

CHEMICAL AND RADIOLOGICAL CHARACTERISATION OF SANTOS ESTUARY SEDIMENTS

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ABSTRACT

Samples from Santos Estuary, an industrial area located in São Paulo State, Southwest Brazil, were analysed by neutron activation analysis and gamma spectrometry for elements As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zr, and radionuclides ^{226}Ra , ^{228}Ra , ^{210}Pb and ^{40}K , with the intent of characterise and identify possible contaminated areas due to industrial activities. With this goal, the results were analysed by means of Pearson's correlation coefficient and using iron concentration as a reference to normalise the determined elements.

INTRODUCTION

Estuaries may accumulate material transported by rivers, including substances of natural or industrial origin, such as major, minor or trace elements. Industries like phosphoric acid and fertiliser producers, could also contribute to the enhancement of radioactive elements content in the environment, as shown by McNabb *et al.* (1979) and Periañez and Leon (1993).

Santos estuary, located in São Paulo State, Southwest Brazil, and comprising three main counties (Santos, São Vicente and Cubatão), is considered one of the most important industrial regions of Brazil.

This work aims to determine the chemical and radiological composition of sediments samples collected along Santos Estuary and to evaluate possible contaminated areas.

METHODOLOGY

Heighten sediment samples were collected by Companhia Brasileira de Saneamento Básico (CETESB), in points showed in figure 1. All samples were analysed by neutron activation analysis (NAA), for determination of the following elements: As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zr. The elements determination was made by irradiation of approximately 150mg of each sample, during 16 hours at a neutron flux of 10^{12} n.cm⁻².s⁻¹, at Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. The induced radioactivity was measured with a Ge-hyperpure detector, Intertechnique, with 2.1 keV resolution for the 1332 keV ^{60}Co photopeak. The concentration of the analysed elements was determined by comparing activities obtained in the sediment samples with standard materials Buffalo River Sediment (NIST-2704) and Soil-7 (IAEA).

Among the collected samples, 13 were analysed by gamma spectrometry for radionuclides determination (^{226}Ra , ^{228}Ra , ^{210}Pb and ^{40}K). For this determination samples were sealed in polyethylene containers for about four weeks prior to the measurement, in order to ensure that equilibrium has been reached between ^{226}Ra and its decay products of short half-life, ^{214}Bi e ^{214}Pb . The ^{228}Ra content of the samples was determined by measurement of ^{228}Ac photopeaks and the concentrations of ^{210}Pb and ^{40}K were carried out by measuring the activity of their own photopeaks. Samples were measured by using a Ge-hyperpure detector, EGNC

15-190-R from Eurisy, with 15% efficiency, during 60.000s. The detector was calibrated using natural soil and rock spiked with radionuclides certified by Amersham. The system background was obtained by measuring the same sample counting geometry for 300.000s. The gamma spectra obtained were analysed by using WinnerGamma program.

