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Reconnaissance of submarine groundwater discharge at Ubatuba coast, Brazil, using ^{222}Rn as a natural tracer

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Abstract

Submarine groundwater discharge (SGD), which includes fresh groundwater and recycled seawater, has been recognized as a widespread phenomenon that can provide important chemical elements to the ocean. Several studies have demonstrated that SGD may approach or even exceed freshwater sources in supplying nutrients to coastal zones. This work reports preliminary results of a study carried out in a series of small embayments of Ubatuba, São Paulo State, Brazil, covering latitudes between 23°26′S and 23°46′S and longitudes between 45°02′W and 45°11′W. The main aims of this research were to set up an analytical method to assess ^{222}Rn and ^{226}Ra activities in seawater samples and to apply the excess ^{222}Rn inventories obtained to estimate SGD. Measurements made during the summer of 2001 included ^{222}Rn and ^{226}Ra in seawater, ^{226}Ra in sediment, seawater and sediment physical properties, nutrients and seepage rates. A continuous ^{222}Rn monitor was also used to determine in situ collection of data to study short-term changes at one location. All methods indicated significant inflow of subsurface fluids at rates in excess of several cm per day.

Keywords: ^{222}Rn and ^{226}Ra in seawater; Natural radionuclides as tracers of oceanographic processes; Submarine groundwater discharge; Brazil; Isotopes in the environment

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1. Introduction

Over the past decades, trace elements and isotopes have found widespread applications in oceanography. In most cases, through the application of reliable models, their use has led to a better understanding of many oceanic processes, like chemical inputs to the ocean, chemical fluxes through the water column, particulate-dissolved-matter exchanges and water mass circulation. Several studies have been conducted on the groundwater transport of trace elements in order to predict the behavior and the environmental impact of anthropogenic contaminants, since some naturally occurring U, Th and Ra isotopes can serve as analogues for radioactive pollutants (King et al., 1982; Osmond and Cowart, 1992; Osmond and Ivanovich, 1992). These isotopes have a wide range half-lives and their inter-relationships in the ^{238}U and ^{232}Th decay series can be used to constrain groundwater supply and removal rates over different time-scales.

Although not as obvious as river discharge, continental groundwater also discharges directly into the ocean. The discharge of groundwater is a relatively common phenomenon, occurring wherever an aquifer with a positive head is connected to overlying surface waters through permeable bottom sediments or fissures. The impact of groundwater discharge is expected to be greatest closer to shore, because discharge rates decrease exponentially with distance from shore. Submarine groundwater discharge (SGD), which includes recycled seawater as well as fresh groundwater, can provide chemical constituents to coastal zones, representing an important material flux pathway from land to sea in some regions (Johannes, 1980). It may influence the geochemical cycles of some major and minor elements either by the direct discharge of fresh groundwater into the sea or by chemical reactions that occur during the re-circulation of seawater through a coastal aquifer system (Burnett et al., 2001). Unfortunately, this source is often ignored in mass balances performed at nearshore environments, as it is still difficult to quantify the groundwater flow using traditional hydrologic methodologies.

At least in some cases, the SGD may be a pathway for diffuse pollution to coastal marine systems, where coastal aquifers become impacted by domestic effluents (septic systems and other releases) or other sources of pollution (Buddemeier, 1996; Rutkowski et al., 1999). The groundwater flow through coastal marine sediments may be both volumetrically and chemically important (Burnett et al., 2001). Estimates of global SGD vary widely; some estimates are as high as 10% of the river flow, while most are considerably lower. The SGD fluxes also change with time, due to natural, seasonal and anthropogenic variations in the source functions, such as sea level, tides, rain, permeability, porosity of the bottom sediments or dredging activities.

Three basic approaches have been used to estimate SGD inputs to coastal marine systems:

1. Hydrologic modeling, including simple water balance calculations;
2. Direct measurements, basically restricted to seepage meters; and
3. Tracing techniques, using either natural or artificial species.

Natural radionuclides from ^{238}U and ^{232}Th decay series are increasingly being used

to evaluate groundwater inputs to the ocean (Cable et al., 1996; Corbett et al., 2000; Moore, 1996; Moore, 1998; Moore and Shaw, 1998; Moore, 1999; Rama and Moore, 1996). Geochemical tracers, like ^{222}Rn and ^{226}Ra, when measured in coastal ocean waters, are advantageous for regional-scale assessments of SGD, because their signals represent values integrated through the water column. These radionuclides are enriched in groundwater compared to seawater, can be measured at very low concentrations and are conservative. In applying geochemical tracing techniques, several parameters must be assessed or defined, including boundary conditions (i.e., area, volume), water and constituent sources and sinks, residence times of the surface water body, and end-member concentrations of the tracer. Sources or end-members may include ocean water, river water, groundwater, precipitation, in situ production, horizontal water column transport, sediment mixing and resuspension, or diffusion from bottom sediments. Sinks may include in situ decay, horizontal water column transport, horizontal or vertical eddy diffusivity, and atmospheric evasion. Through simple mass balances or box models incorporating both sediment advection and water column transport, the geochemical approach represents a sensitive pathfinder to assess SGD.

The ^{222}Rn levels usually found in groundwater are 3–4 orders of magnitude higher than those radon levels observed in seawater. Besides that, ^{222}Rn is a natural short-lived radioisotope ($t_{1/2}$ = 3.83 days) that is chemically inert and may be easily measured. The radon tracing method is an excellent qualitative tool for identifying areas of spring or seepage inputs in most coastal environments. It can also be a good quantitative tool in shallow marine environments characterized by large amounts of SGD (including recirculated seawater) under certain conditions. The approach is particularly sensitive for inner shelf environments when a strong pycnocline is present, as this greatly inhibits radon loss.

