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Article

^{228}Ra and ^{226}Ra in Coastal Seawater Samples from the Ubatuba Region - Brazilian Southeastern Coastal Region

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O presente trabalho apresenta os resultados de ^{226}Ra e ^{228}Ra obtidos durante o 4º experimento de intercomparação referente à descarga submarina de água subterrânea (Submarine Groundwater Discharge, SGD) realizado em Ubatuba (SP), em novembro/2003. Este experimento visava testar, em um sistema de rochas cristalinas fraturadas, as diferentes metodologias existentes de determinação da SDG. Embora com objetivo distinto, decidiu-se participar deste experimento de modo a verificar se os isótopos de rádio poderiam ser empregados no estudo de mistura de águas na região e, também, testar a capacidade analítica do laboratório, visando uma futura validação de modelos de dispersão marinha para o local de instalação dos reatores nucleares de Angra dos Reis, distantes apenas setenta quilômetros da região do experimento. Além das concentrações de ^{228}Ra e ^{226}Ra, resultados de salinidade, bário e sílica também são apresentados e suas relações com a concentração de ^{228}Ra são discutidas.

The present work reports ^{228}Ra and ^{226}Ra results obtained during the 4th Submarine Groundwater Discharge (SGD) intercomparison experiment realized in Ubatuba, November 2003, aiming to test the methodologies on a fractured crystalline rocks system. Although with distinct objectives, it was decided to participate in this experiment in order to verify if radium isotopes could be used to determine water mixing rates in this region and to test the laboratory capability to perform, later on, a marine dispersion model validation at Angra dos Reis reactor site, located nearby. The results show that the SGD model constrains seems to be valid, at least for a distance of 20 km offshore, that corresponds to the distance between the reactor site and Ilha Grande, a 193-km^2 island existing at this site and probably an additional SGD source. Salinity, barium and silica results are also reported and their relation to ^{228}Ra concentrations is discussed.

Keywords: ^{228}Ra, ^{226}Ra, seawater, submarine groundwater discharge, Brazil

Introduction

The Angra dos Reis nuclear power plant site is located 130 km south from Rio de Janeiro city. There are two pressured water reactors in operation at the site: the first one started operation in 1985 and has a nominal capacity of 660 MWe and the second one is a 1300 MWe unit and started its operation in 2000. Seawater is used as cooling water for both units; the cooling water is pumped from Itaorna Bay and discharged into Piraquara de Fora Bay, together with the liquid effluents from the two NPP.

The dispersion of discharged radionuclides was modeled by Fernandes *et al.*[1] in order to allow the assessment of the committed dose incurred by the local population in case of normal operation and accidents. The results obtained suggested that conservative radionuclides released, such as ^{137}Cs and ^{3}H, are efficiently exported to the open ocean.

In order to validate this model, it was first thought to use the released tritium as a tracer. However, due to the actually achieved tritium detection limit (2 kBq m^{-3}),

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its potential application was restricted to the Piraquara de Fora Bay. For a longer distance an alternative was needed. With the development of the research related to the importance of the submarine groundwater discharge (SGD) as an relevant source of substances to the coastal region and, in particular, with the consequent use of radium isotopes for the determination of coastal mixing rates,[2] it was decided to investigate its potential application as a way to validate the dispersion model.

An updated review of SGD in seawater was published by Burnett *et al.*[3] In order to compare the different SGD assessment methodologies the Intergovernmental Oceanographic Commission of UNESCO (IOC), the International Hydrological Program (IHP) and the International Atomic Energy Agency (IAEA) are sponsoring intercomparison experiments at different locations around the world. The previous SGD intercomparison experiments were performed in Gulf of Mexico, Florida (2000); Cockburn Sound, western Australia (2000) and eastern Long Island, New York (2002). The experimental setup and results of the Gulf of Mexico SGD intercomparison experiment are found in Biogeochemistry volume 66, number 1-2, November 2003, a special issue dealing with it. The Ubatuba experiment was realized in November 2003 and aimed to test the methodologies on a fractured crystalline rocks system. The first experiments on SGD at the Ubatuba coast were performed by Oliveira *et al.*[4] and indicated a significant inflow of several cm per day.

