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Distribution of U and Th decay series and rare earth elements in sediments of Santos Basin: Correlation with industrial activities

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Santos Basin, located in Southwest Brazil, is considered the most important industrial region of the country. Among the industrial activities present, phosphate fertilizer plants are 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 as well as rare earth elements originally present in the phosphate rock used as raw material. This study aims to evaluate the environmental impact of such activities in the sediments of the estuarine system by measuring the concentration of U, Th and rare earth elements and activity concentration of radionuclides ^{226}Ra, ^{228}Ra, ^{228}Th and ^{210}Pb.

Introduction

In the last decades considerable attention has been given to technologically enhanced natural occurring radioactive material (TENORM). Within this frame, of particular concern are the coal-fired power plants and the phosphate fertilizer industry.[1,2] The phosphate fertilizer industry includes the mining and processing of phosphate ore to produce phosphoric acid and phosphate fertilizers and as by-product, calcium sulphate (phosphogypsum) that have limited economic or environmental application and contain appreciable amount of radioactive material, originally present in the phosphate rock. The Brazilian phosphate industry has produced so far 69 million tons of phosphogypsum, which are stockpiled and presents a potential threat to the surrounding environment.

Environmental radioactive exposure from phosphate fertilizer comes from the fact that phosphate rock, which is the raw material for all phosphate products, is enriched in U and Th and its decay products. According to MAZZILLI et al.,[3] in the Brazilian fertilizer production the radionuclides ^{226}Ra, ^{210}Pb, ^{210}Po and thorium isotopes fractionate preferentially to the phospho-gypsum, with percentages (to ore rocks) of 90% for ^{226}Ra, 80% for ^{232}Th and ^{230}Th, 100% for ^{210}Pb and 78% for ^{210}Po. The distribution of thorium seems to depend strongly upon chemical processes. The uranium is predominantly incorporated in phosphoric acid as uranyl phosphate, sulphate or fluoride complexes.

Another group of elements related to Brazilian phosphate rocks are rare earth elements (REEs),[4] which have been observed in enhanced concentrations in the surrounding phosphate deposits.[5] Even though REEs have been considered to be of low toxicity, their environmental pollution has already been observed in some mineralized areas and soils affected by long term application of sludge.[6,7] REEs have proven to be beneficial in crop production in adequate concentrations,[7,8] but how they affect human health via food chain or directly through water or air, remain unclear.

This work aims to characterize and identify possible technologically enhanced sources of natural radiation in Santos Basin by measuring natural U, ^{232}Th and its decay products in sediments throughout the estuary region. As a complementary study REE are also determined in the same samples.

Description of the study area

Santos Basin, located in Southwest Brazil, São Paulo State, comprizing the counties of Santos (725 km^2), São Vicente (131 km^2) and Cubatão (160 km^2), is considered the most important industrial region of the country. However, such activities represent a potential threat to the surrounding environment.[9–11] A considerable amount of material, such as major and trace metals and other pollutants discharged by the local industrial activity, is transported by rivers and is deposited in its estuarine system.

Figure 1 shows the study area and the sampling location. For a better understanding of the results, the sediment samples were divided according to their provenance, from rivers (identified by R), from Santos Channel (CS), from São Vicente Channel (SV) and from Santos Bay (B). The rivers samples were divided into R-samples, which represent sediments from the estuary, RC-samples which represent sediments from Cubatão River and RM-samples, which represent sediments from Mogi River. In the surrounding of Cubatão and Mogi rivers a large number of industries is located including phosphate fertilizer plants and in Santos Canal lies the most important Brazilian harbor.