The main purpose of this research is the application of excess ^{222}Rn inventories to estimate SGD in a series of small embayments of Ubatuba, São Paulo State, Brazil, covering latitudes between 23°26'S and 23°46'S and longitudes between 45°02'W and 45°11'W. The study area comprises the northernmost part of São Paulo Bight, southeastern Brazil, and is considered a tropical coastal area. 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).

The Ubatuba coastal area was originally known to be oligo-meso-trophic, because the primary production was limited by the lack of inorganic compounds of nitrogen and phosphorus (Braga and 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 limits the local primary production. Occasionally, intrusions of nutrient and oxygen-rich South Atlantic Central Water (SACW) from the open ocean thermocline may reach the shelf edge, and may be further transferred by coastal upwelling, providing a third source of nutrients for primary production.

However, as a cultural symptom of demographic expansion of the Brazilian coastline, waste disposal, domestic and industrial releases, infiltration of septic plumes through the coastline and uncontrolled management of the watersheds, have been

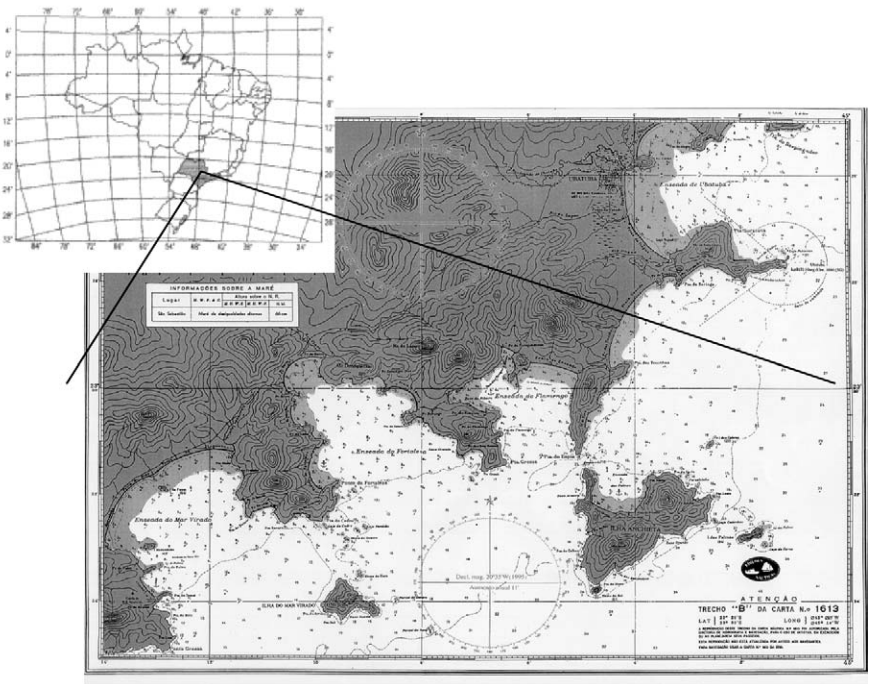

Fig. 1. Location of the four embayments studied at Ubatuba coastal area: Flamengo Bay, Fortaleza Bay, Mar Virado Bay and Ubatuba Bay. Ubatuba County is located around 270 km north from São Paulo city, southeast Brazil.

affecting these coastal environments, particularly increasing the nitrogen concentrations observed in nearshore waters from restricted bays and sounds. Excess nutrient inputs to the embayments of the region via groundwater discharge may be responsible for the increased turbidity recently observed in these waters. For all these reasons, assessments of SGD inputs are necessary for the future management of these bays.

To our knowledge, the quantification of SGD in Brazilian coastal areas is completely undocumented. Even if SGD fluxes at Ubatuba coastal area were modest, pollutant concentrations in groundwater may be sufficiently high (mostly in summer season, when anthropogenic nitrogen fluxes rise) to have an important impact on the fate of contaminants delivered to the local embayments.

2. Scenario

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 1000 meters), which reaches the shore in almost all of the study area, and limits the extension of the drainage systems and of the 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 with the passage of cold fronts over the area and are the most important in terms of the 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 the fact that they can all be considered enclosed bays. The terrestrial input of sediments is strongly dependent on the rainfall regime, leading to a higher contribution of sediments during the 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 1803 mm, the maximum rainfall rates being observed in February. Sea level varies from 0.5 to 1.5 m, the highest values occurring in August/September due to greater volume of warm waters of the Brazil Current (Mesquita, 1997).

3. Materials and methods

The assessment of SGD using ^{222}Rn as a tracer includes:

1. Measurement of the ‘excess’ (unsupported by ^{226}Ra) ^{222}Rn inventory in water column;
2. Identification of any ^{222}Rn sources and sinks in the system studied;
3. Determination of the total input flux of ^{222}Rn to balance the measured inventories, including corrections for atmospheric losses; and
4. Calculation of the advective transport required to account for the estimated total input flux.

The main aim of our initial research was to set up the analytical methodologies to assess ^{222}Rn and Ra isotopes activities in seawater samples and to apply the excess ^{222}Rn and ^{226}Ra inventories obtained to estimate SGD. Measurements made until now included ^{222}Rn and Ra isotopes in seawater, ^{226}Ra in sediment, seawater and sediment physical properties, nutrients and seepage rates via standard seepage meters. The development of this project is offering an opportunity to better understand groundwater–seawater interactions, the input of pollutants from septic systems and other sources, and will allow regional assessment of subsurface fluid flow.

