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Seasonal variations of ^{222}Rn and SGD fluxes to Ubatuba embayments, São Paulo

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We describe here an application of excess ^{222}Rn to estimate submarine groundwater discharge in a series of small embayments of Ubatuba, São Paulo State, Brazil. Excess ^{222}Rn inventories obtained in 11 vertical profiles varied from $(3.3\pm1.1)\cdot10^3$ to $(19\pm5)\cdot10^3$ dpm·m^{-2}. The estimated total fluxes required to support the inventories varied from $(0.6\pm0.2)\cdot10^3$ to $(3.4\pm0.9)\cdot10^3$ dpm·m^{-2}·d^{-1}. Considering these results, the submarine groundwater discharge advective rates necessary to balance the sub-pycnocline fluxes calculated in Ubatuba embayments ranged from 0.06 to 1.9 cm·d^{-1}. During the period of this investigation (from March/03 to May/2004), the highest ^{222}Rn in excess inventories were observed late in the summer season (March). Taking into account all vertical profiles established, the relative variability was 67%. Although, if we consider only the fluxes determined in both Flamengo and Fortaleza embayments, the relative variation was 21%.

Introduction

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 the greatest close to shore, because discharge rates decrease exponentially with distance from shore.

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 coastal zones, representing an important material flux pathway from land to sea in some areas.[1] 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 recirculation of seawater through a coastal aquifer system.[2] Over the past few years, it has been recognized that groundwater discharge 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.[3] The groundwater flow through coastal marine sediments may be both volumetrically and chemically important.[4] 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 have been applied to trace and to quantify groundwater inputs to the ocean.[5–11] Geochemical tracers, like ^{222}Rn and ^{226}Ra, are advantageous for regional-scale assessments of SGD, because their signals represent values integrated through the water column that removes small-scale variations. These radionuclides are usually enriched in groundwater compared to seawater, can be measured at very low concentrations and are conservative.

This research project has as its main purpose the application of ^{222}Rn to trace SGD into the marine environmental studies performed in a series of small embayments of Ubatuba, São Paulo State. 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.[12] 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.

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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.

As a cultural symptom of demographic expansion, waste disposal, domestic and industrial releases, infiltration of septic plumes through the coastline and uncontrolled management of the watersheds have been affecting these coastal environments, causing eutrophication. Nutrient inputs to the embayments of the region via groundwater discharge may be responsible for increased turbidity observed in these waters. For all those reasons, the application of ^{222}Rn as a tracer technique is critical for the assessment of SGD inputs and the future management of groundwater-borne nutrients.

The development of this project offered an opportunity to better understand groundwater–seawater interactions in the study area, seasonal variations of SGD, the input of pollutants from septic systems and other sources, and allowed a regional assessment of subsurface fluid flow.

Methodology

Estimating the groundwater discharge using ^{222}Rn as a natural tracer

A potential means of determining groundwater pathways and flux rates into the coastal zone is the application of ^{222}Rn as a natural tracer. The ^{222}Rn levels often found in groundwater are 2–4 orders of magnitude higher than those radon levels observed in seawater. Besides that, ^{222}Rn is a natural short-lived radionuclide ($T_{1/2} = 3.83$ d) and is chemically inert. 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 under certain conditions. The approach is particularly sensitive for inner shelf environments when a strong pycnocline is present, as this greatly inhibits radon loss to the atmosphere.

The source of ^{222}Rn in groundwater is from continuous decay of its parent ^{226}Ra ($T_{1/2} = 1620$ y), which is present both in the solid and solution phase of an aquifer. ^{226}Ra is part of the ^{238}U decay series and consequently is well distributed in sediments and rocks. Some rock types concentrate more ^{226}Ra than others, so the amount of ^{222}Rn produced will be partially based on the distribution of its parent. As ^{226}Ra on or near the surface of mineral grains decays, ^{222}Rn diffuses or is injected into the rock pore waters by recoil processes and becomes part of the solution phase of the aquifer. Concentrations of ^{222}Rn increase as water flows through the aquifer until an equilibrium level (production = decay) is reached, which is almost always in great excess of secular equilibrium with its parent ^{226}Ra. After removal from the aquifer, the primary loss of radon occurs due to decay.

