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Geochronology of anthropogenic radionuclides in Ribeira Bay sediments, Rio de Janeiro, Brazil

Franciane de Carvalho Gomes [a], José Marcus Godoy [b,c,*], Maria Luiza D.P. Godoy [b], Zenildo Lara de Carvalho [b], Ricardo Tadeu Lopes [a], Joan-Albert Sanchez-Cabeza [d,1], Iolanda Osvath [d], Luiz Drude de Lacerda [e]

[a] Programa de Engenharia Nuclear, COPPE/UFRJ, Cidade Universitária, Caixa Postal 68.509, 21945-970 Rio de Janeiro, Brazil
[b] Instituto de Radioproteção e Dosimetria (IRD), Caixa Postal 37750, Barra da Tijuca, 22642-970 Rio de Janeiro, Brazil
[c] Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Rua Marquês de São Vicente 225, 22453-900 Rio de Janeiro, Brazil
[d] IAEA Marine Environment Laboratories, 4 Quai Antoine Premier, MC98000 Principality of Monaco, Monaco
[e] Laboratório de Ciências do Mar, Universidade Federal do Ceará, Fortaleza, Ceará, Brazil

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ABSTRACT

Ribeira Bay is located approximately 130 km south of the city of Rio de Janeiro and receives discharges of liquid effluent from the Angra dos Reis nuclear power plant (NPP) site, where two pressurized water reactors are located. To test whether the presence of anthropogenic radionuclides in sediments in Ribeira Bay could be correlated to the NPP operations, we sampled seven sediment cores and determined accumulation rates and chronologies. Only one sediment core did not exhibit a superficial mixing layer; this sample was used for dating purposes. Cesium-137 and ^{207}Bi were observed in this sediment profile, but their presence was associated with atmospheric fall-out rather than the nearby NPP. The exponential decay of ^{210}Pb concentration with sediment layer depth was verified below a superficial mixing layer for all other sediment cores. Calculated accumulation rates ranged from 1.2 mm y^{-1} in the inner bay to 6.2 mm y^{-1} close to its entrance.

1. Introduction

Ribeira Bay is a large cove of Ilha Grande Bay, which is an important tourist resort area for southern Rio de Janeiro State. Ribeira Bay has an irregular coastline and is surrounded by the Serra do Mar Mountains, which reach elevations of up to 1000 m. However, the bay receives freshwater only from small creeks. Ribeira Bay is relatively deep, with a mean depth of 8 m, and it contains several small islands (Nogueira et al., 1991). The local climate is humid-tropical, with a mean annual temperature above 19 °C, and rainfall occurs primarily from December to March (IBGE, 1977).

There are currently two co-located nuclear power plants (NPP) in operation in Brazil. The first, with 660 MWe of generating capacity, began operation in 1982, while the second plant, with 1350 MWe of capacity, began in 2000. Together, they represent approximately 3% of Brazil's electricity production. Another 1350-MWe plant is under construction at the same reactor site. The reactor site is located at Itaorna Beach, Angra dos Reis, which is approximately 130 km from the city of Rio de Janeiro. The reactors draw in seawater for cooling and then discharge the water through a tunnel into an adjacent cove called Piraquara de Fora. Due to the strong current caused by the cooling water discharges, non-conservative radionuclides are thought to be deposited outside Piraquara de Fora, into the Ribeira Bay (Fig. 1).

When construction began on the second reactor unit in 1992, the area around the NPP was declared an environmental protection area. Therefore, despite the presence of several condominiums, marinas and the Almirante Alvaro Alberto Nuclear Power Plant effluent discharge point, the region remains relatively well preserved (Gomes et al., 2009), with significant remnants of Atlantic forests. According to Dias et al. (1990), the existing sediments in Ribeira Bay can be classified as muddy sediments.

The presence of the NPP has motivated multiple environmental impact studies in the Ribeira Bay region. Past studies have examined the influence of cooling water discharges on the plankton

* Corresponding author. Instituto de Radioproteção e Dosimetria (IRD), Caixa Postal 37750, Barra da Tijuca, 22642-970 Rio de Janeiro, Brazil.
E-mail address: jmgodoy@ird.gov.br (J.M. Godoy).
[1] Present address: Institute of Environmental Science and Technology, and Physics Department, Autonomous University of Barcelona, ES-08193 Bellaterra, Spain.