Seawater samples were collected at the center of Ubatuba embayments in four top-to-bottom vertical profiles, in February 2001. The embayments studied at Ubatuba coastal areas are shown in Fig. 1: Flamengo Bay, Fortaleza Bay, Mar Virado Bay and Ubatuba Bay. Temperature and salinity profiles (Fig. 2) were obtained at the same stations using a Micro CTD, from Falmouth Scientific Inc. We collected seawater samples for radon analyses at 1–2 m depth intervals using a peristaltic pump and 4 L evacuated glass bottles. Seawater was purged for 5 min from the hose at each depth prior to filling the sampling bottles, and they were immediately sealed to prevent radon losses. ^{222}Rn was extracted and counted using a modified emanation technique (Cable et al., 1996) described by Mathieu et al. (1988). Once extracted, the radon gas was collected in a liquid nitrogen cold trap and transferred from the trap to an alpha scintillation cell. After radon stripping and transfer into alpha scintillation cells, samples were stored for 3 h to allow ^{222}Rn daughters, ^{218}Po and ^{214}Po to equilibrate and counting was performed using a portable radon monitor RDA-

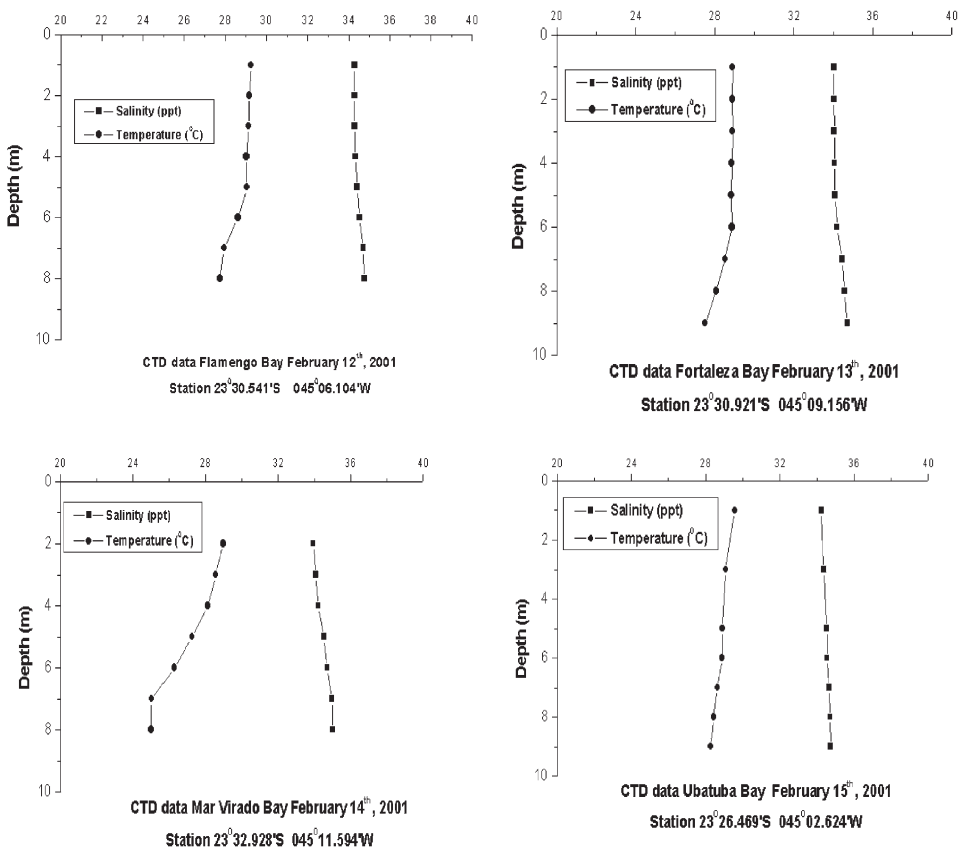

Fig. 2. Seawater temperature, salinity, depth profiles for Flamengo Bay (Ubatuba Marine Lab site), Fortaleza Bay, Mar Virado Bay and Ubatuba Bay.

200, from Scintrex. From the initial radon analysis, the samples were sealed and stored for at least five days for ^{222}Rn ingrowth and then sparged again in order to determine the ^{226}Ra activity. Excess radon was determined as the difference between the total ^{222}Rn in samples and the supported ^{222}Rn, assumed to be equal to the ^{226}Ra activity. These values were decay-corrected back to the time of sampling in order to assess the in situ excess radon concentrations. The following expressions (Eq. 1 and 2) were used to calculate the total ^{222}Rn activity concentration and the ^{222}Rn activity concentration supported by ^{226}Ra:

$$A\,{}^{222}_{Total}Rn = \frac{C-Bg}{3.E.V} x \frac{1}{e^{-\lambda t_1}} x \frac{\lambda t_2}{1-e^{-\lambda t_2}}. \quad (1)$$

Where:

- C: counting rate of the alpha scintillation cell, 3 h after the end of the degassing procedure (cpm)

$$A^{226}Ra = \frac{C-Bg}{3.E.V} x \frac{1}{(1-e^{-\lambda t_1})\,(e^{-\lambda t_2})} x \frac{\lambda t_3}{1-e^{-\lambda t_3}}; \quad (2)$$

- Bg: background count rate of the alpha scintillation cell on the portable monitor RDA-200, prior to the radon emanation (cpm);
- E: overall radon extraction efficiency (cpm dpm^{-1});
- V: sample volume (L);
- λ: radioactive decay constant of ^{222}Rn (1.235×10^{-4} min^{-1});
- t_1, t_2, t_3: time between the sample flushing and the beginning of sample counting, ^{222}Rn ingrowth correction, and counting time, respectively (min);
- A_{Total} ^{222}Rn: total activity concentration of ^{222}Rn (dpm L^{-1}); and
- A^{226}Ra: activity concentration of ^{222}Rn supported by ^{226}Ra (dpm L^{-1}).

The calibration of the degassing emanation system was performed using ^{226}Ra standard solution and blanks, in order to determine the extraction efficiencies, the precision, the accuracy, and the lower limits of the detection. Total extraction efficiencies were determined by repetitive measurement of several ^{226}Ra reference solutions. Precision of these results ranged from 6 to 13%. Lower limits of detection (estimated at 0.47 dpm L^{-1}) were evaluated by measurement of ^{226}Ra-free deionized water (purified by processing through MnO_2-coated fiber to extract radium).

