2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

ASSESSMENT OF SUBMARINE GROUNDWATER DISCHARGE AND SEASONAL OSCILLATIONS IN SEAWATER ^{222}Rn INVENTORIES OF UBATUBA, BRAZIL

Patrícia da Costa Lopes[1] and Joselene de Oliveira[1]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
jolivei@ipen.br

ABSTRACT

In order to assess submarine groundwater discharge (SGD) and evaluate seasonal oscillations of such fluxes, measurements of the naturally occurring ^{222}Rn in Ubatuba embayments were carried out from March/03 through July/2005. In this area, the main geologic/geomorphologic feature is the presence of pre-Cambrian granites and migmatites of Serra do Mar. The coastal aquifer is a fractured rock aquifer, covered by Pleistocene and Holocene sediments. The discharge pattern of this kind of aquifer is spatially heterogeneous, with preferential flow paths along rock fractures. During this investigation ^{222}Rn in excess inventories obtained in 24 vertical profiles varied from 345 ± 24 dpm m^{-2} to 18,700 ± 4,900 dpm m^{-2}. The highest inventories of ^{222}Rn in excess were observed both in Flamengo and Fortaleza embayments, during summer campaigns. The estimated total fluxes required to support inventories measured varied from 62 ± 4 to 3,385 ± 880 dpm m^{-2} d^{-1}. SGD fluxes calculated in Ubatuba embayments ranged from 0.1×10^{-1} to 1.9 cm d^{-1}. Taking into account all fluxes estimated, the percentual variability was 89% (seasonal variation in 3 years period, n = 24 measurements). Although, if we consider each year of study separately, the respective percentual variabilities estimated are 72% in 2003 (n = 10 measurements), 127% in 2004 (n = 6 measurements) and 97% in 2005 (n = 8 measurements).

1. INTRODUCTION

Submarine groundwater discharge (SGD) is the direct flow of groundwater into the coastal ocean. Like surface water, groundwater flows down gradient and SGD occurs wherever a coastal aquifer is connected to the sea. SGD consists of various mixtures of fresh groundwater and seawater and is a widespread coastal feature. Most SGD occurs as diffuse seepage and identifying discharge sites or quantifying flux rates across sediment-water interface has proven difficult. Regional parameters that may affect the occurrence and magnitude of SGD are climate, geology, topography, soil and sediment type and their hydraulic conductivity, hydraulic head of the underlying aquifer, tidal range and other oceanic forces. There is also indication that substantial groundwater inputs may occur in river-dominated margins.

SGD has recently been recognized as a phenomenon that can strongly influence coastal water and geochemical budgets and drive ecosystem change [1-3]. For example, the discharge of nutrient-enriched groundwater into coastal waters may contribute significantly to eutrophication and blooms of harmful algae. Similarly, the quantity of SGD can also directly affect the availability of fresh water to coastal communities, impact fragile coastal ecosystems such as estuaries and coral reefs, and influence geomorphology of shoreline features.

Coastal aquifers may consist of complicated arrays of confined, semi-confined and unconfined systems. Simple hydrogeologic models do not consider the anisotropic nature of coastal sediments, dispersion and tidal pumping. Moreover, cycling of seawater through the coastal aquifer may be driven by the flow of freshwater from coastal uplands. As freshwater flows through an aquifer driven by an inland hydraulic head, it can entrain seawater that is diffusing and dispersing up from the salty aquifer that underlies it. Superimposed upon this terrestrially driven circulation are a variety of marine-induced forces that result in flow into and out the seabed even in the absence of a hydraulic head. Such “subterranean estuaries” will be characterized by biogeochemical reactions that influence the transfer of nutrients to coastal zone in a manner similar to that of surface estuaries.

SGD forcing has both terrestrial and marine components. The following drivers of fluid flow through shelf sediments may be considered: (1) the terrestrial hydraulic gradient (gravity) that results in water flowing downhill; (2) water level differences across a permeable barrier; (3) tide, wave, storm, or current-induced pressure gradients in the near-shore zone; (4) convection (salt-fingering) induced by salty water overlying fresh groundwater in some near-shore environments; (5) seasonal inflow and outflow of seawater into the aquifer resulting from the movement of the freshwater-seawater interface in response to annual recharge cycles; and (6) geothermal heating.

