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Determination Of Naturally Occurring Ra Isotopes In Ubatuba-SP, Brazil To Study Coastal Dynamics And Groundwater Input

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Abstract. The four naturally occurring Ra isotopes were measured in seawater, river and groundwater samples collected in a series of small embayments of Ubatuba coastal region, covering latitudes between 23°26'S and 23°46'S and longitudes between 45°02'W and 45°11'W, in order to estimate coastal mixing rates and groundwater discharge fluxes. During the period of this investigation, the activity concentrations of ²²³Ra in surface seawater varied from 2.7 to 41 mBq 100 L⁻¹, ²²⁴Ra in excess from 8.5 to 624 mBq 100 L⁻¹, ²²⁶Ra from 131 to 187 mBq 100 L⁻¹ and ²²⁸Ra from 109 to 409 mBq 100 L⁻¹. The activities of ²²³Ra, ²²⁴Ra, ²²⁶Ra and ²²⁸Ra in a surface river water sample (Escuro River), which reaches the coast on the local area, were 46 mBq 100 L⁻¹, 954 mBq 100 L⁻¹, 229 mBq 100 L⁻¹ and 745 mBq 100 L⁻¹, respectively. Groundwater samples from monitoring wells presented activity concentrations up to 2,033 mBq 100 L for ²²³Ra, 72,540 mBq 100 L⁻¹ for ²²⁴Ra in excess, 2,722 mBq 100 L⁻¹ for ²²⁶Ra and 35,688 mBq 100 L⁻¹ for ²²⁸Ra. The ²²³Ra/²²⁴Ra activity ratios observed in seawater samples ranged from 0.7x10⁻¹ to 0.46, whereas ²²⁸Ra/²²⁶Ra AR varied in the interval from 0.6 to 1.9. These results seems to indicate that Ra isotopes from ²³²Th series prevail in a major number of samples, when compared with Ra isotopes from ²³⁸U and ²³⁵U series. Based on this data, shore-perpendicular profiles of ²²³Ra and ²²⁴Ra in surface waters along the coast were modeled to yield eddy diffusion coefficients. These coefficients allow an evaluation of cross-shelf transport and provide further insight on the importance of groundwater to coastal regions.

INTRODUCTION

The fate of contaminants and natural compounds in estuarine and coastal ocean is determined by a set of biological, geochemical and physical interactions. Although scientists have a basic understanding of the major sources, sinks, and transformations for many substances, to assess offshore fluxes of dissolved materials we need to know coastal water residence times. Until today to quantify residence times in coastal areas remains as a difficult task, since few methodologies are available to assess water

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exchange in this dynamic region, where currents, waves, tides, river flow and groundwater discharge usually play together a complex role.

The cycling of Ra in oceans can be considered as the most interesting phase of radium geochemistry. The fact that in oceans ^{226}Ra and ^{228}Ra exist in excess of their respective parents, ^{230}Th and ^{232}Th (more than tenfold in excess for ^{226}Ra), led some authors to hypothesize that the excess radium was being supplied by diffusion from deep sea sediments. This hypothesis was later confirmed by deficiencies of the radium isotopes observed in deep sea sediments. It was recognized the potential of these isotopes for studying oceanic circulation because they are the only ones amongst other natural tracers which are injected directly into bottom water from underlying sediments.

The first measurements of radium in the ocean water were made due not so much to its radiological significance, but to the promising role of oceanic radium as a tool for understanding marine geochemical processes. It was Koczy (1958) who first proposed using Ra as a natural tracer in the ocean for the calculation of vertical diffusion coefficients in the water column. This was extended later by Koczy & Szabo (1962) for estimating the renewal time of water masses in the Pacific and Indian Oceans. Numerous investigations have been conducted since then to obtain a fuller understanding of ^{226}Ra distributions in the major oceans of the world, with considerable attention devoted to the variability of ^{226}Ra concentrations with regard to depth and latitude, correlation with barium, silica concentrations, salinity, etc. (Broecker *et al.*, 1967).

^{226}Ra concentrations in surface seawater (0-500 m) appear to be in a narrow range, and nearly uniform in the Pacific (0.74-3.7 mBq L⁻¹) and Atlantic Oceans (0.74-2.96 mBq L⁻¹). However, the Indian Ocean has levels of ^{226}Ra which cover a narrower range (1.11-2.22 mBq L⁻¹). At the increasing depths, a trend of increasing concentrations is observed uniformly in all of the oceans, which, according to most investigators, results from the injection of ^{226}Ra from thorium (^{230}Th) bearing sediments in the ocean floor.

Reports of an interesting correlation of silica and barium concentrations with those of Ra in collateral seawater samples have been made by some researchers, calling attention to the parallel geochemical behavior among these elements. It appears that radium behavior in the marine environment closely parallels that of barium, both of which are carried by marine diatoms, which are highly siliceous organisms.

^{226}Ra concentrations in coastal waters are slightly higher relative to open ocean water. Radium is released by coastal sediments, which form an important source of ^{226}Ra migration to the ocean. This was corroborated by measurements in South Carolina (USA) by Elsinger & Moore (1980) who concluded that a desorption mechanism can quantitatively explain the increase of ^{226}Ra in brackish water. Moore (1981) in his interesting investigations at Chesapeake Bay, demonstrated the clear influence of salinity on the desorption of ^{226}Ra from particulates: at salinities lower than 0.5 ‰, about 12 % of ^{226}Ra in the water is in the soluble phase, while above 5 ‰ salinity, over 80 % is in the dissolved phase.

The spread of ^{226}Ra in coastal waters is more or less uniform (0.74-6.6 mBq L⁻¹), except for estuarine and shelf water in west central Florida. There the ^{226}Ra levels can vary from 1.83 to 53.8 mBq L⁻¹ for surface water and from 1.83 to 22.0 mBq L⁻¹ for

deep water. These high concentrations are attributed to the geology of that area, known for its rich phosphate deposits, seepage of groundwater and to the existence of active geothermal springs.

It is generally observed that nearshore water, particularly from restricted bays and sounds, has higher ^{228}Ra levels than does open ocean surface water. However, these concentrations tend to become lower as one moves away from the coast, thus showing a close correlation between concentration and proximity to land (coastal activities ranging from 0.7 to 11.5 mBq L^{-1}). Some nearshore Indian coastal waters displays significant ^{228}Ra levels (13.7-38.1 mBq L^{-1}) due to significant occurrence of monazite sands.

Moore (1969) has discussed the use of ^{228}Ra in the oceans as a natural tracer for studying marine processes occurring within a 3-30 year time-scale. He has also described the applicability of $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios as tracers for studying lateral and vertical movements within the ocean.