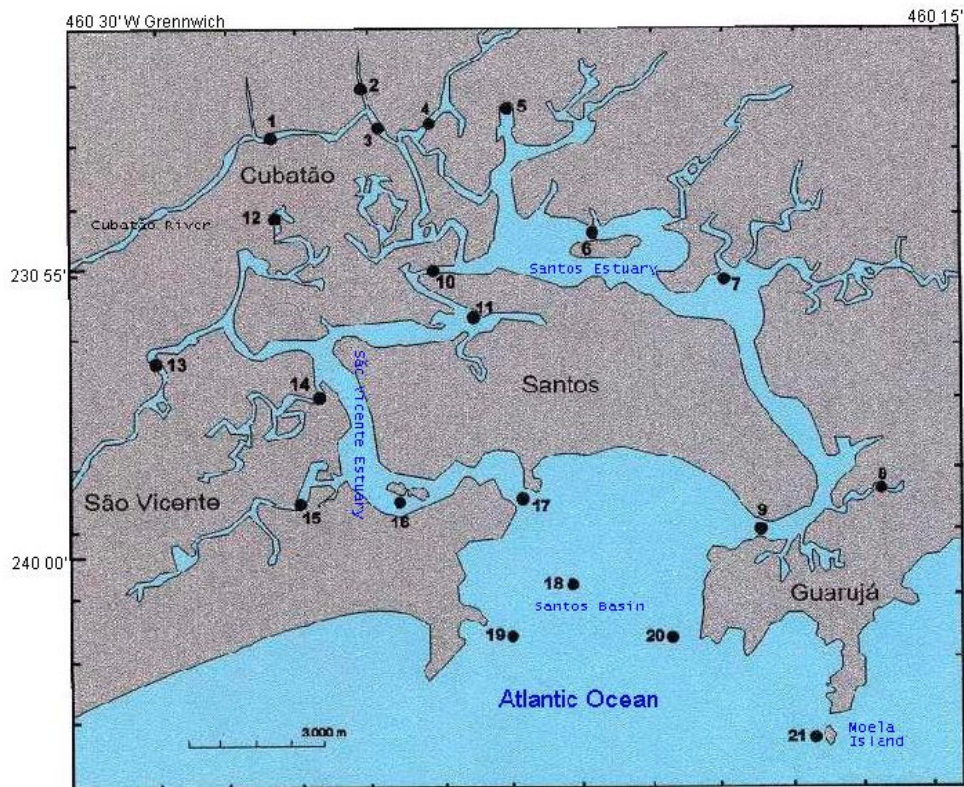


Figure 1: Santos estuary and location of the sampling points.

Self-absorption correction for ^{210}Pb was applied since the attenuation for its low energy gamma rays is highly dependent upon sample composition. The approach used was modified from that suggested by Cutshall et al. (1983).

As organic matter is a good absorber of metals and radionuclides, its amount was also determined in the samples by heating at $360^\circ\text{C} - 370^\circ\text{C}$ for 2 hours.

All sediment samples studied were prepared by drying at a temperature of 110°C to constant mass, ground to a grain-size of less than $250\ \mu\text{m}$ for gamma spectrometry, $105\ \mu\text{m}$ for NAA and finally homogenised.

RESULTS AND CONCLUSIONS

Table 1 shows the results obtained in the samples measurement by NAA, the mean values, the relative standard deviation and the range of values. It can be seen that the elements Br and U presented higher variations and Ba the smallest one, although for the majority of the analysed elements the variations obtained were bigger than 50%, reflecting the complexity of this kind of environment.

Elbaz-Poulichet and Dupuy (1999) showed that phosphate deposits contribute to the enhancement of rare earth elements in the environment. In a previous paper, the same authors presented the concentration of rare earth elements in the same sediment samples (Silva *et al.*,

2001). An increase in rare earth elements was found in points 1, 2 and 3, probably due to their release together with Th and Ra isotopes from phosphogypsum stockpiled in the surrounding.

Table 1: Mean value, relative standard deviation and range obtained for sediments by NAA ($\mu\text{g/g}$).

	mean	rsd	Range
As	6	61	2 - 11
Ba	329	27	116 - 488
Br	50	84	2 - 133
Ce	64	56	8 - 136
Co	6	50	1,3 - 12
Cr	35	55	7 - 78
Cs	3	56	0,5 - 8
Eu	0,9	39	0,2 - 1,5
Fe(%)	2	49	0,4 - 4
Hf	6	62	1,2 - 13
K(%)	1,2	40	0,4 - 1,8
La	28	61	6 - 65
Lu	0,3	54	0,04 - 0,6
Na	10443	78	1674 - 33037
Nd	31	61	4 - 73
Rb	69	51	17 - 180
Sb	0,4	52	0,2 - 0,8
Sc	7	54	0,8 - 13
Se	0,5	60	0,2 - 1,4
Sm	5	65	1,0 - 12
Ta	0,8	44	0,1 - 2
Tb	0,4	57	0,1 - 0,9
Th	10	63	1 - 24
U	3	86	0,9 - 14
Yb	2	54	0,5 - 4
Zr	188	50	43 - 385

The correlation coefficient was also determined indicating that: a) the rare earth elements are strongly correlated between themselves and also with trace metals, Fe, Zr and Th; b) the elements U and Th are well correlated between themselves, Th is strongly correlated with all rare earth elements, trace metals and Fe; c) U is well correlated only with Cs and Ta, among the trace metals.

Fe is generally well correlated with all trace metals. Therefore, it can be used to normalise experimental results and to identify possible enrichments among the analysed elements. Since aluminium was not detected by NAA, iron was used to normalise the studied elements.

Although there are a lot of possible external sources of iron, the results obtained by using Fe as a normaliser showed good agreement for Co, Ce, Cr, Cs, Eu, La, Lu, Nd, Sc, Sm, Ta, Th, Yb and Zr. Slight enrichments were observed for As in points 17 and 19; for Se in points 7, 9, 16, and 17 and for U in points 12 and 13. An explanation for U enrichment may be the great concentration of organic matter.

Table 2 shows activity concentrations for U, Th, ^{226}Ra , ^{228}Ra , ^{210}Pb and ^{40}K and activity ratios $^{226}\text{Ra}/^{238}\text{U}$ and $^{228}\text{Ra}/^{232}\text{Th}$.