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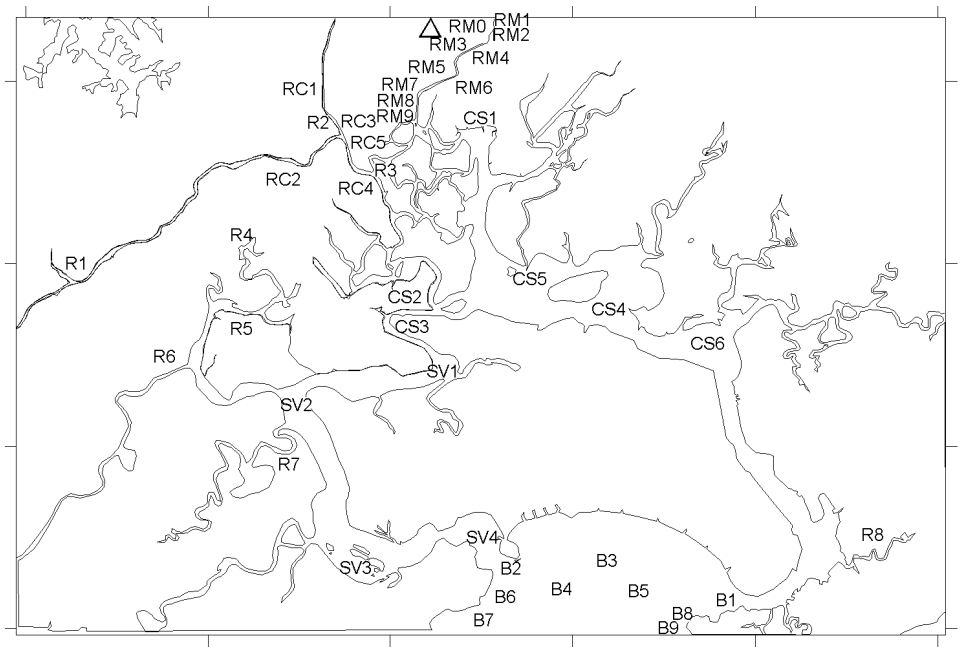

Fig. 1. Study area showing the sampling location and the phosphate fertilizer plant location (Δ); RM, Mogi River samples; RC, Cubatão River samples; R, other estuary river samples; CS, Santos Channel samples; SV, São Vicente channel samples and B, Santos Bay samples

Experimental

Forty-two sediment samples were collected either by dragging or manually. In sampling location RM6, a core was also collected at a depth of 34 cm. This core was sliced every 2 cm. All samples were prepared by drying at a temperature of 60 °C to constant mass, ground to a grain-size of less than 250 μm and finally homogenized prior to analysis.

All samples were analyzed by instrumental neutron activation analysis (INAA), for the determination of La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, ^{232}Th and natural U (called simply U, from now on). The elemental determination was made by irradiation of approximately 150 mg of each sample, during 16 hours at a neutron flux of 10^{12} n·cm^{-2}·s^{-1}, at the Instituto de Pesquisas Energéticas e Nucleares (IPEN) research reactor IEA-R1. Two series of counting were made: the first after one week decay and the second, after 15–20 days. The counting time was 2 hours for each sample and reference material. 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 analyzed elements was determined by comparing activities obtained in the sediment samples with standard reference materials Buffalo River Sediment (NIST SRM 2704) and Soil-7 (IAEA).

Activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{210}Pb were measured by gamma-spectrometry in 31 samples of sediments. Samples were packed in polyethylene containers and sealed for about four weeks prior to measurement in order to ensure that equilibrium has been reached between ^{226}Ra and its decay products of short half-life, ^{214}Bi and ^{214}Pb. Samples were measured by using a hyperpure germanium detector (EGNC 15-190-R from Eurisys), with 15% efficiency for 50,000 seconds. The gamma-spectra obtained were analyzed by using WinnerGamma program.[12]

^{226}Ra activity was determined by taking the mean activity of three separate photo peaks of its daughter nuclides: ^{214}Pb, at 295.21 keV and 351.93 keV, and ^{214}Bi at 609.32 keV. The ^{228}Ra content of the samples was determined by measuring the intensities of the 911.07 and 968.90 keV gamma-ray peaks from ^{228}Ac. ^{228}Th content was determined by the mean activity for ^{212}Pb (2338.6 keV) and ^{208}Tl (583.2 keV).

