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Determination of residence time and mixing processes of the Ubatuba, Brazil, inner shelf waters using natural Ra isotopes

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Abstract

Coastal waters contain elevated dissolved activities of short-lived radium isotopes, ^{223}Ra and ^{224}Ra, having half-lives of 11.4 and 3.66 days, respectively. The input of these isotopes near the coast must be balanced by decay and mixing into the open ocean, where excess activities are zero. Since the decay rate is known, in the ideal case the mixing rate may be determined from the offshore distribution of these isotopes. This study found that samples collected in June 2000 followed the expected exponential decrease with distance offshore. We assign a dispersion coefficient of 28–39 $m^2\ s^{-1}$ for this study. During January 2002 and November 2003, there was not a consistent decrease of activity with distance offshore. This is likely due to the ruggedness of the coastline, where many bays and small islands interrupt simple mixing patterns. To estimate exchange rates during 2002 and 2003, we used a model based on the decrease in the ^{224}Ra/^{223}Ra activity ratio (AR) with time for samples isolated from fresh inputs of Ra. This model yielded residence times of 1–2 weeks for samples collected within 20 km of the coast. We used this residence time to calculate the flux of ^{228}Ra (half-life = 5.7 years) to the study area necessary to maintain the enrichment relative to ocean water. This enrichment is a factor of ten greater than the flux of ^{228}Ra expected from submarine groundwater discharge (SGD) occurring within 50 m of shore.

Keywords: residence time; mixing; Ra isotopes; submarine groundwater discharge; Brazil

1. Introduction

Chemical differences between coastal and offshore waters occur as a result of several processes. The inflow from rivers and desorption from riverborne particles enrich coastal waters in some elements, while the chemical reactions associated with this mixing may remove other constituents. Anthropogenic inputs associated with industry, shipping, mining, sewage (treated or untreated), and a host of other factors contribute pollutants to these waters. Another factor that is becoming recognized as a significant control on coastal water chemistry is submarine groundwater discharge (SGD). This process may contribute both natural and anthropogenic components and may also remove certain components as coastal waters circulate through shallow aquifers.

The distribution of naturally occurring radionuclides can provide important insights into the mobility of pollutants and the rates of natural geochemical processes. Modeling of local mass balance by physical and tracer techniques can supply quantitative estimates of transport rates.

The exchange rate between coastal waters and the open ocean is a key parameter that must be known in order to estimate chemical fluxes between the continent and the ocean. Knowing the exchange rates allows oceanographers to estimate fluxes of conservative tracers and reaction rates of nonconservative

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components. These exchange rates may be derived from physical measurements, models, and tracers. In this paper we utilize two short-lived, naturally occurring isotopes of radium, ^{224}Ra (half-life = 3.66 days) and ^{223}Ra (half-life = 11.4 days), to estimate exchange rates.

The rates of submarine groundwater discharge along coastal margins are controlled by inland recharge rates, the underlying geologic framework, and oceanographic processes on the coast (Michael et al., 2005; Moore and Wilson, 2005). Fresh water that flows down gradient from the water table toward the sea may discharge either as diffuse seepage close to shore, or directly into the sea either as submarine springs or wide-scale seepage. The hydraulic gradient that drives fresh water toward the sea can also drive seawater that has intruded into the underlying deposits back to the ocean, creating a saltwater circulation cell. Wherever multiple aquifers and confining units co-exist, each aquifer will have its own freshwater/saltwater interface, and deeper aquifers will discharge farther offshore. SGD can be spatially as well as temporally variable, since there exists a variety of both natural and anthropogenic influences (e.g., sea level, tides, storms, precipitation, dredging, groundwater withdrawals) that can have strong effects. In areas like Ubatuba, where crystalline rocks outcrop beyond the shoreline, flow through fractures may produce irregular patterns of SGD.

An ideal SGD tracer should be highly enriched in groundwater relative to seawater, behave conservatively, and be easy to measure. The four Ra isotopes and ^{222}Rn follow these constraints reasonably well and have recently been used to identify and quantify SGD to various coastal areas (see Moore, 1999 for review). One strong advantage of these radiotracers is that the coastal water column effectively integrates the SGD signal over broad spatial and temporal scales.

We report three studies conducted near the marine laboratory of the Oceanographic Institute of the University of São Paulo near the city of Ubatuba, Brazil. The study site is characterized by fractured granite cliffs descending into the Atlantic Ocean. There is only a thin veneer of coarse-grained sediment that makes up beaches within the numerous bays along the coast. The 2003 study was part of a collaborative multinational program designed to investigate submarine groundwater discharge using different techniques tested in different hydrogeologic settings. This intercomparison was sponsored by the Scientific Committee on Oceanic Research (SCOR), the Land–Ocean Interactions in the Coastal Zone (LOICZ), the International Atomic Energy Agency (IAEA), and UNESCO's Intergovernmental Oceanographic Commission (IOC) and International Hydrologic Program (IHP). The primary objective of this last program was an improved understanding of scientific and technical aspects that will enable SGD measurements to be addressed with a higher degree of confidence, including the development and implementation of nuclear and isotopic techniques to assess submarine groundwater discharges. Local benefits of this program extended into the fields of hydrology and coastal oceanography, improving the information already available in São Paulo coastal area.

2. Theory

Moore (2000a) used the distribution of the short-lived Ra isotopes to estimate exchange rates in the coastal ocean. The change in concentration or activity (A) with time (t) as a function of distance offshore (x) for a radioactive tracer with decay constant (λ) may be expressed as a balance of advection, dispersion, and decay, as follows:

$$\frac{dA}{dt} = K_h \frac{\partial^2 A}{\partial x^2} - \omega \frac{\partial A}{\partial x} - \lambda A \tag{1}$$

If net advection can be neglected, this reduces to

$$\frac{dA}{dt} = K_h \frac{\partial^2 A}{\partial x^2} - \lambda A \tag{2}$$

where K_h is the dispersion coefficient.

The criterion for setting $\omega = 0$ is based on the offshore distribution of conservative tracers such as ^{226}Ra (half life = 1600 yr) and ^{228}Ra (half life = 5.7 yr). These long-lived isotopes decay little during the residence time of coastal waters. A constant offshore concentration gradient of these tracers provides evidence that dispersion dominates offshore or onshore advection (Moore, 2000a,b). In the case where $\omega = 0$, the boundary conditions of eq. (2) are as follows:

$A = A_i$ at $x = 0$
$A \to 0$ as $x \to \infty$

If K_h is constant and the system is steady state,

$$A_x = A_0 \exp\left[- x \sqrt{\frac{\lambda}{K_h}} \right] \tag{3}$$

where A_x = activity at distance x from coast, A_0 = activity at distance 0 from coast, and λ = decay constant.

