# <sup>210</sup>Pb and <sup>137</sup>Cs geochronologies in the Cananeia-Iguape Estuary (São Paulo, Brazil)

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Sediment cores were collected at the Cananeia-Iguape Estuary and the levels of  $^{210}$ Pb,  $^{226}$ Ra and  $^{137}$ Cs were measured by gamma-ray spectrometry. The total  $^{210}$ Pb levels in sediments varied from 13.5 to 122.5 Bq·kg<sup>-1</sup>, for  $^{226}$ Ra ranged from 2.4 to 28 Bq·kg<sup>-1</sup> and for  $^{137}$ Cs from 0.28 to 6.1 Bq·kg<sup>-1</sup>. Sedimentation rates were calculated from the slope of the excess  $^{210}$ Pb profile in the core. The values obtained varied from 5 to 10 mm·y<sup>-1</sup>, depending on the sediment deposition inputs in the local of sampling.

### Introduction

The use of <sup>210</sup>Pb to date sediments up to 100 years is a very important tool to establish a geochronology of the coastal environment.<sup>1,2</sup> Usually, <sup>210</sup>Pb is present in excess in relation to <sup>226</sup>Ra (unsupported <sup>210</sup>Pb), because <sup>226</sup>Ra, an intermediate in the decay series, <sup>222</sup>Rn is volatile and escapes from soil to the atmosphere. So, <sup>222</sup>Rn and <sup>210</sup>Pb are deposited in the marine environment and its activity decrease with the core depth and this gradient gives information about sediment dating.

<sup>210</sup>Pb formed by <sup>226</sup>Ra decay is in radioactive equilibrium with <sup>226</sup>Ra (supported <sup>210</sup>Pb). Unsupported <sup>210</sup>Pb is the difference between total <sup>210</sup>Pb concentration and <sup>226</sup>Ra measured in the sediment . <sup>137</sup>Cs is often used to determine sedimentation rates<sup>1</sup> in addition to those provided by <sup>210</sup>Pb measurements. As a result of atmospheric fallout,<sup>1</sup> <sup>137</sup>Cs presented a maximum deposition over the world between 1963–1964 years. Since these years, its atmospheric emission decreased and its deposition has been constant over decades.

In this paper, <sup>210</sup>Pb and <sup>137</sup>Cs dating was conducted in order to elucidate the sedimentation process in the Cananeia-Iguape Estuary. The estuary is situated along the Southern coast of Brazil ( $25^{\circ}$  S–48° W), in an area of 200 km<sup>2</sup>, including 3 natural islands (Cardoso, Cananeia (27 km of extension), Comprida (70 km of extension) and an artificial island (Iguape), separated by lagoons and rivers that flow to the ocean.

The Ribeira of Iguape River is the principal source of sediment transport into the estuary. The higher sedimentation dynamic is near Iguape Island, that presents high levels of lead resulting from wastes from ore processing industries.<sup>3</sup>

Sediment cores were collected in four stations, considering different sediment deposition inputs. The core was sectioned into 2 cm thick layers and the levels of <sup>210</sup>Pb, <sup>226</sup>Ra and <sup>137</sup>Cs were measured by gamma-ray spectrometry.<sup>4,5</sup> <sup>210</sup>Pb analysis was carried out by means of its low-energy gamma-emission (47 keV), while <sup>226</sup>Ra was analyzed via its granddaughter <sup>214</sup>Bi, at a photopeak of 609 keV. <sup>137</sup>Cs radionuclide was determined by means of its 661 keV photopeak. The methods consisted of several steps: detector calibration, determination of detector counting efficiency, accumulative counting of both background and sample in regular intervals of counting time and photopeak smoothing.

The sedimentation rates were calculated from the slope of the unsupported  $^{210}$ Pb profile in the core as well as by using the  $^{137}$ Cs as a time marker.

## **Experimental**

## Equipment

Gamma-ray spectrometer, low background Ge detector, EG&G Ortec, GEM 60120P Model.

