^{210}Pb and ^{210}Po levels in sediments, water, and bioindicators in the Cananeia-Iguape estuary – Sao Paulo – Brazil

R. T. SAITO AND I. I. L. CUNHA

Radiochemistry Division – IPEN-CNEN/SP – Caixa Postal 11049 Pinheiros,
05508-900 – São Paulo – Brazil, e-mail: macunha@ipt.br

R. C. L. FIGUEIRA

Cruzeiro do Sul University (UNICSUL), São Paulo – Brazil

M. G. TESSLER

Oceanographic Institute – São Paulo University – Brazil

The purpose of this work was to determine levels of ^{210}Pb and ^{210}Po in seawater, sediment cores, fish and seafood as well as to estimate the concentration factors and the bioindicators for ^{210}Pb and ^{210}Po in marine organisms collected in the estuary. ^{210}Pb levels in seawater varied from 2.1 to 6.2 mBq.L^{-1} and for ^{210}Po ranged from 1.6 to 4.1 mBq.L^{-1}. ^{210}Pb concentration factors in fish varied from 0.5×10^2 to 0.8×10^3, in crustaceans from 0.5×10^3 to 0.2×10^4 and in shellfish from 0.2×10^4 to 0.3×10^4. ^{210}Po concentration factors in fish varied from 0.9×10^2 to 0.5×10^4, in crustaceans from 0.5×10^4 to 0.2×10^5 and in shellfish from 0.3×10^5 to 0.9×10^5. The results obtained to the concentration factors indicated that shellfish and crustaceans are good bioindicators for the radionuclides studied. Some species of fish also accumulated significantly quantities of these radionuclides.

1 Introduction

The Cananeia – Iguape estuary (25° S – 48° W) is separated from the ocean by Comprida Island, a barrier island approximately 70 kilometers long. In the NE of this coastal system, the largest drainage system of the southeastern Brazilian seashore, the mouth of the Ribeira de Iguape river drains all the mountainous crystalline-rock complex at the backside of the coastal plain. It is linked to the Cananeia-Iguape estuary only through an artificial canal, built over 150 years ago. About 60% of the Ribeira de Iguape river discharge flows in the internal canals of the estuary, causing an increasing silt up of the canals by the muddy sediments in suspension.

Estuarine areas, as the one of this Coastal System, generally present a great biodiversity constituted of many organisms that can concentrate radionuclides. Some of these organisms, as fishes, crustaceans and molluscs, can be used as food source by the human beings, and therefore, be a source of radionuclide ingestion [1,2]. Therefore, it is important to estimate the levels of some present radionuclides in the marine samples to evaluate the possible risks that the ingestion of those organisms can cause, namely because these studies are scarce in Brazilian estuarine areas.

2 Experimental

Sediment cores were collected by the Oceanographic Institute from the University of Sao Paulo, Brazil, at four stations of the estuary that show different sediment inflows to the coastal system. The cores were sliced into 2 cm thick layers, dried and homogenised, and transferred to plastic containers appropriate for γ counting. The contents of organic matter and humidity, as well as sand and mud contents (silt and clay) were determined in every core.

Several types of techniques and equipment were used for the collection of the organisms, in order to allow a significant sampling of the species. The collected animals were identified, conditioned in plastic bags and frozen until the analysis.

During the field works sampling of superficial water was also carried out in six localities of the studied area. The seawater was conditioned in a gallon of polyethylene and acidified with hydrochloric acid.

In the sediments, ^{210}Pb was measured by γ counting by means of its photo-peak of 47 keV by using a GMX (25190P) Ortec γ detector (γ resolution of 1.90 keV for 1332 keV ^{60}Co peak, ^{210}Pb efficiency was of 0.17%). The method consisted of detector calibration, determination of detector counting efficiency, cumulative counting of both background and samples in regular intervals of counting time, photo-peak smoothing, linear regression and correction for the self-absorption effect of the sample [3].

Marine organisms samples were dissolved by using a microwave digestor (open system, Star Cem Coorporation) employing 8M nitric acid and hydrogen peroxide.