In the coastal zone, discharges influenced by terrestrial and marine forces are typically coincident in time and space but may differ significantly in magnitude. Since the hydraulic gradient of a coastal aquifer, tidal range, and position of the freshwater-seawater interface change over time; it is possible that the situation in any one area could shift (e.g., seasonally) between terrestrially governed and marine dominated systems.

Although the importance of SGD has been well recognized, studies on this issue have been hampered by the lack of measurement tools on a large space and time scale. General tools for SGD assessment include hydrological considerations [4], seepage measurements [5-6], and mass balance modeling using tracers such as Ra isotopes, ^{222}Rn and CH_4 [7-8]. An advantage of groundwater tracers is that they present an integrated signal as they enter marine water column via various pathways in the aquifer. Although small-scale variability is a serious drawback for the use of seepage meters or piezometers, such small spatial scale variations tend to be smoothed out over time and space in the case of tracer methods. On the other hand, natural tracers require that all other tracer sources and sinks except groundwater be evaluated, an often difficult exercise.

Natural geochemical tracers have been applied in two ways to evaluate groundwater discharge rates into the ocean. First is the use of enriched geochemical tracers in the groundwater relative to the seawater. In other words, the concentration of a solute in a receiving water body is attributed to inputs of that component derived only from groundwater [9-10]. A second approach is the use of vertical profiles of the geochemical compositions in sediment pore waters under the assumption that its distribution can be described by a vertical, one-dimensional advection-diffusion model [11]. However, this is usually limited to the case of homogeneous media.

Over the past few years, several studies used natural radium isotopes and ^{222}Rn to assess groundwater discharge into the ocean. Ideally, in order to provide a detectable signal, a groundwater tracer should be greatly enriched in the discharging groundwater relative to coastal marine waters, conservative and easy to measure. In applying geochemical tracing techniques, several criteria 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 concentrations of the tracer. Sources may include ocean water, river water, groundwater, precipitation, in situ production, horizontal water column transport, sediment re-suspension, or sediment diffusion. Sinks may include in situ decay or consumption, horizontal water column transport, horizontal or vertical eddy diffusivity and atmospheric evasion. Through simple mass balance or box models incorporating both sediment advection and water column transport, the geochemical approach can be quite useful in assessing SGD.

We report in this paper SGD assessment studies carried out from March/2003 through July/2005 in Ubatuba embayments, Brazil, using ^{222}Rn as a natural tracer. The study site is characterized by fractured granite cliffs descending into the Atlantic Ocean. There is only a thin veneer of coarse-grained sediment that makes up beaches within the numerous bays along the coast. The 2003 study was part of a collaborative multinational program designed to investigate submarine groundwater discharge using different techniques tested in different hydrogeologic settings. This intercomparison was sponsored by the Scientific Committee on Oceanic Research (SCOR), the Land-Ocean Interactions in the Coastal Zone (LOICZ), the International Atomic Energy Agency (IAEA), and UNESCO's Intergovernmental Oceanographic Commission (IOC) and International Hydrologic Program (IHP). The primary objective of this last program was an improved understanding of scientific and technical aspects that will enable SGD measurements to be addressed with a higher degree of confidence, including the development and implementation of nuclear and isotopic techniques to assess submarine groundwater discharges. Local benefits of this program extended into the fields of hydrology and coastal oceanography, improving the information already available in São Paulo coastal area.

2. EXPERIMENTAL

2.1. Geological Setting and Sampling

The field work has been carried out in a series of small embayments near Ubatuba, São Paulo State, Brazil. All samples studied here were taken in the selected area between latitudes 23°26'S and 23°46'S and longitudes 45°02'W and 45°11'W, in order to estimate coastal mixing rates and groundwater discharge fluxes. The main embayments selected to be studied in this work were Flamengo Bay (Ubatuba Marine Laboratory site), Fortaleza Bay, Mar Virado Bay and Ubatuba Bay

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 [12]. 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 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), 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 [13]. In the study area the coastal aquifer system can be classified as a fractured rock aquifer, covered by Pleistocene and Holocene sediments. The discharge pattern of this kind of aquifer is spatially heterogeneous, with preferential flow paths along rock fractures.

