold over this interval.

If the increase in short-lived radium isotopes were related to SGD, or even to sediment release, one would wonder why the ^{222}Rn did not follow a similar trend. One possibility is that the discharge was located close to shore and we were sampling at the end of a very long (~140 m) pier. So if groundwater seepage was occurring within a narrow (say 50 m or less) zone close to shore and was being transported offshore to where our measurements were being made, radon could have been lost due to atmospheric evasion. This is a real possibility as the winds were fairly high that day (up to 8 m/s during our measurement interval). Radium, not having a gas phase, would be unaffected by this process.

If we make the assumption that the increase in ^{224}Ra noted above was due to SGD, we can make some rough estimates of the magnitude of groundwater discharge based on a series of assumptions. While speculative, we feel the exercise is useful in order to: (1) make a first-order estimate of the importance of SGD to the BTS system; and (2) to identify the data gaps that need to be filled in order to make this kind of estimate with a higher degree of certainty.

We list the measurements and assumptions used for the calculation in Table 4. We estimate the ^{224}Ra flux per day at 1020 dpm/m^2 day based on the increase of the ^{224}Ra inventory from 14:00 to 18:00 (Fig. 8B) of 255 dpm/m^2 hr multiplied by an assumed 4-h period per day when seepage is active during down going tides. This is conservative as the tides in BTS are mostly semi-diurnal and thus often have two transitions from high to low tide per day. In order to estimate the seepage rate, we must know something about the width of seepage from the shoreline. Such information can be obtained by modeling or seepage meter measurements (Burnett et al., 2006). Since this information does not exist as yet for BTS, we make a conservative estimate of 50 m for the seepage face. Thus, there is a 50 m^2 seepage area per unit width of shoreline. Using our measured groundwater ^{224}Ra activity of 720 dpm/m^3 from the open well at Marina, we estimate a seepage rate of 1.42 m/day (equivalent to 1.42 m^3/m^2 day) by dividing the ^{224}Ra flux per day by the groundwater ^{224}Ra activity concentration. Multiplying this derived seepage rate by 50 m^2 area per unit width of shoreline results in an estimate of 71.1 m^3 per day per 1 m width of shore. Finally, we multiply this value by the estimated total length of BTS shoreline (estimated in 362 km including Ribeira and Aratu Bays on the eastern side of BTS) to derive an estimate of about 300 m^3/s total groundwater flux to BTS. This is a very significant number when compared to the river discharge. The Paraguaçu