Basically, an assessment of SGD via radon tracing involves 4 steps: (1) measurement of the water column inventory of ^{222}Rn; (2) an accounting of any ^{222}Rn inputs and outputs to the study area by other processes; (3) a calculation of the total input flux of ^{222}Rn to balance the measured inventories (together with any estimated losses); and (4) a calculation, using estimated fluid concentrations for ^{222}Rn and an advection-diffusion model of the advective transport required to account for the estimated total input flux. A schematic radon mass balance for a coastal environment is shown in Fig. 1.

Measurement of the radon concentrations in the water column may be accomplished by standard oceanographic sampling and analysis techniques for measurement of ^{222}Rn, taking the special care required for trace gas sampling.[5] The determination of ^{226}Ra, the parent nuclide of ^{222}Rn, is recommended in order to correct for the "supported" activity of ^{222}Rn, i.e., the amount due to ingrowth from the ^{226}Ra dissolved in the water column. Once the concentrations have been determined, ideally as a complete profile through the water column, the inventory is calculated by integrating the excess radon concentrations over water depth.

Since radon occurs virtually everywhere in the environment, an accounting of the input and loss terms for the area studied is an important part of this approach. Additional inputs include ingrowth from the ^{226}Ra dissolved in the water column, and any benthic inputs from diffusion or via physical mixing (bioturbation, sediment re-suspension). An important loss term, at least in a shallow water environment, is loss to the atmosphere. Water mass movement can, of course, transport radon-rich or radon-depleted waters into an area of interest. For the purposes of this discussion, it is assumed that horizontal gradients are small and a one-dimensional approach is used to calculate inputs and outputs.

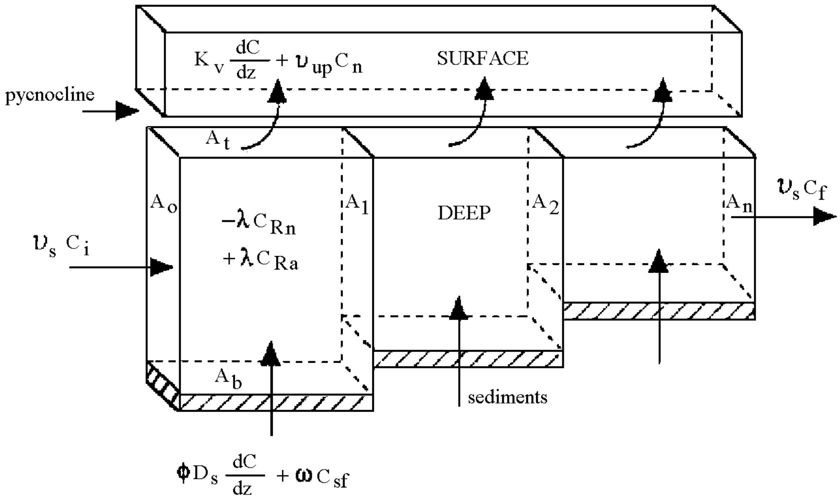

Fig. 1. An incremental mass balance of ^{222}Rn in the sub-pycnocline water column was applied using this box model, which allows the sub-pycnocline water column to change with distance up the continental shelf. Sources and sinks considered for ^{222}Rn were (1) total advective–diffusive benthic input processes [wC_{sf}, ϕ Ds (dC/dz)]; (2) horizontal transport ($\upsilon_s C_i$; $\upsilon_s C_f$); (3) radon production and decay ($\pm\lambda C$); and (4) loss across the pycnocline [K_v (dC/dz) + $\upsilon_{up} C_n$]

The total flux of radon required to support the inventory measured in the system can be estimated by:

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

where J is the the total flux of ^{222}Rn (dpm·m^{-2}·d^{-1}), I is the inventory (dpm·m^{-2}), and λ is the decay constant of ^{222}Rn (0.181 d^{-1}).

At high t values (several half-lives of ^{222}Rn), this equation reduces to the inventory divided by 5.5-day mean life [I/(1/λ)] or simply the inventory multiplied by the decay constant, $I \cdot \lambda$. This calculation thus assumes a steady-state situation on a time scale of weeks. This condition has been observed in coastal environments in Florida.[6] The main loss from the measured ^{222}Rn inventory will typically be 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:

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

where C is the radon concentration (activity) in the sediments, z is the depth positive downwards, K_z 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 ($P = \lambda C_{eq}$, where C_{eq} is the activity of ^{222}Rn in equilibrium with wet sediment determined experimentally, dpm·m^{-3} wet sediment); and λC is the radioactive decay of ^{222}Rn.

