

# Origin and transport of radium in the water column of Buena Coastal Lagoon

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## Introduction

The radium concentration in surface waters normally ranges from 0.01 to 0.1 Bq.l<sup>-1</sup> (Iyengar, 1990), with high values found in waters close to uranium mining and milling (Iyengar, 1990; Paschoa *et al.*, 1979 and Benes, 1990). In groundwater, the Ra concentration can reach values up to 38 Bq.l<sup>-1</sup>, depending on factors such as the kind of aquifer rock as well as chemical and physical characteristics of water (Gascoyne, 1989). Based on groundwater data, a correlation between salinity and radium is expected (Kramer and Reid, 1984; Langmuir, 1985); therefore, among others the lower concentration of radium in surface waters than in ground waters could be credited to the lower values of salinity normally found in surface waters. Well known is the increase of the dissolved radium concentrations in the estuarine region due to salinity effects (Hancock and Murray, 1996; Moore and Shaw, 1998).

The so-called Buena Lagoon is a high salt coastal lagoon located close to the border between Rio de Janeiro and Espirito Santo States, Brazil, in a monazite rich region. Its waters are used by a hydrogravimetric monazite sand separation mill. In the waters of

Buena lagoon abnormal concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were found, which at first could be credited to the activities at this mill. However, the high chemical and mechanical stability of the monazite is responsible for the negligible releasing of radionuclides from it and consequently the short contact time of the water with the sand minerals during the hydrogravimetric processing would not be sufficient to promote the releasing of radionuclides from the ore. Additionally, higher radium concentrations were observed upstream instead of downstream from the effluent discharge point. So, the aim of this research was to identify the origin of the observed high radium concentrations and to study its transport in the water column of the lagoon.

## Material and methods

### *The study area*

Buena Lagoon is located in Rio de Janeiro State, Brazil, between the coordinates  $21^{\circ} 23'$ -  $21^{\circ} 24'$  S and  $41^{\circ} 00'$ -  $41^{\circ} 03'$  W (Figure 1). Its watercourse surface area is  $0.11 \text{ km}^2$  ( $113\,000 \text{ m}^2$ ), its length is 5.4 km and it is on average 21 m wide. Its wetland has an area of  $0.67 \text{ km}^2$ , largely covered by aquatic vegetation, mainly *Typha Dominguesis* Pers., and its catchment area comprises  $7.5 \text{ km}^2$ . The lagoon is separated from the ocean by a barrier of sand approximately 15 meters wide. Once or two times a year, fishers open its mouth and its water inflows in the direction of the sea. A physical separation plant aiming the heavy mineral separations uses the water of Buena Lagoon and after the water is used, it is returned to the place where it was taken from (sampling station 5, Figure 1). The regions climate is tropical, warm and wet, with rainy (approximately October-February) and dry (approximately March-September) seasons. Mean annual rainfall is about 760 mm.

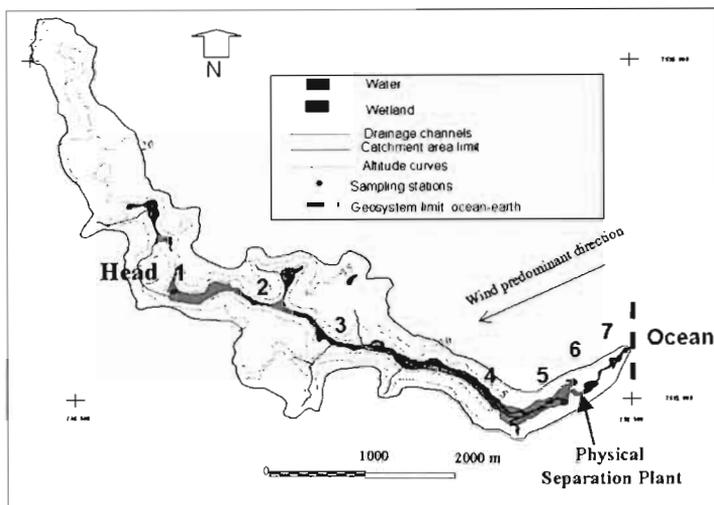


Figure 1  
Map of Buena lagoon containing the localization  
of the sampling points.