Determining coastal mixing rates using radium isotopes [2]

The change in concentration or activity (A) with time (t) as a function of distance offshore (x) for a conservative, non reactive tracer may be expressed as a balance of advection and diffusion:

$$\frac{dA}{dt} = K_h \cdot \frac{\partial^2 A}{\partial x^2} + \omega \cdot \frac{\partial A}{\partial x} \quad (1)$$

where K_h is the eddy diffusion coefficient and ω is the advective velocity. Lateral effects are ignored in this one-dimensional approximation. If K_h and ω are constant, the offshore distribution of a conservative tracer may be used to determine the relative importance of these processes in moving the signal offshore (advection) and diluting if (diffusion). If the offshore distribution is dominated by diffusion with constant K_h, a plot of activity vs. distance will be a straight line connecting the end members. Offshore advection will cause positive curvature and onshore advection will cause negative curvature to this plot. This model assumes there is no additional input of the tracer beyond the nearshore. The existence of a termocline isolate the surface water from inputs from below. Once added to nearshore waters, the two long-lived radium isotopes, ^{226}Ra ($t_{1/2}$ = 1620 years) and ^{228}Ra ($t_{1/2}$ = 5.7 years), are conservative tracers.

For the short-lived radium isotopes, ^{223}Ra ($t_{1/2}$ = 11.3 days) and ^{224}Ra ($t_{1/2}$ = 3.66 days), a decay term must be included in the equation describing their distributions. Equation (2) describes the distribution of the activity of a radioactive tracer with decay constant λ in the same context:

$$\frac{dA}{dt} = K_h \cdot \frac{\partial^2 A}{\partial x^2} + \omega \cdot \frac{\partial A}{\partial x} - \lambda \cdot A \quad (2)$$

If net advection can be neglected, this reduces to:

$$\frac{dA}{dt} = K_h \cdot \frac{\partial^2 A}{\partial x^2} - \lambda \cdot A \quad (3)$$

In this case, the boundary conditions are:

$A = A_o$ at $x = 0$

$A \rightarrow 0$ as $x \rightarrow \infty$

If K_h is constant and the system is in steady state:

$$A_x = A_0 \cdot \exp\left(-x \cdot \sqrt{\frac{\lambda}{K_h}}\right) \quad (4)$$

where A_x is the activity at distance x from the coast, A_o is the activity at distance 0 from the coast and λ is the decay constant.

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

$$\ln(A_x) = \ln(A_0) - x \cdot \sqrt{\frac{\lambda}{K_h}} \quad (5)$$

In this case, the slope is $\sqrt{\lambda/K_h}$.

Therefore, using long-lived radium isotopes in coastal waters it is possible to verify which mixing mechanics (diffusion and advection) are present. Where the exchange is dominated by diffusion, applying short-lived radium isotopes it is possible to determine the eddy diffusion coefficient.

This methodology was successful applied to Yeoja Bay, morphologically similar to Ribeira Bay, including the presence of several islands inside and nearby the bay outlet, in order to estimate nutrient inputs to.[5] Although with distinct objectives, it was decided to participate in this SGD experiment in order to verify if these constraints are valid in this region and to test the laboratory capability to perform, later on, the marine dispersion model validation at the Angra

dos Reis reactor site, located only 70 km from Ubatuba.

At Angra dos Reis reactor site, two others radium sources have to be taken into account at Angra dos Reis reactor site, Ilha Grande SGD and the current flowing though the Ilha Grande/Angra dos Reis channel. But, despite any morphological difference between Ubatuba and Ribeira bay, the radium contribution from the shoreline should be such that it could be differentiated from the open sea end-member, and this can be evaluated with the Ubatuba SGD experiment due to the geological similarity between both locals (Figure 1), with the presence of granites and migmatites of mountain chains (Serra do Mar), which reaches the shore throughout almost all the study area, and limits the extension of the drainage systems and of the Quaternary coastal plains.

