

Environmental contamination by technologically enhanced naturally occurring radioactive material – TENORM: A case study of phosphogypsum

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In the last decades considerable attention has been given to technologically enhanced natural occurring radioactive material (TENORM). Within this frame, of particular concern is the phosphate fertilizer industry, located in Cubatão, São Paulo State, Southwest Brazil. This industry is responsible for the production of 69 million tons of phosphogypsum waste, which is stockpiled in the surrounding environment. This waste concentrates radionuclides of the natural series originally present in the phosphate rocks used as raw material. This study aims to evaluate the environmental impact of such activities in the sediments of the estuarine system. Contents of natural radionuclides from thorium and uranium series were measured in sediments from Cubatão estuarine system, using high-resolution gamma-spectrometry. U and Th were determined by instrumental neutron activation analysis (INAA). It was observed that U and Th concentration is higher in the rivers close to the phosphogypsum piles, at least five points were identified as being affected by anthropogenic factors.

Introduction

The mining and processing of phosphate rock that is processed to phosphoric acid production generate TENORM containing residues. This intermediate is then further processed into phosphate fertilizers, detergents, animal feeds, food additives, pesticides and other phosphorous chemicals. Phosphate fertilizers are primarily derived from phosphate rock mined as naturally occurring ores. The principle constituent of the Brazilian phosphate rock is the mineral apatite (carbonatite). The fresh rock is a phoscorite cut by abundant carbonatitic veins. The typical phosphate (P_2O_5) concentration of the rock is of the order of 15–30%, with clay, sand, carbonate and other impurities present in varying quantities. Processing of phosphate ore in order to produce intermediate products can be done by acid leaching of the ore resulting in phosphoric acid. Most acidulation is done with sulphuric acid, which leads to the formation of phosphogypsum ($CaSO_4 \cdot xH_2O$), which is not very soluble in the resulting reaction mixture. Solid gypsum crystals precipitate and can be easily separated from the raw phosphoric acid by filtration following a washing step. This waste is then moved to nearby storage areas, the so-called gypsum stacks. In Brazil, two main industries (named here A and C) are responsible for the production and storage of about 4,000 ton per day on several stacks in Cubatão City, located in Santos Basin. The amounts of radioactivity that are fractionated to phosphogypsum vary significantly. MAZZILLI et al.¹ found percentages (phosphogypsum to ore rocks) of 90% for Ra isotopes, 100% for ^{210}Pb and 80% for Th isotopes, in the

phosphogypsum stored in Cubatão. Several papers have already been published concerning the characterization of the Brazilian phosphogypsum.^{1–3} Mean activity concentrations of the same order of magnitude was observed for ^{226}Ra and ^{210}Pb (849 Bq·kg⁻¹ and 837 Bq·kg⁻¹ for industry A and 357 Bq·kg⁻¹ and 342 Bq·kg⁻¹ for industry C) and for ^{232}Th and ^{228}Ra (222 Bq·kg⁻¹ and 229 Bq·kg⁻¹ for industry A and 172 Bq·kg⁻¹ and 163 Bq·kg⁻¹ for industry C).³

SANTOS et al.³ evaluated the environmental impact of the storage of phosphogypsum stacks in Cubatão. The aquatic environment near the disposal area was assessed by measuring natural radionuclide activities in groundwater, river water and sediment samples in the vicinity of gypsum stack from industry C. They found that the most critical pathway between phosphogypsum and the environment was through water contamination. Sediments from rivers, in the area of influence of the stacks, presented higher concentrations of U and Th, when compared with reference values.

In order to verify the extent of such influence, this paper is concerned with the measurement of natural radionuclides of the U and Th series in the sediments of the region. In Fig. 1 are depicted the location of the two industries, the surrounding aquatic system and the location where sediments were collected.

The study area

Santos Basin, located in Southwest Brazil, São Paulo State, comprising the counties of Santos (725 km²), São Vicente (131 km²) and Cubatão (160 km²), is considered the most important industrial region of the country.