For ^{210}Pb analysis, after sample dissolution, 10 mg of lead, bismuth, barium and strontium carriers were added. Pb was precipitated as sulphate, converted to carbonate, and precipitated as hydroxide, and finally precipitated as lead sulphate. The ^{210}Bi β counting was performed with a low background Geiger-Müller detector (Risø, Denmark, GM-25-5 Model, ^{210}Bi efficiency was of 24%, background counting less than 0.7 cpm) after the establishment of the radioactive equilibrium. Lead recovery was calculated by gravimetric analysis. Blank analysis was also run for every kind of sample [4,5]

For polonium analysis, after sample dissolution with nitric acid, 20 mg lead carrier and ^{208}Po tracer were added. Nitric acid was removed by evaporating the solution and concentrated hydrochloric acid was added. This process was repeated several times. The residue was dissolved by 10M hydrochloric acid and diluted to 40 ml (pH 1.5), in the presence of 300 mg ascorbic acid. The solution was transferred into a plastic cell (disposable plastic tube), which contained a silver disc (20 mm diameter). This cell was placed in a water bath at 70-90°C, under mechanical agitation, and the plating time was 6 hours. ^{210}Po was counted by α-spectrometry (Si detector, Ortec, 576 A Model, α resolution of 26.4keV for ^{241}Am, ^{210}Po efficiency of the 31%). Polonium recovery was calculated using the ^{208}Po tracer. Analysis of the blank was also run periodically [4,5]. The analyses of the samples were carried out in triplicate .

3 Results

Figure 1 shows the different islands in the Cananeia-Iguape estuary as well as the localization of the Ribeira de Iguape River. Table 1 presents the ^{210}Pb levels in cores sampled in different points. ^{210}Pb levels varied from 7.2 to 167.5 Bq.kg^{-1}. The levels of ^{210}Pb in the cores generally decrease with depth, with some oscillations. The levels found in the sediments are in good agreement with the results obtained in other areas. Ravichandran et al. [6] found in sediments of the estuary Sabine-Neches (USA) levels of ^{210}Pb varying from 30 to 87 Bq. kg^{-1}. Somayajulu et al. [7] observed levels of ^{210}Pb varying from 5 to 402 Bq.kg^{-1} in sediments of the Sea of Arabia.

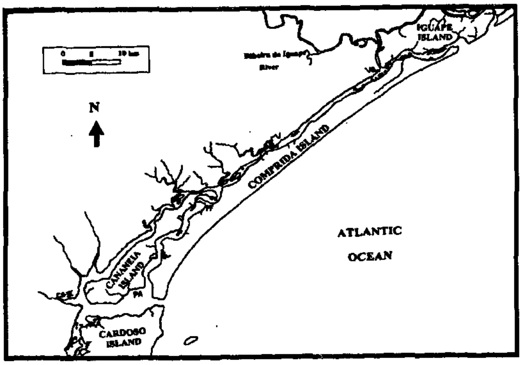

Fig. 1. The Cananeia-Iguape Estuary.

^{210}Pb and ^{210}Po levels in the superficial waters of the estuary varied from 2.1 to 6.2 mBq.L^{-1} and from 1.6 to 4.1 mBq.L^{-1}, respectively (Table 2). The highest values were found at Valo Grande station. These values reflect Ribeira's River bigger influence, besides a possible consequence of the agricultural activity, developed along the river, which according to Parfenov [8] contributes to the increase in the concentration of ^{210}Pb and ^{210}Po in the soil, due to the high levels of radionuclides of the uranium series in the phosphatic rock, present in this area.

Carvalho [9] found levels of ^{210}Po in the top layer of the water, of the coast of Portugal and of the Madeira Island, varying from 1 to 4 mBq.L^{-1}, with the average of 1.1 mBq.L^{-1}. He also observed levels of ^{210}Pb and ^{210}Po in waters of the Tagus estuary, Portugal, varying between 0.02 and 0.49 mBq.L^{-1} and from 0.01 to 0.31 mBq.L^{-1}, respectively [10].