In the future, in order to evaluate the relative influence of these two other sources, 2-3 transects at Ribeira bay surroundings will be performed, one of them, from Mambucaba beach, crossing the bay, in direction to open sea through the channel between Ponta de Juatinga and Ilha Grande. Since multiple tracers as short and long-lived radium isotopes, barium, silica and salinity will be used it should be possible to evaluate their relative contributions.[5]

Experimental

The Ubatuba SGD experiment was performed during the period 16-22 November 2003, at the same region described by Oliveira *et al.*[4] Samples of surface ocean water were obtained during two cruises, the first one realized on 18th November from Flamengo Bay to Vitoria Island (31 km offshore) and, next day, the second one from Vitoria Island to Fortaleza Bay (Figure 1 and 2). The distance between each sampling station was about 5 km and a total of 16 samples were taken. The R/V Albacora (Instituto de Oceanografia, Universidade de São Paulo) was used on both cruises and each sampling station localization was recorded by an on-board GPS, the distances to the coast were calculated based on these records. At each sample station 100 L seawater was taken and pumped through on-line filter cartridge (2 μm pre-filter and 0.45 μm filter) followed by a column of manganese coated acrylic fiber (Mn fiber), to quantitatively remove radium.[6] The Mn fibers were leached with HCl and hydroxylamine hydrochloride was added in order to produce a clear solution. Radium was co-precipitated with $BaSO_4$ and ^{228}Ra and ^{226}Ra determined by gross beta and alpha counting as described by Godoy *et al.*[7] The detection limit achieved was 0.02 and 0.3 Bq m^{-3} for ^{226}Ra and ^{228}Ra, respectively, and the relative measurement error ranges were between 5-10%. Additionally, a seepage meter (10 L), an artesian well and Picinguaba river (20 L) water sample were collected, in order to obtain the $^{228}Ra/^{226}Ra$ activity ratio signature of the surface and groundwater end members. Seawater samples for ^{228}Ra and ^{226}Ra were also collected under the MOMAM program during the year 2003,[8] in order to determine its variability across the Brazilian Southeastern coast.

At each sampling site, a 100 mL sample was taken and kept frozen for the determination of salinity, silica and barium. Barium and silica were determined by inductively coupled plasma atomic emission spectrometry (Perkin-Elmer ICP-AES Optima 2000 DV), salinity by titulation with silver nitrate.

Results and Discussion

Figure 1. Ubatuba-Angra dos Reis nautical chart showing the seawater sampling points and the Angra dos Reis reactor (CNAAA) site (adapted from the Brazilian nautical chart #81).

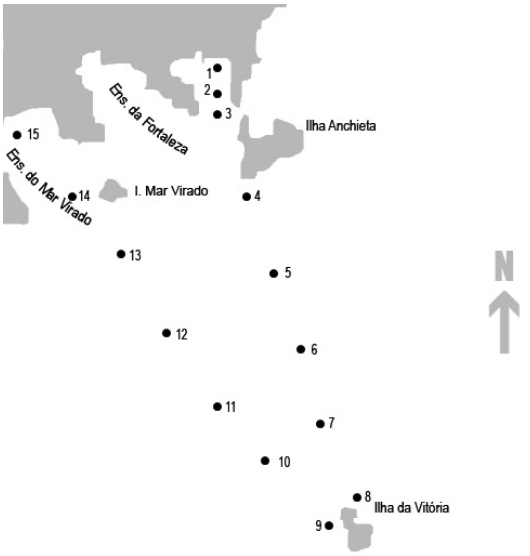

Figure 2. Detail of the Ubatuba nautical chart with the seawater sampling points.

Table 1. Ubatuba SGD experiment collected samples and obtained results (uncertainty = one sigma expanded uncertainty)