Points 1, 2 and 3 presented concentrations for ^{226}Ra and ^{228}Ra above the mean value of the region, probably due to releases from stockpiled phosphogypsum originated in the

phosphoric acid industries. This contamination is supported by the results obtained for the activity ratio $^{226}\text{Ra}/^{238}\text{U}$ and $^{228}\text{Ra}/^{232}\text{Th}$ in the same points, which were higher than usually expected due to the solubility of radium isotopes in estuarine systems (Gascoyne, 1982; Moore, 1981). This enrichment can also be seen when normalising the activity concentrations of Ra isotopes with iron concentration. The correlation coefficient analysis shows that Ra isotopes have a strong correlation with rare earth elements, Fe, Zr and trace metals.

Table 2: Activity concentrations (Bq/kg) for U, Th, ^{226}Ra , ^{228}Ra , ^{210}Pb and ^{40}K and activity ratios $^{226}\text{Ra}/^{238}\text{U}$ and $^{228}\text{Ra}/^{232}\text{Th}$.

	U	Th	^{226}Ra	^{228}Ra	^{210}Pb	^{40}K	$^{226}\text{Ra}/^{238}\text{U}$	$^{228}\text{Ra}/^{232}\text{Th}$
A 1	69 ±6	79 ±4	44 ±5	77 ±6	49 ±9	379 ±30	1,3 ±0,1	0,98 ±0,05
A 2	109 ±8	96 ±5	43 ±5	73 ±6	44 ±9	392 ±32	0,81 ±0,07	0,76 ±0,04
A 3	86 ±7	60 ±3	40 ±5	59 ±6	41 ±8	546 ±39	0,96 ±0,09	0,99 ±0,06
A 6	87 ±8	37 ±2	-	-	-	-	-	-
A 7	48 ±13	15 ±1	-	-	-	-	-	-
A 8	95 ±27	44 ±4	19 ±4	25 ±5	60 ±11	430 ±38	0,4 ±0,2	0,6 ±0,1
A 9	43 ±4	32 ±2	13 ±3	15 ±3	37 ±7	341 ±29	0,6 ±0,1	0,47 ±0,06
A 10	103 ±9	44 ±2	20 ±4	29 ±4	47 ±9	418 ±34	0,40 ±0,07	0,66 ±0,05
A 12	348 ±27	77 ±4	31 ±5	36 ±5	114 ±21	486 ±39	0,18 ±0,04	0,47 ±0,04
A 13	145 ±20	41 ±2	20 ±4	24 ±4	47 ±10	428 ±31	0,28 ±0,08	0,58 ±0,06
A 14	116 ±16	42 ±2	15 ±3	20 ±3	95 ±18	370 ±30	0,27 ±0,08	0,48 ±0,05
A 15	84 ±13	34 ±2	15 ±3	16 ±4	69 ±14	315 ±31	0,4 ±0,1	0,47 ±0,08
A 16	26 ±13	10,2 ±0,4	8 ±2	10 ±3	27 ±4	189 ±21	0,6 ±0,4	1,0 ±0,1
A 17	23 ±5	4,5 ±0,2	6 ±2	8 ±3	13 ±0	186 ±20	0,5 ±0,2	1,8 ±0,2
A 18	43 ±10	29 ±1	-	-	-	-	-	-
A 19	26 ±8	11,0 ±0,4	-	-	-	-	-	-
A 20	31 ±8	21 ±1	-	-	-	-	-	-
A 21	74 ±18	41 ±2	13 ±5	23 ±6	73 ±8	377 ±40	0,4 ±0,2	0,6 ±0,1

- not measured yet

For U distribution, points located in the vicinity of the industrial area presented mean activity concentration of 117Bq/kg, whereas more distant points (9, 16, 17, 18, 19 and 20) presented concentrations below 50Bq/kg, with mean value of 32Bq/kg.

The results obtained for the correlation coefficients between Th and Ra-isotopes, U and Ra isotopes and organic matter and Ra isotopes show that points 1, 2 and 3 present anomalous concentrations of Ra-isotopes and Th.

The correlation analysis for ^{210}Pb showed that this element correlates with rare earth elements, trace metals and Fe and it seems to be enriched just in the areas with high organic matter content. ^{40}K showed the same trend as ^{210}Pb .

CONCLUSIONS

The results obtained reflect the complexity of the region, however good correlation was observed between Fe concentration and Co, Ce, Cr, Cs, Eu, La, Lu, Nd, Sc, Sm, Ta, Th, Yb, Zr, and Ra-isotopes content. These results corroborate the already observed enrichment of ^{226}Ra , ^{228}Ra and Th in the surroundings of the phosphoric acid industries located in the region, both by the correlation analysis and by the iron normalisation. It can also be seen, that the organic matter content, in the estuary sediment, is a powerful trap for nuclides U and ^{210}Pb .

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