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ASSESSMENT OF NATURAL RADIUM ISOTOPES AND ^{222}Rn IN WATER SAMPLES FROM CANANÉIA-IGUAPE ESTUARINE COMPLEX, SÃO PAULO

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ABSTRACT

Radium isotopes and radon are among the most important natural radionuclides in the environment from both radioprotection and geo-hydrological points of view. These radionuclides are a powerful tool for studying coastal processes and have been used intensively as tracers of groundwater sources that discharge into the ocean. In this paper, naturally ocurring radium isotopes and ^{222}Rn were determined to trace water exchange and SGD in Cananéia-Iguape estuarine complex, a shallow coastal plain estuary in southern São Paulo area. The research work was carried out during the 1st semester of 2009 and covered stations located both in Cananéia and Iguape outlets, as well as samples collected in Ribeira of Iguape River and groundwater. Activity concentrations of ^{226}Ra in estuarine waters from Cananéia outlet varied from 2.9 mBq L^{-1} to 4.7 mBq L^{-1}, while ^{228}Ra concentrations ranged from 22 mBq L^{-1} to 45 mBq L^{-1}. In Iguape outlet, activities of ^{226}Ra ranged from 1.6 mBq L^{-1} to 6.6 mBq L^{-1}; ^{228}Ra varied from 13 mBq L^{-1} to 20 mBq L^{-1}. Activities of Ra were slightly higher in samples collected at 5 m depth than at the surface water level. Groundwater activity concentrations of ^{226}Ra ranged from 0.63 mBq L^{-1} to 12 mBq L^{-1} and for ^{228}Ra from 18 mBq L^{-1} to 39 mBq L^{-1}. In groundwater, the ^{228}Ra/^{226}Ra activity ratios varied from 3.3 to 31.7. ^{222}Rn activities in groundwater up to 747 Bq L^{-1} were observed. Increased nitrate contents were observed in groundwater samples collected in Cananéia and Comprida Island.

1. INTRODUCTION

Nowadays, the importance of coastal regions and their resources hardly needs argument. The challenge lies in arriving at enduring solutions to the complex problems facing these unique areas, where considerably ecosystem services and high human population pressure coincide. The marine environment is one of the most important natural resource: tourism, industry, fishing and maritme transport are strictly linked to the quality of the ecosystem. It is then crucial to preserve the marine environment and the coastal area from natural and anthropogenic impacts. Several countries are urged to develop strategies and methodologies for the assessment of the coastal area as a base for sustainable development. This implies multidisciplinary investigations on the present/ past history of the pollutants in the marine system to identify present environmental impacts and to predict the time-evolution of the ecosystem.

Chemical differences between coastal and offshore waters occur as a result of several processes. The inflow from rivers and desorption from riverborne particles enrich coastal waters in some elements, while the chemical reactions associated with this mixing may remove other constituents. Anthropogenic inputs associated with industry, shipping, mining, sewage (treated or untreated), and a host of factors contribute pollutants to these waters. Another factor that is becoming recognized as a significant control on coastal water chemistry is submarine groundwater discharge.

The direct discharge of groundwater into the coastal zone called "submarine groundwater discharge (SGD)" can be an important component of water balance between land and sea. Although not as obvious as river discharge, a significant percentage of the total freshwater discharge into the oceans comes in the form of SGD (for the Mediterranean Sea, this proportion is about 70%). As a result, SGD may contribute as an important factor in sustainable management of coastal fresh water aquifers in many highly populated areas of the world. Depending on the location, SGD may be of greater ecological significance than surface runnof, and a significant pathway for nutrient and contamination transport from land-based activities to coastal zones. Inputs of the nutrients nitrogen and phosphorous are important to the overall nutrient economy, and their presence in SGD may contribute to the development of phytoplankton blooms and algal mats.

The distribution of naturally occurring radionuclides can provide important insights into the mobility of pollutants and the rates of natural geochemical processes. Modelling of local mass balance by physical and tracer techniques can supply quantitative estimates of transport rates.