^{210}Pb was determined by measuring the activity of its low energy peak (46.54 keV). Self-absorption correction was applied since the attenuation for low energy gamma-rays is highly dependent upon sample composition. The approach used was modified from that suggested by CUTSHALL et al.[13]

Results and discussion

It is a common practice for geochemists and environmentalists to use shale elemental concentration to study upper crust materials. Normalization with shale eliminates natural variations in the absolute concentrations, making it easier to see how each

elemental concentration varies with respect to the other elements, especially for chemically correlated species.[14]

For normalization purposes Post-Archean Average Australian Shale (PAAS)[15] was used for REEs, U and Th and the baseline (30–34 cm depth) values obtained from the core collected in point RM6 were used for U, ^{232}Th, ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th. Both normalizations presented the same trend for Th and U. The distribution pattern of radionuclides and REEs over Santos Estuary are shown in Figs 2 and 3. It can be seen that Santos Estuary Rivers and Santos Channel samples (Fig. 2a, b, c, and d) showed the highest concentration for analyzed elements and radionuclides. São Vicente Channel and Santos Bay sediment samples (Fig. 3a, b, c and d) presented lower concentrations, although Santos Bay results showed higher variation and mean values than the former.

Even considering the geochemical differences in the studied environments (such as salinity, tide influence, etc.), the variation obtained between them is higher than expected for non-perturbed areas.[16,17] In this area are located, among others, two phosphate fertilizer plants, a steel industry and the biggest harbor of the southern hemisphere – Santos harbor.

In river samples, U and Th presented values generally greater than both normalizers (ratios are higher than 1) and U tends to be enriched downstream of the Mogi River in relation to the other points. Point RM1 is located upstream Mogi River and was chosen as blank for river compartments. ^{226}Ra, ^{228}Ra and ^{228}Th present similar trends, being enriched in Cubatão and Mogi River related to other river samples. ^{210}Pb presented rather spread values around the normalizer.