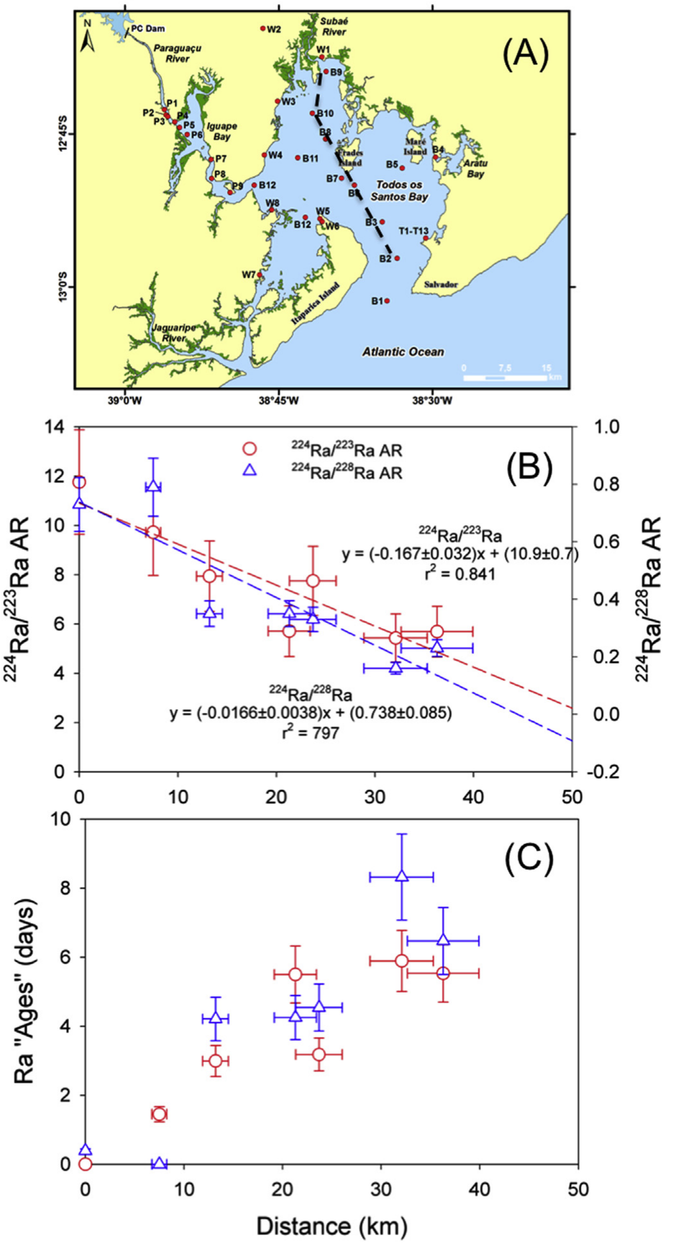

Fig. 7. (A) Sequence of 7 stations (dashed line) from the northern interior of BTS (station B9) to the main bay entrance (station B2) where samples for radium isotopes were collected; (B) ^{224}Ra/^{223}Ra (circles) and ^{224}Ra/^{228}Ra (triangles) activity ratios versus distance along dashed line; and (C) apparent radium "ages" (days) based on both ARs along the line from the interior (B9) to the entrance of BTS (B2). Errors shown are ±1σ based on counting statistics.

River alone averages 93 m^3/s and all rivers combined contribute about 120 m^3/s to BTS. One could also estimate a minimum SGD by only including the shoreline length where we observed high radon and reduced salinity (Figs. 2 and 3). Our shoreline estimate for these areas is 28 km and that translates to a groundwater discharge of 2 × 10^6 m^3/day or 20 m^3/s. Our estimated range is thus 20–300 m^3/s for SGD into BTS.

Is it possible that SGD provides about 3-fold more flow to BTS than all the rivers? Although the estimate made here is admittedly rough, the high value includes several conservative assumptions, and should indicate that SGD is a viable mechanism of water and dissolved material inputs to this bay. In addition, the calculated groundwater discharge is for total flow, not only terrestrial fresh water discharge. Much of the SGD indicated by the short-lived radium is likely saline. Note that we did not see any significant reduction in salinity during our time series measurements (Table 2). With additional measurements, we should be able to provide better estimates for both the fresh and saline components of SGD into BTS.

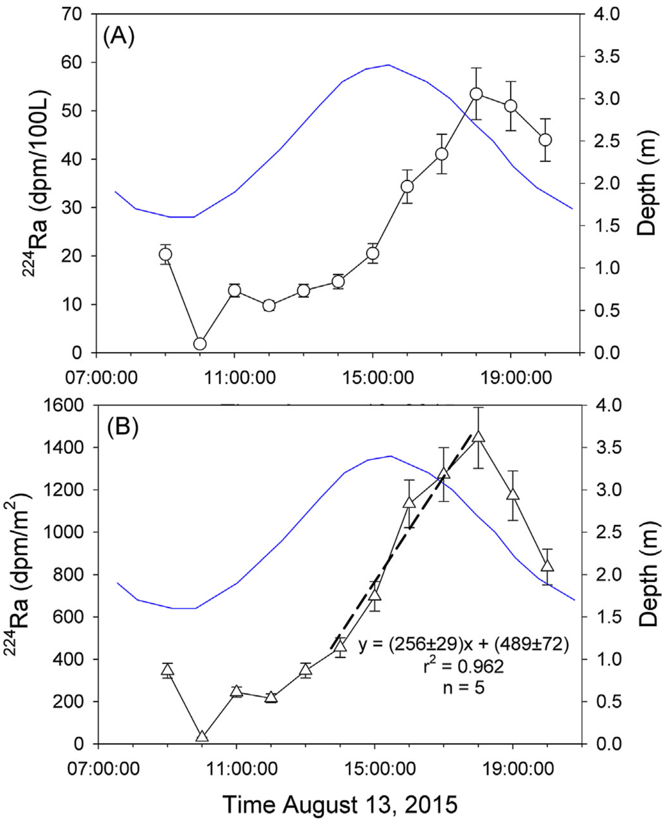

Fig. 8. Time-series trend of (A) ^{224}Ra activities; and (B) ^{224}Ra inventories (activity x water depth) over a tidal cycle (smooth solid line). The near linear increase in ^{224}Ra inventories from 14:00 to 18:00 may indicate groundwater inputs as the tide was turning. Based on the slope of a linear regression through these points, the ^{224}Ra flux during this 4-h period was 256 dpm/m^2 hr. Errors shown are ±1σ based on counting statistics.

4. Conclusions & recommendation for future work

These are the first measurements of radon and radium isotopes in the Paraguaçu Estuary and BTS. While some of the assumptions and interpretations are not constrained as much as one would like, the process of fitting these pieces of information together has resulted in important insights into the BTS system not previously available.