Nearshore water, such as surface water close to continents and coastal water in contact with terrigenous sediments where it is observed limited circulation with open ocean, appear to have very high $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios. For example, some of the highest $^{228}\text{Ra}/^{226}\text{Ra}$ ratios (7.1) have been measured in the brackish water of Mississippi Sound. Similar enhanced ratios have also been observed in Chesapeake Bay (1.8); Long Island Sound (1.4); Davis Bay, Mississippi (2.5); Narragansett Bay, Rhode Island (2.0); Wellington Harbour, New Zealand (1.7); Penang Harbour, Malaysia (2.0) and few other places (Moore, 1969).

When nearshore water mixes with oceanic water, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio goes down. However, within surface water, large variations in this activity ratio have been observed by Moore (1969). Atlantic surface water generally has higher ratios than Pacific surface water. For example, the Atlantic has activity ratios of 0.09-2.41 and the Pacific 0.011-0.2. According to Moore, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio is determined by a balance between the supply of ^{228}Ra to the water body and the lateral and vertical mixing rates. The activity ratios in the Atlantic and Pacific Oceans indicate that the mixing rate of the surface water is considerably longer than ten year mean life of ^{228}Ra .

The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios in the surface water of the Mediterranean, Caribbean and Black Seas are all less than unity and are also in a close range. Inversely, the surface water of the Indonesian seas show typically enhanced ratios, from 0.26 to 3.8, which is due to considerable diffusion of ^{228}Ra from the continental shelves. Other regions such as New York Bight (0.39-1.99), Chesapeake Bay (1.17-4.08), Kalpakkam, India (2.4-4.9) and Bombay, India (1.6-1.9) further support the fact that estuarine and coastal water is rich in ^{228}Ra owing to diffusion from nearshore and estuarine sediments, thereby leading to enhanced $^{228}\text{Ra}/^{226}\text{Ra}$ ratios, as observed. Moore (1981), following his studies in Chesapeake Bay on ^{226}Ra and ^{228}Ra flux rates and comparing his data with those from other bay and estuarine regions, has proposed that the flux rate of ^{228}Ra from the sediments should be greater than that of ^{226}Ra owing to the faster growth of ^{228}Ra from its parent ^{232}Th and the effects of bioturbation.

This paper reports the determination of ^{223}Ra , ^{224}Ra , ^{226}Ra and ^{228}Ra in a series of small embayments of Ubatuba, São Paulo State-Brazil. The main aim of this

preliminary work was to apply these isotopes as tracers to assess coastal mixing rates and groundwater input. Concurrent analysis of ^{226}Ra in sediment, seawater and sediment physical properties, besides nutrients improved the evaluation carried out in this coastal region.

MATERIAL AND METHODS

The field work was carried out during January 2002 (summer), in a series of small embayments of Ubatuba, covering latitudes between $23^{\circ}26'S$ and $23^{\circ}46'S$ and longitudes between $45^{\circ}02'W$ and $45^{\circ}11'W$. The main embayments selected to be studied in this project are Flamengo Bay (Ubatuba Marine Laboratory site), Fortaleza Bay, Mar Virado Bay and Ubatuba Bay (Fig.1).

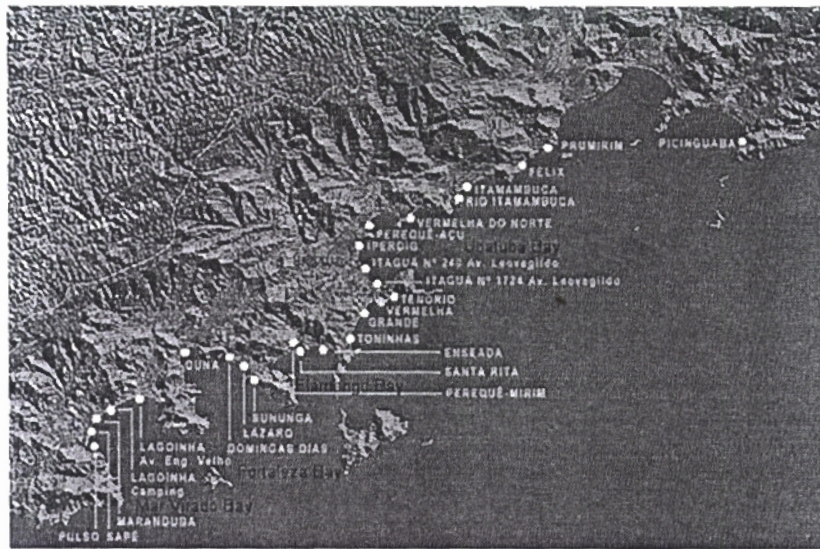


FIGURE 1. Location of the four embayments studied at Ubatuba coastal area: Flamengo, Fortaleza, Mar Virado and Ubatuba. Ubatuba county is located 250 km north from São Paulo city, southeastern Brazil.

The study area comprises the northernmost part of São Paulo Bight, southeastern Brazil, and is considered a tropical coastal area. The geological/geomorphologic characteristics of the area are strongly controlled by the presence of granites and migmatites of a mountain chain locally called Serra do Mar (altitudes up to 1,000 meters), which reaches the shore in almost all of the study area, and limits the extension of the drainage systems and of Quaternary coastal plains (Mahiques, 1995). In most of the area, the sediments contain mainly silt and very fine sand, and few samples show coarse sand or a clay modal distribution. 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. Two main wave directions affect the area. Waves coming from S-SE are associated to the passage of cold fronts over the area and are the most important in terms of reworking of sediments previously deposited. Waves coming from E-NE are mainly generated by trade winds and also during post-frontal periods and are believed to be important to the bottom dynamics. The interaction of wave directions with the extension and orientation of bay mouths and the presence of islands in the inner shelf lead to the occurrence of sensible variations in the dynamics characteristics of the bays, despite that they can all be considered as enclosed bays. The terrestrial input of sediments is strongly dependent on the rainfall regime, leading to a higher contribution of sediments during summer season. During this period, the advance of the South Atlantic Central Water (SACW) over the coast leads to the displacement of the Coastal Water (CW) (Castro Filho *et al.*, 1987), rich in continental suspended materials, and to the transportation of these sediments to the outer portions of the continental shelf. During winter, the retreat of the SACW and the decreasing of the rainy levels restrict the input of sediments from the continental areas. The mean annual rainfall is roughly 1,803 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/September due to greater volume of warm waters of Brazil Current (Mesquita, 1997).