A plot of ln ^{223}Ra or ln ^{224}Ra as function of distance from the coast may be used to estimate K_h if the exchange is dominated by dispersion rather than advection and if the system is steady state:

$$\ln A_x = \ln A_0 - x \sqrt{\frac{\lambda}{K_h}} \tag{4}$$

In this case the slope,

$$m = \sqrt{\frac{\lambda}{K_h}} \tag{5}$$

This model requires that the system be at steady state over the time scale of the short lived isotopes and that there are no additions of these isotopes beyond the nearshore zone. Hancock et al. (2006) expanded this model to include offshore additions of the tracers that decreased with increasing distance. This model is probably not appropriate for our study area because the presence of offshore islands raises the possibility that such additions may occur only at some distance from shore.

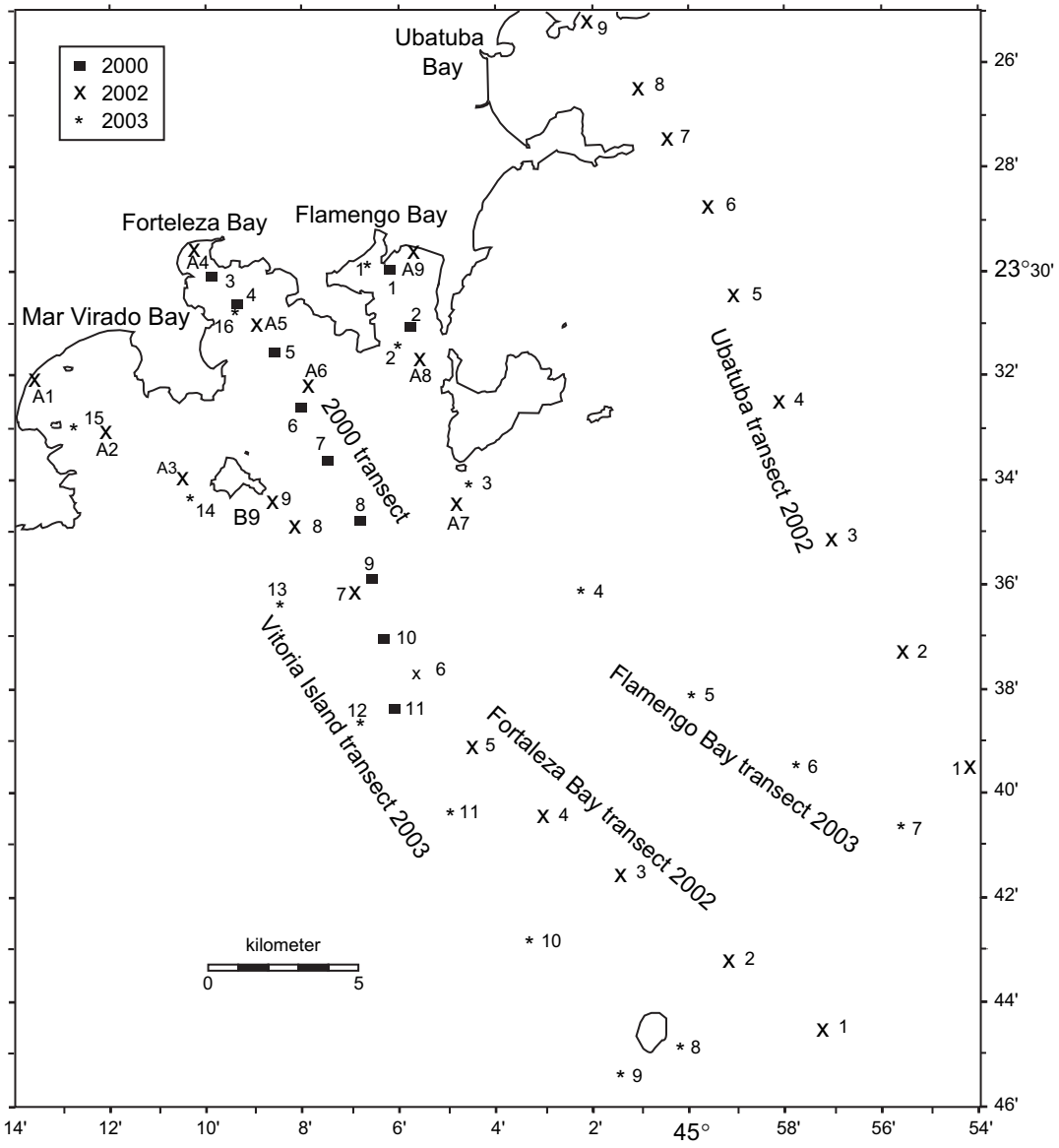

Fig. 1. Map of the study area showing cruises conducted in 2000 (■), 2002 (×), and 2003 (*). The offshore transects are labeled. The labels for samples collected in various bays in 2002 have an A prefix.

An alternate way to use the short-lived Ra isotopes is to utilize the $^{224}Ra/^{223}Ra$ AR to estimate the ages of shelf waters (Moore, 2000b) This method is based on the assumptions that the $^{224}Ra/^{223}Ra$ AR is initialized to a constant value near shore and only changes by decay as the water is isolated from the radium source. The $^{224}Ra/^{223}Ra$ AR decreases with an apparent half life of 5.4 days, as follows:

$$\left(\frac{^{224}Ra}{^{223}Ra}\right)_{measured} = \left(\frac{^{224}Ra}{^{223}Ra}\right)_{initial} \frac{e^{-\lambda_{224}t}}{e^{-\lambda_{223}t}} \quad (6)$$

This model is also sensitive to offshore additions of the tracers.

3. Geologic setting

This research was carried out in a series of small embayments near Ubatuba, São Paulo State, Brazil. All samples studied here were taken in the selected area between latitudes 23°26′ S and 23°46′ S, and longitudes 45°02′ W and 45°11′ W, in order to estimate coastal mixing rates and submarine groundwater discharge fluxes.