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 July 2005, 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 L 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.

2.2. Methods

^{222}Rn was extracted and counted using a modified emanation technique [14]. 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 analysis, 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.

The methodology was validated through the participation in a proficiency test organized by the Analytical Quality Control Services (AQCS) of the International Atomic Energy Agency (IAEA), called the "Interlaboratory Study on Determination of Radium and Uranium Radionuclides in Water", in January 2003. A total of six water samples (3 natural and 3 synthetic) were diluted with Milli-Q purified water. These samples were measured for ^{226}Ra using the Rn-emanation technique described previously. Uncertainties were lower than 5%. The final evaluation of our results reported in this intercomparison indicated they were in a good agreement with IAEA reference values and were not biased by a systematic error, both with low and high ^{226}Ra activities.

3. RESULTS AND DISCUSSION

Pore water radon activities and diffusive fluxes were estimated by sediment equilibration experiments [15]. Six sediment samples collected in Ubatuba embayments were equilibrated with bay water for periods over three weeks, long enough for radioactive equilibration between ^{226}Ra and ^{222}Rn. A porosity (ϕ) of 0.51 ± 0.07 was determined for sediment samples (n = 2) in Flamengo bay. The corresponding activity of ^{222}Rn in equilibrium with wet sediment determined experimentally (C_{eq}) was 1.8×10^5 dpm m^{-3} of wet sediment. This is equivalent to a pore water ^{222}Rn activity of 243 dpm L^{-1}. The porosity (ϕ) values estimated for Fortaleza bay and Mar Virado bay were 0.49 ± 0.07 (n = 2) and 0.57 ± 0.07 (n = 2), respectively. In the same way, the activities of ^{222}Rn in equilibrium with wet sediments (C_{eq}) were 8.5×10^4 dpm m^{-3} and 1.3×10^5 dpm m^{-3}. The corresponding pore water ^{222}Rn activities for Fortaleza and Mar Virado embayments were of 170 dpm L^{-1} and 230 dpm L^{-1}.

Considering the results obtained in the vertical profiles established, the excess ^{222}Rn inventories were estimated for the embayments studied. These data are shown in **Tab.1**, together with the total fluxes required to support the measured inventories and SGD rates necessary to balance the total fluxes. In these SGD calculations we assumed that ^{222}Rn vertical profiles were reasonably in steady-state and supported by a combination of advection and diffusion. The ^{222}Rn depth profiles indicated that the water column was relatively well mixed in these shallow embayments. During the period of this investigation, ^{222}Rn in excess inventories obtained in 24 vertical profiles varied from 345 ± 24 dpm m^{-2} to 18,700 ± 4,900 dpm m^{-2}. The highest ^{222}Rn in excess inventories were observed both in Flamengo and Fortaleza embayments, during summer campaigns, mostly in March, which corresponds exactly to the month of highest pluviometry (about 344.9 mm). The annual pluviometric rate at Ubatuba region varies from 1,500 to 2,000 mm, August is the only month presenting pluviometry lower than 100 mm.

Applying an one-dimensional advection-diffusion model [10, 14] with porosity and pore water values mentioned earlier, the estimated total fluxes required to support inventories measured varied from 62 ± 4 to 3,385 ± 880 dpm m^{-2} d^{-1}. Considering these results, SGD advective rates necessary to balance the sub-pycnocline fluxes calculated in Ubatuba embayments ranged from 0.1×10^{-1} to 1.9 cm d^{-1}. It is important to notice that the SGD fluxes obtained for Fortaleza bay were slightly higher than to that one observed at Flamengo bay, since this parameter is function of the bottom sediment porosity.

The seasonal oscillations in seawater ^{222}Rn inventories measured in Ubatuba from March /2003 through July/2005 and consequent variations on SGD fluxes were evaluated taking into account all values reported in **Tab.1**. The assessment of the seasonal variation considering all fluxes obtained resulted in a relative percentual variability of 89% (3 years period, n = 24 measurements). Although, if we estimate seasonal oscillations taking into account each year of study separately, the respective relative percentual variabilities were 72% in 2003 (n = 10 measurements), 127% in 2004 (n = 6 measurements) and 97% in 2005 (n = 8 measurements).