Once the concentrations have been determined, usually as a complete profile through the water column, the corresponding inventories were calculated by integrating the excess radon concentrations over water depth (Fig. 3).

In each profile, samples for the determination of phosphate, silicate, ammonium and nitrate were also collected. Water samples were frozen until the time of analysis. The analytical procedures adopted for these determinations were vanadium reduction followed by chemiluminescence detection of NOx for nitrate-nitrite, phenate method for ammonia and ascorbic acid method for phosphate. Fig. 4 shows the nutrient vertical profiles obtained at the four embayments studied in this work.

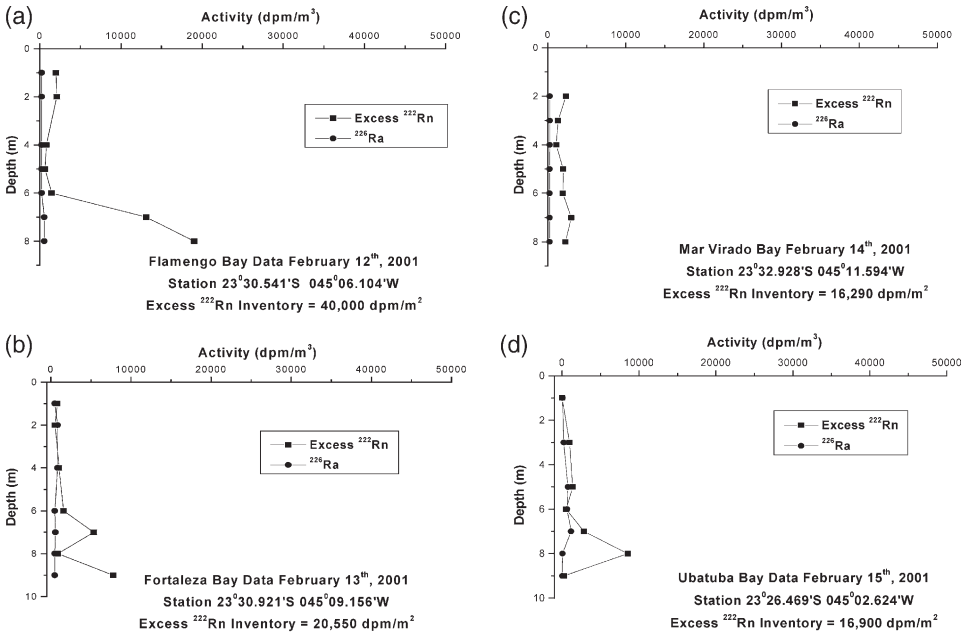

Fig. 3. Representative water column profiles at the four Ubatuba coastal embayments studied in this work. The activity concentrations of excess ^{222}Rn are represented by black squares and ^{226}Ra by red circles.

Bottom sediment grab samples were also obtained at each site in order to assess potential diffusive fluxes of ^{222}Rn from sediments. Diffusion of ^{222}Rn from bottom sediments into the overlying seawater may be an important source of radon and must be evaluated as part of an overall radon budget. These diffusive ^{222}Rn fluxes will be obtained using a sediment equilibration technique described by Martens et al. (1980).

The response of seepage meters was evaluated near the coastline at Flamengo Bay. Six standard seepage meters were set up in two transects (A and B), perpendicular to the shoreline. The meters consisted of open-bottom chambers (0.25 m^2) implanted in bottom sediments. These chambers had an open port where a plastic bag was attached to collect seepage over measured time intervals. Direct measurement of groundwater seepage was done using 1000 mL pre-filled plastic bags. The volume in the collection bags was converted to a seepage flux, as the sampling time intervals and seepage area were known. Fig. 5 shows seepage rates results from time-series measurements carried out in the two transects.

Nearshore ^{222}Rn concentrations in the air and in the seawater were also assessed at Flamengo Bay using two continuous ^{222}Rn monitors (RAD-7, Durrigde Company). This equipment was used to collect in situ data during a one-week period, to study short-term changes. The results from six days of continuous radon measurements of coastal seawater from Flamengo Bay Marine Laboratory site are shown in Fig. 6.