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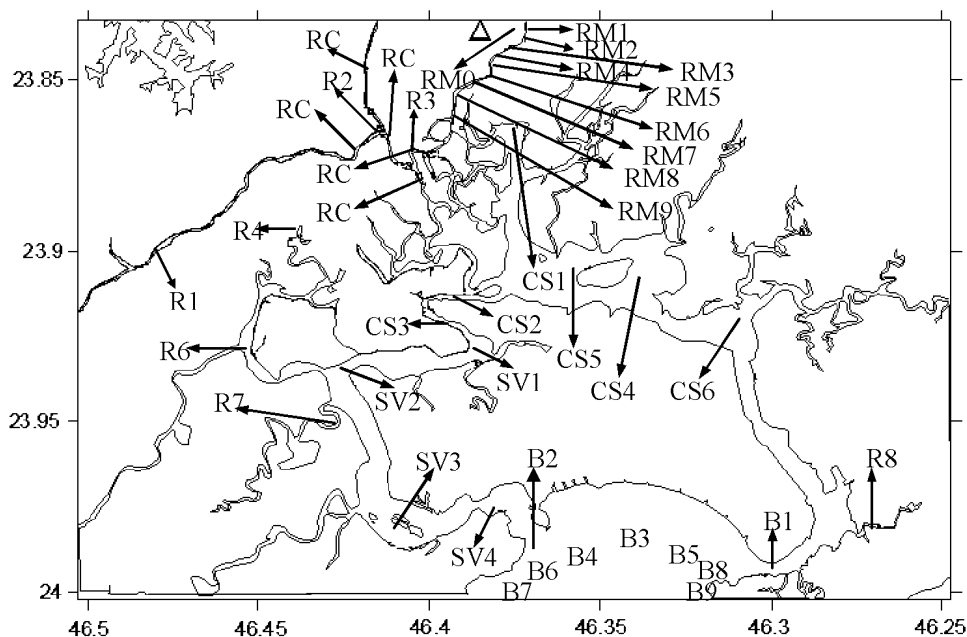


Fig. 1. Study area showing the sampling location. Axes x and y mean geographic coordinates

These man-made activities, on the other hand, represent a potential threat to the surrounding environment. Its estuarine system is responsible for the catchments and deposition of a considerable amount of material loaded by rivers, such as major and traces metals and other pollutants discharged by the local industrial activity.

For a better understanding of the results, in Fig. 1 the study region was divided in rivers (identified by R), Santos Channel (CS), São Vicente Channel (SV) and Santos Bay (B). The rivers samples were divided into RC-samples, which represent sediments from Cubatão River; RM-samples, which represent sediments from Mogi River and R-samples, which represent sediments from others estuarine rivers that are subjected to tidal effects, and, therefore, possess salinity values higher than the former rivers. In Santos and São Vicente Channel the salinity ranges from 0.5 to 35‰ and Santos Bay possesses salinity of 35‰. In the surrounding of Cubatão and Mogi rivers a large number of industries are located including two phosphate fertilizer plants, which are the object of this study. In Santos Channel the most important Brazilian harbor is located. The sampling locations were chosen according to the monitoring program established by “Companhia de Tecnologia de Saneamento Ambiental” CETESB, which is the state company responsible for formulation and application of public health measures; and the location of the phosphate fertilizer plants (Fig. 2).

Experimental

Samples were collected in 1999 in Santos and São Vicente estuary with a Van Veen grab and in 2002 in Cubatão and Mogi Rivers using PVC core with 20 cm of length and 4 cm diameter. All samples were maintained under 4 °C before laboratory treatment. Samples were dried at temperature of 65 °C till constant weigh and sieved to a grain size of 150 mesh. Part of the sample was packed in plastic vessels for gamma-spectrometry, for the determination of radium isotopes and ^{210}Pb . Approximately 150 mg were used for Th and U measurement by neutron activation analysis.

Activity concentrations of ^{226}Ra , ^{228}Ra and ^{210}Pb were measured by gamma-spectrometry with a hyper-pure germanium detector, EGNC 150-190 R, from Eurisy Measures, with resolution of 1.8 keV for the 1332 keV ^{60}Co photopeak, for 4096-channels. The detector was calibrated using natural soil spiked with radionuclides certified by Amersham. Samples were packed in 100 cm³ cans and sealed 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. The ^{226}Ra activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides: ^{214}Pb at 295 keV and 352 keV, and ^{214}Bi at 609 keV. The ^{228}Ra content of the samples was determined by measuring the

intensities of the 911 keV and 968 keV gamma-ray peaks from ^{228}Ac . The concentration of ^{210}Pb was determined by measuring the activity of its low energy peak (47 keV). Self-absorption correction was applied since the attenuation for low energy gamma-rays is highly dependent upon the composition of the sample. The approach used was that suggested by CUTSHALL et al.⁴ Typical lower limits of detection for gamma-spectrometry were $4.5 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{226}Ra , $3.1 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{228}Ra and $25 \text{ Bq}\cdot\text{kg}^{-1}$ for ^{210}Pb , for a counting time of 50,000 seconds. U and Th were determined by instrumental neutron activation analysis (INAA) by irradiation of approximately 150 mg of each sample, during 8 hours in a neutron flux of $10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, at the Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. The induced radioactivity was measured with a Ge-hyperpure detector (Inter technique), with 2.1 keV resolution for the 1332 keV ^{60}Co photopeak. The concentration of the elements was determined by comparing activities obtained in the samples with standard materials Buffalo River Sediment (NIST-2704) and Soil-7 (IAEA). All uncertainties presented correspond to propagation of errors.