Specifically, we found that: (a) the radon/salinity survey measurements identified areas off Ribeira Bay on the eastern shore of BTS and nearby the São Paulo river mouth and Coqueiro Grande in the northern region of the bay where SGD may be enhanced (Figs. 2 and 3); (b) an unusual water composition in the lower part of the Paraguaçu Estuary (station P8) with relatively high DIN and ^{224}Ra and low PO_4^{3-} may be a result of SGD; (c) radium isotope ratios provided net transit times through the Paraguaçu Estuary of approximately 3–4 days to travel the 20 + km from near zero salinity to BTS (Fig. 7); (d) radium isotope trends from the northern interior to the entrance of BTS suggested a flushing time, at least for the near surface waters, of about 6–8 days; and (e) an approximate

Table 4
Measurements and assumptions used to make a rough estimate of the magnitude of SGD for the entire BTS as well as just the areas with high radon and lower salinity.

Measurements/Assumptions	Values	Units	Notes
^{224}Ra flux per hour =	256	dpm/m^2 hr	based on slope (Fig. 8B)
^{224}Ra flux per day =	1024	dpm/m^2 day	assume 4 h per day
Assume seepage face =	50	m	seepage limited to 50-m wide zone
Seepage area per 1 m shoreline =	50	m^2/m	seepage area per 1 m width of shoreline
^{224}Ra in groundwater =	720	dpm/m^3	measured at open well Marina do Bonfim
Seepage rate =	1.42	m/day (m^3/m^2 day)	^{224}Ra flux divided by Ra activity
Seepage per 1 m shoreline =	71.1	m^3/day m	seepage rate x area per 1 m width
Shoreline length of BTS =	362[a]	km	estimated via GIS from a map 1:50,000 and Landsat images
Approx. total seepage for BTS =	2.6 E+07[a]	m^3/day	seepage per 1 m width x shoreline length
Final estimate =	300[a]	m^3/s	unit conversion

[a] Note: If we apply this approach to just the areas where enhanced SGD is indicated by high radon and lowered salinity (Figs. 2 and 3), the estimated shoreline length is 28 km and the calculated SGD solely from those areas would be 20 m^3/s.

SGD estimate of 20–300 m^3/s for either the high radon areas or the entire BTS shoreline was made based on the systematic increase in ^{224}Ra during a portion of our time series measurements and extrapolating these results to the entire coast (Table 4; Fig. 8).

The 6–8 day flushing time for BTS is much shorter than estimated by a salt balance approach (Cirano and Lessa, 2007) that ranged seasonally between 38 days (winter) to 62 days (summer). A numerical model predicted a range from 68 to 340 days with the lower flushing times in the winter when river flows are higher and stronger winds are present (Santana et al., 2015). However, we found that the radium 'ages' indicated flushing times that are consistent with a simple tidal prism approach. The tidal prism approach is usually more valuable to make comparisons between magnitudes of fluxes between bays than to estimate flushing times. However, it serves as an alternative estimation that agreed well with our results, indicating that more studies should be pursued to better refine the flushing times estimates for BTS.

The total shoreline SGD estimate (300 m^3/s) may seem high relative to average river inputs into BTS. Most assumptions made in the estimate, with the possible exception of the shoreline length, were conservative. Thus, the SGD estimate could be considered low. Since the flow estimated is total SGD, not only fresh water flow, the estimate seems realistic. Recirculated bay water, driven into the subsurface by tidal forcing, can return to the bay as the tide turns. This mechanism has been observed in many tidal environments and is often much higher than terrestrial fresh water groundwater flow driven by gravity (Burnett et al., 2003; Moore, 2010).

Based on the results reported here, we suggest that future investigations of BTS include the following: (i) additional time-series experiments especially in areas where significant SGD has been indicated by the ^{222}Rn/salinity surveys; (ii) assess importance of deep drainage channels and fault regions as possible conduits of SGD (we only considered along shore seepage thus far); (iii) analyze additional groundwater samples not only for radon, but radium isotopes and nutrients as well; (iv) collect sediment from several areas in order to perform sediment equilibration experiments to determine the non-SGD radon flux and pore water ^{222}Rn activities; (v) collect depth profile samples to assess possible vertical structure of radon and radium isotopes; (vi) collect a series of radium samples along a transect from the entrance of the bay to its northern most extreme during an outgoing tide (samples were collected on an incoming tide in the present study which may have biased the results towards more of an 'oceanic' signal); and (vii) evaluate the importance of SGD, especially in areas identified as possible SGD hotspots (e.g., station P8 and areas showing radon anomalies) as a source of nutrients and contaminants to BTS. The insights gained during this initial study have allowed us to make preliminary evaluations and develop a sound strategy for more detailed investigations.

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