The main geologic/geomorphologic feature in the Ubatuba region is the presence of pre-Cambrian granites and migmatites of a mountain chain locally called Serra do Mar (altitudes up to 1000 m), which reaches the shore in almost all of the study area and limits the extension of the drainage systems and of Quaternary coastal plains. Wave action is the most effective hydrodynamic phenomenon responsible for the bottom sedimentary processes in the coastal area as well as in the adjacent inner continental shelf (Mahiques, 1995). The terrestrial input of sediments is strongly dependent on the rainfall regime, leading to a higher contribution of sediments during summer season. During the summer (November through February), the advance of the South Atlantic Central Water

Table 1
Ra activities (dpm per 100 L) in surface waters. The ages (days) are based on assumed initial $^{224}Ra/^{223}Ra$ activity ratio of 21 (from seepage meters). Distance is in km

Sample	Location	Date	Salinity	Distance	^{226}Ra	^{228}Ra	ex^{224}Ra	^{223}Ra	224/223 AR	Age
2000										
Transect										
UB-1	Flamengo Bay	19-Jun-00	35.696	1.0			28.03	2.23	12.6	3.9
UB-2	Flamengo Bay	19-Jun-00	35.881	3.0			20.52	1.75	11.7	4.5
UB-3	Fortaleza Bay	19-Jun-00	35.699	0.9			29.74	2.53	11.8	4.5
UB-4	Fortaleza Bay	19-Jun-00	35.198	3.0			42.82	2.70	15.9	2.2
UB-5	Transect	19-Jun-00	35.932	5.1			13.75	1.20	11.5	4.7
UB-6	Transect	19-Jun-00	35.965	7.2			8.77	1.12	7.8	7.6
UB-7	Transect	19-Jun-00	35.977	9.3			5.98	0.60	10.0	5.7
UB-8	Transect	19-Jun-00	35.998	11.5			3.69	0.43	8.6	6.9
UB-9	Transect	19-Jun-00	36.001	14.1			1.50	0.43	3.5	13.8
UB-10	Transect	19-Jun-00	36.034	16.4			0.84	0.15	5.6	10.2
UB-11	Transect	19-Jun-00	36.061	18.6			3.29	0.20	16.5	
2002										
Nearshore										
A-1	Mar Virado Bay	23-Jan-02	34.80	1	9.91	24.52	38.53	2.56	15.0	2.6
A-2	Mar Virado Bay	23-Jan-02	35.14	4	9.72	12.66	2.52	0.35	7.2	8.3
A-3		23-Jan-02	34.95	7	9.04	15.47	7.82	0.75	10.4	5.4
A-4	Fortaleza Bay	23-Jan-02	34.22	1	9.96	22.22	27.06	1.62	16.7	1.8
A-5	Fortaleza Bay	23-Jan-02	35.11	4	8.96	14.80	8.07	1.02	7.9	7.5
A-6		23-Jan-02	34.89	7	10.03	18.43	7.06	0.52	13.6	3.4
A-7		23-Jan-02	35.16	13	8.49	10.02	1.06	0.41	2.6	16.1
A-8	Flamengo Bay	23-Jan-02	34.82	6	10.01	18.77	8.46	0.94	9.0	6.5
A-9	Flamengo Bay	23-Jan-02		1	9.79	23.54	31.81	2.48	12.8	3.8
Fortaleza Bay Transect										
B-1	Transect	22-Jan-02	35.34	30.6	9.20	9.55	1.97	0.45	4.4	12.1
B-2	Transect	22-Jan-02	35.39	27.9	8.82	7.95	1.69	0.16	10.5	5.3
B-3	Transect	22-Jan-02	35.35	23.5	7.16	6.54	0.65	0.10	6.3	9.3
B-4	Transect	22-Jan-02	34.92	20.4	7.83	7.38	3.08	0.35	8.8	6.7
B-5	Transect	22-Jan-02	35.05	17.4	9.79	14.65	4.96	0.79	6.2	9.3
B-6	Transect	22-Jan-02	35.00	14.4	10.05	16.05	6.93	0.56	12.3	4.1
B-7	Transect	22-Jan-02	35.03	11.5	9.45	18.27	7.10	0.69	10.3	5.5
B-8	Transect	22-Jan-02	35.03	9.3	8.43	15.32	6.82	0.85	8.0	7.4
B-9	Transect	22-Jan-02	35.02	8.4	10.39	17.11	7.98	0.87	9.2	6.4
Ubatuba Bay Transect										
J-1	Transect	25-Jan-02	35.73	30	9.05	9.57	1.51	0.33	4.6	11.6
J-2	Transect	25-Jan-02	35.55	25	9.49	14.12	3.74	0.58	6.5	9.0
J-3	Transect	25-Jan-02	35.37	20	8.93	16.28	6.51	0.64	10.2	5.6
J-4	Transect	25-Jan-02	35.53	15	9.47	17.89	8.59	1.16	7.4	8.0
J-5	Transect	25-Jan-02	35.65	11	9.55	13.25	7.04	0.79	9.0	6.6
J-6	Transect	25-Jan-02	35.58	8	8.88	14.13	5.41	0.67	8.1	7.3
J-7	Transect	25-Jan-02	35.34	5	11.22	6.54	6.55	0.98	6.7	8.8
J-8	Transect	25-Jan-02	35.67	3	8.88	15.35	6.80	0.61	11.2	4.8
J-9	Ubatuba Bay	25-Jan-02	35.75	1	9.36	18.15	21.83	0.95	23.0	-0.7
2003										
Flamengo Bay Transect										
1	Flamengo Bay	18-Nov-03	34.3	0.3	9.73	19.98	21.39	1.61	13.31	3.5
2	Transect	18-Nov-03	34.0	0.7	8.10	16.28	10.85	0.92	11.80	4.4
3	Transect	18-Nov-03	34.0	0.8	9.57	17.06	10.87	0.82	13.21	3.6
4	Transect	18-Nov-03	34.7	5.5	7.84	13.62	2.16	0.46	4.66	11.6
5	Transect	18-Nov-03	34.7	10.3	8.31	12.76	1.15	0.32	3.58	13.6
6	Transect	18-Nov-03	34.6	14.5	7.65	12.41	1.42	0.40	3.55	13.7
7	Transect	18-Nov-03	34.6	18.5	7.11	12.30	1.09	0.34	3.24	14.4
7A	Transect	19-Nov-03	34.9	18.5	8.03	14.42	1.38	0.40	3.47	13.8
Vitoria Island Transect										
8	Transect	19-Nov-03	34.5	23.0	8.56	11.99	0.32	0.16	2.02	18.0
9	Transect	19-Nov-03	34.6		8.35	12.68	0.57	0.20	2.84	15.4
10	Transect	19-Nov-03	34.7	17.0	8.17	13.40	1.43	0.28	5.12	10.9
11	Transect	19-Nov-03	34.4	12.2	8.01	15.69	4.68	0.70	6.68	8.8
12	Transect	19-Nov-03	34.5	8.8	8.96	13.77	1.07	0.31	3.48	13.8
13	Transect	19-Nov-03	34.5	4.0	8.30	14.68	1.76	0.39	4.54	11.8
14	Transect	19-Nov-03	34.1	0.5	8.45	18.94	16.27	1.33	12.23	4.2
15	Mar Virado Bay	19-Nov-03	34.0	1.5	8.87	18.18	15.88	1.47	10.78	5.1
16	Fortaleza Bay	19-Nov-03	33.6	1.2	8.30	19.94	15.15	1.33	11.43	4.7