# Sediment sampling

Sediment cores were collected by the Oceanographic Institute from the University of São Paulo, Brazil, at four stations. The core formed mainly by pure sand was sliced into 5 cm thick layers while the others were sliced into 2 cm thick layers, dried and homogenized, and transferred to plastic pots. The contents of organic matter, moisture, sand and mud content (silt and clay) were determined in every core.

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# Methodology for <sup>210</sup>Pb analysis

<sup>210</sup>Pb was analyzed by means of its photo-peak at 47 keV. Detector calibration was performed by means of several gamma-ray emitting nuclides. IAEA reference materials (IAEA-300, IAEA-315, IAEA-327, IAEA-368 and IAEA/SD-N-2) were employed to determine the detector counting efficiency in the studied photopeak region.

A study of background radiation variation in the region of the <sup>210</sup>Pb photopeak as a function of time was performed by means of the MAESTRO II software. Background counting was carried for 250,000 seconds, in intervals of 10,000 seconds. After photopeak smoothing, the activity as a function of counting time was plotted. A linear regression was fitted through data ranging from 70,000 to 250,000 seconds; statistical errors are very high for data relative to total counting times below the inferior limit of 70,000 seconds.

The same process was repeated for the sediment. About 50 g of the sediment was placed in plastic pots appropriated for gamma counting (diameter = 7.5 cm, thickness = 1.0 cm). Comparison between the linear regression curves of background and the sediment sample allowed the determination of sediment activity, discounting background activity for each registered time.

Analyses of <sup>226</sup>Ra and <sup>137</sup>Cs were performed as above mentioned. <sup>226</sup>Ra analysis via <sup>214</sup>Bi required an airtight housing and a waiting time of 21 days to allow radioactive equilibrium.

# Results

Analysis of IAEA reference materials showed precision ranging from 2 to 7%. The methodology presented good precision and accuracy and it can be considered satisfactory, specially as small photopeaks appear in the gamma-spectrum.



Fig. 1. Sedimentation rate and <sup>210</sup>Pb unsupported and <sup>137</sup>Cs levels in Ponta of Arrozal station



Fig. 2. Sedimentation rate and <sup>210</sup>Pb unsupported and <sup>137</sup>Cs levels in Ponta of Frade station



Fig. 3. Sedimentation rate and <sup>210</sup>Pb unsupported and <sup>137</sup>Cs levels in Carapara River station



Fig. 4. Sedimentation rate and <sup>210</sup>Pb unsupported and <sup>137</sup>Cs levels in Valo Grande Channel station

Depth, cm	H <sub>2</sub> O, %	O. M., %	Granulo	metry	Depth, cm	H <sub>2</sub> O, %	O. M., %	Granul	ometry
	2		Sand, %	Silt and clay, %		2		Sand, %	Silt and clay, %
0–2	50.7	11.00	59.3	28.6	44-46	23.3	2.30	90.3	3.8
2–4	61.7	3.76	47.8	36.9	46-48	23.0	3.00	91.7	3.9
4-6	49.5	2.84	60.6	29.2	48-50	23.7	3.00	90.4	3.6
6–8	51.8	1.68	56.7	30.2	50-52	22.8	4.34	91.0	3.3
8-10	41.4	0.67	72.8	16.2	52-54	23.3	3.00	90.2	3.8
10-12	37.4	0.72	80.9	11.3	54-56	25.9	1.93	89.8	4.1
12-14	36.3	0.60	77.7	14.2	56-58	22.2	3.31	90.0	4.0
14–16	32.6	0.97	86.3	6.4	58-60	22.1	1.83	91.2	3.8
16-18	43.8	1.55	72.2	17.9	60-62	22.7	0.90		
18-20	42.6	0.42	74.5	17.1	62–64	23.1	1.66		
20-22	37.8	1.56	76.1	16.3	64–66	22.3	2.32		
22-24	37.2	0.57	79.5	13.9	66–68	21.7	1.68		
24-26	30.1	0.55	82.6	10.9	68-70	20.2	1.90		
26-28	32.2	0.82	84.2	9.8	70-72	18.8	1.56		
28-30	31.5	0.41	83.4	10.3	72–74	21.2	1.26		
30-32	33.7	5.71	85.8	7.9	74–76	23.0	0.81		
32-34	25.9	3.10	91.6	3.3	76–78	27.4	4.00		
34-36	25.4	2.60	91.8	3.1	78-80	23.4	3.10		
36-38	21.9	2.04	93.4	2.0	80-85	22.8	7.47		
38-40	30.0	2.10	89.7	4.1	85-90	27.5	4.18		
40-42	31.5	3.00	88.5	5.3	90–95	27.0	2.00		
42–44	26.0	2.64	88.4	5.5	95-100	23.1	2.53		