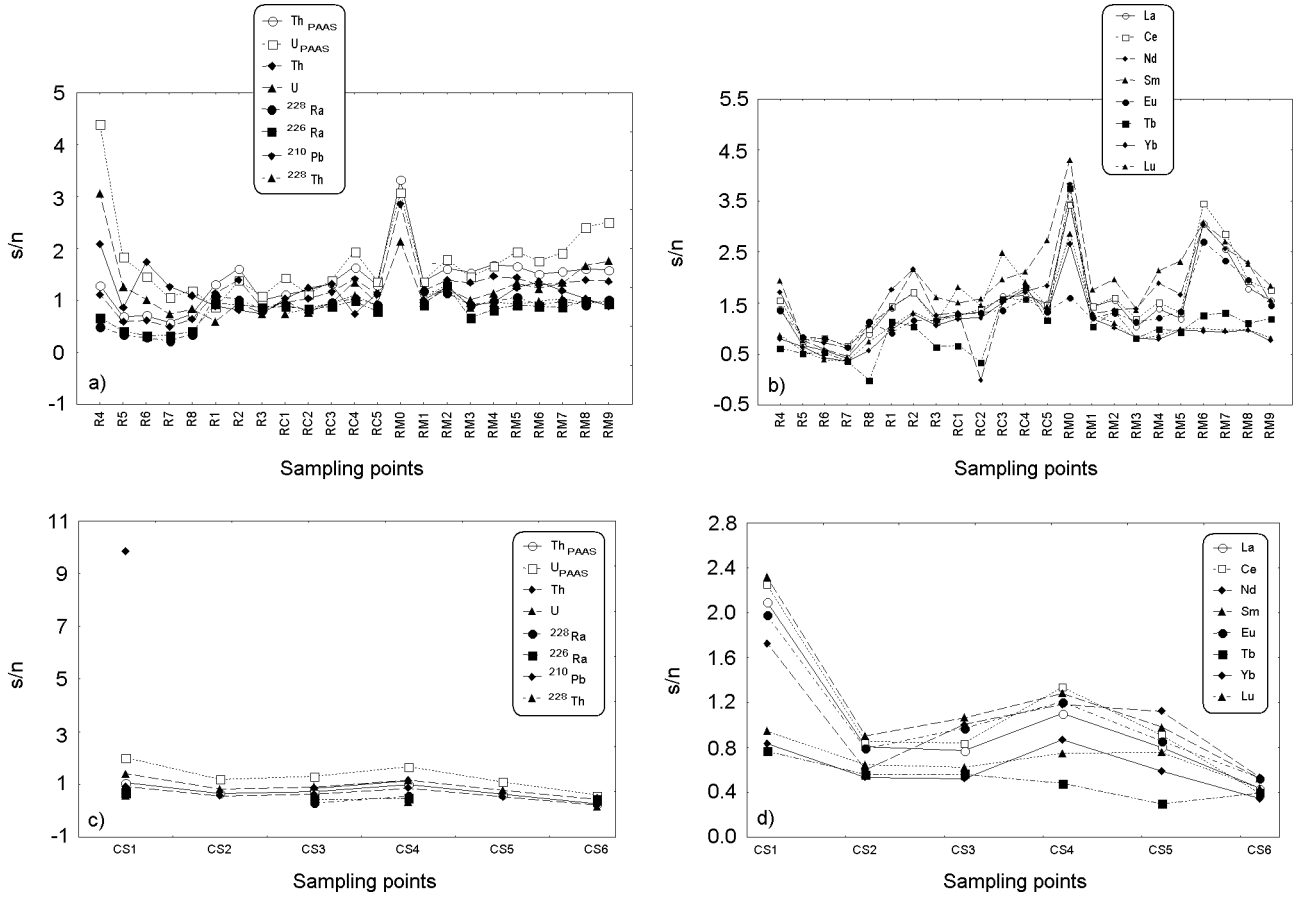

Fig. 2. Normalized distribution of radionuclides (s/n, where s is the content of the sample and n the content in the normalizer in Bq·kg^{-1}), and REEs, (s/n, where s is the content of the sample and n the content in the normalizer in μg·g^{-1}) for samples collected in Santos Rivers (a and b) and Santos Channel (c and d)