Results and discussion

Table 1 shows the activity concentrations of U, ^{226}Ra , ^{210}Pb , Th and ^{228}Ra obtained in the sediment samples for the six compartments studied (Santos Channel-CS, São Vicente Channel-SV, Santos Bay-B, Cubatão River-RC, Mogi River-RM and river samples-R). In the same table are also presented reference values obtained for a deep core profile collected in the region.⁵ These values were considered as the background of the region (BG), since no data is available in the literature so far.

In Fig. 3 are depicted the results obtained for the sediment concentration normalized by the reference values. A normalized value higher than one indicates enrichment in the sediment compared to the background values and is generally used as an indicator of anthropogenic contribution. Despite the geochemical differences, such as salinity and tide, it can be observed identical behavior for ^{226}Ra and ^{228}Ra , with the following distribution among the studied compartments:

$$[\text{RM}] \approx [\text{RC}] > [\text{R}] \approx [\text{CS}] \approx [\text{SV}] \approx [\text{B}]$$

for U and Th the distribution:

$$[\text{RM}] > [\text{RC}] > [\text{R}] > [\text{CS}] > [\text{SV}] \approx [\text{B}]$$

and for ^{210}Pb the distribution:

$$[\text{RM}] \approx [\text{RC}] \approx [\text{R}] \approx [\text{CS}] \approx [\text{SV}] \approx [\text{B}]$$

Statistical analysis was used for the comparison of the compartments studied.⁵

Considering all the analyzed samples, the activity concentration of U varied from 14 ± 3 to $348 \pm 27 \text{ Bq}\cdot\text{kg}^{-1}$ (points B4 and R4, respectively); the activity concentration of ^{226}Ra varied from 6 ± 2 to $60 \pm 3 \text{ Bq}\cdot\text{kg}^{-1}$ (points B2 e RM2, respectively); ^{210}Pb varied from <13 to $538 \pm 96 \text{ Bq}\cdot\text{kg}^{-1}$ (points B2 and CS1, respectively); Th activity varied from 6.6 ± 0.3 to $198 \pm 9 \text{ Bq}\cdot\text{kg}^{-1}$ (points SV3 and RM0, respectively), for ^{228}Ra the variation was from 8 ± 3 to $86 \pm 5 \text{ Bq}\cdot\text{kg}^{-1}$ (points B2 and RM0, respectively).

Box plot graphic was used to evaluate the behavior of the radionuclides in the studied compartments (Fig. 4). It can be observed that the higher concentrations and variations of Th occur in the samples from Mogi River, followed by Cubatão River. Higher concentration and variation for U are observed in samples R, probably due to the influence of an industry that manufacture residues from a steel plant in the nearby, close to point R4; followed by samples from Mogi River, Santos Channel and Cubatão River. The higher concentration of ^{210}Pb in samples from Santos Channel is due to the influence of a steel plant near point CS1.

Radium isotopes present the same pattern in the samples belonging to the compartments Santos Bay, São Vicente Channel and rivers R. Slightly higher values were observed in samples from Santos Channel, Cubatão and Mogi rivers. Such result can be explained by desorption process and dissolution of Ra as salinity increases.⁶ In these samples, a slightly increase in the concentration of ^{228}Ra in relation to ^{226}Ra can be observed, in comparison with the same ratio in other compartments.

As a general trend, it can be seen that the concentration of these elements generally decreases downstream Mogi River, showing good correlation with the estuarine system salinity gradient. Nevertheless, sampling point MR0 deserves special attention. It is located in a small stream, Bugre River, tributary of Mogi River, and is the closest point to the phosphogypsum piles. This point is enriched in all determined nuclides.