In this situation, K_z 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 to Eq. (2) may be represented by:

$$C = \frac{(C_o - C_{eq})(e^{\frac{z}{2z^*}}) \sinh(\frac{A(z_{eq} - z)}{2z^*})}{\sinh(\frac{Az_{eq}}{2z^*})} \qquad (3)$$

where C_0 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}), z_{eq} is a depth in the sediments much deeper than the depth where C_{eq} 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.[6]

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}, than 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 to be similar to those measured in groundwater from the coastal aquifer.

Experimental

Geological setting and sampling

The field work have been carried out in a series of small embayments of Ubatuba, covering latitudes between 23°26'S and 23°46'S and longitudes between 45°02'W and 45°11'W. The main embayments selected for this work were Flamengo Bay (Ubatuba Marine Laboratory site), Fortaleza Bay, Mar Virado Bay and Ubatuba Bay (Fig. 2).

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.[13] 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),[14] 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.[15]

Measurements made until now included ^{222}Rn and ^{226}Ra in seawater, ^{226}Ra in sediment, seawater and sediment physical properties, nutrients and seepage rates via standard seepage meters. For the purposes of this study, seawater samples were collected at several stations in Ubatuba embayments from March 2003 to May 2004, in order to assess SGD and evaluate seasonal variations. Temperature and salinity profiles were obtained at each station using a 2.00" Micro CTD, from Falmouth Scientific, Inc. Seawater samples were collected at 1–2 m depth intervals using a peristaltic pump to purge the sampling tubes and then drawn into 4-liter evacuated glass bottles. Seawater was purged for 5 minutes 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.[5] 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 hours to allow ^{222}Rn daughters, ^{218}Po and ^{214}Po to equilibrate and counting was performed using a portable radon monitor RDA-200, Scintrex. After the initial radon determination, the samples were sealed and stored for at least five days for ^{222}Rn ingrowth and then flushed 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. Once the concentrations have been determined, ideally as a complete profile through the water column, the inventory was calculated by integrating the excess radon concentrations over water depth intervals. Bottom sediment grab samples were also obtained at each site in order to assess potential diffusive fluxes of ^{222}Rn from sediments.