Table 1. Excess ^{222}Rn inventories, total fluxes required to support inventories measured and SGD rates necessary to balance the sub-pycnocline fluxes estimated in Ubatuba embayments (2003/2005).

VERTICAL PROFILE Water Column Depth (m)	I^{222}Rn in excess (dpm m^{-2})	Flux ^{222}Rn in excess (dpm m^{-2} d^{-1})	SGD (cm d^{-1})
March 2003			
Mar Virado bay (8 m)	5,200 ± 1,900	941 ± 338	0.36
Fortaleza bay (8 m)	13,100 ± 2,800	2,371 ± 498	1.3
Sete Fontes (Flamengo bay) (8m)	18,700 ± 4,900	3,385 ± 880	1.9
Refúgio do Corsário (Fortaleza bay) (8 m)	3,300 ± 1,100	597 ± 179	0.06
Domingas Dias (Flamengo bay) (6 m)	7,400 ± 1,800	1,339 ± 326	0.65
Flamengo bay (8 m)	5,700 ± 2,100	1,032 ± 380	0.43
Praia Grande (Anchieta Island) (8 m)	5,300 ± 1,800	952 ± 323	0.37
November 2003			
Flamengo bay - FB1 (5 m)	6,100 ± 1,600	1,104 ± 290	0.48
Flamengo bay - FB2 (8 m)	12,800 ± 3,600	2,317 ± 649	1.3
Flamengo bay - FB3 (11 m)	12,200 ± 3,900	2,208 ± 706	1.2
May 2004			
Flamengo bay - FL (9 m)	12,400 ± 3,600	2,244 ± 651	1.2
August – 2004			
Fortaleza bay (8 m)	3,720 ± 260	673 ± 47	0.74
Perequê-Mirim (Flamengo bay) (5 m)	2,730 ± 166	429 ± 30	0.20
Perequê-Mirim left side (2.7 m)	1,155 ± 81	209 ± 15	0.03
Perequê-Mirim right side (3.2 m)	345 ± 24	62 ± 4	0.01
Flamengo bay (8 m)	3,940 ± 244	632 ± 44	0.10
March – 2005			
Fortaleza bay (9 m)	8,330 ± 583	1,508 ± 106	1.9
Flamengo bay(8.2 m)	3,390 ± 237	614 ± 43	0.08
Perequê-Mirim left side (2.4 m)	5,400 ± 378	977 ± 68	0.39
Perequê-Mirim right side (2.4 m)	4,500 ± 315	815 ± 57	0.26
July - 2005			
Fortaleza bay – A1(2.4 m)	4,080 ± 286	738 ± 52	0.83
Fortaleza bay- A2 (12 m)	6,030 ± 442	1,091 ± 76	1.3
Flamengo bay (8.2 m)	2,630 ± 184	476 ± 33	0.24
Perequê-Mirim (4 m)	3,280 ± 230	594 ± 42	0.27

4. CONCLUSIONS

Geochemical tracers can provide important information on hydrological processes and mixing rates in coastal areas. This paper described the application of ^{222}Rn to study submarine groundwater discharge (SGD) patterns in a series of coastal Ubatuba embayments, São Paulo, Brazil. Since SGD can be an important source of dissolved solutes into the coastal zone, there is a concern of its influence on the water balance on land and biogeochemical inputs to the ocean. Although the assessment of SGD and its associated chemical mass fluxes remains difficult due to a high degree of uncertainty in available methodologies, the ^{222}Rn technique used in this study provided good results, and has shown to be appropriated for such measurements in natural waters over a wide range in salinity and radium activities.

In order to evaluate seasonal oscillations, several vertical profiles were established in Ubatuba embayments from March/2003 through July/2005. The results obtained showed highest inventories of ^{222}Rn in excess occurring late in the summer season (March), which corresponds exactly to the month of highest pluviometry and consequently, highest discharge. It seems to indicate that the main control on temporal variations in groundwater flow to Ubatuba embayments is precipitation, since recharge was governed largely by this phenomenon. Once both tidal and seasonal oscillations can induce changes in SGD fluxes through coastal aquifers, large data sets are frequently necessary to accurately predict temporal variations in groundwater discharge and its associated chemical budget.