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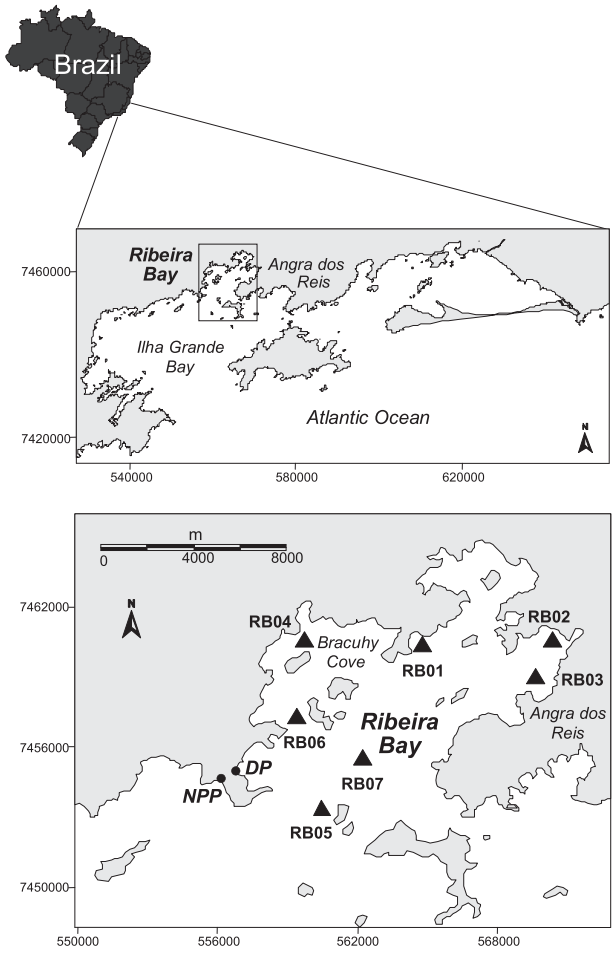

Fig. 1. Sediment coring stations in Ribeira Bay (NPP = Nuclear Power Plant and DP = Effluent Discharge Point).

community (Dias and Bonecker, 2008), heavy metals in sediments (Freret-Meurer et al., 2010; Gomes et al., 2009; Cardoso et al., 2001) and HPAs in sediments (Azevedo et al., 2007). Very few studies have considered artificial radionuclides such as ^{137}Cs and ^{60}Co in seaweeds (Guimarães and Penna-Franca, 1985).

For environmental monitoring related to the NPP operation, knowledge of existing sedimentation areas and sedimentation rates in Ribeira Bay is of foremost importance for selecting the locations of sediment sampling stations and sampling procedures. Therefore, the aims of this study were to obtain this information and ascertain the deposition pattern of artificial radionuclides and its relationship to the NPP operation.

2. Material and methods

We used a gravity corer to sample seven sediment cores in Ribeira Bay (Fig. 1). During the first sampling campaign, in 2007, four sediment cores (RB01-RB04) were taken, each of which were sliced into 3-cm layers. Three additional sediment cores (RB05-RB07) were obtained during the second sampling campaign, in 2008, and were sliced into 2-cm layers. The slices were lyophilized and homogenized using an agate mortar. All of the slices were weighed wet and dry; the observed dry weight was divided by the corer area to calculate the superficial density (g cm^{-2}).

Lead-210 concentrations were determined according to the following procedure described by Godoy et al. (1998): 5-g aliquots were taken and leached with 50 mL 0.5 M HBr for 2 h at 80 °C. The resulting solution was separated, and the residue was leached with 50 mL 0.5 M HBr + 1.0 g hydroxylamine hydrochloride for 2 h at 80 °C. A lead carrier was added to the resultant solution, and the mixture was transferred to an ion-exchange column containing Dowex 1X8, 50–100 mesh. This stage was followed by a cleaning step with 0.5 M HBr + 1.0 g hydroxylamine hydrochloride and further elution with 1 M HNO_3. There is no interference from other beta-emitting radionuclides because the ion-exchange separation in bromidic acid is quite selective for lead (Godoy et al., 1998). Lead then precipitated as chromate, after which the chemical yield could be obtained gravimetrically.