Table 1. Activity concentration (in Bq·kg⁻¹) in sediments from Mogi (MR) and Cubatão River (CR), Santos Channel (CS), São Vicente Channel (CV), Santos Bay (B) and other rivers (R) from the Santos and São Vicente estuary

Sample	U	²²⁶ Ra	²¹⁰ Pb	Th	²²⁸ Ra
R4	348 ± 27	31 ± 5	114 ± 21	77 ± 4	36 ± 5
R5	145 ± 20	20 ± 4	47 ± 10	41 ± 2	24 ± 4
R6	116 ± 16	15 ± 3	95 ± 18	42 ± 2	20 ± 3
R7	84 ± 13	15 ± 3	69 ± 14	34 ± 2	16 ± 4
R8	95 ± 27	19 ± 4	60 ± 11	44 ± 4	25 ± 5
R1	69 ± 6	44 ± 5	49 ± 9	79 ± 4	77 ± 6
R2	109 ± 8	43 ± 5	44 ± 9	96 ± 5	73 ± 6
R3	86 ± 7	40 ± 5	41 ± 8	60 ± 3	59 ± 6
RC1	113 ± 7	42 ± 2	56 ± 9	66 ± 3	64 ± 4
RC2	89 ± 6	39 ± 2	68 ± 9	71 ± 3	59 ± 3
RC3	109 ± 7	42 ± 2	72 ± 10	80 ± 4	68 ± 27
RC4	154 ± 16	46 ± 2	40 ± 8	98 ± 5	74 ± 4
RC5	108 ± 8	37 ± 14	62 ± 9	77 ± 4	65 ± 4
RM0	243 ± 22	43 ± 2	ND	198 ± 9	86 ± 5
RM1	109 ± 11	43 ± 2	55 ± 9	82 ± 4	86 ± 5
RM2	141 ± 13	60 ± 3	68 ± 10	96 ± 5	82 ± 5
RM3	115 ± 13	31 ± 2	49 ± 8	92 ± 4	65 ± 4
RM4	131 ± 9	39 ± 2	52 ± 8	100 ± 5	71 ± 4
RM5	153 ± 11	43 ± 2	68 ± 9	99 ± 5	75 ± 4
RM6	140 ± 12	41 ± 2	74 ± 10	89 ± 4	66 ± 4
RM7	152 ± 13	41 ± 3	65 ± 13	93 ± 4	70 ± 6
RM8	190 ± 20	47 ± 2	57 ± 9	95 ± 4	65 ± 4
RM9	199 ± 17	44 ± 2	48 ± 8	95 ± 4	73 ± 4
BG	54	45	57	61	71
B1	59 ± 9	13 ± 3	37 ± 7	25 ± 1	15 ± 3
B2	21 ± 2	6 ± 2	<13	9.9 ± 0.5	8 ± 3
B3	37 ± 5	ND	ND	36 ± 2	ND
B4	43 ± 10	ND	ND	29 ± 1	ND
B5	14 ± 3	ND	ND	14.6 ± 0.6	ND
B6	19.7 ± 3.5	ND	ND	15.8 ± 0.7	ND
B7	26 ± 8	ND	ND	11.0 ± 0.4	ND
B8	31 ± 8	13 ± 5	73 ± 8	21.2 ± 0.8	23 ± 6
B9	74 ± 18	ND	ND	41 ± 2	ND
CS1	159 ± 21	32 ± 2	538 ± 96	63 ± 3	58 ± 4
CS2	94 ± 14	ND	ND	39 ± 2	ND
CS3	103 ± 9	20 ± 4	47 ± 9	44 ± 2	20 ± 4
CS4	133 ± 10	22 ± 1	62 ± 23	59 ± 3	40 ± 2
CS5	87 ± 18	ND	ND	37 ± 2	ND
CS6	48 ± 13	20 ± 2	26 ± 12	15.1 ± 0.8	26 ± 2
SV1	16 ± 2	ND	ND	11.5 ± 0.5	ND
SV2	46 ± 5	ND	ND	10.9 ± 0.5	ND
SV3	26 ± 13	8 ± 2	27 ± 4	10.2 ± 0.4	10 ± 3
SV4	16 ± 2	ND	ND	6.6 ± 0.3	ND

R: Other rivers samples; RC = Cubatão River samples; RM = Mogi River samples except RM0 that correspond to Bugre river; B = Santos Bay samples; CS = Santos Channel samples; SV = São Vicente Channel samples.

ND: Not determined.

Associated uncertainties refer to propagation of errors.