Sample	Latitude	Longitude	Offshore Distance (km)	Si (µmol L^{-1})	Ba (nmol L^{-1})	Salinity (psu)	^{226}Ra (Bq m^{-3})	^{228}Ra (Bq m^{-3})	AR
1	S23°29.938	W45°06.998	0.5	6.77	54.6	34.74	0.73±0.10	2.72±0.25	3.74±0.61
2	S23°30.000	W45°06.350	2	4.84	56.1	35.62	1.04±0.14	3.34±0.32	3.20±0.52
3	S23°32.124	W45°04.624	4	3.55	56.1	35.94	1.00±0.12	3.29±0.29	3.30±.0.50
4	S23°36.108	W45°02.185	9	2.13	50.2	36.38	0.83±0.11	2.50±0.25	3.01±0.49
5	S23°38.064	W45°00.015	14	2.00	52.4	36.25	0.90±0.09	2.27±0.22	2.52±0.36
6	S23°39.445	W44°57.850	19	2.16	51.7	36.25	0.66±0.08	2.12±0.20	3.21±0.50
7	S23°40.627	W44°55.595	24	2.29	51.0	36.32	0.75±0.08	1.71±0.19	2.29±0.36
8	S23°40.582	W44°55.600	31	1.71	51.0	36.57	0.91±0.10	1.78±0.22	1.96±0.32
9	S23°44.930	W45°00.040	31	1.84	50.2	36.89	1.09±0.11	2.03±0.25	1.86±0.29
10	S23°45.258	W45°01.476	26	1.87	52.4	37.26	0.99±0.10	3.02±0.26	3.05±0.41
11	S23°42.895	W45°03.213	21	2.68	52.4	36.32	1.05±0.10	2.89±0.25	2.75±0.36
12	S23°40.383	W45°04.942	16	2.58	50.2	36.57	1.15±0.11	2.16±0.26	1.88±0.29
13	S23°38.685	W45°06.825	11	2.10	53.9	37.2	0.83±0.09	2.54±0.22	3.04±0.42
14	S23°36.354	W45°08.384	6	3.55	55.3	36.57	0.79±0.09	2.59±0.21	3.29±0.45
15	S23°34.238	W45°10.368	1	4.52	53.9	36.57	1.04±0.10	3.27±0.26	3.15±0.40
16	S23°32.594	W45°12.741	1	5.16	54.6	36.00	0.85±0.09	3.19±0.23	3.76±0.49
17			Well	258	72.8	n. d.	0.10±0.03	0.67±0.07	6.8±1.9
18			Seepage	41.9	109	26.60	6.65±0.77	50.2±2.6	7.56±0.95
19			Picinguaba river	145	94.7	n. d.	5.09±0.51	<2	

n.d. = not determined.

The obtained results are shown in Table 1. The artesian well was located on the granite hills close to the Marine Laboratory, due to its very low radium concentration, the contribution of groundwater coming from these mountains to the radium content of coastal water discharged at this region seems to be not relevant. Similarly, Picinguaba river has crystalline waters with; also, low radium content, and cannot be taken as a relevant radium source for the coastal seawater. On the other hand, the ^{228}Ra content on the seepage water was 15-20 times higher than that observed seawater concentrations. The ^{228}Ra/^{226}Ra activity ratio (AR) in the seepage and the artesian well water are similar to the ^{232}Th/^{238}U AR observed in monazite samples taken at the Rio de Janeiro coast,[9] therefore, it is valid to suppose that the monazite leaching by groundwater moving to the beach is the reason of the high radium concentration observed in the seepage water sample, and this groundwater can be taken as the coastal end member.

Figure 3 shows the ^{228}Ra and ^{226}Ra concentrations as a function of distance offshore. For ^{226}Ra there is not a clear function of the distance offshore as observed for ^{228}Ra. For ^{228}Ra the data within 20 km of the coast fit a line of (-0.0714) Bq m^{-3} km^{-1} having R^2 = 0.889, there is a break in the slope at 21 km and another at 26 km but only the first break is observed for the ^{228}Ra/^{226}Ra ratio (Figure 4). These two breaks could be due to the existence of offshore groundwater discharge. A break at 21 km is also observed for silica (Figure 5) that reinforces this possibility for this particular sampling point. Nevertheless, the results show that at least for a distance of 20 km offshore, a straight line connecting the end members was observed, showing that the offshore distribution is dominated by diffusion with constant K_h. This distance corresponds to the distance between the reactor site and Ilha Grande, a 193 km^2 island existing at this site and probably an additional SGD source.