The concentration of ^{210}Pb was determined from its decay product, ^{210}Bi, after a two week in-growth period, using beta counting on a ten-channel low-level proportional counter Perkin–Elmer Prof. Berthold. LB-750. This technique has a detection limit of 1 Bq kg^{-1} per 1000 min of counting time, and the method's repeatability is estimated at 10% (Godoy et al., 1998). The ^{210}Pb method is routinely submitted on a quarterly basis for interlaboratory exercises (Tauhata et al., 2006). The RB04 samples were also analyzed using gamma spectrometry at the IAEA-Monaco underground low-level counting laboratory for environmental radionuclides (Povinec et al., 2005).

The sediment core chronologies were determined using the Constant Flux – Constant Sediment Accumulation Rate (CF:CS) method (see, for example: Joshi and Shukla, 1991; Appleby and Oldfield, 1992; Sanchez-Cabeza et al., 2000). First, logarithmic plots of ^{210}Pb concentration versus sediment depth were made. Then, the excess ^{210}Pb was calculated by subtracting the constant value observed in the core bottom, as shown in Fig. 2a–g and described by Godoy et al. (1998).

For all seven cores, ^{210}Pb flux was calculated by multiplying the total $^{210}Pb_{excess}$ inventory by the ^{210}Pb decay constant. Additionally, the RB04 ^{210}Pb flux was also calculated with a CF:CS model, as proposed by Krishnaswany et al. (1971) and Gökmen et al. (1996) (equation (1)):

$$\left(^{210}\text{Pb flux}\right) = \left[^{210}\text{Pb}\right]_0 .S.\rho.\left(1\text{-}\phi_0\right) = \left[^{210}\text{Pb}\right]_0 .\omega, \qquad (1)$$

where:

$[^{210}Pb]_0$ = ^{210}Pb concentration on the first layer (mBq g^{-1})
S = sediment accumulation rate, cm y^{-1}
ρ = sediment density, (g cm^{-3})
ϕ_0 = porosity of the first layer
ω = mass accumulation rate, g cm^{-2} y^{-1}

3. Results and discussion

3.1. Pb-210 sediment dating

The ^{210}Pb concentration depth profiles in the seven sediment cores from Ribeira Bay are shown in Fig. 2a (RB01) through 2 g (RB07). If the sediment records in Ribeira Bay are well preserved and no surface mixing layer is present, then as long as constant ^{210}Pb flux and sediment accumulation rates exist, the CF:CS model should be valid, and the ^{210}Pb concentration with mass depth should vary exponentially. In fact, despite the presence of a surface mixing layer (SML) in all cores, except RB04, every core exhibited an exponential decay signature. Under the assumption that no mixing occurs below the SML, mass accumulation rates were estimated by fitting the ^{210}Pb concentration profile to an exponential curve (Gökmen et al., 1996). Estimated mass accumulation rates varied from 0.0571 ± 0.0097 g cm^{-2} y^{-1} (1.26 ± 0.20 mm y^{-1}) in RB01 to