ACKNOWLEDGMENTS

The authors wish to thank the personnel at the marine laboratory of the University of São Paulo who were very helpful during the sampling program. Financial support for this project was provided by the International Atomic Energy Agency (IAEA) through its Cooperative Research Program (CRP) "Nuclear and Isotopic Techniques for Charactherization of Submarine Groundwater Discharge (SGD) in Coastal Zones", Research Contract 12151. Logistical support was also provided by UNESCO's Intergovernmental Oceanographic Commission (IOC) and International Hydrological Program (IHP). Science support was provided by Fundação de Amparo à Pesquisa no Estado de São Paulo (FAPESP) grant n°02/08902-9 and project n°02/08154-9.

REFERENCES

1. C.F. D'Elia, K.L. Webb, J.W. Poter, "Nitrate-rich groundwater inputs to Discovery Bay, Jamaica: A significant source of N to local coral reefs?," *Bulletin of Marine Science*, **31**, pp.903-910 (1981).
2. I. Valiela, J. Costa, K. Foreman, J.M. Teal, B.L. Howes, D.G. Aubrey, "Transporto f groundwater-borne nutrients from watersheds and their effects on coastal waters", *Biogeochemistry,* **10**, pp.177-197 (1990).
3. W.C. Burnett, H. Bokuniewwicz, M. Huettel, W.S. Moore, M. Taniguchi, "Groundwater and pore water inputs to the coastal zone", *Biogeochemistry*, **66,** p.3-33 (2003).
4. J.A. Oberdorfer, M.A. Valentino, S.B. Smith, "Groundwater contribution to the nutrient budget of Tomales Bay, California", *Biogeochemistry,* **10,** pp.199-216 (1990).
5. J.E. Cable, W.C. Burnett, J.P. Chanton, D.R. Corbett, P.H. Cable, "Field evaluation of seepage meters in the coastal marine environment", *Estuar.Coast.Shelf Sci.*, **45,** pp.367-375 (1997).
6. M. Taniguchi, "Tidal effects on submarine groundwater discharge into the ocean", *Geophys.Res.Lett.*, **29,** (doi:10.1029/2002GL014987).
7. D.R. Corbett, K. Dillon, W.C. Burnett, J.P. Chanton, "Estimating the groundwater contribution into Florida Bay via natural tracers, ^{222}Rn and CH_4", *Limnol.Oceanogr.*, **45,** pp.1546-1557 (1997).

8. G. Kim, D.W. Hwang, “Tidal pumping of groundwater into the coastal ocean revealed from submarine ^{222}Rn and CH_4 monitoring”, *Geophys.Res.Lett.*, **29,** (doi:10.1029/2002GL015093).
9. W.S. Moore, “Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments”, *Nature,* **380,** pp.612-614 (1996).
10. J. Cable, G. Bugna, W. Burnett, J. Chanton, “Application of ^{222}Rn and CH_4 for assessment of groundwater discharge to the coastal ocean”, *Limnol.Oceanog.*, **41,** pp.1347-1353 (1996).
11. R.J. Cornett, B.A. Risto, D.R. Lee, “Measuring groundwater transport through lake sediments by advection and diffusion”, *Water Res.,* **25,** pp. 1815-1823 (1989).
12. M.M. Mahiques, M.G. Tessler, V.V. Furtado, “Characterization of Energy Gradient in Enclosed Bays of Ubatuba Region, South-eastern Brazil”, *Estuarine, Coastal and Shelf Science,* **47,** pp.431-446 (1998).
13. A.R. Mesquita, “Marés, circulação e nível do mar na Costa Sudeste do Brasil”, Relatório Fundespa, São Paulo, (1997).
14. J. Oliveira, W.C. Burnett, B.P. Mazzilli, E.S. Braga, L.A. Farias, J. Christoff, “Reconnaissance of submarine groundwater discharge at Ubatuba coast, Brazil, using ^{222}Rn as a natural tracer”, *Journal of Environmental Radioactivity,* **69,** pp.37-52 (2003).
15. C.S. Martens, G.W. Kipphut, J. Klump, “Sediment-water chemical exchange in the coastal zone traced by in-situ ^{222}Rn flux measurements”, *Science,* **208,** pp.285-288 (1980).