Table 2
Ra activities (dpm per 100 L) in estuary, seepage, and groundwater

Sample	Location	Date	Salinity	^{226}Ra	^{228}Ra	ex^{224}Ra	^{223}Ra	224/223 AR
UB-GW	Hillside seep	20-Jun-00	0.0			80.8	3.3	24.3
P-1	Ubatuba city well	24-Jan-02	0.8	25.1	37.2	38.4	0.9	41.3
P-2	Ubatuba city well	24-Jan-02	0.1	13.7	93.9	104	3.5	29.7
P-3	Ubatuba city well	24-Jan-02	0.1	11.3	22.6	24.1	2.2	11.1
P-4	Ubatuba city well	24-Jan-02	0.1	11.0	47.4	50.8		
PM-01	Lab well PM-01	24-Jan-02		102	91.2	78.0		
PM-06	Lab well PM-06	24-Jan-02		28.7	124	187		
PM-03	Lab well PM-03	24-Jan-02	25.5	14.5	873	1056	55.9	18.9
PM-08	Lab well PM-08 (3B)	25-Jan-02	26.0	71.5	2141	2284	122	18.7
PM-04	Lab well PM-04 (2A)	25-Jan-02	26.7	163	1440	4524		
PM-05	Lab well PM-05 (3A)	25-Jan-02		163	1440	2161		
PM-09	Lab well PM-09	25-Jan-02		62.1	1207	2330	28.4	82.0
Rio Escuro	Estuary	26-Jan-02	30.6	13.8	44.7	57	2.8	20.4
17	Seep meters	19-Nov-03	26.4	19.1	402	1221	65	18.8
18	Lab well PM-07 (2B)	20-Nov-03	31.0	135	2377	2718	133	20.4
19	Lab well PM-08 (3B)	20-Nov-03	32.8	76.0	1116	978	32	30.6
20	Lab well PM-04 (2A)	20-Nov-03	32.9	159	2862	2939	100	29.3
21	Lab well PM-05 (3A)	20-Nov-03	33.1	207	1321	2374	60	39.6
22	Seep meters	20-Nov-03	26.6	26	435	1716	75	22.9

(SACW) over the coast leads to the displacement of the Coastal Water (CW), rich in continental suspended materials, and to the transportation of these sediments to the outer portions of the continental shelf. During winter (May through August), the retreat of the SACW and the decreasing rain restrict the input of sediments from the continental areas. The mean annual rainfall is roughly 1800 mm, the maximum rainfall rates being observed in February. Sea level varies from 0.5 to 1.5 m, the highest values occurring in months August and September due to greater volume of warm waters of the Brazil Current (Mesquita, 1997).

In the study area the coastal aquifer system can be classified as a fractured rock aquifer, covered by Pleistocene and Holocene sediments. The discharge pattern of this kind of aquifer is spatially heterogeneous, with preferential flow paths along rock fractures.

In a preliminary study carried out to determine the equivalent concentrations of primordial radionuclides in sediments of the continental shelf off São Paulo, it was found that the content of U varied from 0.2 to 2.5 ppm and Th from 0.2 to 15 ppm. The ^{234}U/^{238}U activity ratio varied from 0.6 to 1.7 (Pereira et al., 1986).

4. Experimental methods

Large-volume (60–200 L) samples were pumped from 1–2 m below the surface into plastic drums. After measuring salinity and temperature and recording sample volume, the water was pumped at <1 L min^{-1} through a column of manganese-coated acrylic fiber (Mn fiber) to quantitatively capture Ra (Moore, 1976).

Additional samples were obtained from a set of monitoring wells and from seepage meters installed in Flamengo Bay in 2003. These samples were processed in the same manner as the surface samples.

The samples collected in June 2000 were sent by express mail to the University of South Carolina at Columbia, SC, for measurement. Samples from January 2002 and November 2003 were measured at the University of São Paulo Marine Laboratory in Ubatuba. Each Mn fiber sample was partially dried with a stream of air and was placed in a closed-loop air circulation system as described by Moore and Arnold (1996). Helium was circulated over the Mn fiber to sweep the ^{219}Rn and ^{220}Rn generated by ^{223}Ra and ^{224}Ra decay through a 1-L scintillation cell where alpha particles from the decay of Rn and daughters were recorded by a photomultiplier tube (PMT) attached to the scintillation cell. Signals from the PMT were routed to a delayed-coincidence system. The delayed-coincidence system utilizes the difference in decay constants of the short-lived Po daughters of ^{219}Rn and ^{220}Rn to identify alpha particles derived from ^{219}Rn or ^{220}Rn decay and hence to determine activities of ^{223}Ra and ^{224}Ra on the Mn fiber. The expected error of the short-lived Ra measurements is 10%.

After the ^{223}Ra and ^{224}Ra measurements were complete, the Mn fiber samples were aged for 2–6 weeks to allow initial excess ^{224}Ra to equilibrate with ^{228}Th adsorbed to the Mn fiber. The samples were measured again to determine ^{228}Th and thus to correct for supported ^{224}Ra.

Later, the Mn fibers were leached with HCl in a Soxhlet extraction apparatus to quantitatively remove the long-lived Ra isotopes. The Ra was coprecipitated with $BaSO_4$. The precipitant was aged for at least 2 weeks to allow ^{222}Rn and its daughters to equilibrate with ^{226}Ra. The samples were measured in a gamma-ray spectrometer to assess the activities of ^{226}Ra and ^{228}Ra (Moore, 1984). The expected error of the long-lived Ra measurements is 7%.