The ^{210}Pb levels measured in fishes (Table 3) varied from MDC (Minimum Detectable Concentration) to 1.84 Bq.kg^{-1} and of ^{210}Po ranged from 0.15 to 7.76 Bq.kg^{-1}. The levels of ^{210}Pb and ^{210}Po in crustaceans (Table 4) varied from 2.9 to 3.8 Bq.kg^{-1} and 10.4 to 33.4 Bq.kg^{-1}, respectively. In molluscs (Table 5), the levels of ^{210}Pb varied from 4.5 to 7.4 Bq.kg^{-1} and ^{210}Po from 52.5 to 148.6 Bq.kg^{-1}. In all the analyzed species, the amount of ^{210}Po was higher than the one of ^{210}Pb.

SAITO [5] reported ^{210}Po levels in fish of the north coast of the State of São Paulo varying from 0.5 to 5.3 Bq.kg^{-1}. CARVALHO [10] determined the concentration of ^{210}Po activities in different species of fish of Portugal and Madeira Island coast, obtaining values from 0.08 to 21 Bq.kg^{-1}. The International Agency of Atomic Energy (IAEA), through the MARDOS Project [11], published a report containing the concentration of

Table 1. ^{210}Pb levels in the cores (dry weight)

Depth (cm)	^{210}Pb Ponta do Arrozal Bq.kg^{-1}	^{210}Pb Ponta do frade Bq.kg^{-1}	^{210}Pb Rio Carapara Bq.kg^{-1}	Depth (cm)	^{210}Pb Valo Grande Bq.kg^{-1}
0 – 2	167.5 ± 15.1	47.5 ± 3.9	101.8 ± 9.5	0 – 4	115.7 ± 10.5
2 – 4	116.5 ± 11.5	41.9 ± 4.1	101.3 ± 10.2	4 – 7	118.8 ± 11.2
4 – 6	128.3 ± 11.9	52.6 ± 5.0	94.5 ± 9.2	7 – 10	120.0 ± 9.7
6 – 8	81.7± 8.1	35.6 ± 3.1	83.2 ± 8.2	10 – 13	91.7 ± 8.8
8 – 10	75.7 ± 5.1	29.7 ± 2.6	77.1 ± 7.2	13 – 16	81.7 ± 7.9
10 – 12	77.0 ± 7.8	26.2 ± 2.7	57.4 ± 4.9	16 – 19	70.5 ± 7.2
12 – 14	53.1 ± 5.3	28.0 ± 2.7	60.5 ± 6.2	19 – 22	61.0 ± 6.2
14 – 16	54.8 ± 5.4	26.5 ± 2.6	43.6 ± 4.2	22 – 25	71.8 ± 7.0
16 – 18	21.1 ± 2.0	18.2 ± 1.8	44.1 ± 4.2	25 – 28	68.2 ± 6.9
18 – 20	37.4 ± 3.4	16.2 ± 1.6	33.7 ± 4.0	28 – 31	70.7 ± 6.8
20 – 22	41.1 ± 4.0	7.2 ± 0.7	36.1 ± 2.9	31 – 34	80.2 ± 7.5
22 – 24	40.7 ± 4.0	10.2 ± 1.0	30.0 ± 3.6	34 – 37	69.8 ± 6.7
24 – 26	35.8 ± 2.8	10.5 ± 0.5	25.6 ± 2.5	37 – 40	70.6 ± 6.8
26 – 28	28.8 ± 2.8	9.6 ± 1.0	25.4 ± 2.7	40 – 43	58.2 ± 5.2
28 – 30	38.4 ± 2.5	8.5 ± 0.9	18.6 ± 1.8	43 – 46	48.7 ± 4.2
30 – 32	58.7 ± 4.9	15.9 ± 1.6	31.0 ± 2.2	46 – 49	69.8 ± 5.5

Table 2. ^{210}Pb and ^{210}Po levels in seawater

Station	^{210}Pb (mBq.L^{-1})	^{210}Po (mBq.L^{-1})
A1 (Oceanographic Institute pier)	2.1 ± 0.2	1.6 ± 0.1
A2 (Cananeia sea)	3.3 ± 0.2	2.1 ± 0.1
A3 (Trapande bay)	3.7 ± 0.3	2.9 ± 0.2
A4 (Cananeia barra)	2.5 ± 0.2	1.7 ± 0.1
A5 (Valo Grande channel)	6.2 ± 0.6	4.1 ± 0.4
A6 (Valo Grande channel)	5.8 ± 0.5	3.6 ± 0.3