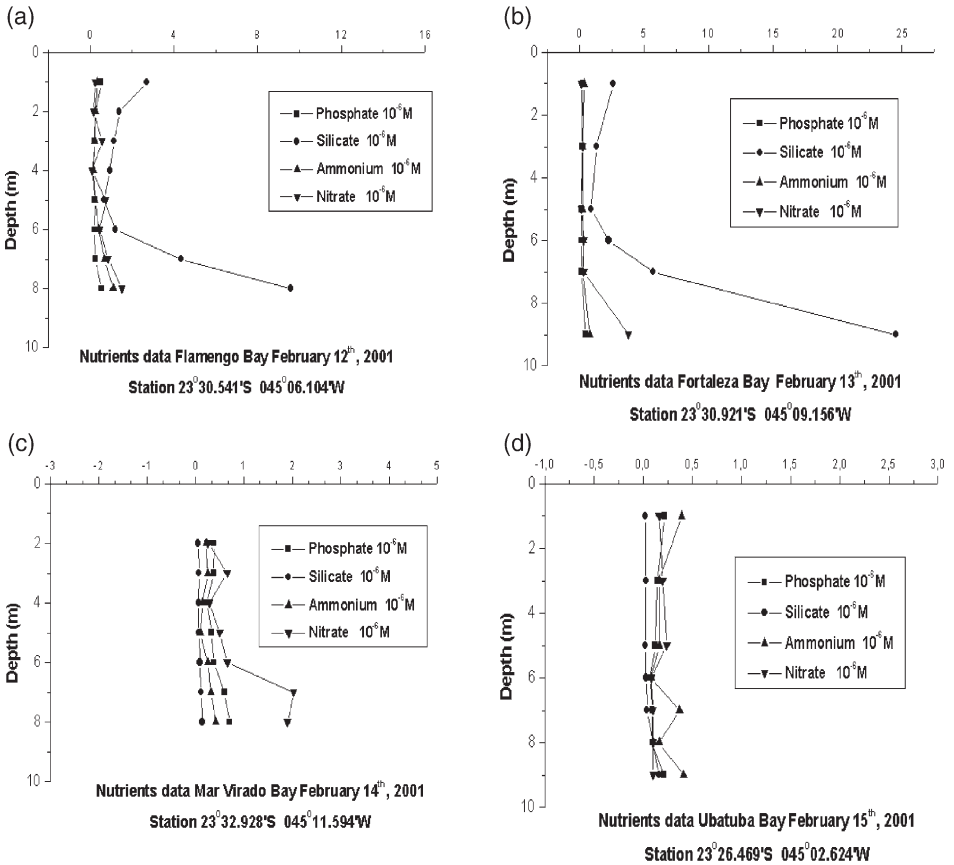

Fig. 4. Representative nutrient water column profiles at the four embayments studied at Ubatuba region: concentrations (10^{-6} mol L^{-1}) of phosphate are represented by black squares, silicate by red circles, ammoniun by green triangles and nitrate by blue triangles.

4. Results and discussion

The total flux of radon required to support the inventory measured in the system can be estimated by the following equation (Eq. 3):

$$J = \frac{I}{(1 - e^{-\lambda t}/\lambda)}. \tag{3}$$

Where J=the total flux of ^{222}Rn (dpm m^{-2} d^{-1}); I=inventory (dpm m^{-2}), and λ=the decay constant of ^{222}Rn (0.181 d^{-1}). At high values of t (several half-lives of ^{222}Rn), this equation reduces to the inventory divided by 5.5-day mean life $[I/(1/\lambda)]$ or simply the inventory multiplied by the decay constant, $I\lambda$. This calculation thus assumes a steady-state situation on a time scale of weeks. This condition have been

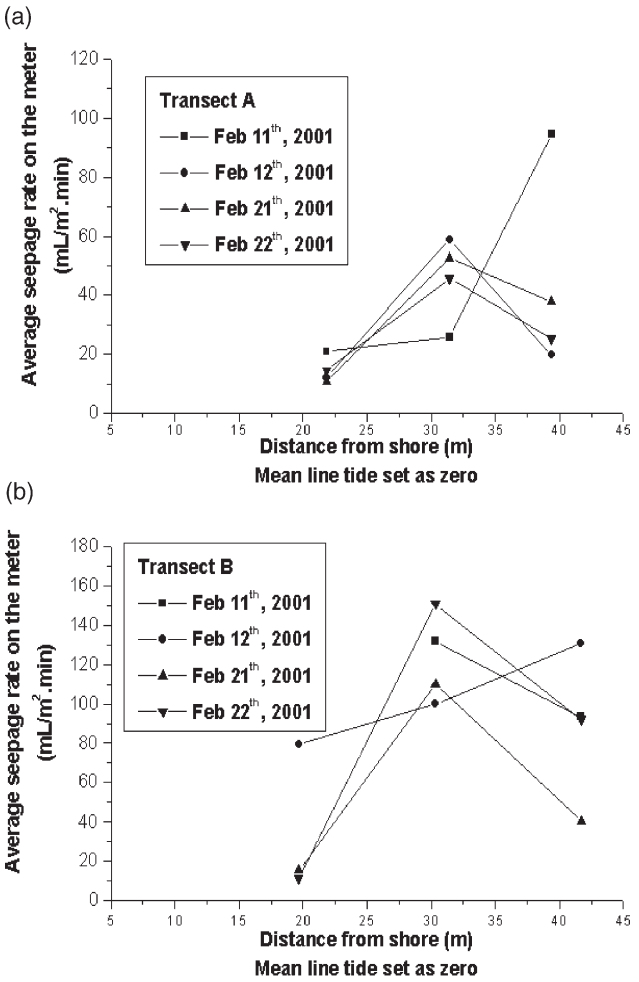

Fig. 5. Transect A (a) and transect B (b) seepage rates vs distance from shore (m) at Flamengo Bay, Marine Laboratory, Ubatuba, measured with six manual seepage meters deployed perpendicular to the shoreline. Four liter plastic bags, pre-filled with one liter of seawater were used for all measurements.

observed in coastal environments in Florida (Corbett et al., 2000). The main loss from the measured ^{222}Rn inventory will typically be that due to atmospheric evasion.

With this estimate of the required total benthic flux of radon, calculations can be made of the advective component required by using an advection-diffusion equation (Eq. 4):

$$\frac{dC}{dt} = K_z\frac{\partial^2 C}{\partial z^2} + \omega\frac{\partial C}{\partial z} + P + \lambda C. \quad (4)$$

Where C is the radon concentration (activity) in the sediments; z is the depth positive