5. Results

Three sampling campaigns were organized to assess the temporal and spatial distribution of the tracers. The sample

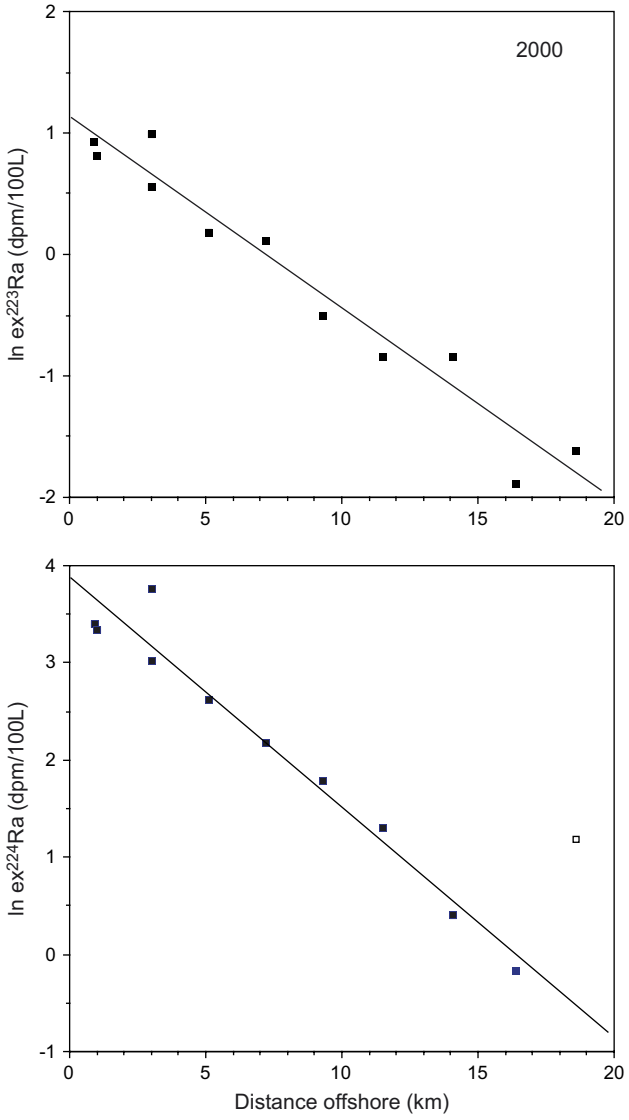

Fig. 2. The ln Ra activity as a function of distance offshore for samples collected in 2000. The best-fit line for ^{223}Ra ($R^2 = 0.949$) yields $K_h = 28$ m^2 s^{-1}. The best-fit line for ^{224}Ra ($R^2 = 0.961$) yields $K_h = 39$ m^2 s^{-1}.

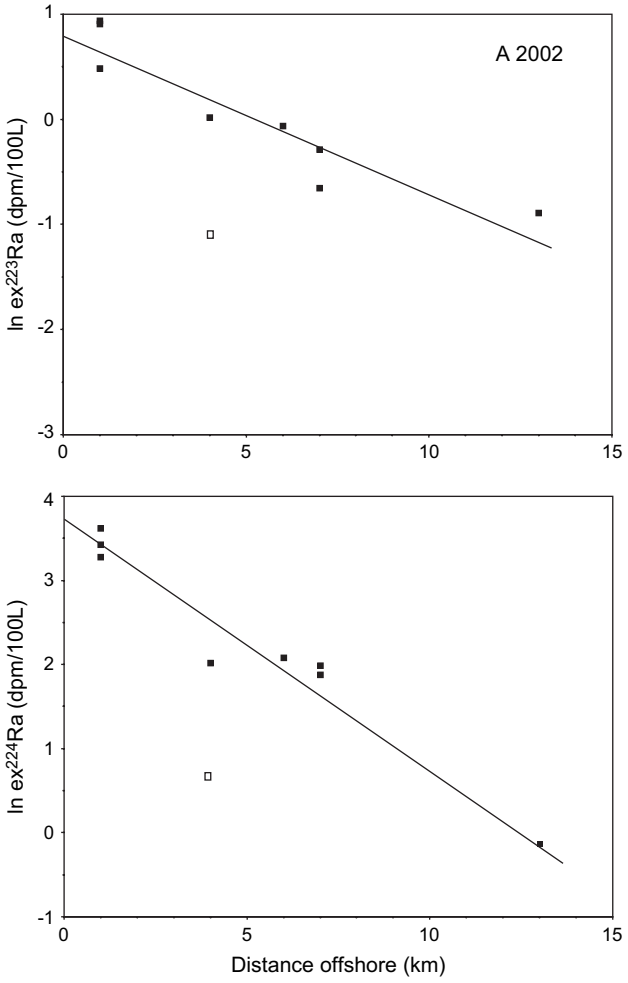

Fig. 3. The ln Ra activity as a function of distance offshore for samples collected within 13 km of shore in 2002. The best-fit line for ^{223}Ra ($R^2 = 0.862$) yields $K_h = 24$ m^2 s^{-1}. The best-fit line for ^{224}Ra ($R^2 = 0.950$) yields $K_h = 31$ m^2 s^{-1}.

locations are shown on Fig. 1. In June 2000 we collected one transect from Fortaleza Bay to 19 km offshore. In January 2002 we sampled Mar Virado, Fortaleza, and Flamengo Bays, ran one transect north of Vitoria Isand, and a second transect off Ubatuba Bay. We also sampled some monitoring wells in Flamengo Bay. In November 2003 we ran one transect out of Flamengo Bay and a second transect extending to Vitoria Island. We again sampled the Flamengo Bay wells and also measured samples obtained from seepage meters in Flamengo Bay. The results are given in Table 1 (surface water samples) and Table 2 (wells and seepage meters).

5.1. June 2000

Both ln ^{223}Ra and ln ^{224}Ra exhibited a strong relationship with distance offshore on this transect (R^2 for ^{223}Ra = 0.949 and for ^{224}Ra = 0.961, with the exception of the most distant point, UB-11) (Fig. 2). The slope of ln ^{223}Ra indicated a dispersion coefficient of 2.4 km^2 day^{-1} (28 m^2 s^{-1}). The ln ^{224}Ra data yielded a K_h of 3.4 km^2 day^{-1} (39 m^2 s^{-1}).

5.2. January 2002

For samples collected within the three bays, the offshore distributions of both isotopes were similar to the June 2000 plots (Fig. 3). The plot of ln ^{223}Ra vs. distance yielded a dispersion coefficient of 2.7 km^2 s^{-1} ($R^2 = 0.86$). The ln^{224}Ra vs. distance plot yielded 2.1 km^2 s^{-1} ($R^2 = 0.95$). In both plots, one low Ra sample (A-2) from 4 km was excluded.