The Ubatuba coastal area is known to be oligo-mesotrophic, because the primary production is limited by the lack of inorganic compounds of nitrogen and phosphorous (Braga & Muller, 1998). The region has been reported to receive nutrient inputs by atmospheric contribution mainly in nitrogenous compounds, and in minor degree by terrestrial contribution, which limit the local primary production. However, from time to time, intrusions of nutrient and oxygen-rich South Atlantic Central Water (SACW) from the open ocean thermocline may reach the shelf edge, and may further be transferred by coastal upwelling, that is driven by northeasterly winds, providing a third source of nutrients for primary production.

For the purposes of pre-concentration of Ra isotopes from large volume of seawater samples described in this paper, Acrylic fibre (Cia. Sudamericana do Brasil, 3.0 denier) was treated with a hot solution of saturated KMnO_4 for approximately 10 minutes. The KMnO_4 oxidizes specific sites on the acrylic molecule and deposits MnO_2 at these sites. The prepared fibre was washed with purified water free of radium and was kept in plastic bags for use. This produces Mn-fibre having sub-micrometric sized particles of MnO_2 chemically bonded to the fibre. The MnO_2 constitutes 8-10% by mass of the Mn-fibre. This procedure was conducted in a 5 L beacker scale.

To assess the spatial distribution of the Ra tracers, five shore-perpendicular transects were sampled in January 2002, the horizontal profiles were collected up to about 30 km from shore (Fig.2). Large volume seawater samples (196 L) were pumped from 5 m below the surface into plastic drums on the R/V Velliger II. The sample volume was recorded and the seawater was percolated through a column of manganese coated acrylic fibre to quantitatively remove radium from seawater (Moore, 1996). Temperature and salinity profiles were obtained at each station using a 2.00" Micro CTD, from Falmouth Scientific Inc. Samples for salinity and nutrients were also collected in each station.

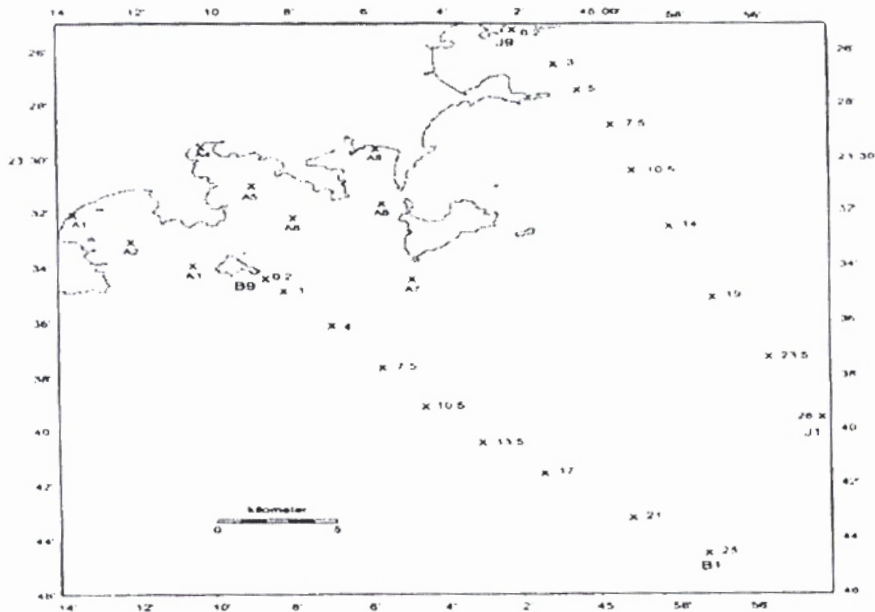


FIGURE 2. Location of the horizontal profiles established for Ra isotopes in Ubatuba region (Jan. 2002).

In each profile, samples for the determination of phosphate, silicate, ammonium, nitrite and nitrate were also collected. Water samples were frozen until time of analysis. The analytical procedures adopted for these determinations were vanadium reduction followed by chemiluminescence detection of NO_x for nitrate-nitrite, phenate method for ammonia and ascorbic acid method for phosphate.

In an onshore laboratory each Mn fibre sample was partially dried with a stream of air and placed in an air circulation system described by Moore & Arnold (1996). Helium was circulated over the Mn fibre to sweep ²¹⁹Rn and ²²⁰Rn generated by ²²⁴Ra and ²²³Ra decay in a 1.1 L scintillation cell. The alpha particles from the decay of radon and its daughters were recorded by a photomultiplier tube (PMT) attached to the scintillation cell described previously. Signals from the PMT were routed to a delayed coincidence counter system adapted for Ra measurements (Moore & Arnold, 1996). The delayed coincidence system utilizes the difference in decay constants of the short-lived Po daughters of ²¹⁹Rn and ²²⁰Rn to identify alpha particles derived from ²²³Ra and ²²⁴Ra captured on the Mn fibre. The expected error of the short-lived Ra isotope measurement is 10%.

After completing the ²²⁴Ra and ²²³Ra measurements, the Mn fibre samples were aged for 5 weeks to allow excess ²²⁴Ra to equilibrate with ²²⁸Th adsorbed to the Mn

fibre. The samples were measured again to determine ^{228}Th activity and this value was used to correct the ^{224}Ra activity to its unsupported activity.

Following these analyses, the Mn fibre was leached in a beaker with 200 mL HCl under controlled heating, to quantitatively remove the longer-lived Ra isotopes. For the radiochemical separation of ^{226}Ra and ^{228}Ra , carriers of stable barium (20mg) and lead (20 mg) were added to the water sample in the presence of 5 mL of 1 M citric acid and 5 mL of 40% hydroxylamine hydrochloride solutions. The radium was co-precipitated as Ba,Pb(Ra)SO_4 by adding 50 mL of 3 M H_2SO_4 . The precipitate was dissolved with alkaline EDTA. When the pH is adjusted to 4.5 with glacial acetic acid, Ba(Ra)SO_4 is re-precipitated, while interfering elements remain in the solution. The Ba(Ra)SO_4 precipitate was transferred to a 2 mL polypropylene tube and sealed to avoid the escape of ^{222}Rn . ^{226}Ra and ^{228}Ra were measured by gamma spectrometry of a Ba(Ra)SO_4 precipitate in a WeGe well germanium detector, after 21 days from the precipitation. The detector is a 78 cm^3 coaxial intrinsic germanium crystal with a 1 cm diameter and 4 cm deep well produced by Princeton Gamma Tech.. The ^{226}Ra activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides: ^{214}Pb at 295.2 keV and 351.9 keV, and ^{214}Bi at 609.3 keV. The ^{228}Ra content of the samples was determined from the 911 keV and 968 keV gamma-ray peaks of ^{228}Ac . Both measurements were performed at the Radioisotope Geochemical Laboratory of the University of South Carolina.