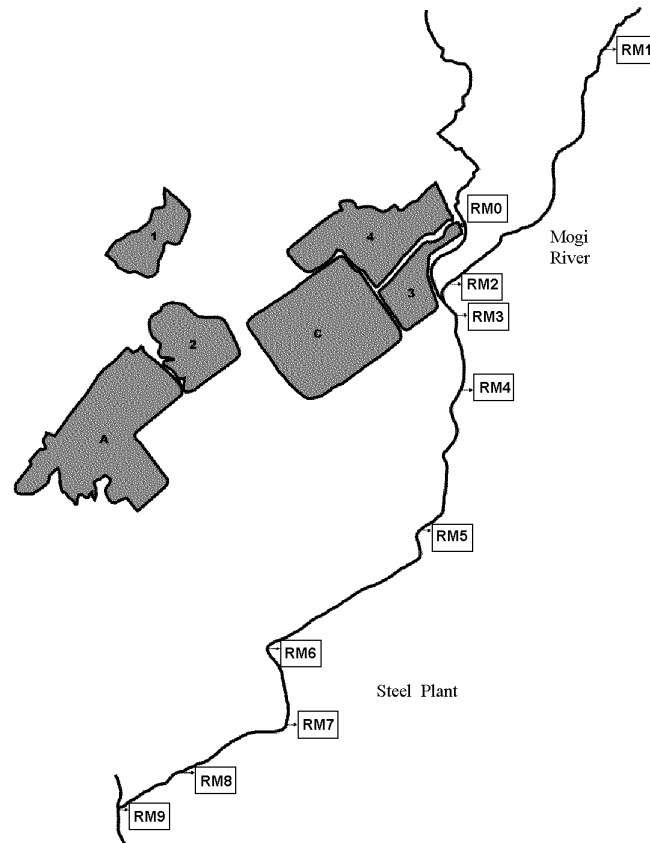


Fig. 2. Detailed map of the phosphate fertilizer plants (A and C) and phosphogypsum stacks (1, 2, 3 and 4) showing collection points at Mogi and Bugre (RM0) rivers and the location of the steel plant