Over the past few years, several studies have employed the use of the natural U decay-series nuclides ^{226}Ra and ^{222}Rn to assess groundwater inputs to the ocean [1-5]. Moore [2] first showed that ^{226}Ra onshore-to-offshore gradients develop because of inputs via SGD and subsequent mixing (either via advection or eddy diffusion) with lower concentration waters offshore. One may determine water exchange rates from independent observations (such as tidal wedge calculations) or use the distribution of the short-lived isotopes of radium to estimate the mixing coefficients. These mixing rates can then be used to calculate the offshore flux of ^{226}Ra. Assuming that the radium gradients are steady-state, at least over the time scale of the mixing processes, and that the excess radium is supplied by SGD near the coast, one can estimate the groundwater discharge by dividing the radium flux by the concentration of radium in the groundwater.

In river water and fresh groundwater Ra strongly adsorb to particles; in seawater they are primarily dissolved. These differences in chemical behavior are due to a change in the adsorption coefficient of Ra between fresh and salt water and to a change in the average particle concentration between terrestrial and ocean waters. As particles encounter salty water in the estuary, Ra is desorbed from their surface.

Radon is also a good natural tracer of SGD because: its concentration is very high in groundwater but low in seawater; it behaves conservatively; and it is relatively easy to measure. Assessment of possible temporal trends of radon is important because groundwater flow is known to be extremely variable – in some cases even reversing direction in response to external forcing (tides, change in water table height, etc.). The short-lived radium isotopes can be used with radon to constrain the mixing losses.

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 waterbody, 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 can be quite useful in assessing submarine groundwater discharge.

In our study, naturally ocurring radium isotopes and ^{222}Rn were determined to trace water exchange and SGD in Cananéia-Iguape estuarine complex, a shallow coastal-plain estuary in southern São Paulo area.

2. MATERIAL AND METHODS

2.1. Study site

This research work was carried out in Cananéia-Iguape estuary, located at the continental shelf of southern coast of São Paulo State, Brazil. This is a complex, mangrove-surrounded estuary system covering a total area of 110 km^2. Water circulation in the estuary channels is brought about by tidal flow and inflow of freshwater from continental drainage of several small rivers. The average tidal amplitude in the system is 0.82 m. The annual average temperature of the region is 21.2°C and the annual average precipitation 2200 mm, with a maximum average precipitation of 266.9 mm occurring between January and March, and a minimum average precipitation of 95.3 mm occurring in July and August.

Comprida Island, a barrier island, separates Cananéia-Iguape (25°S- 48°W) from the ocean and is approximately 70 kilometers long. From the transgressive Holocene maximum, when the coastal line retirement to its present level, a long barrier island was formed (Comprida Island), towards NE, by the action of seaside moving currents causing the formation of the Cananéia-Iguape estuary, at the back of the present coastal line. In the northeast of this estuarine system is located the mouth of the Ribeira of Iguape River. The largest drainage system of the southeastern Brazilian seashore, draining all the crystalline coastal mountainous complex behind the coastal plain, is connected to Cananéia-Iguape estuary only through an artificial channel (Valo Grande) built over 150 years ago [6]. This artificial channel connects the Ribeira of Iguape River directly to the Mar Pequeno channel.

The Cananéia-Iguape estuary receives freshwater from Ribeira de Iguape River and mixes with seawater through two inlets: Icapara sandbanks (Iguape county) and Cananéia sandbanks (Cananéia county). The coastal plain of Cananéia-Iguape forms one of the exception sectors of the long Atlantic coast of Brazil. Before the cemented offshore sandbars had been created the ocean had gone through a few shallow penetrations into the braided landforms of the entire regional coast, reaching up to the foot hills of the Serra do Mar and its spurs during the principle Holocenic transgressions. This is why present day hills and coastal masses were islanded near the end of the Pleistocene and the middle of the Holocene, in the

form of insular masses. The majority of further involution remained in the extreme southern portion of the São Paulo coastline where three generations of cemented offshore sandbars were formed, interspersed with long lagoons, with one case possessing interconnections between the outer sea, the inner sea and the Itapitangui Sea. The majority of these narrow inner "seas" possessed connections with the waters of Trepandé Bay, and endowed with a "zonal" salinity within its waters.