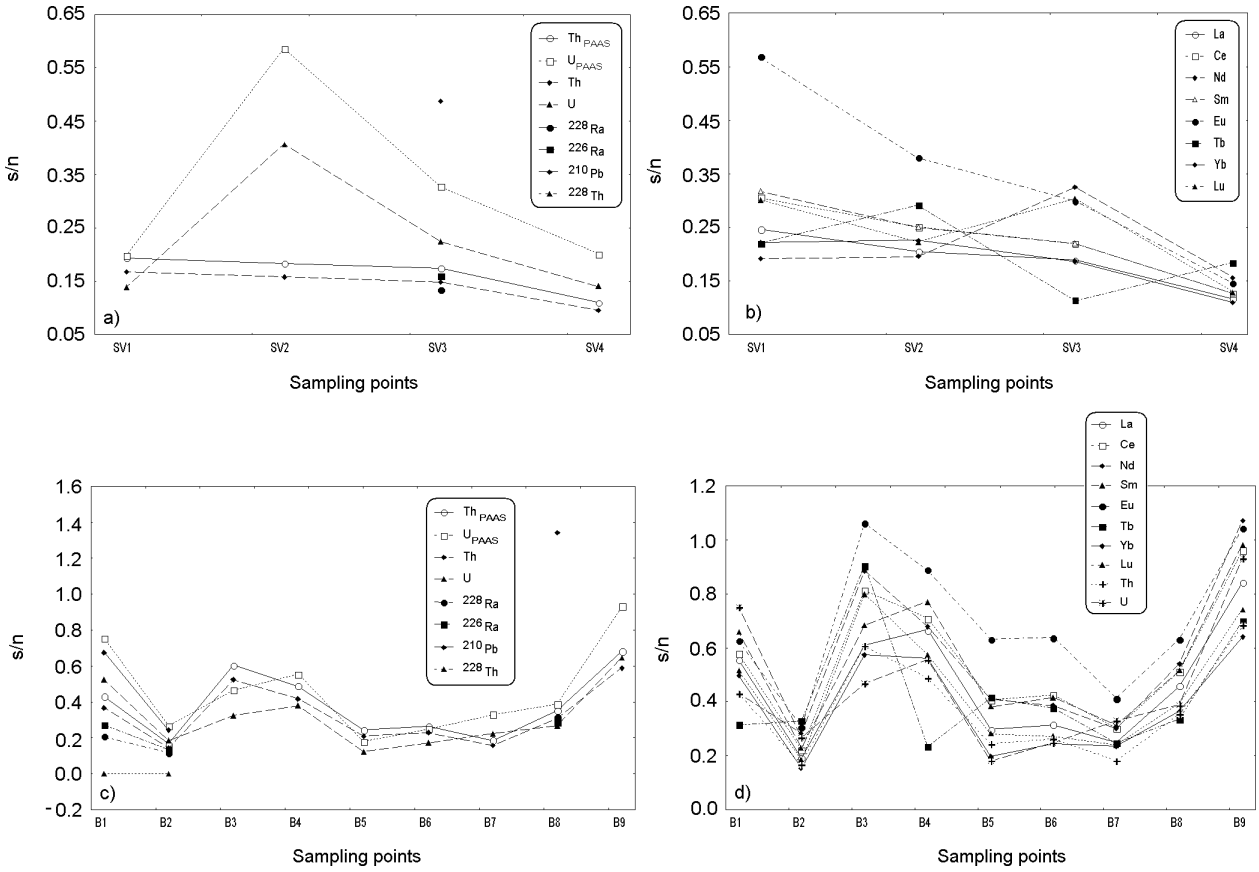

Fig. 3. Normalized distribution of radionuclides (*s*/*n*, where *s* is the content of the sample and *n* the content in the normalizer in $Bq \cdot kg^{-1}$), and REEs, (*s*/*n*, where *s* is the content of the sample and *n* the content in the normalizer in $\mu g \cdot g^{-1}$) for samples collected in São Vicente Channel (a and b) and Santos Bay (c and d)

A clear enrichment in light rare earth elements (LREEs, from La to Eu) is observed downstream of RM3. An enrichment of Lu and Sm is also noted in Cubatão River. The ratio between ΣLREEs and ΣHREEs (HREE from Tb to Lu) presented a mean value and standard deviation of 62±22 (range 36–126). These values are quite higher than that found for PAAS (39.3), showing a strong fractionation between LREE and HREE. SANTOS[4] showed that LREEs are enriched in phosphogypsum during the phosphoric acid production and this could explain the higher concentrations observed. Point RM0, which is the closest point to the phosphogypsum stacks, presented enhanced values for all analyzed elements. The higher values observed for point R4 are probably due to its organic matter content.[18]

Santos Channel samples (Fig. 2c and d) show small variations in relation to the baseline normalization, except for CS1 sample that presents the highest ^{210}Pb content of all analyzed samples. This point is located close to a steel plant that uses coal in its high temperature furnaces. The discharge of ^{222}Rn from these furnaces could be responsible for ^{210}Pb levels in the surrounding sediments. Furthermore, this point, which receives sediment load from Cubatão and Mogi rivers, is enriched in LREEs. The geochemical composition of these rivers could affect CS1 characteristics. The ΣLREE/ΣHREE ratio presented a mean value and standard deviation of 66±18 (range 47–99).