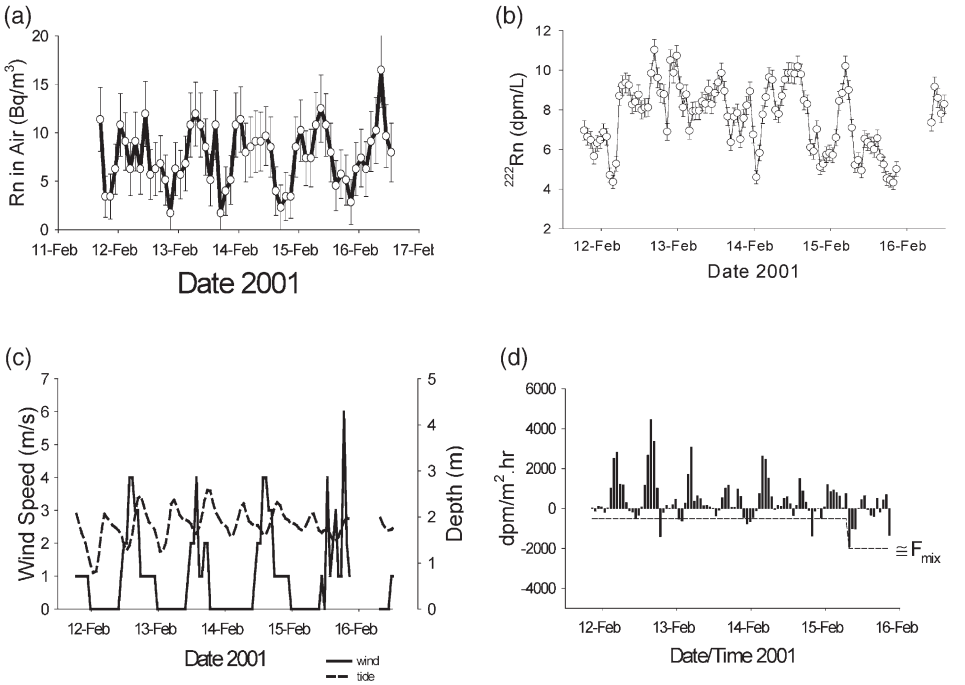

Fig. 6. Results from six days of continuous RAD-7 radon measurements of coastal seawater and air collected at Flamengo Bay Marine Laboratory site. The plot on the left top presents the ^{222}Rn activity concentrations measured in the air during the monitoring period of this experiment, while the plot on the right top shows the ^{222}Rn activity concentrations found in seawater. The plot on the left bottom shows the wind speed measurements, represented by the green line and the tide flutuations, represented by the blue dashed line. The bar plot presented on the right bottom shows the calculated ^{222}Rn fluxes into the seawater during the period of study, where the blue dashed line represents the estimated losses of radon by mixing with lower concentration waters offshore.

downwards, Kz is the vertical diffusivity; $\partial^2 C/\partial z^2$ and $\partial C/\partial z$ are the ^{222}Rn concentration gradients across the sediment-water interface for diffusion and advection, respectively; ω is the vertical advective velocity; P is the production of ^{222}Rn in pore fluids which is due to recoil after production by ^{226}Ra decay in mineral grains ($P = \lambda$Ceq, where Ceq is the activity of ^{222}Rn in equilibrium with wet sediment determined experimentaly, dpm m^{-3} wet sediment); and λC is radioactive decay of ^{222}Rn. In this situation, Kz is set equivalent to Ds, the effective wet sediment diffusion coefficient which is corrected for temperature and sediment tortuosity. Advection, ω, and radioactive decay, λ, represent losses from the sediments and are thus defined as negative terms. The solution of Eq. (4) may be represented by the following:

$$Cbent = \frac{(Co-Ceq)\left(e^{\frac{z}{2z*}}\right)\sinh\left(\frac{A(zeq-z)}{2z*}\right)}{\sinh\left(\frac{Azeq}{2z*}\right)}. \quad (5)$$

Where *Co* is the radon activity (dpm m^{-3}) in the overlying water, at the sediment-water interface, multiplied by the sediment porosity to obtain a value corresponding to the ^{222}Rn in wet sediment (dpm m^{-3}); *zeq* is a depth in the sediments much deeper than the depth where Ceq initially occurs; $z*$ is a one-dimensional mixing parameter described by Ds/ω; and $A = [1 + 4z*(\lambda/\omega)]^{0.5}$, which includes radioactive decay and advection (Corbett et al., 2000). When advection of the fluids through sediments is considered, information regarding the radon concentration associated with the subsurface fluids is necessary to estimate accurately the fluid flux across the sediment-water interface. Thus, the estimate of the extent of the water flux through sediments into the overlying water depends critically upon the evaluation of the ^{222}Rn activity in these fluids. If SGD is thought to occur mainly via slow seepage through sediments, a process typically measured at rates on the order of cm d^{-1}, then a reasonable estimate of the fluid radon concentration may be made from the sediment equilibration approach or from pore water measurements. If more rapid entry points to the sea floor, such as submarine springs, are present than expected radon activities in the discharging fluids would more likely be similar to those measured in groundwaters from the coastal aquifer.

The potential diffusive fluxes of ^{222}Rn from sediments at each station were obtained using the same emanation methodology described previously. In these calculations, corrections for sediment porosity and tortuosity were made. These diffusive ^{222}Rn fluxes are presented in Table 1.

Considering the results obtained in the four vertical profiles established, the excess ^{222}Rn inventories were estimated for the embayments studied. These data are shown in Table 2. Table 2 also presents the total ^{222}Rn fluxes required to support inventories measured (calculated by Eq. (3)) and the groundwater advective velocity rates to balance the sub-pycnocline fluxes (assessed using Eq. (4)) in Ubatuba embayments.