Today, about 60% of the Ribeira of Iguape River discharge flows in the internal channels of Cananéia-Iguape estuary, causing an increasing silting up of these channels by the deposition of the muddy sediments in suspension carried by the drainage of the Ribeira of Iguape. Thus, the continental material is transferred to the maritme system on the southern seashore of São Paulo State, not only in the mouth of the Ribeira of Iguape River but also in the river mouths of the Cananéia-Iguape estuary.

Sediments continue to be deposited in the channels and internal seas, mainly in the Mar Pequeno channel, and along the islands in the channels. The silting up of the area is taking place so fast that whereas, some decades ago large ships were able to dock in Iguape city, crossing the Cananéia bar, this is now impossible, due to the increasing obstruction at two regions towards Icapara bar and at Cananéia. In consequence, the present depth of the lagoons and channels is of less than 15 m. The Valo Grande channel was completed in 1852, then about 4 meters wide and 7 meters deep. Now, it is 250 m wide and 15 m deep [7].

2.1.1. Sampling and experimental methods

For the purposes of this study in the estuarine region of Cananéia-Iguape, at least two sampling campaigns were planned per year: the first one covers the summer and the second one the winter seasons. The first sampling trip, which data will be presented and discussed in this paper, was carried out from 9 to 15 February 2009 and covered stations both in Cananéia and in Iguape outlets (**Fig. 1**). Another sampling trip was performed from 13 to 14 April 2009 to assess the levels of ^{222}Rn, ^{226}Ra and ^{228}Ra in groundwater samples in Cananéia and Comprida Island.

For Ra isotopes, about 10 L of river-estuarine waters and/or groundwater were collected at each location. These samples were passed through a column packed with MnO_2 acrylic fiber to extract Ra isotopes quantitatively. Following the pre-concentration, ^{223}Ra and ^{224}Ra were determined in water samples by using a delayed coincidence system, RaDeCCSys from Scientific Computer Inc. The overall uncertainties of these measurements were bellow 10%. After the ^{223}Ra and ^{224}Ra measurements were complete, the Mn fibers were leached in a mixture of 5% NH_2OH + HCl and 6 M HCl to remove the long-lived Ra isotopes and then co-precipitated with $Ba(Ra)SO_4$. The precipitate was aged for 21 days to allow ^{222}Rn and its daughters to equilibrate with ^{226}Ra. The samples were measured in a gamma-ray spectrometer to assess the activities of ^{226}Ra and ^{228}Ra [5]. The expected error of the long-lived Ra measurement is 7%.

^{222}Rn concentrations were determined in groundwater samples by a liquid scintillation method. For this analysis, a volume of 10 mL of raw water sample was carefully transferred directly from the source to the counting vials, in which the same volume of the universal LSC-cocktail Ultima Gold had been previously added. The samples were measured in a

liquid scintillation analyser, where the spectrum of ^{222}Rn and daughter products was determined. Typical lower limit of detection (LLD) for ^{222}Rn determination was $1.9x10^{-1}$ Bq L^{-1}, at a 95% confidence level [8, 9].