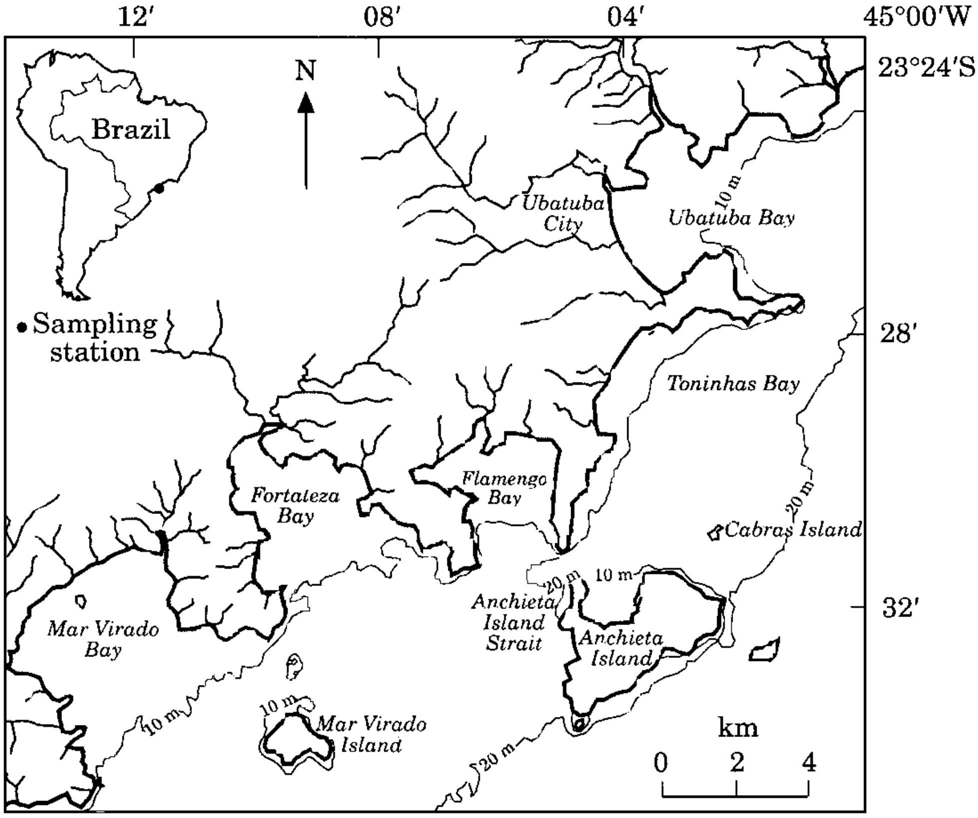

Fig. 2. Location of the four embayments studied at Ubatuba coastal area: Flamengo Bay, Fortaleza Bay, Mar Virado Bay and Ubatuba Bay. Ubatuba County is located around 270 km north from São Paulo city, southeast Brazil

Results and discussion

The potential diffusive fluxes of ^{222}Rn from sediments are presented in Table 1.

Excess ^{222}Rn inventories are given in Table 2, together with the total fluxes required to support the measured inventories, estimated using Eq. (1) and groundwater advective velocity rates necessary to balance the total fluxes, assessed using Eq. (2).

During the period of this investigation, the excess ^{222}Rn inventories varied from $(3.3\pm1.1)\cdot10^3$ to $(19\pm5)\cdot10^3$ dpm·m^{-2}. The highest ^{222}Rn in excess inventories were observed both in Flamengo and Fortaleza embayments (Table 2). The respective fluxes of excess ^{222}Rn in the water column ranged from $(0.6\pm0.2)\cdot10^3$ to $(3.4\pm0.9)\cdot10^3$ dpm·m^{-2}.

The groundwater advective velocity rates necessary to balance the fluxes of excess ^{222}Rn bellow the pycnocline by advection (ω) calculated for Ubatuba embayments varied from 0.06 to 1.9 cm·day^{-1}. However, it is important to notice that the corresponding advective velocity rate of groundwater obtained for Fortaleza Bay was slightly higher than that one observed at Flamengo Bay, since this parameter is a function of the bottom sediment porosity. To evaluate the order of 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 in a study carried out in the northeastern Gulf of Mexico,[5] covering an area of 620 km^2.

The highest inventories of excess ^{222}Rn were observed late in the summer season (March), which corresponds exactly to the month of highest pluviometry (about 350 mm). The annual pluviometric rates at Ubatuba region varies from 1,500 to 2,000 mm, August is the only month presenting pluviometry lower than 100 mm.

Taking into account all vertical profiles established (from March/03 to May/2004), the relative variability was 67%. However, if we consider only the fluxes determined in both Flamengo and Fortaleza embayments, the percentual variation was 21%.

Table 1. Activity of ^{222}Rn in equilibrium with wet sediment determined experimentally, (dpm·m^{-3} wet sediment) (C_{eq}), 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}) (C_0), measured in the Ubatuba embayments sediment. Activity of ^{222}Rn in pore water (dpm·m^{-3}) (A_{pw})

Sediment sample	C_{eq}, dpm·m^{-3}	Porosity	C_0, dpm·m^{-3}	A_{pw}, dpm·m^{-3}
Flamengo Bay	$1.8 \cdot 10^5$	0.51	$1.9 \cdot 10^4$	$3.6 \cdot 10^5$
Fortaleza Bay	$8.5 \cdot 10^4$	0.49	$7.8 \cdot 10^3$	$1.7 \cdot 10^5$
Mar Virado Bay	$1.3 \cdot 10^5$	0.57	$3.0 \cdot 10^3$	$2.3 \cdot 10^5$
Ubatuba Bay	$1.5 \cdot 10^5$	0.62	$8.5 \cdot 10^3$	$2.4 \cdot 10^5$
Ubatuba Marine Lab	$9.9 \cdot 10^4$	0.41	$8.5 \cdot 10^3$	$2.4 \cdot 10^5$

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 (2003/2004)