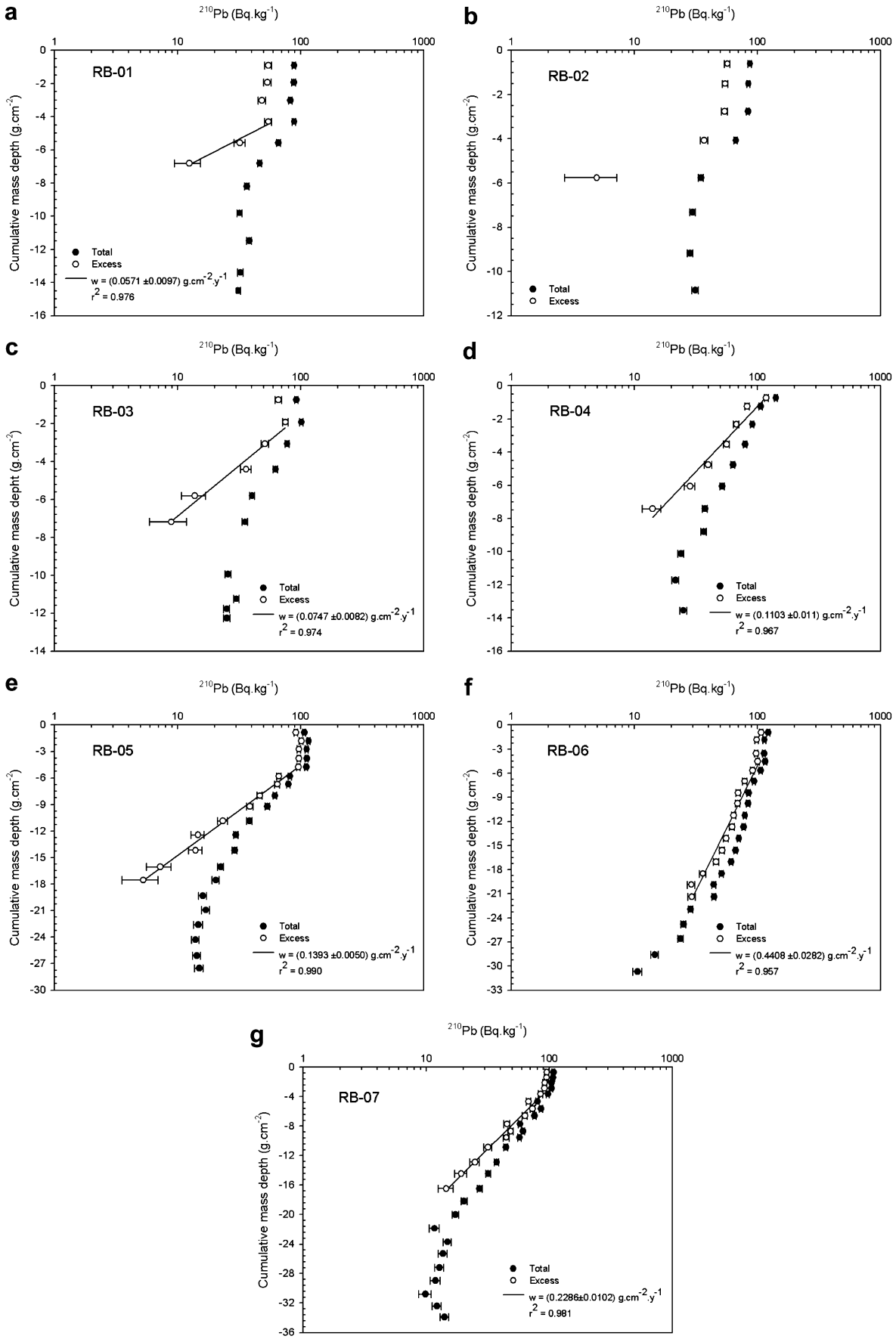

Fig. 2. Excess ^{210}Pb depth profiles for Ribeira Bay sampling points RB01 (a) through RB07 (g).

Table 1
Sediment and mass accumulation rates obtained at each sampling point.

Sampling station	Mass accumulation rate, g cm^{-2} y^{-1}	Sediment accumulation rate, cm y^{-1}
RB01	(0.0571 ± 0.0097)	(0.126 ± 0.020)
RB02	Not calculated	
RB03	(0.0747 ± 0.0082)	(0.167 ± 0.018)
RB04	(0.110 ± 0.011)	(0.268 ± 0.026)
RB05	(0.1393 ± 0.0050)	(0.192 ± 0.011)
RB06	(0.441 ± 0.028)	(0.620 ± 0.040)
RB07	(0.229 ± 0.010)	(0.388 ± 0.031)

0.229 ± 0.010 mg cm^{-2} y^{-1} (3.88 ± 0.31 mm y^{-1}) in RB07 (Table 1). Because no significant river discharge into Ribeira Bay occurs, two sediment sources may exist: sediment remobilization from Ilha Grande Bay during high tides, and soil runoff from the adjacent hills. The existence of the first source can be illustrated by comparing the sedimentation rate from sampling point RB07 with RB05. Both are neighbors, but RB05 is protected by islands and has a lower sedimentation rate, while RB07 is more exposed to the currents between Grande Island and the continent and presents a higher sedimentation rate. Similarly, comparing RB06 and RB07, RB06 has a higher sedimentation rate, most likely due to runoff from the adjacent hills. An example of this runoff occurred in February 1985, when a large amount of soil slid down from the hills in front of Piraquara de Fora Cove, where the NPP effluent discharge point is located, and destroyed the road and the former Nuclear Power Plant's environmental monitoring laboratory in the cove area. The sediment accumulation rate calculated for Bracuhy Cove (RB04) was 3 mm y^{-1}, which is in agreement with a previous estimate by Barbosa (2001).