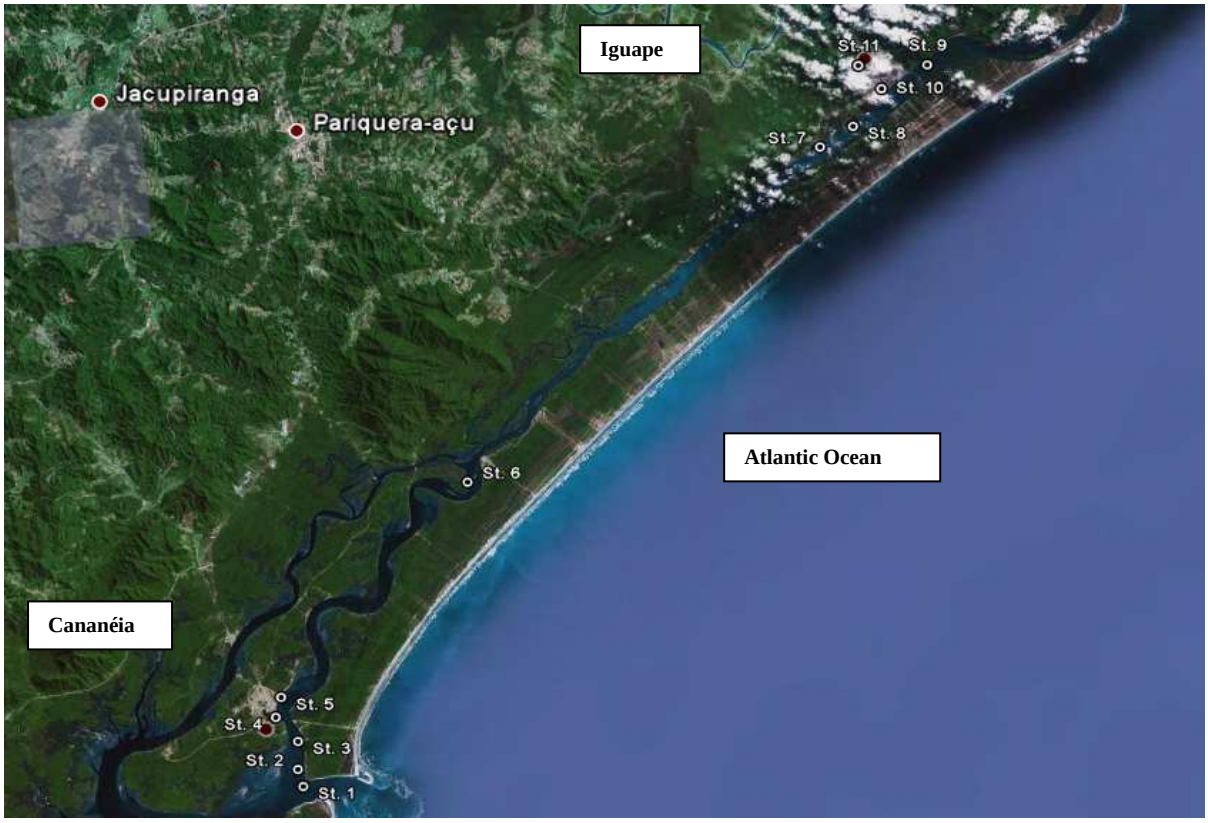

Figure 1. Location of sampling stations in Cananéia and Iguape outlets, February 2009 (satellite view from Google Earth).

The Ra 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 co-precipitation 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.

Water samples for the determination of phosphate, silicate, ammonium, nitrite, nitrate, pH and salinity were also collected. Samples for nutrient were frozen until 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 [10].

3. RESULTS AND DISCUSSION

The location of the surface and groundwater samples collected in the estuarine complex of Cananéia-Iguape during the 1st semester of 2009, as well as the activity concentrations of ^{226}Ra, ^{228}Ra, ^{222}Rn and nutrients are presented in **Tab. 1-8**. Activity concentrations of ^{226}Ra in riverine waters from Ribeira of Iguape river discharging to the Iguape outlet varied from 1.8 mBq L^{-1} to 3.4 mBq L^{-1}, while ^{228}Ra concentrations ranged from 17 mBq L^{-1} to 37 mBq L^{-1}. The highest value of ^{228}Ra/ ^{226}Ra activity ratio of 20.6 was observed in station Ribeira 02 (at salinity 1.0).