## Sampling

About 4.5 l samples, 4 l in a polyethylene bottle and 0.5 l in a dark glass bottle, were collected at each sampling point, in the rainy and in the dry seasons, from June/95 to December/97. Sediment and water samples were collected in the seven sampling stations along the lagoon. Eh, pH and conductivity were measured directly at the site. On a time scale shorter than one hour, the samples were taken to a clean lab and the aliquot storage in the glass bottle was filtered with glass fiber for the determination of nitrate, phosphate and organic and inorganic carbon; afterward the aliquot was again put in a dark glass flask and preserved frozen until the day of the determinations. The other 3.5 l samples were filtered (Millipore membrane) and were then acidified with nitric acid supra pure for the determination of the radionuclides and cations. 0.5 l Samples were stored without acidification for the sulfate and chlorine determination.

## *Chemical analysis methods*

**Anions:** Classical chemical methods were applied to the determination of anions in the water samples. Sulfate was determined by turbidimetry, chloride by the Volhard's argentometric method, nitrate by spectrophotometric method after its reduction to nitrite on a cadmium/copper column and phosphate by the ammonium molybdate/ascorbic acid method and the alkalinity by acid titration (Standard Methods, 1975).

**Organic and inorganic carbon:** Both organic and inorganic carbon were determined by a Carbon Analyzer Beckman 915B.

**Cations:** Cations in general, including major cations, rare earth elements, uranium and thorium were analyzed by inductively coupled plasma-mass spectrometry, ICP-MS, Perkin-Elmer ELAN 5000, after a dilution 1:20 with water quality Milli-Q, applying the so-called "TotalQuant" method using In and Tl as internal standards. A total of 27 elements were used for the equipment mass efficiency calibration.

**$^{228}\text{Ra}$  and  $^{226}\text{Ra}$ :** Using 1-liter sample,  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  were analyzed applying the procedure described by Godoy (1990). The accuracy of such determination is routinely tested by inter-laboratory exercises organized by the EPA/USA and the Radionuclide Metrology Division of IRD/CNEN (Vianna, Tauhata, de Oliveira, Clain and Ferreira, 1998).

## **I** Results and discussion

Among seven and four sampling campaigns were performed at each sampling station, as station one was the last station discovered, only four sampling campaigns were performed at this station. The complete data set was composed by 1065 single measurements of the 28 variables (Na, K, Mg, Ca, Mn, Fe, Al, Si, La, Ce, Pr, Nd, Sm, Th, U,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$ , F<sup>-</sup>, Cl<sup>-</sup>,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ; Dissolved Organic Carbon, Inorganic Carbon, pH, Eh, Alkalinity and Conductivity).

Comparing the values of the variables at the same station, no significant differences among the values in the dry and in the rainy seasons was observed. The normality distribution tests for each variable showed that the data were log-normally distributed. Statistical tests were performed with the data transformed into their logarithms allowing the central tendency and dispersion to be represented by the geometric mean and geometric standard deviation for each station (Wayne, 1990). The exception was the pH data set. The central tendency and dispersion were represented by arithmetic mean and standard deviation as the pH data set was already in the logarithm form. The central tendency and the dispersion for the most representative variables (Th, U,  $^{228}\text{Ra}$ ,  $^{226}\text{Ra}$ , Cl<sup>-</sup> and pH) at the sampling stations are shown in Table 1.

The comparison of the geometric mean and the geometric standard deviation of each variable among the sampling stations (respectively by t-test and F-test) showed four different distribution patterns along the lagoon: *i*) the mean is the representative value of concentration for all stations, including the behavior of Th, Fe, Mn and dissolved organic carbon; *ii*) the highest values of concentration were found at station 1, while in all the other stations the concentrations had the same mean value. The variables of this set are Si, Eh and nitrate. Uranium belongs to this set, however its behavior is a little bit different, since at station 7 its concentration value increased; *iii*) the concentrations increased with the proximity of the sea. To this data set belongs the major ions (Na, K, Ca, Mg, Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and the pH and *iv*); the fourth data set showed a behavior opposite to the last distribution, the values of the concentration decreased with proximity to the sea. To this variable set belongs the radium isotopes and the light rare earth elements.