3.2. Pb-210 chronology validation

In the northern hemisphere, ^{137}Cs is usually used as a tool for ^{210}Pb sediment dating validation (see, for example, Sanchez-Cabeza et al., 1999). However, within the 20–30° latitude band of the southern hemisphere, nuclear bomb fall-out deposition is five times lower than that observed between 40° N and 50° N, for example (UNSCEAR, 1982). For instance, Godoy et al. (2003) report ^{137}Cs concentrations in marine sediments ranging from 3.8 to <0.15 Bq kg^{-1} between 20° S and 30° S. Therefore, the samples from the undisturbed core (RB04) were analyzed at the very low-level, underground gamma spectrometry laboratory IAEA-MEL. The results obtained (Fig. 3) from this analysis indicated a ^{137}Cs plateau after a depth corresponding to 1968(±4), which is close to the 1964–1965 maximum from atomic bomb testing. A ^{207}Bi maximum at a depth corresponding to 1957(±5) was also observed. This spike could be related to the Argus operation in 1958, when three nuclear devices were tested in the South Atlantic between Brazil and South Africa. The clean nuclear weapon tests carried out in the Pacific in late 1958 are another possible ^{207}Bi source (Noshkin et al., 2001).

Descriptions given to early nuclear weapons include the terms "clean" or "dirty". Weapon components used in early tests were usually configured with quantities of natural, depleted or enriched uranium or other potentially fissionable material. The energetic neutrons (>1.5 MeV) produced during fusion (or from fission of the primaries) were capable of inducing fission in ^{238}U (or other fissionable material), which would lead to an increase in fission yield. Weapons configured in this way were known as "dirty" because the end result was a release of larger amounts of radioactive fission products to the environment. In a "clean" device, the ^{238}U is replaced with other high Z nonfissionable material (*e.g.*, lead and bismuth). In a "clean device", most of the energy is derived from fusion, whereas, in a "dirty" device, nuclear fission accounts for the majority of the total yield (Noshkin et al., 2001).

The larger uncertainty associated with ^{137}Cs concentrations makes it impossible to determine whether the NPP operation has actually led to an increase in ^{137}Cs in bay sediments. The sample corresponding to the first layer was measured in Rio de Janeiro and not in Monaco, and, despite the 100% relative efficiency of the applied detector, the 0.5 Bq kg^{-1} ^{207}Bi detection limit for a 24-h

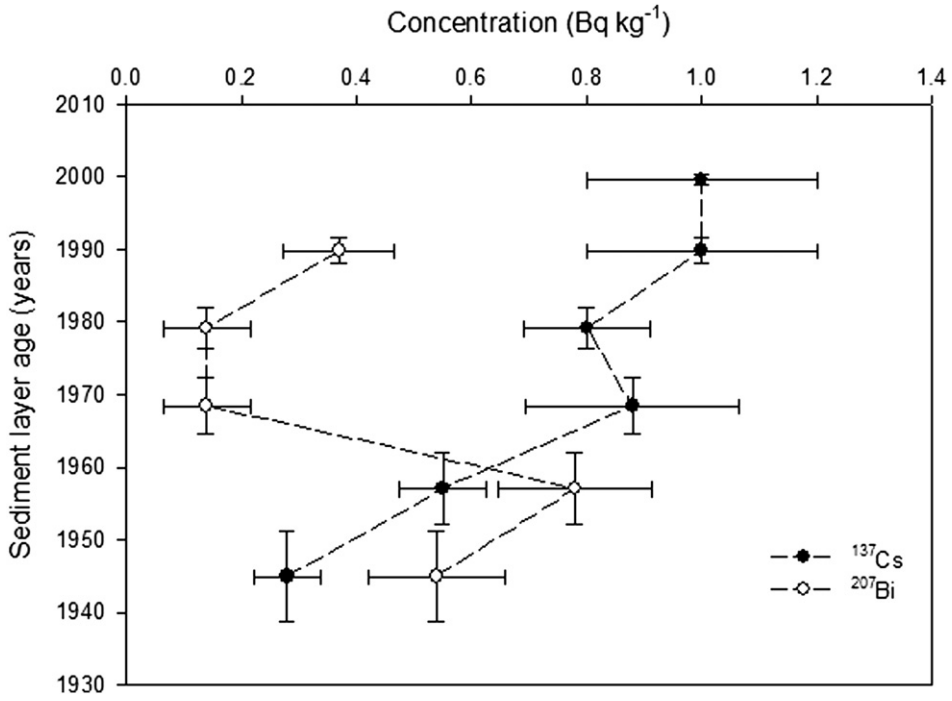

Fig. 3. ^{137}Cs and ^{207}Bi age and depth profiles at sampling point RB04.