The ln Ra activity as a function of distance offshore plots for samples collected on the Fortelaza Bay transect are shown in Fig. 4a. The ^{223}Ra data are reasonably correlated within 20 km of shore, but the correlation breaks down for samples collected between 20 and 30 km. The ln Ra activity as a function of distance offshore for samples collected on the Ubatuba

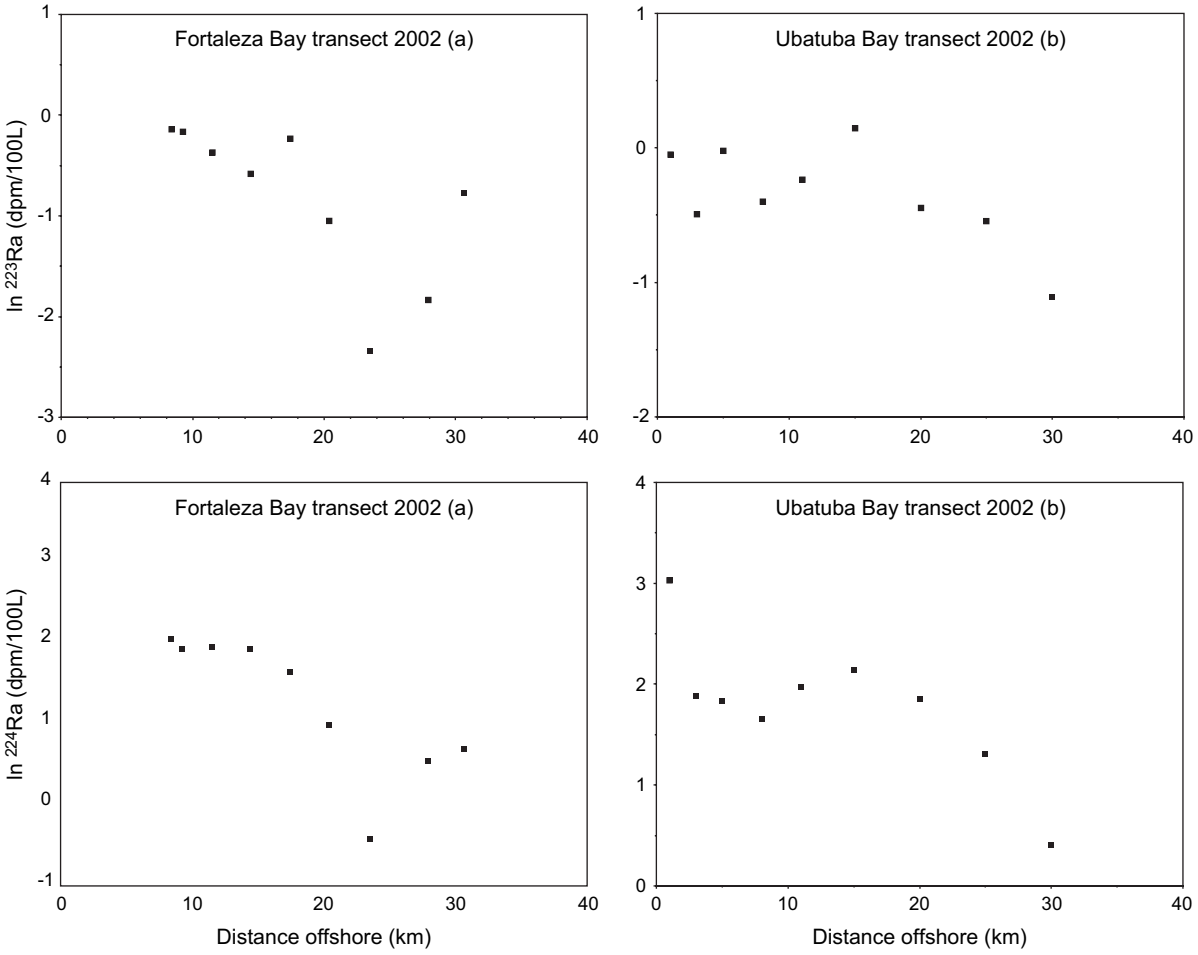

Fig. 4. (a) The ln Ra activity as a function of distance offshore for samples collected on the Fortelaza Bay transect in 2002. The ^{223}Ra data are reasonably correlated within 20 km of shore, but the correlation breaks down for samples collected between 20 and 30 km. (b) The ln Ra activity as a function of distance offshore for samples collected on the Ubatuba Bay transect in 2002. Samples collected within Ubatuba Bay and just shoreward of the bay have activities considerably lower than those of samples collected from the bays lying to the south. Additionally, there is no consistent trend of decreasing activity with distance offshore for these samples.

Bay transect is shown in Fig. 4b. Samples collected within Ubatuba Bay and just shoreward of the bay have activities considerably lower than those of samples collected from the bays to the south. Additionally, there is no consistent trend of decreasing activity with distance offshore for these samples. Because of these problems, we are reluctant to assign a K_h to these transects.

5.3. November 2003

The ln Ra activity as a function of distance offshore plots for samples collected on the Vitoria Island transect are shown in Fig. 5a. There is no consistent trend of decreasing activity with distance offshore for these samples. The ln Ra activity as a function of distance offshore plots for samples collected on the Flamengo Bay transect is shown in Fig. 5b. Samples collected beyond 5 km do not show a decreasing trend of activity with distance. Because of these problems, we are reluctant to assign a K_h to these transects.