The highest ^{222}Rn in excess inventories were observed both in Flamengo (40,000 dpm m^{-2}) and Fortaleza (20,550 dpm m^{-2}) embayments. However, the corresponding advective velocity rate of groundwater obtained for Fortaleza Bay was slightly higher than to that one observed at Flamengo Bay, since this parameter is function of the bottom sediment porosity. The groundwater advective velocity rates calculated for Ubatuba embayments varied from 2.1 to 4.8 cm day^{-1}. To evaluate the order of

Table 1
Activity of ^{222}Rn in equilibrium with wet sediment determined experimentaly, (dpm m^{-3} wet sediment) (Ceq), and radon activity in the overlying water (dpm m^{-3}), at the sediment-water interface, multiplied by the sediment porosity to obtain a value corresponding to the ^{222}Rn in wet sediment (dpm m^{-3}) (Co), measured in the Ubatuba embayments sediment samples

Sediment sample	Ceq (dpm m^{-3})	Porosity	Co (dpm m^{-3})
Flamengo Bay	1.8×10^5	0.51	1.9×10^4
Fortaleza Bay	8.5×10^4	0.49	7.8×10^3
Mar Virado Bay	1.3×10^5	0.57	3.0×10^3
Ubatuba Bay	1.5×10^5	0.62	8.5×10^3
Ubatuba Marine Lab	9.9×10^5	0.41	8.5×10^3

Table 2
Excess ^{222}Rn inventories, total fluxes required to support inventories measured and groundwater advective rates necessary to balance the sub-pycnocline fluxes estimated in Ubatuba embayments (2001)

Vertical profile (depth)	Excess ^{222}Rn (I) (dpm m^{-2})	Excess ^{222}Rn flux (J) (dpm m^{-2} d^{-1})	SGD (ω) (cm d^{-1})
Flamengo Bay (9 m) S23°30.541'/W45°06.104'	40,000	7240	4.30
Fortaleza Bay (10 m) S23°30.921'/W45°09.156'	20,550	3720	4.84
Mar Virado Bay (9 m) S23°32.928'/W45°11.594'	16,290	2949	2.26
Ubatuba Bay (10 m) S23°26.469'/W45°02.624'	16,900	3058	2.09

magnitude of these fluxes, the results obtained in this work were compared to values reported for other authors in Florida. The SGD values found in Ubatuba embayments are three orders of magnitude lower than those estimated by Cable et al. (1996) in a study carried out in the northeastern Gulf of Mexico, covering an area of 620 km^2.

Increased silicate concentrations also were found in Flamengo Bay and Fortaleza Bay bottom waters (Fig. 4). Other authors have reported a strong correlation between increased silicate levels, Ba^{2+}, ^{226}Ra and groundwater discharge (Moore and Shaw, 1998; Moore, 1999).

Manual seepage meter measurements made during February 2001 in transects A and B (Ubatuba Marine Lab. Station), showed a flux interval varying from 10 to 150 mL m^{-2} min^{-1} (Fig. 5), which corresponds to 1.4–21.6 cm day^{-1}.

At the Ubatuba Marine Laboratory station (Flamengo Bay), two continuous radon monitors RAD-7 recorded the ^{222}Rn levels in the air and seawater from 12–17 Feb. 2001. A water level meter was also used to monitor depth variations caused by tidal change, so ^{222}Rn inventories could be assessed over this time. The continuous radon record was used to calculate rates of groundwater seepage by making allowances for losses due to atmospheric evasion and mixing with lower concentration waters. Assuming that the bentic fluxes of radon were driven mainly by groundwater (porewater) advection, we measured the radon concentration in the advecting fluids by sediment equilibration experiments and converted ^{222}Rn fluxes to water fluxes (Fig. 7). Our procedure for estimating groundwater fluxes from continuous radon measurements in the coastal zone may be summarized by the following steps: ^{222}Rn inventories were calculated for each hourly measurement by multiplying the excess ^{222}Rn activity (dpm m^{-3}) by the water depth (m)=(dpm m^{-2}). Excess ^{222}Rn (total ^{222}Rn minus ^{226}Ra) activities in the water column were estimated from spot measurements of ^{226}Ra using the Rn in-growth method. Inventories were corrected for atmospheric evasion losses during each measurement interval. The total flux across the air-water interface depends on the molecular diffusion produced by the concentration gradient across this interface and turbulent transfer, which is dependent on physical processes, primarily governed by wind speed. We used equations that relate gas

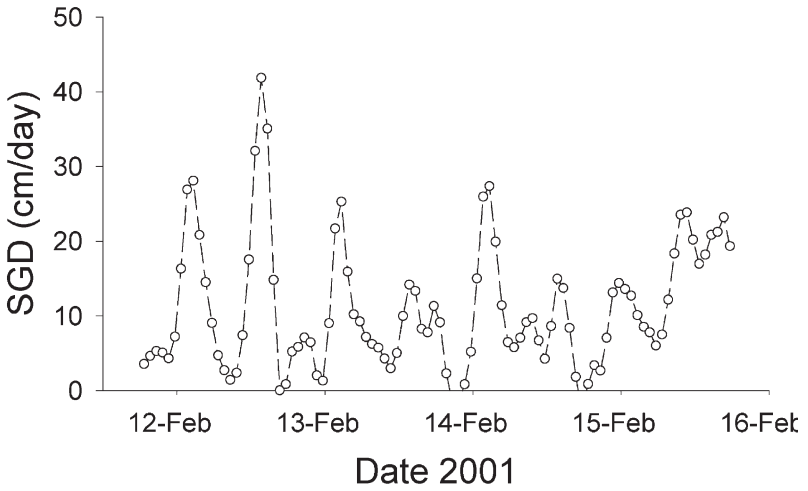

Fig. 7. Calculated SGD rates based on the continuous radon measurements.

exchange across the sea-air interface to the gradient in radon concentration, temperature, and wind speed (Cable et al., 1996). Net ^{222}Rn fluxes were determined by evaluating the change in inventories (dpm m^{-2}) over each time interval (1 h, in this case). These fluxes represent the observed fluxes of ^{222}Rn into the coastal water column with all necessary corrections including a conservative estimate for radon loss via mixing with lower concentration waters offshore. We thus feel that these estimated fluxes are minimum values, as higher mixing losses would have to be compensated for by higher inflow fluxes.