^{210}Po in fish of several oceans. The values varied from 0.1 to 5.8 Bq.kg^{-1}, considering a global geometric average value of 2.4 Bq.kg^{-1}. The concentration of ^{210}Po in crustaceans and molluscs varied from 0.4 to 100 Bq.kg^{-1} and from 0.8 to 57 Bq.kg^{-1}, respectively, with global geometric average value of 6 and 15 Bq.kg^{-1}. Carvalho [10] observed ^{210} Po levels, in some species of crustaceans and molluscs, with average of 122 and 16.5 Bg.kg^{-1} (wet weight), respectively.

Tables 3,4 and 5 show that the concentration factors of ^{210}Pb for fish, crustaceans and molluscs varied from 0.5 .10^2 to 0.8 × 10^3, from 0.5 × 10^3 to 0.2 × 10^4 and from 0.2 ×

10^4 to 0.3×10^4, respectively. The concentration factors of ^{210}Po for fish, crustaceans and molluscs varied from 0.9×10^2 to 0.5×10^4, from 0.5×10^4 to 0.2×10^5 and from 0.3×10^5 to 0.9×10^5, respectively. MARDOS Project [11] established a factor of concentration of ^{210}Po for fish, crustaceans and molluscs to 2×10^3, 5×10^4 and 1×10^4, respectively, although it also establishes a single value for crustacean and mollusk of 3×10^4.

Table 3. Concentration Factors of ^{210}Pb and ^{210}Po in fish

Fish	^{210}Pb		^{210}Po	
	activity (Bq.kg^{-1})	CF	activity (Bq.kg^{-1})	CF
Mycteroperca rubra	< MDC	----	0.15	8.8 x 10^1
Cathorops spixii	1.84	8.0 x 10^2	5.76	3.4 x 10^3
Sciadeichthys luniscutis	0.19	8.3 x 10^1	1.22	7.2 x 10^2
Genidens genidens	0.79	3.4 x 10^2	2.54	1.5 x 10^3
Spheroides testudineus	0.63	2.7 x 10^2	1.85	1.1 x 10^3
Menticirrhus americanus	0.23	1.0 x 10^2	3.68	2.2 x 10^3
Sphyraena guachancho	0.34	1.5 x 10^2	2.54	1.5 x 10^3
Diapterus rhombeus	0.36	1.6 x 10^2	4.26	2.5 x 10^3
Pomadasys croco	0.21	9.1 x 10^1	1.96	1.2 x 10^3
Micropogonias furnieri	0.77	3.4 x 10^2	2.87	1.7 x 10^3
Trinects paulistanus	1.34	5.8 x 10^2	5.61	3.3 x 10^3
Anchoviella lepidentostol	0.33	5.5 x 10^1	2.73	7.0 x 10^2
Larimus breviceps	0.23	1.0 x 10^2	6.94	4.1 x 10^3
Hemiramphus brasiliensis	0.27	1.2 x $10^{2.}$	1.56	9.2 x 10^2
Selene setapinnis	0.77	3.4 x 10^2	3.20	1.9 x 10^3
Selene vomer	0.41	1.8 x 10^2	1.98	1.2 x 10^3
Chaetodipterus faber	0.88	3.8 x 10^2	2.45	1.4 x 10^3
Ogcocephalus vespertilio	0.45	2.0 x 10^2	1.53	9.0 x 10^2
Cynoscion acoupa	0.71	3.1 x 10^2	2.15	1.3 x 10^3
Cynoscion leiarchus	0.62	2.7 x 10^2	3.01	18 x 10^3
Cynoscion microlepdontus	0.22	9.6 x 10^1	1.56	9.2 x 10^2
Centropomus paralellus	< MDC	----	0.87	5.1 x 10^2
Oligoplites saurus	0.17	7.4 x 10^1	1.32	7.8 x 10^2
Sardinella brasiliensis	0.92	4.0 x 10^2	3.22	1.9 x 10^3
Opisthonema oglinum	1.01	4.4 x 10^2	7.76	4.6 x 10^3
Harengula clupeola	1.52	6.6 x 10^2	4.90	2.9 x 10^3
Mugil platanus	0.38	1.7 x 10^2	3.12	1.8 x 10^3