Table 1. Granulometry, moisture and organic matter content in the core CR-III (Carapara River station)

O. M. - Organic matter.

Tuble 2. Granulometry, moisture and organic matter content in PA, PF and VG cores

			Table 2.	Granulometry, 1	moisture and o	organic matter co	ontent in PA, P	F and VG cores				
		Ponta of /	Arrozal (PA)			Ponta c	f Frade (PF)			Valo Grande ch	nannel (VG)	
Depth, cm	H <sub>2</sub> O, %	0. M., %	Granul Sand, % S	lometry Silt and clay, %	H <sub>2</sub> O, %	0. M., %	Granu Sand, %	lometry Silt and clay, %	H <sub>2</sub> 0, %	0. M., %	Granul Sand, %	ometry Silt and clay, %
0–2	65.3	6.75	20.2	59.1	27.5	1.05	91.1	4.7	39.4	2.55	15.2	77.2
2-4	0.69	6.35	17.8	61.7	27.7	2.88	90.7	3.8	47.8	4.07	14.7	78.1
4–6	55.1	10.64	34.3	50.2	34.7	3.22	87.0	5.3	52.1	9.80	14.5	75.8
6-8	61.6	6.35	48.6	37.9	36.7	3.46	72.2	5.3	44.1	3.88	17.5	74.1
8-10	54.6	9.23	51.1	36.3	33.5	1.40	72.4	3.0	46.3	4.11	13.8	76.6
10-12	53.9	3.05	50.0	37.1	31.3	1.21	85.3	4.3	51.7	6.32	10.4	79.3
12–14	52.2	5.21	61.2	27.8	32.6	5.00	89.9	4.4	51.5	6.82	11.2	<i>9.17</i>
14–16	53.0	5.35	66.7	23.8	34.2	4.18	87.9	5.2	48.6	6.20	10.5	80.3
16–18	46.8	0.54	69.0	22.0	31.5	2.86	87.5	6.6	$45.7^{3}$	$4.18^{3}$	15.8	75.3
18-20	37.2	2.70	69.3	22.0	27.7	4.29	92.8	2.8	w. s.	W. S.	w. s.	W. S.
20–22	49.7	2.69	73.7	18.7	26.6	2.80	90.7	3.6	$45.7^{4}$	$5.31^{4}$	16.4	74.4
22–24	46.2	3.05	67.6	23.9	26.2	3.98	91.6	3.9	47.8	5.51	13.2	76.5
24–26	51.0	1.48	51.3	36.8	30.3	3.44	91.3	3.5	50.6	6.98	LL	80.5
26–28	53.7	2.21	43.7	43.6	27.4	2.38	92.3	2.9	44.7	5.31	10.2	80.0
28–30	55.1	6.08	49.5	38.4	21.7	3.65	93.4	1.9	50.3	6.32	6.6	78.9
30–32	59.5	9.30	42.8	43.0	26.1	5.09	93.0	2.1	50.0	6.72	10.7	L.LL
32–34	55.5	7.94	43.0	44.6	$23.8^{2}$	$2.72^{2}$	93.3	2.2	52.7	8.02	6.6	82.0
34–36	45.1	4.70	65.2	26.8	W. S.	W. S.	w. s.	w. s.	57.1	7.95	4.4	83.3
36–38	47.5	2.35	59.6	30.0	W. S.	W. S.	w. s.	w. s.	54.6	7.32	9.8	78.5
38-40	37.0	1.40	83.6	11.3	W. S.	W. S.	W. S.	W. S.	47.1	5.03	14.6	74.9
40-42	$42.6^{1}$	$3.96^{1}$	76.8	17.0	W. S.	W. S.	w. s.	W. S.	46.7	6.36	16.5	72.3
42-44	w. s.	w. s.	w. s.	w. s.	w. s.	w. s.	w. s.	w. s.	51.9	5.80	10.5	78.7
O. M Organic matter.												
w. s Without sample.												
<sup>2</sup> (40–43) cm; <sup>2</sup> (32–35) cm;												
$\frac{3}{4}$ (16–19) cm; $\frac{3}{4}$ (21–23) cm.												