Radium Isotope Disequilibrium to Delineate Coastal Dynamics and Groundwater Input

In the natural radioactive series, there are four radium isotopes: ^{226}Ra ($t_{1/2} = 1620$ years); ^{228}Ra ($t_{1/2} = 5.75$ years); ^{223}Ra ($t_{1/2} = 11.3$ days); ^{224}Ra ($t_{1/2} = 3.66$ days). Each isotope is produced from the decay of a thorium parent: ^{230}Th ($t_{1/2} = 7.54 \times 10^4$ years); ^{232}Th ($t_{1/2} = 1.40 \times 10^{10}$ years); ^{227}Th ($t_{1/2} = 18.7$ days); ^{228}Th ($t_{1/2} = 1.91$ years), respectively.

Because thorium remains tightly bound to particles while radium daughters are mobilized into the marine environment, sediments provide a continuous source of Ra isotopes to seawater, at rates set by their respective decay constants. Measurements of the Th isotope activities in the sediments and the distribution coefficient of Ra between the sediments and water provide a means of quantifying the potential input of each isotope to the ocean.

Two short-lived radium isotopes ^{223}Ra and ^{224}Ra can be used as tracers to measure the rate of exchange of coastal waters (Moore, 1998). Shore-perpendicular profiles of ^{223}Ra and ^{224}Ra in surface waters along the coast may be modeled to yield eddy diffusion coefficients. Coupling the exchange rate with offshore concentration gradients, the offshore fluxes of dissolved materials are estimated. For systems in steady-state, the offshore fluxes must be balanced by new inputs from rivers, groundwater, sewers or other sources. Also, it was observed that barium and ^{226}Ra contents can be powerful indicators of groundwater input in marine systems, since they have high relative concentrations in the fluids and low reactivity in the coastal ocean. An estimate of the ^{226}Ra offshore flux is made applying the eddy diffusion coefficients to the ^{226}Ra offshore gradient. Complementary data of ^{226}Ra in subsurface

fluids provides a mean of calculate the fluid flux necessary to support the ^{226}Ra concentrations found in the marine environment.

The Ra distribution may be expressed by a simple one-dimensional horizontal diffusion model, in which the distribution is in balance between eddy diffusion and radioactive decay (Moore, 1998):

$$\frac{dA}{dt} = K_h \frac{\partial A}{\partial x^2} - \lambda A \quad (1)$$

At the steady-state, this expression can be written as the following:

$$A_x = A_0 \exp \left[-x \sqrt{\frac{\lambda}{K_h}} \right] \quad (2)$$

Where, A_x is the activity at distance x from coast, A_0 is the activity at distance zero from coast, λ is the decay constant and K_h is the horizontal eddy diffusion coefficient.

RESULTS AND DISCUSSION

The location of all stations studied as well as the results of the cruise carried out in January 2002 are shown in **Tab. 1 to 8**.

During the period of this investigation, the activity concentrations of ^{223}Ra in surface seawater varied from 2.7 to 41 mBq 100 L⁻¹, ^{224}Ra in excess from 8.5 to 624 mBq 100 L⁻¹, ^{226}Ra from 131 to 187 mBq 100 L⁻¹ and ^{228}Ra from 109 to 409 mBq 100 L⁻¹. The activities of ^{223}Ra , ^{224}Ra , ^{226}Ra and ^{228}Ra in a surface water sample from Escuro River, which reaches the coast on Fortaleza bay were 46 mBq 100 L⁻¹, 954 mBq 100 L⁻¹, 229 mBq 100 L⁻¹ and 745 mBq 100 L⁻¹, respectively. Groundwater samples from monitoring wells installed in Flamengo bay (in front of the Marine Lab.) presented activity concentrations up to 2,033 mBq 100 L⁻¹ for ^{223}Ra , 72,540 mBq 100 L⁻¹ for ^{224}Ra in excess, 2,722 mBq 100 L⁻¹ for ^{226}Ra and 35,688 mBq 100 L⁻¹ for ^{228}Ra . The $^{223}\text{Ra}/^{224}\text{Ra}$ activity ratios observed in seawater samples ranged from 0.7×10^{-1} to 0.46, whereas $^{228}\text{Ra}/^{226}\text{Ra}$ AR varied in the interval from 0.6 to 1.9. These results seems to indicate that Ra isotopes from ^{232}Th series prevail in a major number of samples, when compared with Ra isotopes from ^{238}U and ^{235}U series.

The ^{226}Ra activity concentrations found in surface seawater samples studied at Ubatuba region are of the same order of magnitude than those reported by other author in the southeastern coast of United States (typical values from 133 to 283 mBq 100 L⁻¹) (Moore, 1999).

TABLE 1. Location of the samples from Transect B, between Mar Virado and Fortaleza embayments, Jan. 2002.

Sample	Date	Volume (L)	Latitude	Longitude	Distance from shore (km)	Salinity (psu)	Temperature (°C)
B-1	22/Jan/02	196	S23°44.592	W44°57.259	30.6	35.337	24.1
B-2	22/Jan/02	196	S23°43.265	W44°59.154	27.9	35.393	24.5
B-3	22/Jan/02	196	S23°41.684	W45°01.435	23.5	35.348	23.5
B-4	22/Jan/02	196	S23°40.445	W45°03.006	20.4	34.917	24.0
B-5	22/Jan/02	196	S23°39.163	W45°04.395	17.4	35.054	24.3
B-6	22/Jan/02	196	S23°37.713	W45°05.697	14.4	35.003	25.0
B-7	22/Jan/02	196	S23°26.233	W45°06.888	11.5	35.003	25.0
B-8	22/Jan/02	196	S23°34.976	W45°08.645	9.3	35.025	25.0
B-9	22/Jan/02	196	S23°34.316	W45°08.645	8.4	35.018	25.0

TABLE 2. Concentration of the natural Ra isotopes, Ra^{223}/Ra^{224} and Ra^{223}/Ra^{226} activity ratios and nutrients determined in the samples from Transect B.