Groundwater activity concentrations of ^{226}Ra ranged from 0.63 mBq L^{-1} to 12 mBq L^{-1} and for ^{228}Ra from 18 mBq L^{-1} to 39 mBq L^{-1}. In groundwater, the ^{228}Ra/^{226}Ra activity ratios varied from 3.3 to 31.7. ^{222}Rn activities in groundwater up to 747 Bq L^{-1} were observed, the highest value found in Cananéia well 03. All groundwater samples collected in Cananéia presented salinities close to zero. In Comprida Island two wells studied showed salinities slightly higher than zero (well 8 and 10, respectively) indicating the influence of the short distance to seashore, once these wells were located a few hundred meters of the beach.

Table 1. Location of Cananéia surface water samples (February 2009).

Sample	Depth (m)	Date	Volume (L)	Temperature (ºC)	Latitude	Longitude	salinity	pH *in situ*
Station 01	0	10/02/2009	2	26.0	25º 26.351'S	47º 54.944'W	31.597	8.361
Station 03	0	10/02/2009	5	28.6	25º 01.908'S	47º 54.895'W	20.081	7.999
Station 04	0	10/02/2009	5	28.0	29º 01. 084'S	47º 55.548'W	19.585	8.132
Station 05	0	10/02/2009	5	27.8	25º 00.467'S	47º 55.308'W	24.032	8.263

Table 2. Activity concentrations of ^{226}Ra, ^{228}Ra and dissolved nutrients in Cananéia surface water samples (February 2009).

Sample	^{226}Ra (mBq L^{-1})	^{228}Ra (mBq L^{-1})	^{228}Ra/^{226}Ra	Ammonium (µmol L^{-1})	Nitrate (µmol L^{-1})	Nitrite (µmol L^{-1})	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})
Station 01	3.8 ± 0.2	45 ± 5	11.8	1.48	0.59	0.20	11.71	0.23
Station 03	2.9 ± 0.3	22 ± 1	7.6	4.70	2.20	0.32	42.07	0.89
Station 04	4.7 ± 1.1	24 ± 4	5.1	5.42	1.33	0.19	35.80	0.80
Station 05	2.9 ± 0.2	22 ± 1	7.5	3.53	0.98	0.18	46.78	0.86

Table 3. Location of Iguape surface water samples (February 2009).

Sample	Depth (m)	Date	Volume (L)	Temperature (ºC)	Latitude	Longitude	salinity	pH *in situ*
Station 06 A	0	12/02/2009	4	29	24º 54. 166'S	47º 48.520' W	7.775	7.278
Station 06 B	5	12/02/2009	4	29	24º 54. 166'S	47º 48.520' W	7.245	7.344
Station 07 A	0	12/02/2009	5	27	24º 44. 505'S	47º 35.952' W	0.066	7.041
Station 07 B	5	12/02/2009	4	27	24º 44. 505'S	47º 35.952' W	0.055	6.963
Station 08 A	0	12/02/2009	5	27	24º 43.940'S	47º 34.811' W	0.031	6.818
Station 08 B	5	12/02/2009	4	27	24º 43.940'S	47º 34.811'W	0.029	6.776
Station 09 A	0	12/02/2009	4	27	24º 42.187'S	47º33.765'W	0.165	6.953
Station 09 B	5	12/02/2009	4	27	24º 42.187'S	47º 32.196' W	0.255	6.973
Station 10 A	0	12/02/2009	5	27	24º 42.823'S	47º 33.765' W	0.046	6.918
Station 10 B	5	12/02/2009	5	27	24º 42.823'S	47º 33.765' W	0.053	6.865
Station 11 A	0	12/02/2009	5	27	24º 42.026'S	47º 34.045' W	0.042	6.727
Station 11 B	5	12/02/2009	5	27	24º 42.026'S	47º34.045' W	0.761	6.758

Table 4. Activity concentrations of ^{226}Ra, ^{228}Ra and dissolvel nutrients in Iguape surface water samples (February 2009).