The ^{228}Ra relationship with other parameters with potential SGD signatures as salinity and barium and silica concentrations are shown in Figure 6a-c. The correlation between ^{228}Ra and barium (Figure 6a) and silica (Figure 6b) is evident and was already reported by other authors.[10,11] However, the same was not observed for ^{228}Ra and salinity (Figure 6c) or with ^{228}Ra/^{226}Ra AR (Figure 6d). Since the seepage water end member has a ^{228}Ra/^{226}Ra AR of 7.5 and a salinity of 26.6, higher the activity ratio higher should be the freshened water contribution, as are related by Moore and Todd.[12] On the other hand, a clear relationship between silica and salinity is observed, the Si-Sal slope of 1.9 µmol

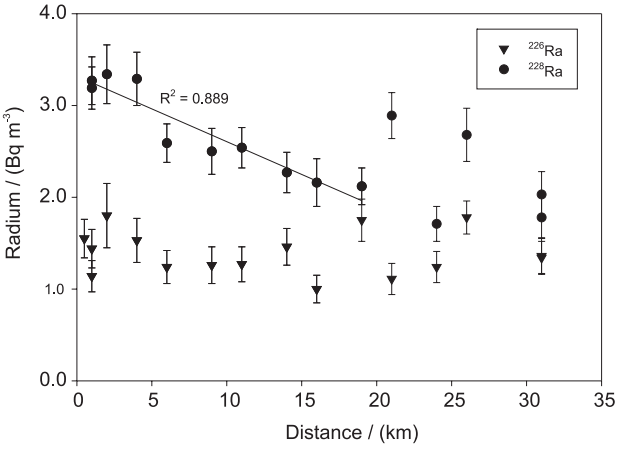

Figure 3. Profiles of ^{228}Ra and ^{226}Ra as a function of distance offshore.

L^{-1} kg^{-1}, for the samples in the 34-37 psu range (Figure 7), is similar to that related by Moore *et al.*[10]

It was also decided to test the influence of the different approaches adopted to calculate the distances, distance to the shoreline taking into account the start point at the shoreline or the distance to the nearest land mass. Using this methodology, as applied by Moore,[13] the initial point, are the sampling points 4 and 14 for the first and second transects, respectively. The distances based on these two methodologies are different as shown in Figure 8, and their influence on the radium, on the $^{228}Ra/^{226}Ra$ and silica relationship with the distance is shown on Figures 9a-f. The point offshore with high $^{228}Ra/^{226}Ra$ activity ratio was omitted in both cases (Figure 9c and 9d). For the sampling points inside the bays there is a large difference for the distance calculate by the different methods. But, in general, taking into account a shift of 8 km for the longest distance achieved, the final results are equivalent as shown in Figures 9c-f.

During the 2003 MOMAM program[8] seawater samples were taken for ^{228}Ra and ^{226}Ra determination and the results obtained are shown in Table 2. It can be seem that the ^{228}Ra and ^{226}Ra concentration in Ubatuba are similar to those obtained for the Ilha Grande Bay sample as initially supposed. Despite the large area comprised by the MOMAM program, from Vitoria (ES) to Santos (SP), 1000 km along the Brazilian southeastern coast, a relationship was observed between $^{228}Ra/^{226}Ra$ AR and salinity (Figure 10). Thorium rich heavy

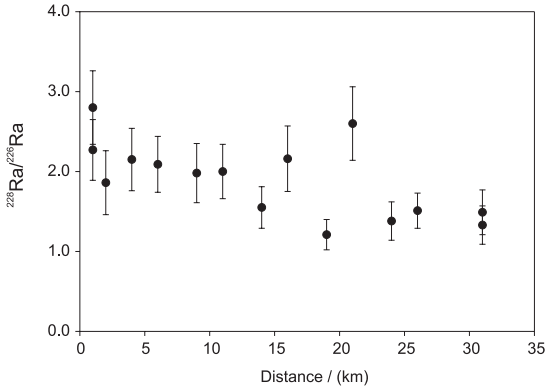

Figure 4. Profiles of $^{228}Ra/^{226}Ra$ activity ratio as a function of distance offshore.

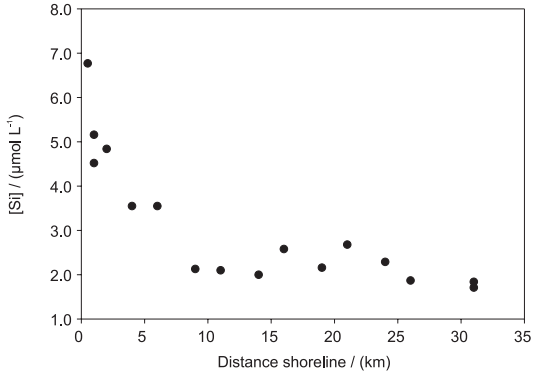

Figure 5. Profile of silica concentration as a function of distance offshore.