Sample	^{223}Ra mBq 100 L ⁻¹	^{224}Ra mBq 100 L ⁻¹	$^{223}Ra/^{224}Ra$	^{226}Ra mBq 100 L ⁻¹	^{228}Ra mBq 100 L ⁻¹	$^{228}Ra/^{226}Ra$	^{232}Th mBq 100 L ⁻¹	Nitrate μ mol L ⁻¹	Nitrite μ mol L ⁻¹	Silicate μ mol L ⁻¹	Phosphate μ mol L ⁻¹
B-1	6.5	29	0.22	153	159	1.0	4.2	0.016	0.096	1.72	0.43
B-2	2.7	22	0.12	147	133	0.90	6.2	0.607	0.098	2.39	0.86
B-3	1.0	8.5	0.12	119	109	0.91	2.3	-	-	5.96	0.33
B-4	5.8	45	0.13	131	123	0.94	6.3	0.241	0.127	2.30	0.51
B-5	13	126	0.10	163	244	1.5	10	0.014	0.049	3.13	0.60
B-6	9.3	107	0.09	168	268	1.6	8.5	0.299	0.069	3.77	0.60
B-7	12	132	0.09	158	305	1.9	12	0.130	0.059	2.78	0.43
B-8	14	106	0.13	141	255	1.8	7.5	0.288	0.059	4.73	0.62
B-9	15	152	0.10	173	285	1.7	8.5	0.028	0.098	2.70	0.51

TABLE 3. Location of the samples from Transects A, inside Mar Virado, Fortaleza and Flamengo embayments, Jan. 2002.

Sample	Date	Volume (L)	Latitude	Longitude	Distance from shore (km)	Salinity (psu)	Temperature (°C)
A-1	23/Jan/02	196	S23°32.089	W45°13.380	1	34.798	25.0
A-2	23/Jan/02	196	S23°33.094	W45°12.015	4	35.136	25.0
A-3	23/Jan/02	196	S23°33.994	W45°10.196	7	34.947	25.5
A-4	23/Jan/02	196	S23°29.823	W45°10.196	1	34.221	26.0
A-5	23/Jan/02	196	S23°31.027	W45°09.057	4	35.114	25.0
A-6	23/Jan/02	196	S23°32.303	W45°07.912	7	34.885	25.0
A-7	23/Jan/02	196	S23°34.397	W45°04.705	13	35.163	26.0
A-8	23/Jan/02	196	S23°34.347	W45°29.629	6	34.820	25.0
A-9	23/Jan/02	196	S23°29.629	W45°05.758	1	-	27.0

TABLE 4. Concentration of the natural Ra isotopes, Ra^{223}/Ra^{224} and Ra^{223}/Ra^{226} activity ratios and nutrients determined in the samples from Transects A.

Sample	^{223}Ra mBq 100 L ⁻¹	^{224}Ra mBq 100 L ⁻¹	$^{223}Ra/^{224}Ra$ mBq 100 L ⁻¹	^{226}Ra mBq 100 L ⁻¹	^{223}Ra mBq 100 L ⁻¹	$^{223}Ra/^{226}Ra$ mBq 100 L ⁻¹	^{228}Ra mBq 100 L ⁻¹	^{228}Th mBq 100 L ⁻¹	Nitrate μ mol L ⁻¹	Nitrite μ mol L ⁻¹	Silicate μ mol L ⁻¹	Phosphate μ mol L ⁻¹
A-1	43	624	0.07	165	409	2.5	19	0.425	0.036	6.08	0.62	0.32
A-2	5.8	34	0.17	162	211	1.3	7.3	0.323	0.048	2.63	0.32	0.33
A-3	13	121	0.10	150	258	1.7	8.8	0.004	0.108	3.25	0.56	0.50
A-4	27	441	0.06	166	370	2.2	14	0.252	0.096	2.63	0.58	0.64
A-5	17	125	0.14	149	247	1.7	9.5	0.008	0.048	7.31	0.50	0.81
A-6	8.7	109	0.08	167	307	1.8	7.5	0.193	0.144	3.83	0.58	0.81
A-7	6.8	11	0.60	142	167	1.2	6.3	1.064	0.060	1.85	0.64	0.81
A-8	16	133	0.12	167	313	1.9	6.0	0.286	0.096	6.02	0.81	0.46
A-9	41	513	0.08	163	392	2.4	17	0.126	0.132	3.91	0.46	0.46

TABLE 5. Location of the samples from Transect J, Ubatuba bay, Jan. 2002.

Sample	Date	Volume (L)	Latitude	Longitude	Distance from shore (km)	Salinity (psu)	Temperature (°C)
J-1	25/Jan/02	196	S23°31.874	W45°09.898	30	35.728	25.0
J-2	25/Jan/02	196	S23°37.426	W44°55.658	25	35.550	26.0
J-3	25/Jan/02	196	S23°35.073	W44°57.099	20	35.368	26.0
J-4	25/Jan/02	196	S23°32.521	W44°58.186	15	35.526	26.0
J-5	25/Jan/02	196	S23°30.453	W44°59.618	11	35.653	26.0
J-6	25/Jan/02	196	S23°28.842	W44°59.618	8	35.581	26.0
J-7	25/Jan/02	196	S23°27.399	W45°00.448	5	35.339	26.0
J-8	25/Jan/02	196	S23°26.545	W45°01.128	3	35.667	26.0
J-9	25/Jan/02	196	S23°25.201	W45°02.246	1	35.752	26.0

TABLE 6. Concentration of the natural Ra isotopes, $^{223}\text{Ra}/^{224}\text{Ra}$, ^{224}Ra , and $^{225}\text{Ra}/^{226}\text{Ra}$ activity ratios and nutrients determined in the samples from Transect J.

Sample	^{223}Ra mBq 100 L ⁻¹	$^{224}\text{Ra}/^{223}\text{Ra}$	^{226}Ra mBq 100 L ⁻¹	^{225}Ra mBq 100 L ⁻¹	^{223}Ra mBq 100 L ⁻¹	$^{224}\text{Ra}/^{226}\text{Ra}$	^{228}Ra mBq 100 L ⁻¹	^{232}Th mBq 100 L ⁻¹	Nitrate $\mu\text{mol L}^{-1}$	Nitrite $\mu\text{mol L}^{-1}$	Silicate $\mu\text{mol L}^{-1}$	Phosphate $\mu\text{mol L}^{-1}$
J-1	5.5	0.24	151	160	1.1	1.1	2.0	0.166	0.040	2.03	0.28	
J-2	9.7	0.18	158	235	1.5	1.5	7.7	0.134	0.098	3.43	0.59	
J-3	11	0.11	149	271	1.8	1.8	15	0.176	0.098	5.55	0.66	
J-4	19	0.15	158	298	1.9	1.9	12	0.587	0.108	10.87	0.67	
J-5	13	0.12	159	221	1.4	1.4	6.0	0.539	0.067	4.01	0.36	
J-6	11	0.14	148	234	1.6	1.6	8.2	0.070	0.058	2.42	0.46	
J-7	16	0.16	187	109	0.6	0.6	6.0	0.383	0.029	2.60	0.35	
J-8	10	0.10	148	256	1.7	1.7	8.0	0.038	0.058	4.00	0.57	
J-9	16	0.46	-	-	-	-	7.0	0.353	0.115	0.40	0.90	

TABLE 7. Location of the groundwater and river samples from Ubatuba region, Jan. 2002.