Vertical profile (depth, m)	I ^{222}Rn excess, dpm·m^{-2}	Flux ^{222}Rn excess, dpm·m^{-2}·d^{-1}	SGD (ω) cm·d^{-1}
March 2003			
Mar Virado Bay (8 m)	$(5.2 \pm 1.9) \cdot 10^3$	$(0.9 \pm 0.3) \cdot 10^3$	0.4
Fortaleza Bay (8 m)	$(13 \pm 3) \cdot 10^3$	$(2.4 \pm 0.5) \cdot 10^3$	1.3
Sete Fontes (Flamengo Bay) (8 m)	$(19 \pm 5) \cdot 10^3$	$(3.4 \pm 0.9) \cdot 10^3$	1.9
Refúgio do Corsário (Fortaleza Bay) (8 m)	$(3.3 \pm 1.1) \cdot 10^3$	$(0.6 \pm 0.2) \cdot 10^3$	0.06
Domingas Dias (Flamengo Bay) (6 m)	$(7.4 \pm 1.8) \cdot 10^3$	$(1.3 \pm 0.3) \cdot 10^3$	0.7
Flamengo Bay Center (8 m)	$(5.7 \pm 2.1) \cdot 10^3$	$(1.0 \pm 0.4) \cdot 10^3$	0.4
Praia Grande (Anchieta Island) (8 m)	$(5.3 \pm 1.8) \cdot 10^3$	$(1.0 \pm 0.3) \cdot 10^3$	0.4
November 2003 – Flamengo Bay			
FB1 (5 m)	$(6.1 \pm 1.6) \cdot 10^3$	$(1.1 \pm 0.3) \cdot 10^3$	0.5
FB2 (8 m)	$(13 \pm 4) \cdot 10^3$	$(2.3 \pm 0.7) \cdot 10^3$	1.3
FB3 (11 m)	$(12 \pm 4) \cdot 10^3$	$(2.2 \pm 0.7) \cdot 10^3$	1.2
May 2004 - Flamengo Bay			
FL (9 m)	$(12 \pm 4) \cdot 10^3$	$(2.2 \pm 0.7) \cdot 10^3$	1.2

Conclusions

The direct discharge of groundwater into near-shore marine environment may have significant environmental consequences because groundwater in many areas has become contaminated with a variety of substances like nutrients (mainly from septic systems), heavy metals, radionuclides and organic compounds. As almost all coastal zones are subjected to flow of groundwater either as submarine springs or disseminated seepage, coastal areas are likely to experience environmental degradation. Transport of nutrients to coastal waters may trigger algae blooms, including harmful algae blooms, having negative impacts on the economy of coastal zones.

Measurements of SGD along the South American coast and over fractured aquifers are especially rare. A reconnaissance of submarine groundwater discharge using ^{222}Rn as a natural tracer disclosed a substantial inflow of groundwater, which includes both fresh and saline pore water.[16] Preliminary measurements carried out at Ubatuba coastal area showed fluxes of groundwater in Flamengo Bay to average 4.3 cubic centimeters of pore water per square centimeter of the sea floor per day (4.3 cm·d^{-1}). Direct measurements of SGD were also made using vented benthic chambers.[16] Measured fluxes were approximately 21 cm·d^{-1}. The disparity between these estimates may be explained by the spatial and seasonal variabilities of SGD documented in that previous study.

In order to evaluate seasonal variations, several vertical profiles were established in Ubatuba embayments (from March/03 to May/2004). The results obtained showed highest excess ^{222}Rn inventories occurring late in the summer season (March), which corresponds exactly to the month of highest pluviometry (about 350 mm) and consequently, highest discharge. It seems to indicate that the main control on temporal variations in groundwater flow in Ubatuba embayments is precipitation, since recharge was governed largely by this phenomenon.

Once both tidal and seasonal oscillations can induce changes in the fluxes of SGD through coastal aquifers, large data sets are frequently necessary to accurately predict temporal variations in groundwater discharge.

During the period of this investigation, the relative variability on SGD fluxes estimated using ^{222}Rn as a tracer was 67%, taking into account all fluxes determined. Although, if we consider only the data set determined in both Flamengo and Fortaleza embayments, the relative variation found was 21%.

This study is a part of a large project that has as a main goal the application of isotopic techniques in coastal oceanography and geochemistry studies developed in São Paulo State coastal area, thus enhancing the understanding of groundwater–seawater interactions in this region, helping environmental managers to identify specific problem areas and its potential resulting impact on local ecosystems.

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