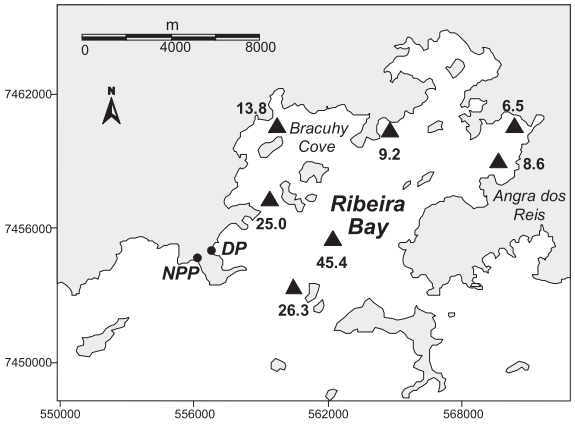

Fig. 4. ^{210}Pb flux variation for sampling stations in Ribeira Bay (values in mBq cm^{-2} y^{-1}).

measurement time was not sufficient to reach the expected ^{207}Bi concentration based on the previous two layers. Therefore, it is only possible to ensure that the ^{207}Bi present day concentration is lower than this value. However, the production of ^{207}Bi on the Angra dos Reis light water pressurized reactor is not expected, because lead and bismuth are not present on the reactor nucleus.

After applying the ^{226}Ra-^{210}Pb results obtained at IAEA-MEL, we observed a sediment accumulation rate of 0.106 ± 0.018 g cm^{-2} y^{-1} for this core, which was statistically equivalent to that obtained with the ^{210}Pb leaching methodology (0.1103 ± 0.0092 g cm^{-2} y^{-1}).

Fig. 4 shows the variations in ^{210}Pb flux at different sampling points. Lower fluxes were observed at the sampling points in the inner part of the bay and were compatible with the expected atmospheric flux for this region, which Preiss et al. (1996) found to be 7 mBq cm^{-2} y^{-1}. Higher values in Bracuhy Cove reveal the contribution of soil runoff from the adjacent hills (RB06) and from small creeks (RB04). As observed with the sedimentation rates, the ^{210}Pb flux contribution from sediments transported from Ilha Grande Bay through the channel, between Ilha Grande and the continent, was particularly evident in sample RB07, especially when compared to RB05, which was located nearby but was protected by islands. For the sampling points located closer to the bay entrance, the observed ^{210}Pb flux range was in agreement with most of the values measured in coastal areas (10–45 mBq cm^{-2} y^{-1}) (Preiss et al., 1996).

The ^{210}Pb flux for core sample RB04 was calculated in two ways: first, by using the total ^{210}Pb$_{excess}$ inventory, and additionally according to Eq. (1). The values obtained with each method were similar, with a flux of 13.1 mBq cm^{-2} y^{-1} for the CF:CS model and 13.8 (±0.7) mBq cm^{-2} y^{-1} from the total inventory. These two flux values can be used to calculate a value of 1.7 years ($\Delta t = 32.2 * \ln(13.1/13.8)$) as the most probable age difference between the CRS and CF:CS ages (Joshi and Shukla, 1991).

4. Conclusions

In Ribeira Bay, the sediment accumulation rate increases from 0.12 cm y^{-1}, at sampling point RB01 in the inner part of the bay, to 0.62 cm y^{-1}, at sampling point RB06 close to the entrance. This gradient may have originated from a combination of sediment flux through the channel between Ilha Grande (Grande Island), and the continental and soil runoff from the adjacent hills. The sediment input through this channel is even more evident when the values obtained at sampling points RB05 and RB07 are compared.

Only one sediment core did not exhibit a superficial mixing layer (RB04); this sample was used for dating purposes. A variety of methods were successfully applied as validation tools, including ^{210}Pb determination through two independent methods, ^{137}Cs and ^{207}Bi profiles, ^{210}Pb flux calculation and age calculation by two different methods, CF:CS and CRS.

The larger uncertainty associated with ^{137}Cs concentrations makes it impossible to determine whether the NPP operation has actually led to an increase in ^{137}Cs in bay sediments. The ^{207}Bi peak, at a depth corresponding to 1957(±5), has two possible sources: the Argus operation, carried out in the South Atlantic between the Brazilian and South African coasts in 1958, and the Poplar test on Bikini atoll, in July 1958, which was the fifth largest U.S. test ever (http://nuclearweaponarchive.org/Usa/Tests/Hardtack1.html).

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