### *Investigating the radium origin*

In order to identify the main sources of ions to the lagoon water, factor analysis was employed, using the complete data set. Factor analysis is a technique suitable for simplifying large and complex data sets, creating a limited number of factors, each representing a cluster of interrelated variables within a data set (Zhu *et al.*, 1997). For the extraction methods the Principal Component Analysis method (PCA)

Station	Distance from the Lagoon head (m)	Th μg.l <sup>-1</sup>	U μg.l <sup>-1</sup>	<sup>226</sup> Ra Bq.l <sup>-1</sup>	<sup>228</sup> Ra Bq.l <sup>-1</sup>	La μg.l <sup>-1</sup>	PH	Cl <sup>-</sup> mg.l <sup>-1</sup>
1	0	0.05	1.10	0.36	1.52	26	4.2	487
		(1.50)	(2.39)	(1.23)	(1.33)	(1.86)	(0.1)	(1.76)
2	800	0.14	0.04	0.26	0.63	2.37	5.9	650
		(4.41)	(4.38)	(1.20)	(1.35)	(2.51)	(0.2)	(2.40)
3	1900	0.08	0.03	0.25	0.49	1.75	5.9	864
		(3.06)	(5.70)	(1.93)	(1.68)	(5.89)	(0.2)	(2.22)
4	3700	0.14	0.03	0.15	0.20	0.16	6.3	1217
		(4.31)	(6.09)	(1.32)	(1.41)	(3.25)	(0.2)	(1.37)
5	4500	0.08	0.04	0.17	0.18	0.54	6.7	1060
		(3.58)	(3.65)	(2.31)	(1.82)	(7.14)	(0.2)	(1.85)
6	4900	0.07	0.12	0.14	0.10	0.09	6.9	1627
		(2.00)	(1.50)	(1.46)	(1.47)	(5.59)	(0.4)	(1.26)
7	5400	0.10	0.42	0.08	0.12	0.14	7.3	2295
		(3.08)	(2.24)	(1.36)	(1.27)	(3.17)	(0.3)	(1.61)

( ) standard deviation

Table 1

Values of the geometric mean and geometric standard deviation of the Th, U, <sup>226</sup>Ra, <sup>228</sup>Ra and Cl<sup>-</sup> concentrations and of the arithmetic mean and standard deviation of pH in the lagoon water.

was applied and those variables with a large number of values close or below the detection limits, such as Th and Al, were excluded. The extraction showed that 82 % of the variance could be explained by only three components (Component 1: 39 %, Component 2: 32 % and Component 3: 11 %). Component 1 joins all the light rare earth elements and the radium isotopes, showing a strong relationship with the constituent elements of the monazite. Component 2 aggregates the set of seawater variables and it represents the seawater influence on the lagoon water composition and Component 3 unites elements which can be released from the rock weathering such as Fe and Mn (Figure 2). Uranium has two different sources, one from the same source of the Component 1 and the other from the Component 2 (sea water).

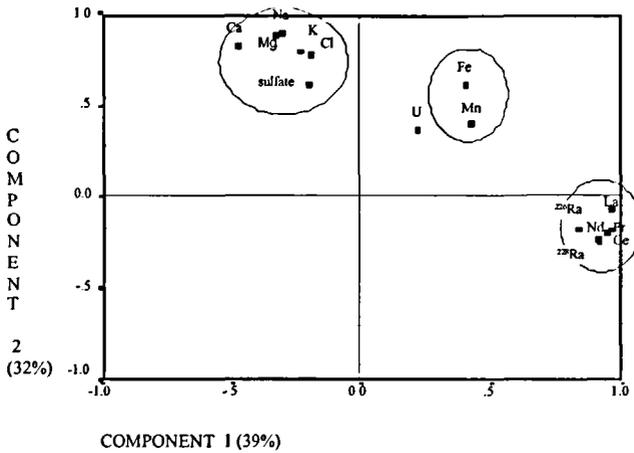


Figure 2  
Plot of loadings on component 1 to 2.