6. Discussion

The solution to eq. (1) depends on several conditions. The system must be steady state, dispersion must be constant throughout the study area, and there can be no addition of Ra beyond the point taken for the initial activity. The transect collected in 2000 appears to obey these conditions as there is an excellent correlation between ln Ra and distance offshore and there is reasonable agreement between the values derived for dispersion from the two isotopes. But this is not the case for the offshore data collected in 2002 and 2003. In 2003 there was no consistent trend of decreasing activity with distance offshore. In 2002 the samples collected within 20 km of shore showed the expected decrease of activity with distance, but the correlation broke down for samples collected between 20 and 30 km. The samples from Ubatuba Bay were significantly lower in activity than the samples collected in the more southern bays. SGD studies in Ubatuba Bay in 2001 indicated lower fluxes compared with the other bays (Oliveira et al., 2003), but the differences were not enough to explain

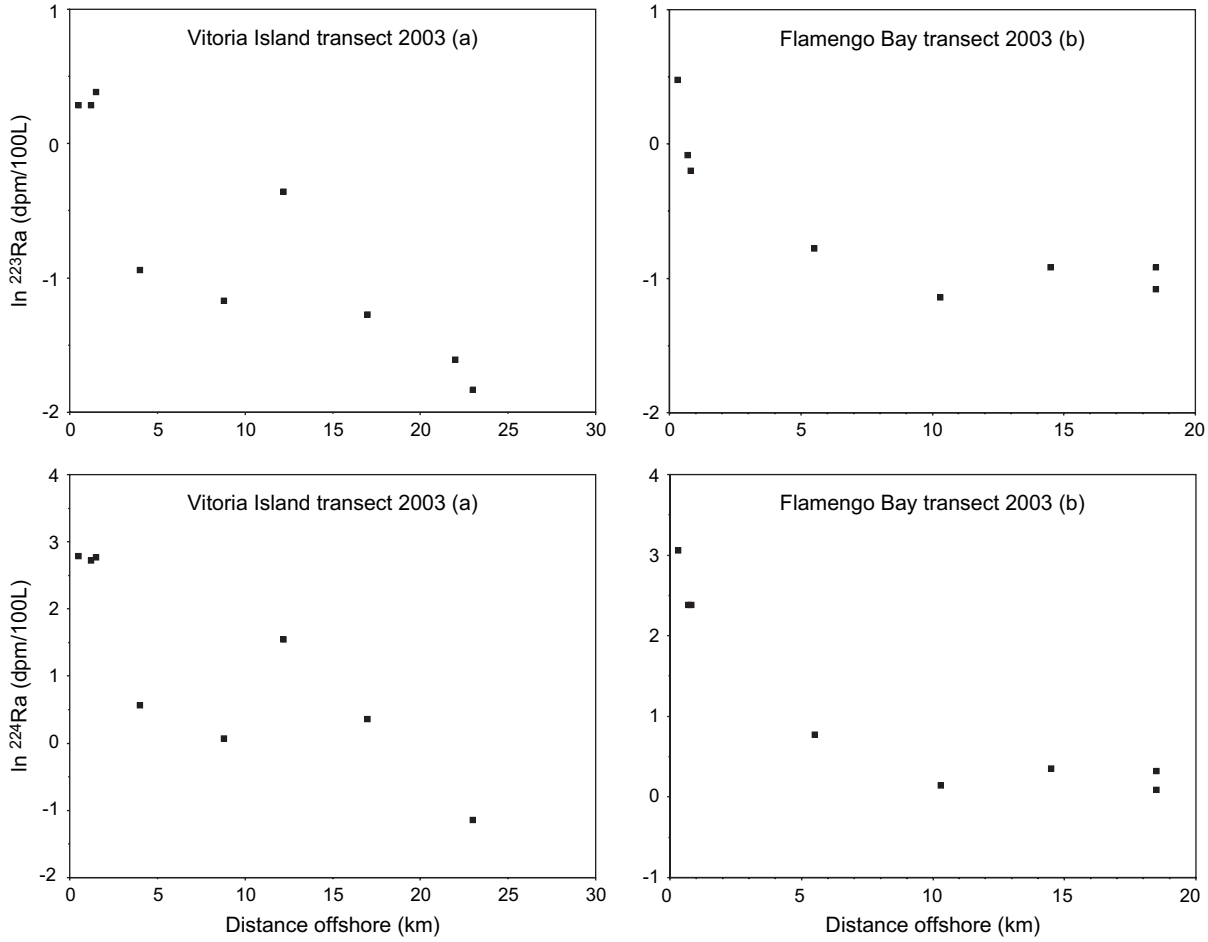

Fig. 5. (a) The ln Ra activity as a function of distance offshore for samples collected on the Vitoria Island transect in 2003. There is no consistent trend of decreasing activity with distance offshore for these samples. (b) The ln Ra activity as a function of distance offshore for samples collected on the Flamengo Bay transect in 2003. Samples collected beyond 5 km do not show a decreasing trend of activity with distance.

the differences measured in 2002. This leads us to conclude that during the 2002 and 2003 sampling campaigns, one or more of the conditions necessary for the use of eq. (1) were not met. Therefore we must seek alternative ways to estimate exchange times.

The $^{224}Ra/^{223}Ra$ age model does not depend on steady state conditions or constant mixing patterns. We used samples collected from seepage meters in Flamingo Bay in 2003 to initialize the age model. These samples had a $^{224}Ra/^{223}Ra$ AR = 21. Because the natural $^{238}U/^{235}U$ AR = 21.7 and the natural abundance $^{232}Th/^{238}U$ AR ~1, the supported $^{224}Ra/^{223}Ra$ AR = 21.7, close to the value measured in the seepage water.

The calculated age vs. distance offshore for all samples is shown in Fig. 6. Samples collected in the bays have ages in the range of 2–10 days relative to the water collected in the seepage meter. Further offshore there is a trend of increasing age with distance. Most samples from 10 to 25 km offshore have ages in the range 7–15 days. The one exception to this was a sample collected near Vitoria Island in 2003. This sample must reflect recent additions of ^{224}Ra and ^{223}Ra with an activity ratio greater than surrounding waters.

The primary objective for the study using short-lived Ra was to provide an estimate of rates of exchange between the coastal waters and the open ocean to use in models of SGD. Tracer concentrations in coastal waters depend on the flux of SGD, the concentration of the tracer in the SGD, and how quickly the signal is lost by exchange with the open ocean. We can use measurements of a long-lived Ra isotope, ^{228}Ra, to illustrate how this works. The average ^{228}Ra activity in the coastal water to 25 km offshore in 2003 was 15.5 ± 2.72 dpm per 100 L (Table 1). The ocean endmember (12.15 ± 0.22 dpm per 100 L) can be estimated from the most distant samples from shore, 7 and 8 (Table 1). Thus, the enrichment of ^{228}Ra in the coastal water is 3.36 ± 2.73 dpm per 100 L. The known volume that exhibits this enrichment is 14 km alongshore × 25 km offshore × 10 m depth, or 3.5×10^9 m^3. The total ^{228}Ra enrichment is $1.2 \pm 1.0 \times 10^{11}$ dpm. If the residence time is taken as 10 days, the average flux of ^{228}Ra is $1.2 \pm 1.0 \times 10^{10}$ dpm day^{-1}.