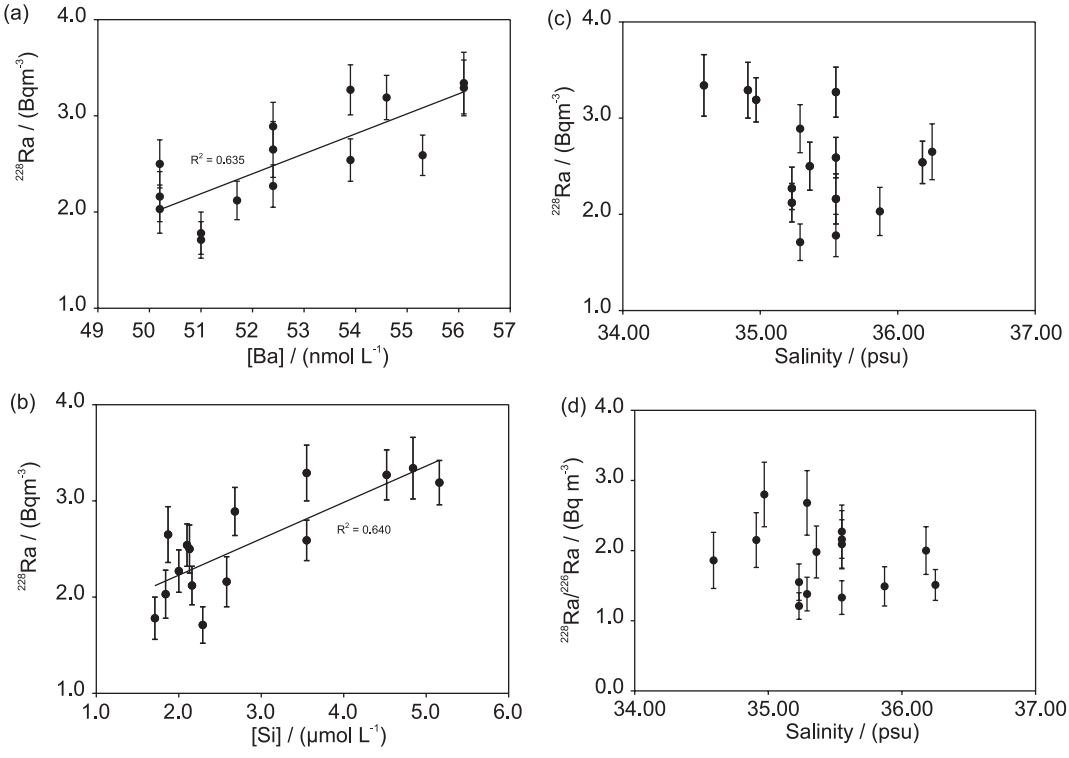

Figure 6. The ^{228}Ra concentration *versus* barium (a) silica (b) and salinity (c) and $^{228}Ra/^{226}Ra$ activity ratio *versus* salinity (d) relation in seawater samples collected in Ubatuba, 2003.

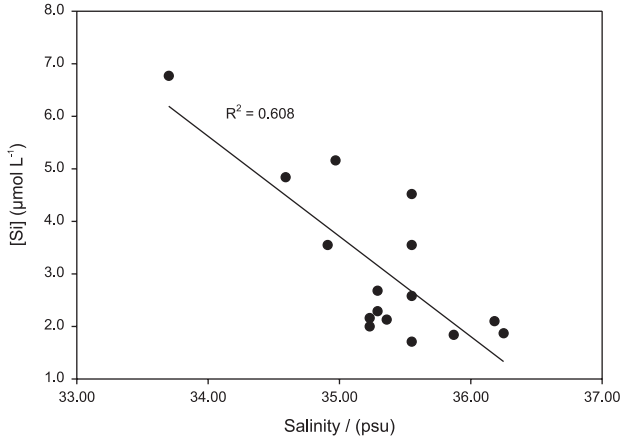

Figure 7. Silica and salinity relation in seawater samples collected in Ubatuba, 2003.