MDC - Minimum detectable concentration (MDC) 0.17 Bq.kg^{-1}

Table 4. Concentration Factors of ^{210}Pb and ^{210}Po in crustaceans

Species	^{210}Pb (Bg.kg^{-1})	CF	^{210}Po (Bg/kg^{-1})	CF
Penaeus sp	3.2	1.4 x 10^{3}	10.4	6.1 x 10^{3}
Callinectes sp	2.9	4.8 x 10^{2}	21.3	5.5 x 10^{3}
Ucides sp	3.8	1.7 x 10^{3}	33.4	2.0 x 10^{4}

Table 5. Concentration Factors of ^{210}Pb and ^{210}Po in molluscs

Species	^{210}Pb (Bg.kg^{-1})	CF	^{210} Po (Bg/kg^{-1})	CF
Lolipo sp	4.5	2.0 x 10^{3}	52.5	3.1 x 10^{4}
Mytilus sp	7.4	3.2 x 10^{3}	148.6	8..7 x 10^{4}
Crassostrea sp	5.1	2.2 x 10^{3}	77.4	4.6 x 10^{4}

4 Conclusions

The ^{210}Pb and ^{210}Po activities in sediment cores collected in the Cananeia-Iguape estuary reflect Ribeira de Iguape's River influence and the possible impact of the agricultural activity along the river.

During the study 27 species of fish, 3 of crustaceans and 3 of molluscs were sampled. Most of these organisms are used in human diet. In all the analysed species the amount of ^{210}Po was higher than that of ^{210}Pb.

The comparison of the values of ^{210}Pb and ^{210}Po obtained for fish, crustaceans and molluscs, sampled in the Cananeia-Iguape estuary with other areas of the world, shows that the data presented here are in agreement with the values of the literature. They could serve as reference levels for the Cananeia-Iguape System. Among the different collected organisms, molluscs present the highest CF. The highest concentrations observed in the mussel can be related with the habitat of this organism that lives buried at the swamp.

A periodic monitoring of the radionuclide levels is necessary, namely for the organisms that were defined as bio-indicators, as the molluscs, crustaceans and some fish.

References

[1] Clulow, F. V., Davé, N. K., Lim, T. P. and Avadhanula, R.: Environmental Pollution *99* (1998) 199.

[2] Yamamoto, M. et al.: J. Radioanal. Nucl. Chem. *178* (1994) 81.

[3] Figueira R. C. L., Silva L. R. N., Figueiredo A. M. G. and Cunha I. I. L.: *In*: Conferęncia Internacional – "Goiânia – 10 anos depois", Goiânia, Brasil, 1997.

[4] Saito R. T. and Cunha I. I. L.: J. Radioanal. Nucl. Chem., *220* (1997) 117.

[5] Saito, R. T.: Dissertação (Mestrado) – Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, São Paulo, 1996.

[6] Ravichandran M., Baskaran M., Santschi P. H. and Bianchi T. S.: Chem. Geology, *125* (1995) 291.
[7] Somayajulu B. L. K., Bhushan R., Sarkar A., Burr G. S. and Jull A. J. T.: Sci. Total Environ., *237/238* (1999) 429.
[8] Parfenov, Y. D.: At. Energy Rev., *12* (1974) 75.
[9] Carvalho, F. P.: Sci. Total Environ., *159* (1995) 201.
[10] Carvalho, F. P.: Radiat. Prot. Dosimetry, *24* (1988) 113.
[11] International Atomic Energy Agency (IAEA): Sources of radioactivity in the marine environment and their relative contributions to overall dose assessment from marine radioactivity (MARDOS Project). (IAEA-MEL-R2/94), IAEA, Vienna, 1994.