Nearshore SGD fluxes were estimated from seepage meters (Bokuniewicz et al., 2008) and ^{222}Rn (Burnett et al., 2008). These studies concluded that the average nearshore SGD flux was 13 ± 6 cm^3 cm^{-2} day^{-1}. The total shoreline length of the

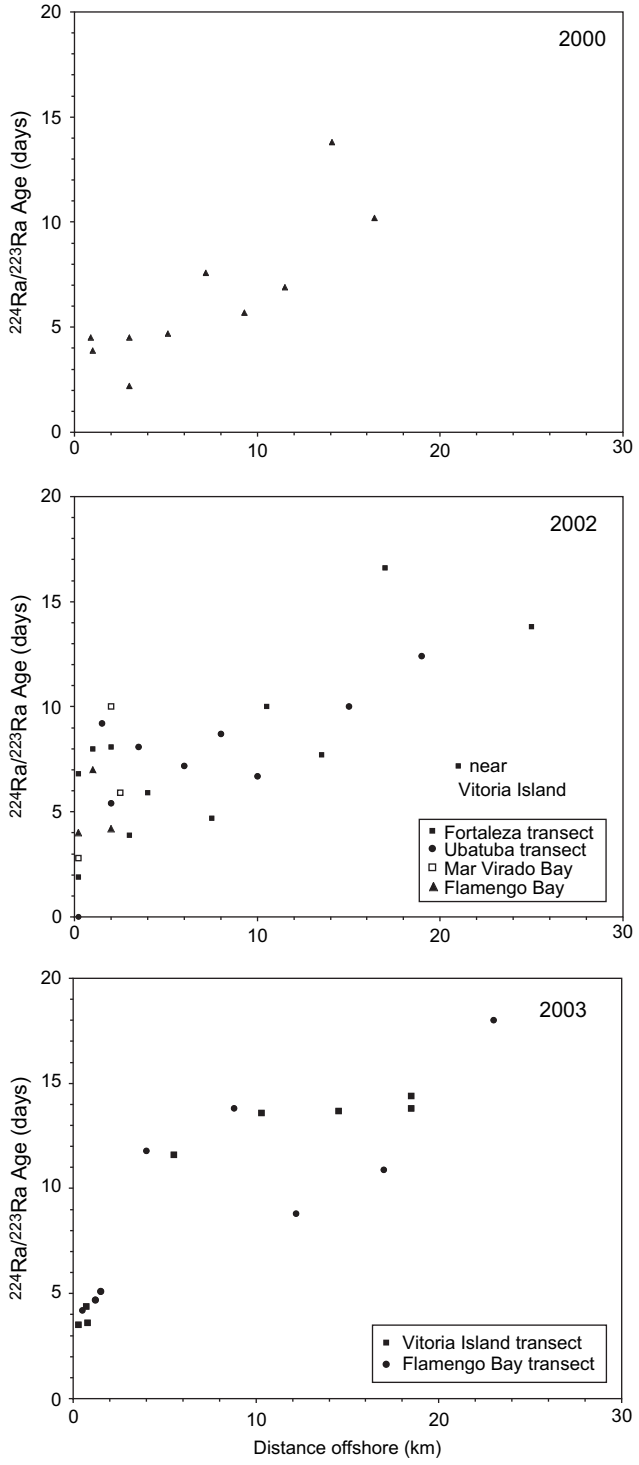

Fig. 6. Age vs. distance offshore for all samples. Samples collected in the bays have ages in the range 2–10 days relative to the water collected in the seepage meter. Farther offshore there is a trend of increasing age with distance. Most samples from 10 to 25 km offshore have ages in the range of 7–15 days.

14 km long study area is ~40 km due to the rugged nature of the coastline. If the nearshore SGD flux occurs between this shoreline and 50 m offshore (Stieglitz et al., 2008; Bokuniewicz et al., 2008), the total nearshore SGD flux is $2.7 \pm 1.2 \times 10^5$ m^3 day^{-1}. We can translate this nearshore SGD flux into a ^{228}Ra flux using the activities of ^{228}Ra measured in water emerging from seepage meters. Two samples of this water had almost identical ^{228}Ra activity = 415 dpm per 100 L (Table 2). If the ^{228}Ra enrichment is caused by the SGD flux of water with this composition, the nearshore SGD ^{228}Ra flux must be $1.1 \pm 0.5 \times 10^9$ dpm day^{-1}. Using a 10-day residence time, this nearshore SGD flux can support an excess ^{228}Ra inventory in the 3.5×10^9 m^3 study area of $1.1 \pm 0.5 \times 10^{10}$ dpm. In spite of the large uncertainty associated with each estimate, it is clear that the estimated nearshore seepage cannot support the measured excess ^{228}Ra in the coastal water. The seepage estimate is only 10% of the measured ^{228}Ra enrichment, implying that either the SGD flux >50 m offshore is ten times more important than the nearshore flux or that the methods based on seepage meters and radon missed significant sites of nearshore SGD. It is also possible that the samples from the seepage meters did not provide a representative sample of SGD to use for the ^{228}Ra endmember. We prefer to estimate the SGD ^{228}Ra endmember based on the seepage meters rather than wells, because this is the closest we can come to sampling SGD entering the ocean. Admittedly, two samples do not provide a robust assessment. But even if we used a high estimate of ^{228}Ra activity in the groundwater, 2000 dpm per 100 L, the Ra-based SGD flux would still exceed the nearshore estimate by a factor of 2.

7. Conclusions

Although the ^{224}Ra/^{223}Ra age method does not yield tightly defined ages, it provides an estimate of 1 to 2 weeks for the residence time of water within 25 km of shore. It also illustrates that the ages do not follow a single trend with distance offshore. This is likely due to the ruggedness of the coastline, where many bays and small islands interrupt simple mixing patterns. As water circulates through these bays, small-scale eddies may develop and propagate onto the shelf. Changes in wind direction must also have a strong effect on the eddy formation and the circulation. The likelihood of achieving steady state on a time scale of days to weeks is small. Thus it is not surprising that the advection-diffusion model yields inconsistent results. We used the residence times of the coastal water and the enrichment of ^{228}Ra relative to the ocean to estimate the flux of ^{228}Ra necessary to maintain this enrichment. Our results indicate that the nearshore (0 to 50 m) SGD flux could support only 10% of the measured ^{228}Ra enrichment. This implies that there is considerable offshore SGD or sites of enhanced SGD nearshore that were missed by the seepage meter and radon studies.

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