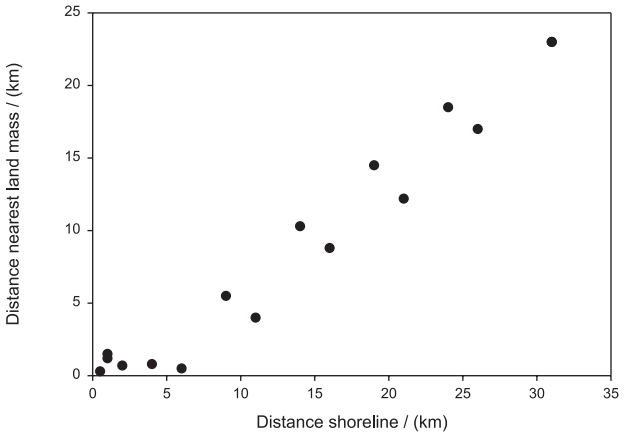

Figure 8. Relationship between the distance calculated based on the shoreline and based on the nearest land mass.

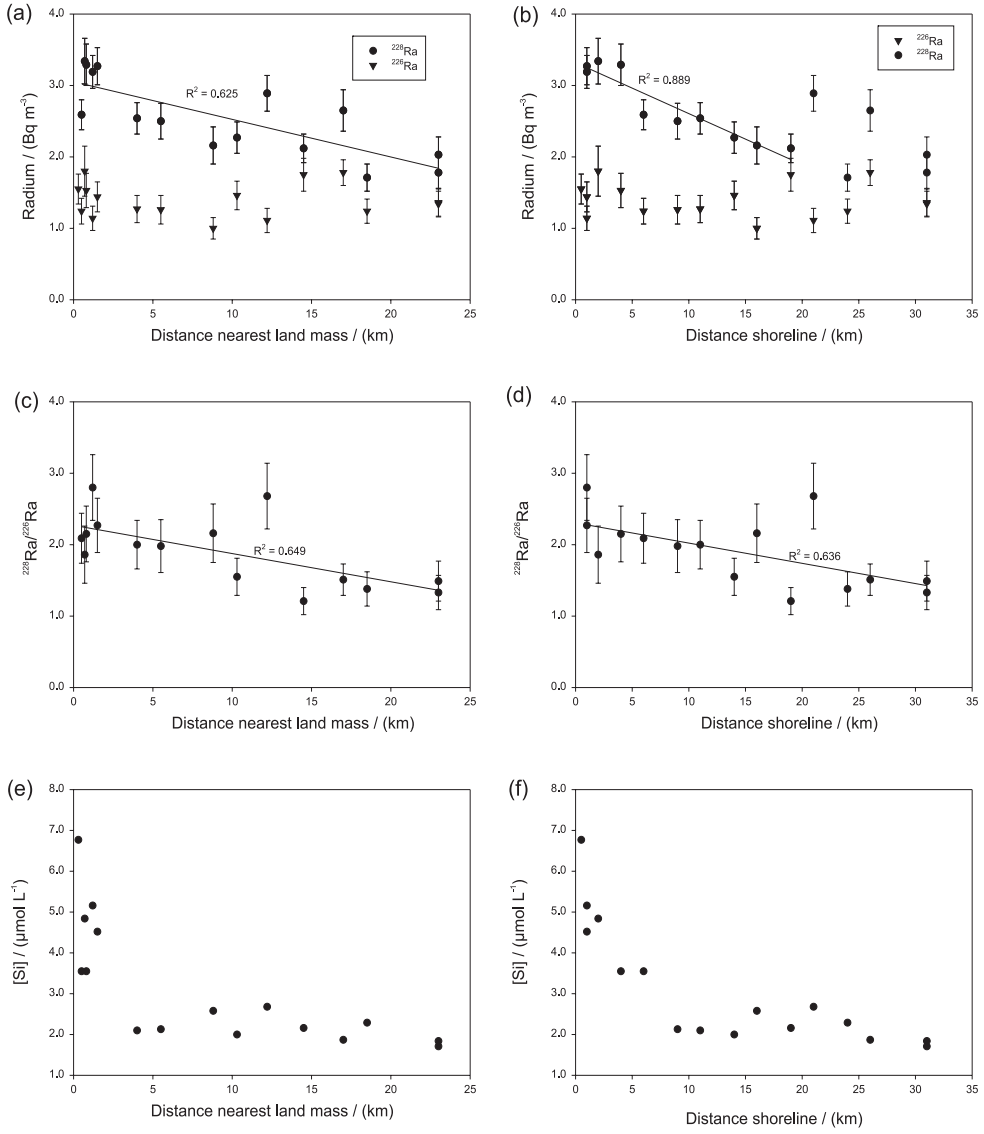

Figure 9. Influence of the distance measurement method on the radium results (a and b), ^{228}Ra/^{226}Ra activity ratio (c and d) and silica profiles (e and f) as a function of the distance.

Table 2. ^{228}Ra and ^{226}Ra in seawater samples collected during 2003 MOMAM program [7] (uncertainty = one sigma expanded uncertainty)

Local	Salinity	^{226}Ra (Bq m^{-3})	^{228}Ra (Bq m^{-3})	AR
	(psu)			
Santos	31.88	1.95±0.19	3.03±0.42	1.55±0.26
São Sebastião	33.25	1.03±0.11	2.85±0.25	2.78±0.38
Ubatuba	33.44	0.58±0.07	1.75±0.18	3.01±0.50
Ilha Grande Bay	32.78	0.48±0.08	2.04±0.19	4.25±0.79
Sepetiba Bay	31.47	1.07±0.12	5.18±0.33	4.86±0.64
Vitória	36.00	1.27±0.12	2.88±0.29	2.26±0.31
Itaóca	36.08	1.23±0.12	1.78±0.29	1.45±0.28
Atafona	34.87	1.39±0.13	1.88±0.28	1.35±0.24
Macaé	35.31	1.17±0.10	2.25±0.27	1.92±0.23

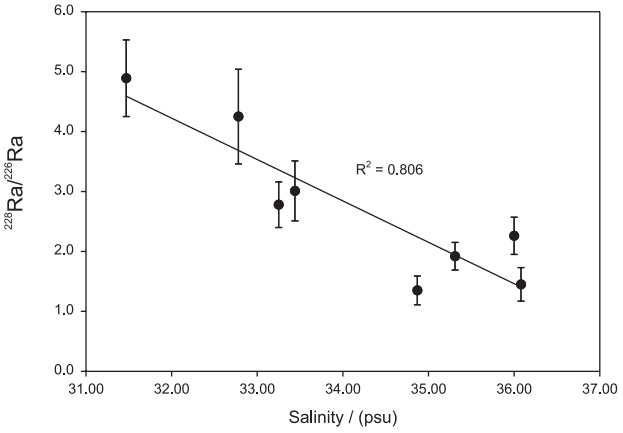

Figure 10. ^{228}Ra/^{226}Ra activity ratio *versus* salinity relation in seawater samples collected during the 2003 MOMAM program (Santos sample omitted).

minerals are found along all over the Brazilian southeastern coast[14,15] giving rise to the observed ^{228}Ra/^{226}Ra AR higher than 1.

Conclusions

The results have shown that the shoreline supply of radium through submarine groundwater discharge in Ubatuba, region nearby the Angra dos Reis nuclear power reactor, is such that it can be used as a tracer for the determination of coastal mixing rates and, consequently, be applied as a tool for the validation of the existing marine dispersion model for this site. However, due to the potential influence of two others radium sources, Ilha Grande SGD and the current flowing through the Ilha Grande/Angra dos Reis channel, additional SGD tracers as short-lived radium isotopes, silica and barium will be needed.

Elevated silica, barium and ^{228}Ra concentrations and ^{228}Ra/^{226}Ra AR were observed in the seepage water end member. Statically valid correlation between ^{228}Ra and others SGD tracers as barium and silica was observed.

Along the Brazilian southeastern coast, a good relationship between ^{228}Ra/^{226}Ra AR and salinity was observed. ^{228}Ra/^{226}Ra AR was always higher than 1, probably, as consequence of the thorium rich heavy minerals found all over the Brazilian southeastern coast.

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