São Vicente Channel and Santos Bay (Fig. 3a and b), as mentioned before, presented the smallest contents of the analyzed elements. Both are depleted relative to the normalizer for radionuclides and REEs. The relatively elevated value for U in SV2 is probably due to the mixture of sediments brought from rivers (points R4, R5 and R6). The observed fractionation between light and heavy REEs is less apparent in these samples, which presented ΣLREE/ΣHREE ratio mean values and standard deviation of 44±6 (range 38–50) and 52±6 (range 46–61), respectively. Enrichment was observed only in points B3, B4 and B9. Point B3 is located near submarine sewage sludge and points B4 and B9 are ancient deposits for sediment drainage from Santos Harbor area.

Figure 4 shows the results of the cluster analyses performed using *z*-normalization to values for all samples. Three main groups were formed comprising: (1) Cubatão and Mogi River, R4 and CS1 samples, (2) other rivers, Santos Channel and locations with high content from Santos Bay and (3) the last group formed by São Vicente Channel and Santos Bay with less content samples. In group 1, it is possible to identify a sub-group formed by samples: RM0, RM6, RM7 and SC1. These samples, that present higher REEs, U and Th concentrations, are close to the phosphogypsum stacks and possibly represent anthropogenic contamination.

Principal component analysis shows that ^{210}Pb is the lesser significant in the observed variance, as shown in Fig. 5. In the same figure the extracted factors can be seen. Comprising factor 1 are REE, U and Th, which contribute for 53% of variance, factor 2 comprises ^{226}Ra, ^{228}Ra, ^{228}Th and explain 22% of observed variance. As already observed for these samples[19] the ^{210}Pb behavior seems to be more correlated with organic matter content.

Figure 6 shows the results normalized for the baseline values for the collected core (RM6). It can be seen that all radionuclides, LREEs and Tb are enriched in the first 10 cm and around 22 cm. Radionuclides and REEs present values approximately constant below 28 cm which justify its use as a baseline value. No significant variations were observed for Yb and Lu in all depths.

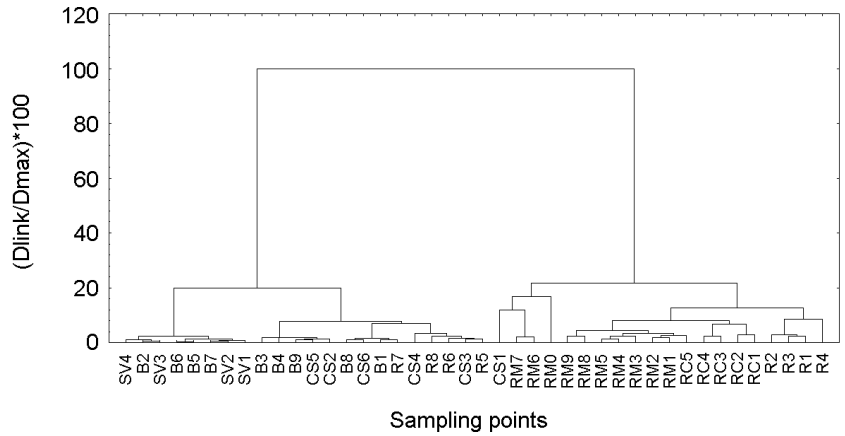

Fig. 4. Cluster analysis obtained for Santos Estuary samples. Ward's method, Euclidean distances