Sample	Date	Volume (L)	Latitude	Longitude	Salinity (psu)
P-1	24/Jan/02	20	S23°29.952	W45°07.093	0.75
P-2	24/Jan/02	20	S23°31.893	W45°09.891	0.079
P-3	24/Jan/02	20	S23°31.886	W45°09.873	0.060
P-4	24/Jan/02	20	S23°31.872	W45°09.901	0.059
PM-01	24/Jan/02	8	S23°30.009	W45°07.113	-
PM-03	24/Jan/02	15	S23°30.008	W45°07.105	-
PM-04	25/Jan/02	8	S23°30.013	W45°07.095	-
PM-05	25/Jan/02	10	S23°30.018	W45°07.085	-
PM-06	24/Jan/02	8	S23°29.999	W45°07.107	-
PM-08	25/Jan/02	10	S23°30.007	W45°07.093	-
PM-09	25/Jan/02	8	S23°30.012	W45°07.084	-
Escuro River	26/Jan/02	40	S23°29.466	W45°09.830	30.6

TABLE 8. Concentration of the natural Ra isotopes, Ra^{223}/Ra^{224} and Ra^{223}/Ra^{226} activity ratios and nutrients determined in groundwater and river samples from Ubatuba region.

Sample	^{223}Ra mBq 100 L ⁻¹	^{224}Ra mBq 100 L ⁻¹	$^{223}Ra/^{224}Ra$	^{226}Ra mBq 100 L ⁻¹	^{228}Ra mBq 100 L ⁻¹	$^{226}Ra/^{228}Ra$	$^{223}Ra/^{226}Ra$	^{228}Th mBq 100 L ⁻¹	Nitrate $\mu mol L^{-1}$	Nitrite $\mu mol L^{-1}$	Silicate $\mu mol L^{-1}$	Phosphate $\mu mol L^{-1}$
P-1	16	609	0.03	224	-	-	21	146	13	57.5	0.57	
P-2	58	1,561	0.04	314	-	-	63	12.9	11	12.1	0.42	
P-3	36	334	0.11	168	-	-	27	90	11	7.1	0.61	
P-4	13	801	0.02	-	-	-	32	-	-	-	0.20	
PM-01	19	1,211	0.02	479	-	-	70	-	-	-	-	
PM-03	931	16,244	0.06	242	14,533	60	433	96	8	9.6	0.25	
PM-04	1,408	72,540	0.02	1,192	35,688	30	1451	16.4	14	54.7	1.63	
PM-05	525	34,659	0.02	2,722	23,995	8.8	826	-	-	-	-	
PM-06	59	2,821	0.02	-	-	-	238	-	-	-	-	
PM-08	2,033	35,405	0.06	933	15,398	17	624	-	-	-	-	
PM-09	473	38,009	0.01	1,035	21,167	20	666	-	-	-	-	
Rio Escurto	46	954	0.05	229	745	3.3	27	50.2	0.57	-	-	

The ^{226}Ra distribution in surface seawater samples from Transect B showed a narrow range along the coast. Since the half-life of ^{226}Ra (1.620 y) is comparable to the mean ocean circulation time established from 750 a 1000 years (Broecker & Peng, 1982), the ^{226}Ra should be very well mixed in seawater (uniform concentrations along the coast). Deviation of this behavior is expected to occur only close to the margins or the bottom (in this case one positive ^{226}Ra signal could be used to identify a groundwater input). In the case of ^{228}Ra , as it has the half-life of 5.7 years, the activities are higher close to the margins, decreasing with distance from shore.

In coastal areas the short-lived Ra isotopes, ^{223}Ra and ^{224}Ra , are flushed from the sediments and are regenerated from their thorium parents in sediments on a time scale of days. This provides a continuous source of ^{223}Ra and ^{224}Ra activity to the overlying seawater that is not accompanied by large additional ^{226}Ra and ^{228}Ra , which are regenerated more slowly. Groundwater discharge directly into sea water may also provide significant additions of Ra activity to the estuaries and ocean shelf bottom water (Moore, 1996; Rama & Moore, 1996).

Fig. 3 shows the distribution of ^{224}Ra in excess vs. ^{223}Ra along the Transect B. This horizontal profile was sampled from the surroundings of Mar Virado Island until 30 km offshore (see Fig. 2). This results demonstrate clearly the influence of a second water mass entering the coastal area during the studied period (Fig. 5-9).

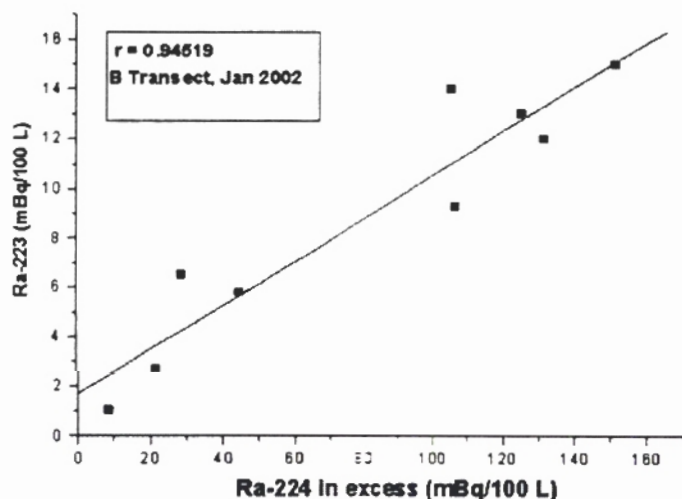


FIGURE 3. ^{224}Ra in excess vs. ^{223}Ra observed in Transect B.

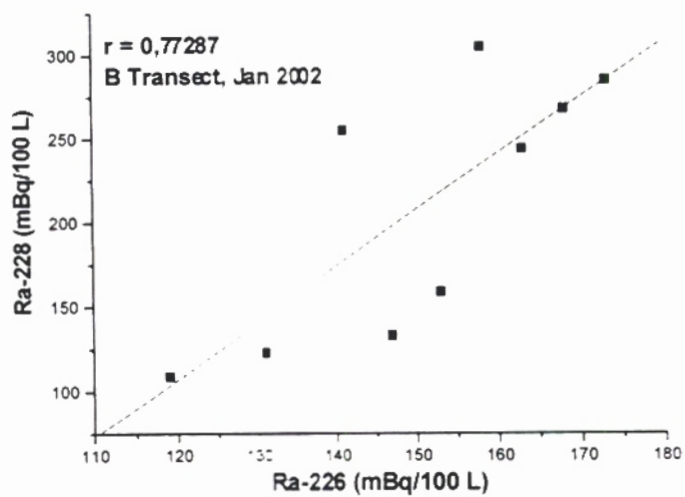


FIGURE 4. Concentrations of ^{226}Ra vs. ^{228}Ra observed in Transect B.