Sample	^{226}Ra (mBq L^{-1})	^{228}Ra (mBq L^{-1})	^{228}Ra/^{226}Ra	Ammonium (μmol L^{-1})	Nitrate (μmol L^{-1})	Nitrite (μmol L^{-1})	Silicate (μmol L^{-1})	Phosphate (μmol L^{-1})
Station 06 A	1.8 ± 0.8	18 ± 1	10.0	4.81	6.35	0.46	121.55	1.69
Station 06 B	2.8 ± 0.6	19 ± 4	6.8	5.31	7.57	0.41	130.91	2.03
Station 07 A	2.3 ± 0.3	13 ± 1	5.7	4.09	15.25	0.30	179.19	1.49
Station 07 B	6.6 ± 0.2	20 ± 2	3.0	4.35	15.50	0.25	193.42	1.38
Station 08 A	2.9 ± 0.2	13 ± 1	4.5	2.51	15.69	0.25	185.05	1.26
Station 08 B	4.4 ± 0.6	14 ± 1	3.2	1.77	15.55	0.20	177.22	1.38
Station 09 A	2.4 ± 1.3	19 ± 2	7.9	1.96	16.47	0.25	113.67	1.52
Station 09 B	1.7 ± 0.1	17 ± 1	10.0	2.02	16.66	0.25	153.08	1.55
Station 10 A	2.0 ± 0.2	15 ± 1	7.5	2.28	16.52	0.20	134.31	1.56
Station 10 B	2.4 ± 0.2	14 ± 2	5.8	1.94	16.08	0.25	150.12	1.52
Station 11 A	1.6 ± 0.4	16 ± 1	10.0	1.66	16.08	0.25	161.45	1.33
Station 11 B	2.9 ± 0.9	19 ± 2	6.6	0.93	15.89	0.25	156.53	1.44

Table 5. Location of Ribeira of Iguape River surface water samples (February 2009).

Sample	Depth (m)	Date	Volume (L)	Temperature (ºC)	Latitude	Longitude	salinity	pH *in situ*
Ribeira 01	0	13/02/2009	5	28.5	24º 42.174'S	47º 42.238' W	0.840	7.065
Ribeira 02	5	13/02/2009	5	27.0	24º 42.174'S	47º 42.238'W	1.000	7.022
Ribeira 03	0	13/02/2009	4	27.5	24º 41.470'S	47º 34.200'W	0.025	6.752
Ribeira 04	0	13/02/2009	5	27.5	24º 41.700'S	47º 36.800'W	0.039	6.787
Ribeira 05	0	13/02/2009	5	26.5	24º 40.250' S	47º 33.860'W	0.031	6.712
Ribeira 06	0	13/02/2009	3	27.0	24º 40. 510'S	47º 34.920'W	0.028	6.823
Ribeira 07	0	13/02/2009	5	28.5	24º 40.750'S	47º 35.750'W	0.025	6.842
Ribeira 08	0	13/02/2009	5	27.0	24º 40. 190'S	47º 36.430'W	0.039	6.855

Table 6. Activity concentrations of ^{226}Ra, ^{228}Ra and dissolved nutrients in Ribeira of Iguape River surface water samples (February 2009).

Sample	^{226}Ra (mBq L^{-1})	^{228}Ra (mBq L^{-1})	^{228}Ra/^{226}Ra	Ammonium (μmol L^{-1})	Nitrate (μmol L^{-1})	Nitrite (μmol L^{-1})	Silicate (μmol L^{-1})	Phosphate (μmol L^{-1})
Ribeira 01	2.1 ± 0.2	21 ± 2	10.0	1.38	15.59	0.25	187.56	1.63
Ribeira 02	1.8 ± 0.2	37 ± 2	20.6	1.41	16.33	0.25	184.11	1.64
Ribeira 03	2.4 ± 0.4	25 ± 2	10.4	1.38	16.38	0.20	225.94	1.46
Ribeira 04	3.4 ± 0.2	17 ± 1	5.0	1.88	16.38	0.20	200.81	1.53
Ribeira 05	2.3 ± 0.1	19 ± 1	8.3	0.62	16.43	0.15	226.48	1.65
Ribeira 06	2.5 ± 0.2	29 ± 2	11.6	1.36	17.11	0.20	207.76	1.83
Ribeira 07	2.5 ± 0.1	18 ± 1	7.2	0.33	16.61	0.15	200.37	2.01
Ribeira 08	2.3 ± 0.2	19 ± 1	8.3	1.08	16.06	0.15	227.91	1.96