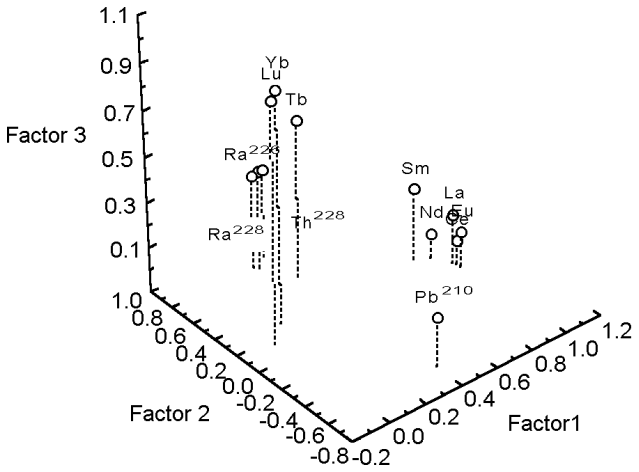

Fig. 5. Factor analysis with the loaded factor for the analyzed elements

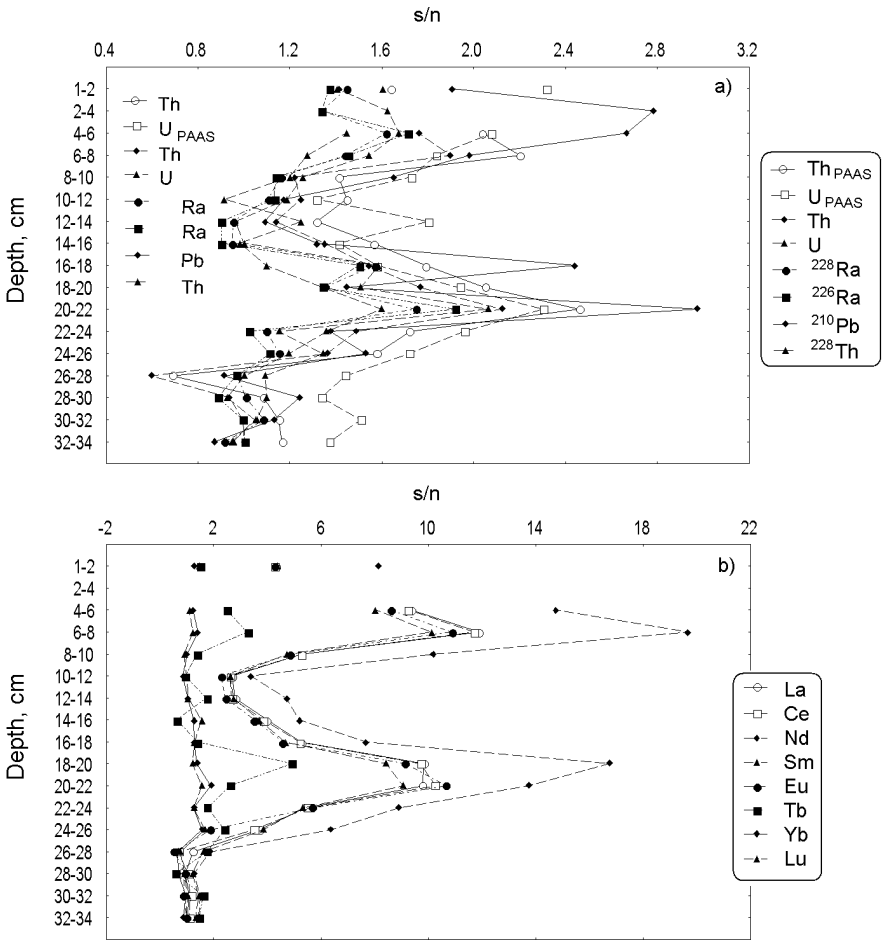

Fig. 6. Normalized distribution of radionuclides (a) (*s*/*n*, where *s* is the content of the sample and *n* the content in the normalizer in $Bq \cdot kg^{-1}$), and REEs (b), (*s*/*n*, where *s* is the content of the sample and *n* the content in the normalizer in $\mu g \cdot g^{-1}$) for the core sample collected in point RM6

The ratio ΣLREE/ΣHREE in the core presents mean value of 150 and range of 43 to 300, approximately four times that found in PAAS. Values found for the baseline (30 to 34 cm) are in the range of 43 to 45, close to PAAS values. These results show that in the upper layers LREEs are strongly fractionated.