Tables 1 and 2 present the moisture percentage and organic matter content in the cores. Sediments presented variable composition in relation to mineralogical composition as well as organic matter content. At Ponta of Frade station the sediments were almost pure sand and the organic matter content was lower than 5%. Valo Grande station sediments presented less than 17.5% sand and more than 70% of silte and clay. The organic matter content varied from 2.5 to 9.8%. The moisture percentage varied from 39 to 57%. The other station, Ponta of Arrozal, showed intermediate values as compared with those two stations. The Carapara station sediment, at a 10 cm depth, was also almost pure sand and the organic matter content ranged from 0.4 to 5.7%.

Figures 1 to 4 present the <sup>137</sup>Cs and <sup>210</sup>Pb levels in the sediments. The total <sup>210</sup>Pb levels in sediments varied from 13.5 to 122.5 Bq·kg<sup>-1</sup>; for <sup>226</sup>Ra ranged from 2.4 to 28 Bq·kg<sup>-1</sup> and for <sup>137</sup>Cs from 0.28 to 6.1 Bq·kg<sup>-1</sup>. <sup>210</sup>Pb, <sup>226</sup>Ra and <sup>137</sup>Cs levels found in the sediments are in good agreement with data published in the literature.<sup>1,2,7</sup>

The highest radionuclide concentrations were found at Valo Grande Channel station whereas lowest concentrations were measured in sediments from Ponta of Frade and Carapara River stations. This is in good agreement with the mineralogical composition of the sediments. Sediments with high levels of sand present low <sup>210</sup>Pb concentrations because natural radionuclides are associated with the organic matter, silt and argile. Natural radionuclide concentrations increase inversely with the size of sediment grains.<sup>7</sup> The sedimentation rates were calculated from the slope by the unsupported  $^{210}$ Pb profile in the core as well as by using the  $^{137}$ Cs peak as a time marker. Figures 1 to 4 show the vertical profiles of <sup>137</sup>Cs and <sup>210</sup>Pb as a function of depth. The sediment rate values obtained by using <sup>210</sup>Pb dating were 5.33 mm·y<sup>-1</sup> (Ponta of Arrozal); 6.22 mm·y<sup>-1</sup> (Carapara River); and 9.80 mm·y<sup>-1</sup> (Ponta of Frade) and by employing  $^{137}$ Cs were 5.45 mm·y<sup>-1</sup> (Ponta of Arrozal); 9.10 mm·y<sup>-1</sup> (Ponta of Frade) and 6.10 mm·y<sup>-1</sup> (Carapara River). The sedimentation rates obtained by employing both dating methods are in good agreement.

For Valo Grande station, it was not possible to determine the sedimentation rate because the depth of the core sampling was not enough or due to the circulation and sediment resuspension in the area. Valo Grande station presented the highest influence of the Ribeira Iguape River in the sediment deposition.

# Conclusions

<sup>210</sup>Pb levels in the PA, CR-III and PF cores decreased with depth, while the Valo Grande core showed an opposite tendency (Figs 1 to 4). Valo Grande station presented the highest radionuclide levels. Ponta do Frade and Carapara III cores showed low radionuclide levels, indicating correlation with the sediment granulometry. The higher sedimentation was noticed at Valo Grande core. This is due to the great influence of the Ribeira de Iguape River, that transport a great amount of sediment in the estuary as well as the dynamic of tide currents. The other stations are located in the opposite side of the estuary, where the influence of sediment resuspension caused by tide currents.

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