Activity concentrations of ^{226}Ra in estuarine waters from Cananéia outlet (Stations 1 to 5) varied from 2.9 mBq L^{-1} to 4.7 mBq L^{-1}, while ^{228}Ra concentrations ranged from 22 mBq L^{-1} to 45 mBq L^{-1}. The highest value of ^{228}Ra/ ^{226}Ra activity ratio of 11.8 was observed in Station 01 (at salinity 31.6). In Iguape outlet (Stations 07 to 11), activities of ^{226}Ra ranged from 1.6 mBq L^{-1} to 6.6 mBq L^{-1}; ^{228}Ra varied from 13 mBq L^{-1} to 20 mBq L^{-1}. Activities of Ra were slightly higher in samples collected at 5 m depth than at the surface water level.

The ^{228}Ra/^{226}Ra activity ratios determined both in surface and in groundwater samples reflect the presence of a higher ^{232}Th content in relation to ^{238}U in sediments and crystalline rocks of the continental shelf off São Paulo [11].

Table 7. Location of groundwater samples collected in Cananéia and Comprida Island (April 2009).

Sample	Date	Volume (L)	Temperature (ºC)	Latitude	Longitude	salinity	pH *in situ*
Cananéia/ Well 1	13/04/2009	5	25	-	-	0.0499	-
Cananéia/ Well 2	13/04/2009	5	26	25º 01.205' S	047º 55.964' W	0.0461	-
Cananéia/ Well 3	13/04/2009	5	24	-	-	0.0155	4.465
Cananéia/ Well 4	13/04/2009	5	24	24º 58.135' S	047º 54.246' W	0.0857	4.384
Cananéia/ Well 5	13/04/2009	5	24	-	-	0.0313	5.122
Cananéia/ Well 6	13/04/2009	5	26	-	-	0.0987	5.360
Cananéia/ Well 7	13/04/2009	5	24	-	-	0.0796	5.562
Comprida Is. / Well 8	14/04/2009	5	26	25º 01.674' S	047º 54.187' W	0.239	5.260
Comprida Is. / Well 9	14/04/2009	5	27	-	-	0.0520	6.489
Comprida Is. / Well 10	14/04/2009	5	27	25º 01.651' S	04º' 53.011' W	0.108	7.415
Comprida Is. / Well 11	14/04/2009	5	25	25º 01.796' S	047º 53.115' W	0.0257	5.515
Comprida Is. / Well 12	14/04/2009	5	29	25º 01.042' S	047º 52.700' W	0.0970	6.639
Comprida Is. / Well 13	14/04/2009	5	28	-	-	0.0149	5.748

Table 8. Activity concentrations of ^{226}Ra, ^{228}Ra in groundwater samples from Cananéia and Comprida Island (April 2009).