Conclusions

The obtained results for sediment samples collected in Santos and São Vicente Channel and Santos Bay showed that the concentration for U, Th and REEs, generally follows the sequence R > CS > B ~ SV (river > Santos Channel > Santos Bay ~ São Vicente Channel samples). Higher values seems to be associated with anthropogenic activities and were observed in the vicinity of the phosphogypsym piles, in Mogi River, except for ^{210}Pb that presented a higher value in point CS1, near the steel industry. In Santos Bay, higher values are associated with the submarine sewage and the harbor dragging activities.

The normalization procedures applied to these results proved to be an efficient tool for identification of sediments affected by human activities in relation to those formed mainly by terriginous materials. REEs can also be used as a signature for a sediment's origin. In this case, the strong fractionation observed in Mogi River samples and in the core collected at RM6 also indicates that anthropogenic processes are affecting the estuary. The results obtained by statistical procedures for radionuclides, in spite of their geochemistry differences, indicate an external source associated with anthropogenic activities.

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References

1. M. S. BAXTER, J. Environ. Radioact., 32 (1996) 3.
2. U. C. MISHRA, J. Environ. Radioact., 57 (2001) 1.
3. B. P. MAZZILLI, V. PALMIRO, C. SAUEIA, M. B. NISTI, J. Environ. Radioact., 49 (2000) 113.
4. A. J. G. SANTOS, Avaliação do impacto radiológico ambiental do fosfogesso brasileiro e lixiviação de ^{226}Ra e ^{210}Pb, PhD Tesis, IPEN, São Paulo, 2002, 165 p.
5. F. ELBAZ-POULICHET, C. DUPUY, Appl. Geochem., 14 (1999) 1063.

6a. Z. M. WU, X. H. TANG, X. X. GAO, K. JIAO, M. P. J. ZHANG, J. Chinese Rare Earth Society, 1 (1983).

6b. C. ZHANG, L. WANG, S. ZHANG, Appl. Geochem., 13 (1998) 451.

7. M. E. ESSINGTON, S. V. MATTIGOD, Soil Sci. Soc. Am. J., 54 (1990) 385.

8a. S. ZHANG, L. J. WANG, C. S. ZHANG, S. J. LIU, Y. Q. WANG, X. X. LI, J. X. SUN, X. Z. QIAN, Press (1994) 199 (in Chinese).

8b. C. ZHANG, L. WANG, S. ZHANG, Appl. Geochem., 13 (1998) 451.

9. CETESB, Poluição da águas no estuário e baia de Santos, (1) 1978.
10. CETESB, Metais pesados na Baia de Santos e estuário de Santos e São Vicente, 1981.
11. CETESB, Sistema Estuarino de Santos e São Vicente, 2001, CD-ROM.
12. INTERWINNER, Spectroscopy Program Family, Version 4.1, released 1st of June, 1998.
13. N. H. CUSTHALL, I. L. LARSER, C. R. OLSEN, Nucl. Instr. Meth., 206 (1983) 309.
14. R. BIDDAU, R. CIDU, F. FRAU, Chem. Geol., 182 (2002) 1.
15. D. S. ALIBO, Y. NOZAKI, Geochim. Cosmochim. Acta, 63 (1999) 363.
16. P. S. ANDERSON, G. J. WASSEBURG, J. H. CHEN, D. A. PAPANASTASSIOU, J. INGRI, Earth Planet. Sci. Lett., 130 (1995) 217.
17. W. S. MOORE, H. ASTWOOD, C. LINDSTROM, Geochim. Cosmochim. Acta, 59 (1995) 4285.
18. B. P. MAZZILLI, P. C. S. SILVA, M. B. NISTI, Radioprot. Colloques, 37 (2001) C1-795.
19. P. S. C. SILVA, B. P. MAZZILLI, D. I. T. FAVARO, Chemical and radiological environmental impact due to industrial activities in Santos Estuary sediments (Brazil), 9th Intern. Symp. on Environmental Radiochemical Analysis – ERA-2002, Kent, UK, 2002.