The factor analysis indicated that the gradient of the variable concentrations along the lagoon were due to two water sources located at opposite sides of the lagoon. The seawater can supply the major ions by seawater infiltration and atmosphere deposition. The groundwater supplies the radium isotopes and the light rare earth elements (LREEs).

Based on this data set, the approximate location of the radium source may be in the area surrounding station one. This was confirmed by the discovery of several water springs feeding a channel (constructed by local farmers) flowing in the direction of the lagoon head (station one). The distance from the springs to the lagoon head was around 100 meters. The channel was totally covered by vegetation, making its location difficult. The spring waters had between 1.7 and 2.5 Bq.l<sup>-1</sup> of <sup>228</sup>Ra and around 0.5 Bq.l<sup>-1</sup> of <sup>226</sup>Ra and its pH value was around 3.7.

The water springs are salt water (salinity 14 ‰) and have a low pH (3.7). It is well established that increasing cation concentrations will lead to competition with Ra for adsorption sites. Consequently, in saline groundwaters, high Ra concentrations have been found (Moore and Shaw, 1998). On the other hand, increases in Ra lea-

ching from ores was observed at a pH lower than 4 (Benes, 1984). The low pH value observed for the water springs can also contribute to the high Ra concentrations in it. The strong relationship among the Ra isotopes, the light rare earth elements and U is compelling evidence that these elements derive from the same source. Then the possibility of the monazite being the source of Ra in the groundwater and consequently to the lagoon water have to be considered.

### *Evaluating the radium transport along the lagoon*

The activity ratio of  $^{228}\text{Ra}/^{226}\text{Ra}$  can be used as a tracer of Ra mobility in the water column if it does not vary with the evaporation, precipitation or biological activity, but varies only with the radium decays. To use this ratio some assumptions must be made: i) the ratio of the concentrations of  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  is constant at the source and ii) there is only one source of radium which is located at the head of the lagoon.

The Ra concentrations observed in other lagoons of the region, located around 20 Km from Buena Lagoon, showed a mean value (for four measurements) of  $^{226}\text{Ra} = 0.16 \pm 0.05$  and  $^{228}\text{Ra} = 0.21 \pm 0.11$  Bq.l<sup>-1</sup>. Considering this concentration as the regions background and subtracting this value from the Ra concentrations at the different stations (Table 1), the "real concentration" of Ra in the water can be estimated as well as the concentration ratios (Table 2).

Once the concentration ratio of the Ra isotopes at each station is known and knowing that the decay of  $^{226}\text{Ra}$  is negligible ( $^{226}\text{Ra}$  half-life 1600 years), the time spent by the radium to move from one station to another can be evaluated (using the activity decay equation). As the distances among the stations are known, the migration velocity can be estimated. Therefore it was estimated a period of around 6.7 years for the radium to move 1900 meters, resulting in a mean migration velocity of 283 meters per year.

$$\left(\frac{\text{Ra}228}{\text{Ra}226}\right)_{\text{station}} = \left(\frac{\text{Ra}228}{\text{Ra}226}\right)_{\text{station}} \cdot \frac{e^{-\lambda_{\text{Ra}228}T}}{e^{-\lambda_{\text{Ra}226}T}}$$

Station	Altitude (m)	Distance from the lagoon head (m)	$^{228}\text{Ra}/^{226}\text{Ra}$	Spent time to move from station 1 (years)	Migration velocity $\text{m.yr}^{-1}$
1	7.5	0	7	-	-
2	5.0	800	4.2	4.4	182
3	1.5	1900	3.1	6.7	478
4	1.0	3700	-	-	-
5	<1.0	4500	-	-	-
6	<1.0	4900	-	-	-
7	<1.0	5400	-	-	-

Table 2

Estimate of the time and migration velocity needed to move Radium from station one to other stations.

From station 4 the  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  concentrations were very close to background one and the migration velocity could not be estimated.