An overall mass balance (Fig. 8) for excess ^{222}Rn during the six-day period shows that the average water column ^{222}Rn inventory was 13,000 ± 4000 dpm m^{-2}. Evasion

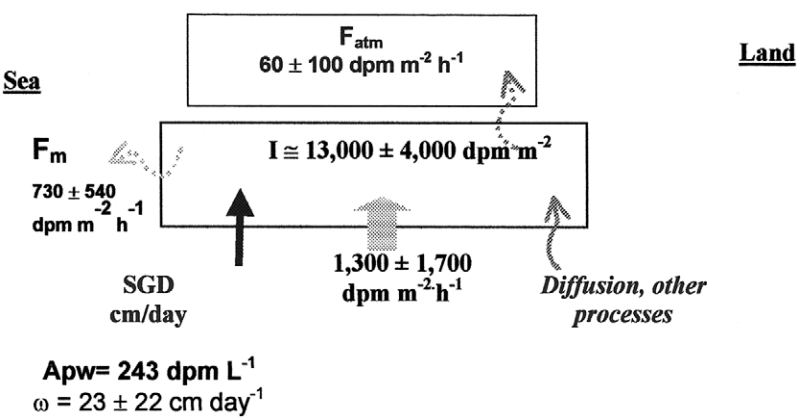

Fig. 8. Overall Rn balance at Ubatuba Marine Laboratory station (Flamengo Bay).

loss to the local atmosphere was, on average, 60 ± 100 dpm m^{-2} h^{-1} while the estimated mixing losses was 730 ± 540 dpm m^{-2} h^{-1}. The mean input fluxes (assumed to be due mainly to advection of pore waters) is 1300 ± 1700 dpm m^{-2} h^{-1}. All of these values have large standard deviations because the influx is apparently very dynamic, probably being heavily influenced by the tidal cycle (Fig. 7). The overall groundwater advective rate necessary to balance the excess ^{222}Rn inventory was estimated at 23 ± 22 cm day^{-1}. This value is in agreement with that interval estimated using the manual seepagemeters method.

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References

Braga, E.S., Muller, T.J., 1998. Observation of regeneration of nitrate, phosphate and silicate during upwelling off Ubatuba, Brazil, 23°S. Continental Shelf Research 18, 915–922.

Buddemeier, R.W., 1996. Groundwater discharge in the Coastal Zone: Proceedings of an International Symposium. LOICZ IGBP. LOICZ/R&S/ 86-8, iv+179 pp. LOICZ, Texel, The Netherlands.

Burnett, W.C., Kim, G., Lane-Smith, D., 2001. A continuous radon monitor for assessment of radon in coastal ocean waters. Journal of Radioanalytical and Nuclear Chemistry 249, 167–172.

Cable, J.E., Burnett, W.C., Chanton, J.P., Weatherly, G., 1996. Modeling groundwater flow into the ocean based on ^{222}Rn. Earth Planet. Sci. Lett 144, 591–604.

Castro Filho, B.M., Miranda, L.B., Miyao, S.Y., 1987. Hydrographic conditions in the continental shelf off Ubatuba: seasonal and medium scale changes. Boletim do Instituto Oceanográfico, São Paulo 35 (2), 135–151.

Corbett, D.R., Kump, L., Dillon, K., Burnett, W., Chanton, J., 2000. Fate of wastewater-borne nutrients in the subsurface of the Florida Keys, USA. Marine Chemistry 69, 99–115.

Johannes, R.E., 1980. The ecological significance of the submarine discharge of groundwater. Marine Ecology Progress Series 3, 365–373.

King, P.T., Michel, J., Moore, W.S., 1982. Groundwater geochemistry of ^{228}Ra, ^{226}Ra and ^{222}Rn. Geochim. Cosmochim. Acta 46, 1173–1182.

Mahiques, M.M., 1995. Sedimentary dynamics of the bays off Ubatuba, State of São Paulo. Boletim do Instituto Oceanográfico, São Paulo 43 (2), 111–122.

Martens, C.S., Kipphut, G.W., Klump, J.V., 1980. Sediment-water chemical exchange in the coastal zone traced by in situ ^{222}Rn flux measurements. Science 208, 285–288.

Mathieu, G.G., Lupton, R.A., Hammond, D.E., 1988. System for measurement of ^{222}Rn at low levels in natural waters. Health Phys 55 (6), 989–992.

Mesquita, A.R., 1997. Marés, circulação e nível do mar na Costa Sudeste do Brasil. Relatório Fundespa, São Paulo, Brazil.

Moore, W.S., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380, 612–614.

Moore, W.S., 1998. Application of ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra in coastal waters to assessing coastal mixing rates and groundwater discharge to oceans. Earth Planet. Sci 107 (4), 343–349.

Moore, W.S., Shaw, T.J., 1998. Chemical signals from submarine fluid advection onto continental shelf. J. Geophys. Res. Oceans 103, 21543–21552.

Moore, W.S., 1999. The subterranean estuary: A reaction zone of groundwater and seawater. Marine Chemistry 65, 111–125.

Osmond, J.K., Cowart, J.B., 1992. Groundwater. In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-series Disequilibrium: application to Earth, Marine, and Environmental Sciences. Oxford Science Publications, pp. 204–245.

Osmond, J.K., Ivanovich, M., 1992. Uranium-series mobilization and surface hydrology. In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-series Disequilibrium: application to Earth, and Environmental Sciences. Oxford Science Publications, pp. 290–333.

Rama, Moore, W.S., 1996. Using the radium quartet for evaluating groundwater input and water exchange in salt marshes. Geochim. Cosmochim. Acta 60, 4245–4252.

Rutkowski, C.M., Burnett, W.C., Iverson, R.L., Chanton, J.P., 1999. The effect of groundwater seepage on nutrient delivery and seagrass distribution in the northeastern Gulf of Mexico. Estuaries 22, 1033–1040.