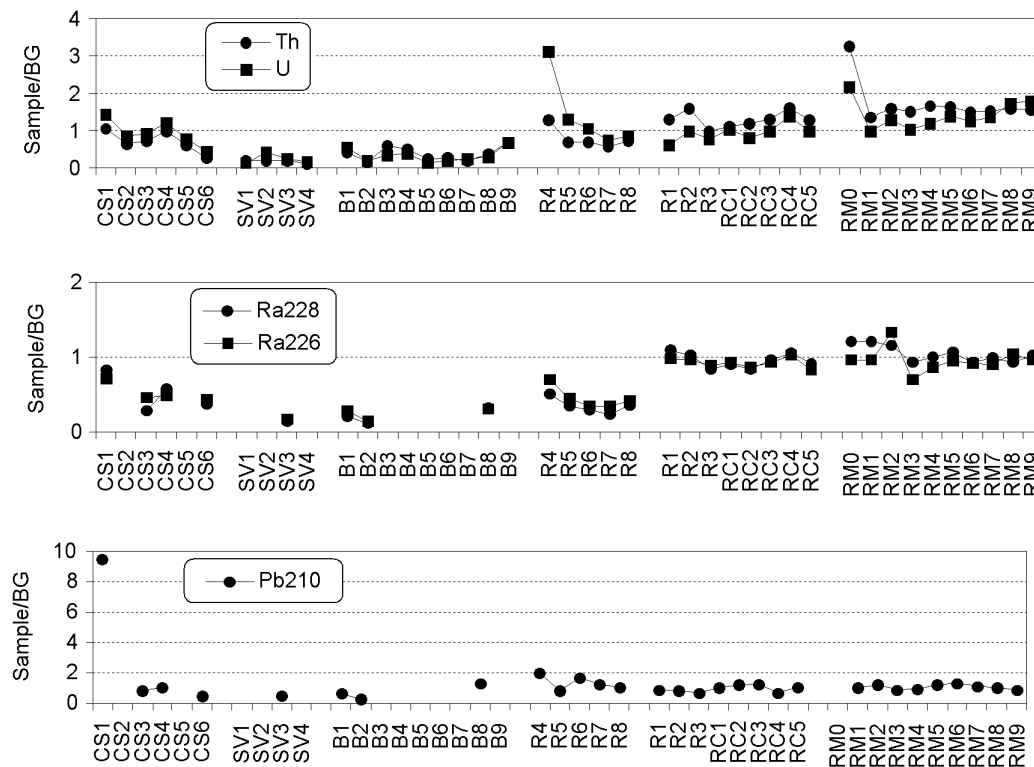


Fig. 3. Radionuclide concentrations normalized by reference values of the region

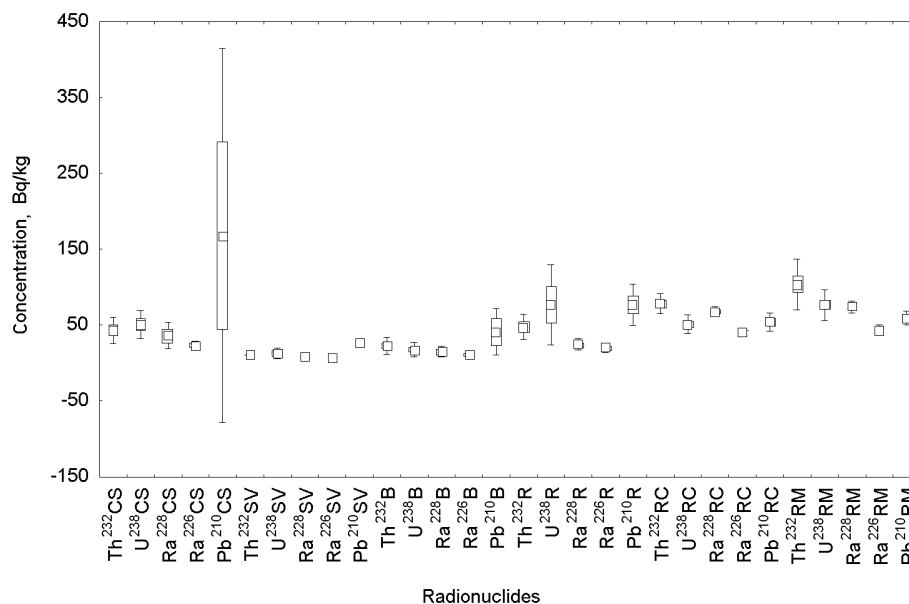


Fig. 4. Box plot showing the average distribution of radionuclides in the compartments studied: CS, SV, B, R, RC and RM

Conclusions

Due to the diversity of the estuarine system studied, sediment samples collected were divided in the following compartments: estuarine river samples, which belong to a region of fresh waters and waters under influence of tides; samples from Santos and São Vicente channels, which represent saline waters with influence from fresh waters from the rivers and from tides; and samples from Bay Santos, which salinity, above 35‰, does not vary with time.

As a general trend, the concentration of these radionuclides in the studied compartments decreases downstream rivers, showing good correlation with the estuarine system salinity gradient.

Radioisotopes of the same element present different nuclear characteristics, such as half-lives, but they present similar chemical properties. They should behave, as a consequence, in the same way in the environment. That is the case of radionuclides ²²⁶Ra and ²²⁸Ra. However, for a better understanding of the environmental behavior of this group, it should be taken in consideration, also, that the Ra isotopes come from different radioactive decay series. ²²⁶Ra and ²²⁸Ra isotopes present average concentrations of the same order of magnitude in sediments from Santos Bay and São Vicente Channel. These values are lower than those observed in sediments from Santos Channel, Cubatão and Mogi rivers, reflecting the influence of desorption

processes and dissolution of radium with the increase in salinity. In this later group it can be also observed a slight enrichment of ²²⁸Ra in relation to ²²⁶Ra. The dispersion of the experimental results around the mean value in the several compartments is very small.

Pb distribution is practically constant along the studied system, anomalous concentrations were observed only in the compartment of Santos Channel where is a steel plant located. This radionuclide did not correlate well with other elements from the same decay series, U and ²²⁶Ra, confirming that its presence in the superficial sediments of the estuarine system is not only due to geochemical differences (as tide influence and salinity) in the compartments studied but it is also dependent upon the atmospheric deposition of this radionuclide. As a potential source, which contributes to an increase in the emanation of ²²²Rn, precursor of ²¹⁰Pb in the ²³⁸U decay series, to the atmosphere, there exist in the region the gaseous effluents from the steel plant, the phosphate fertilizers plants and the phosphogypsum stacks.

The sensitive dispersion around the mean values observed for U in R and MR samples, for Th, in MR samples and for ²¹⁰Pb in CS samples, can be an evidence of the presence of the technologically enhanced naturally occurring radioactive material – TENORM, due to the phosphate fertilizer plants in Mogi River and due to the steel plant in Santos Channel.

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