Sample	^{226}Ra (mBq L^{-1})	^{228}Ra (mBq L^{-1})	^{228}Ra/^{226}Ra	^{222}Rn (Bq L^{-1})	Nitrate (µmol L^{-1})	Nitrite (µmol L^{-1})	Silicate (µmol L^{-1})	Phosphate (µmol L^{-1})
Cananéia/ Well 1	3.6 ± 0.2	20 ± 2	5.6	739 ± 44	42.48	0.04	2.14	0.72
Cananéia/ Well 2	3.8 ± 1.3	24 ± 2	6.3	717 ± 43	41.46	0.03	16.98	0.18
Cananéia/ Well 3	3.9 ± 0.8	21 ± 2	5.4	747 ± 45	0.13	0.03	12.10	0.17
Cananéia/ Well 4	12 ± 1	39 ± 3	3.3	593 ± 35	165.4	0.01	5.41	0.14
Cananéia/ Well 5	5.6 ± 0.8	27 ± 2	4.8	643 ± 39	130.0	0.13	2.74	0.15
Cananéia/ Well 6	2.9 ± 0.5	26 ± 2	8.9	652 ± 39	25.39	0.01	3.86	0.15
Cananéia/ Well 7	2.5 ± 0.6	18 ± 1	7.2	669 ± 40	5.42	0.03	1.65	0.13
Comprida Is. / Well 8	1.8 ± 0.3	25 ± 6	13.9	692 ± 42	0.03	0.18	255.5	5.02
Comprida Is. / Well 9	3.9 ± 3.6	25 ± 6	6.4	595 ± 36	77.30	0.48	98.41	0.55
Comprida Is. / Well 10	0.63 ± 0.08	20 ± 1	31.7	615 ± 37	136.1	3.38	73.30	0.74
Comprida Is. / Well 11	2.0 ± 1.0	23 ± 2	11.5	654 ± 39	5.95	0.01	2.13	0.16
Comprida Is. / Well 12	1.4 ± 0.5	24 ± 2	17.1	643 ± 39	9.62	0.03	4.13	0.18
Comprida Is. / Well 13	2.3 ± 0.1	24 ± 1	10.4	690 ± 41	16.06	0.01	3.37	0.21

The activity concentrations of ^{226}Ra and ^{228}Ra observed both in groundwater and surface water studied in Cananéia-Iguape estuarine complex are of the same order of magnitude than those measured in previous studies carried out in Ubatuba embayments, northern São Paulo coastal area [4, 5, 12].

Taking into account the nutrients results, mainly the nitrate content, we observe that surface waters from the notheastern part of the Cananéia-Iguape estuary is more strongly submitted to the influence of the continental contribution than does southeastern part of the study area. Increased nitrate contents were observed in groundwater samples collected in Cananéia and Comprida Island. Future assessment of nitrogen load to nearshore waters via SGD is necessary for the future management of the local system since in some cases, SGD may result in contamination of the near-shore marine environment from land-based activities. Also, residence time and salinity variations may influence the ecological conditions and production rates in this estuary.

4. CONCLUSIONS

During the last few years, our group have been applied a suite of naturally occurring radionuclides in the U/Th decay series (^{222}Rn, ^{226}Ra and ^{228}Ra) in coastal area to evaluate their utility as groundwater discharge tracers. The major focus of the study presented in this paper was to examine the fluxes of radium isotopes and ^{222}Rn to Cananéia-Iguape estuarine complex. Up until today, groundwater/ surface water exchange of radium isotopes and ^{222}Rn in this area were ungauged.

The activity concentrations of ^{226}Ra and ^{228}Ra observed both in groundwater and surface water studied in Cananéia-Iguape estuarine complex are of the same order of magnitude than those measured in previous studies carried out in Ubatuba embayments, northern São Paulo coastal area.

Both in stations performed in Cananéia and Iguape outlets during the 1st semester of 2009, radium isotopes and nutrient data showed scattered distributions with salinity and distance offshore. This indicates that in this complex system the area is influenced by tidal oscilation and groundwater-seawater mixing. Therefore, the sources of nitrate observed in visited stations are both due to transport of pollutants by local currents and do to possible contributions of SGD. Increased nitrate levels in wells sampled in Cananéia and Comprida Island indicates that nitrogen is fed by coastal contaminated groundwater and re-circulated estuarine water (with different proportions of groundwater in the mixture), which gives rise to potential environmental concern with implications for management of freshwater resources in the region.

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