The data from the decay equation estimates has to be treated carefully and some factors are discussed. The potential influences on Ra isotope activity concentrations in the water column would be the presence of other sources of Ra in the water, such as the contribution from the catchment and the Ra releasing from the sediment.

1) The contribution from the catchment would be: *i)* groundwater flux containing high Ra concentrations along the lagoon: The decrease of Ra concentration along the lagoon suggests the non existence of other groundwater sources, as the ones found at the lagoon head. *ii)* contribution from run off: The low rate of radionuclides released from the monazite sand in normal conditions, for example by the leaching from rain water, makes it difficult to believe that a significant contribution of Ra to the lagoon is due to water run off.

2) The contribution from the sediment: the Ra desorption from the sediment is possible, in such salt waters and the disequilibrium found between  $\text{U}/^{226}\text{Ra}$  (from 1.2 to 2.1) and  $\text{Th}/^{228}\text{Ra}$  (here in two stations -3 and 6- the relation was 0.6, while for the others the relation ranged from 1.2 to 1.6) in the lagoon sediment showed the existence of this process. The Th activity in the Buena sediments is 1.1 to 3.8 more elevated than the U activity. The  $^{228}\text{Ra}$  has a short half-

life and is almost directly produced by the  $^{232}\text{Th}$  decay, while  $^{226}\text{Ra}$  has a long half-life and its ingrowth depends on the decay of three radionuclides of long half-life:  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$ . Because of that, the production rate of  $^{228}\text{Ra}$  in the sediment is more elevated than  $^{226}\text{Ra}$  and probably the  $^{228}\text{Ra}$  amount is also desorpted from the sediment. Thus, the value of the ratio activity  $^{228}\text{Ra}/^{226}\text{Ra}$  found in the water would be due to the decay of the spring's  $^{228}\text{Ra}$  and to the radium desorpted from the sediment. Considering the activity ratio  $^{228}\text{Ra}/^{226}\text{Ra}$  desorpted from the sediment is higher than one, the time and the migration velocity —estimated from equation 1 and presented in Table 2— would be underestimated. The radium migration in the water column of the lagoon is very low and the remaining time in the water column is long. This long radium remaining time in the column water of the lagoon could be explained by the high water salinity and the consequent competition among the cations for the exchange sites of the sediment as observed in salt groundwater.

### *Quantifying the radium amount in the water column*

The distribution of the radium concentrations (Table 1) can be fitted by exponential functions, where the variation of the radionuclide concentrations with the distance can be expressed as:

$$^{228}\text{Ra} \text{ (Bq.m}^{-3}\text{)} = 1180.e^{-0.0005.d} \text{ and } ^{226}\text{Ra} \text{ (Bq.m}^{-3}\text{)} = 351e^{-0.0002.d}$$

where  $d$  is the distance from the sampling point to the head of the lagoon (m). The values of the correlation coefficients were respectively  $R^2 = 0.9565$  and  $0.8632$ .

If these functions were integrated along the 5,400 m of the lagoon, it is possible to estimate the total amount of the radionuclide in the water. The area of the lagoon is 113,000 m<sup>2</sup> and the mean width is around 21 meters. The depth of the lagoon is variable (between 10 cm and 3 m), however it is possible to estimate it at around 0.80 m, resulting in a transverse section of 16.8 m<sup>2</sup>. So in the water of the lagoon the total amount of the Ra isotopes are estimated as :  $3.7 \cdot 10^7$  Bq of  $^{228}\text{Ra}$  (40MBq) and  $1.9 \cdot 10^7$  Bq (20 MBq) of  $^{226}\text{Ra}$ .

## Conclusion

The outcropping of groundwater containing high concentrations of Ra is responsible for the observed Ra concentrations in the water of the lagoon. The water of the lagoon is basically composed by two sources of ions located at opposite sides of the lagoon. The seawater supplies the major ions and the groundwater supplies the radium and the rare earth elements, possibly by the leaching of the monazite. The data points to a slow migration velocity of the radium isotopes in the water column, which could be attributed to the high salinity of the water. A total activity of 40MBq of  $^{228}\text{Ra}$  and 20MBq of  $^{226}\text{Ra}$  remains in the water column.

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