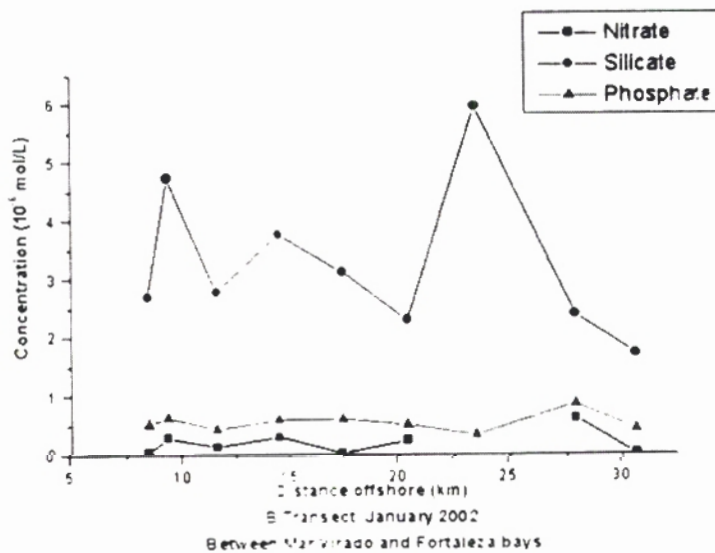


FIGURE 5. Distribution of nutrients along the coast, Transect B.

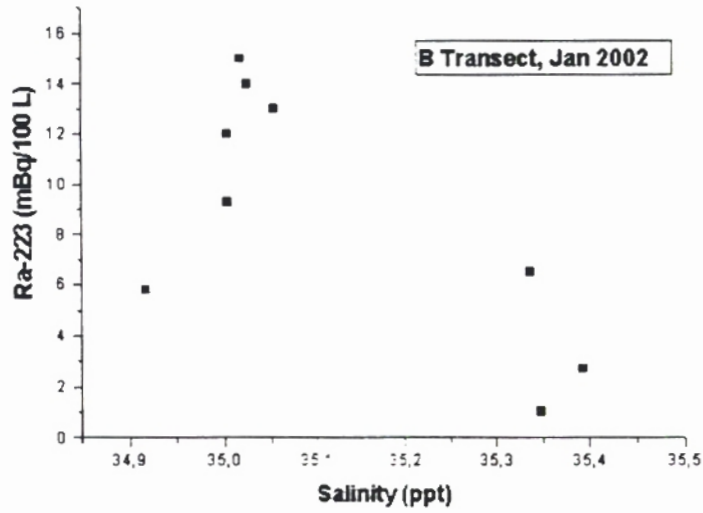


FIGURE 6. A plot of salinity vs. concentration of ^{223}Ra , Transect B.

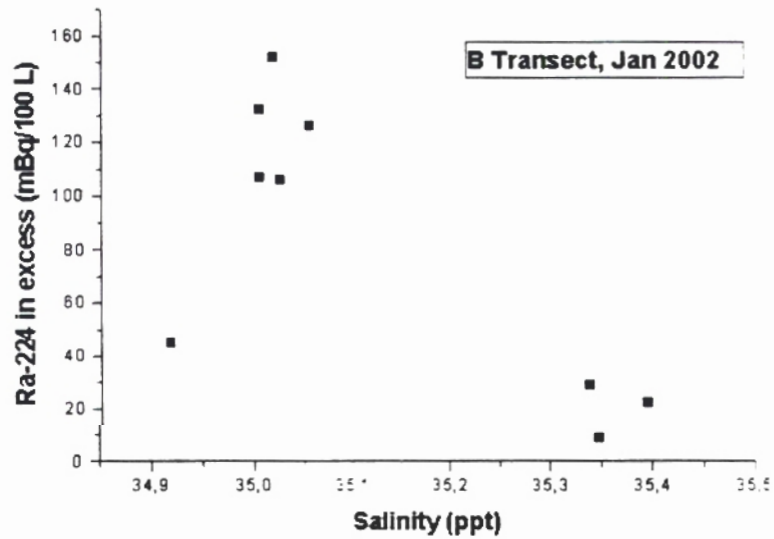


FIGURE 7. A plot of salinity vs. concentration of ^{224}Ra in excess, Transect B.

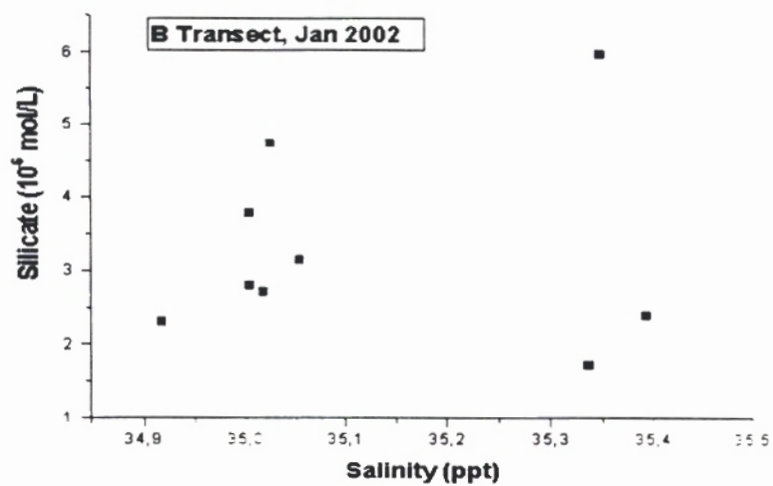


FIGURE 8. A plot of salinity vs. silicate, Transect B.

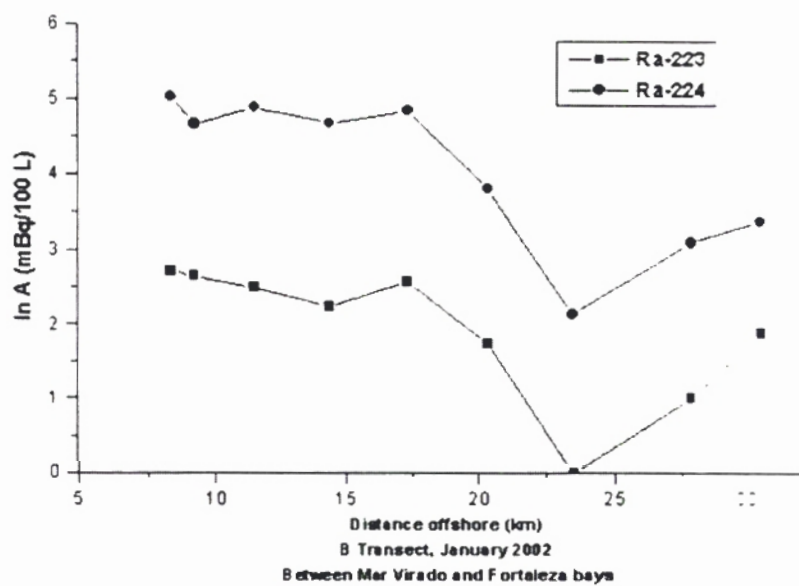


FIGURE 9. The distribution of $\text{In } ^{223}\text{Ra}$ and $\text{In } ^{224}\text{Ra}$ in excess along the coast, Transect B.

As it was presented in **Fig. 3**, there is a strong correlation between the short-lived Ra isotopes in Transect B ($r = 0.94519$). However, the same pattern was not observed for all the samples in a correlation plot of ^{225}Ra vs. ^{226}Ra ($r = 0.77287$) presented in **Fig. 4**.

Regarding the nutrients, it was found increased silicate concentrations in surface seawater around 25 km offshore (**Fig. 5**), which can indicate upwelling of a bottom water mass or submarine groundwater discharge. Although, nitrate and phosphate concentrations measured are comparable to the values usually found in Ubatuba region, classified as oligo-mesotrophic following to the content of (N-P) available to the marine ecosystem productivity (Braga & Muller, 1998). It was not observed any anomalous nitrate concentration in the Transect B samples, which would indicate infiltration of groundwater contaminated by domestic sewage.

It is very well known that occasionally, the upwelling of SACW can bring nutrients for the local embayments of Ubatuba. Thus, the silicate signal noticed at 25 km offshore can be with great probability due to the passage of SACW close to the coast during the summer.

Fig. 9 shows the distribution of $\ln^{223}\text{Ra}$ and $\ln^{224}\text{Ra}$ in excess vs. distance from shore. Theoretically, these concentrations should decrease exponentially with distance offshore. However, it was observed a slight increase of ^{224}Ra and ^{223}Ra activities after 25 km. This fact demonstrates again the presence of a second water mass with distinct characteristics, which could be attributable to SACW upwelling or the circulation pattern of the studied embayments or groundwater discharge. In this case, the existence of an anti-clockwise eddy in opposition to the passage of ocean currents parallel to the coast could carry more fast the short-lived Ra isotopes to this location. The distribution of $\ln^{226}\text{Ra}$ and $\ln^{228}\text{Ra}$ along the coast for Transect B is presented in **Fig. 10**.

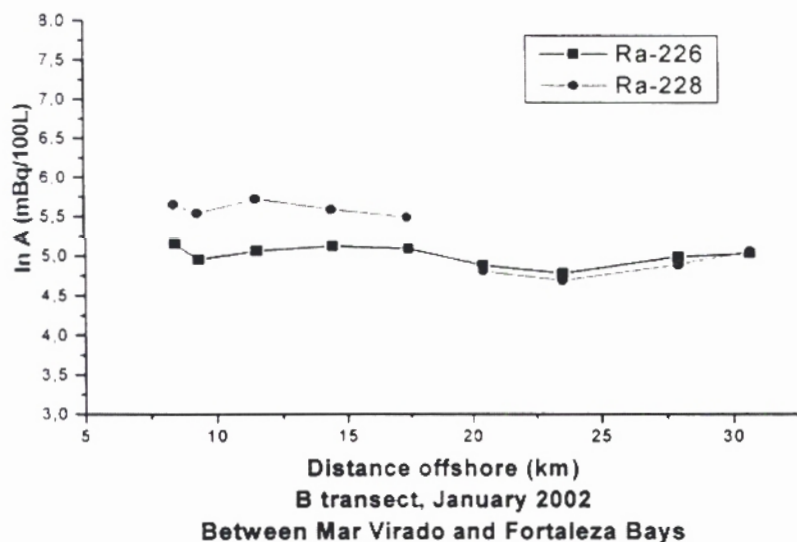


FIGURE 10. The distribution of $\ln^{226}\text{Ra}$ and $\ln^{228}\text{Ra}$ along the coast, Transect B.

The ^{228}Th measurements reveal a marked deficiency of ^{223}Th relative to its parent, ^{228}Ra . This indicates the rapid removal of Th from the water column.

Considering the results obtained in the summer 2002, the exchange time of the surface water masses inside Flamengo, Fortaleza and Mar Virado embayments were estimated using the activity concentrations of ^{223}Ra and ^{224}Ra (small A transects). Apparent ages calculated by this method reflect the time elapsed since the water sample became enriched in Ra and was isolated from the source. This calculations assumed that 100% of the initial concentration of the Ra isotope present in the sediments in the near shore region was transferred to the seawater (end-member fraction=1).

The exchange time obtained using the ^{223}Ra activities were 29.4 days for Flamengo Bay, 18.8 days for Fortaleza Bay and 19.7 days for Mar Virado Bay. Taking into account the ^{224}Ra activities, these apparent ages were respectively: 19.9 days for Flamengo, 7.3 days for Fortaleza and 8.5 days for Mar Virado. However, it is recommended to use the ages determined from the ^{223}Ra profile across the shelf, since the lowest half-life of 3.6 days for ^{224}Ra may be less convenient for this purposes.

The water exchange time in Flamengo Bay was verified using the activities of ^{223}Ra normalized to ^{228}Ra activities to correct for mixing, because its half life is long with respect to the mixing time of near shore waters. This final calculation resulted in an exchange time of 19.4 days for Flamengo Bay. This ages imply that exchange times of the coastal waters across the bays are rapid, of the order of 20 days during the period of investigation.

CONCLUSIONS

The application of the four naturally occurring Ra isotopes and an one-dimensional advection-diffusion model was shown as a tool to assist in the interpretation of coastal ocean circulation and biogeochemistry at Ubatuba region. Since they do not require steady-state conditions with respect to mixing, this isotopic technique can supply useful data which coupled with salinity or any other tracer distributions, provide powerful constraints to follow the circulation patterns and calculate fluxes of several dissolved materials to the ocean. Obviously, additional work during different conditions shall be carried out to estimate average exchange times and seasonal variations.

Once it was indicated and quantified in a previous research work, carried out in Ubatuba using ^{222}Rn as a tracer, that there is a significant inflow of subsurface fluids at rates in excess of several cm per day in the same embayments studied here (Oliveira *et al.*, 2003), we intend to use the Ra data set and the residence times obtained to perform a mass balance (integrating river and groundwater end-member concentrations) to quantify the groundwater input for the same area. This is a research in progress.

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