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Distribution of radionuclides and elements in Cubatão River sediments

P. S. C. Silva,[1] B. P. Mazzilli,[1]* D. I. T. Fávaro[2]

Instituto de Pesquisas Energéticas e Nucleares,
[1] Centro de Metrologia das Radiações, Laboratório de Radiometria Ambiental
[2] Centro do Reator de Pesquisas, Laboratório de Análise por Ativação Neutrônica
Av. Prof. Lineu Prestes 2242, 05508-900 São Paulo, Brazil

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Cubatão River is located in Santos Basin, São Paulo State, Brazil. This region is characterized by the occurrence of estuaries and mangrove. Due to its location, near the coastal line, it is also an important industrial area, where phosphate fertilizer plants, petrol refineries, and chemical and steel industries are present. Such human activities contribute to the enhancement of elemental composition in sediments and, in some cases, also increase the radionuclide concentrations, the so called Technologically Enhanced Natural Occurring Radioactive Materials (TENORM). The contamination of land and sediments by TENORM is of major concern. The activity concentration of U and Th series radionuclides was determined in five sediment samples from Cubatão River. The activity concentration ratio was also determined. Equilibrium was observed for the ratio $^{234}U/^{238}U$. The activity ratios of $Th/^{238}U$, $^{228}Ra/^{226}Ra$ and $^{210}Pb/^{226}Ra$ were higher than the unity. In the first two cases, the observed values are due to the higher activity of Th in the sediment and in the last case are probably due to the atmospheric deposition of ^{210}Pb.

Introduction

Cubatão River is located in Santos Basin, São Paulo State, Southwest Brazil (Fig. 1).[1] This region is characterized by the occurrence of estuaries and mangrove. Due to its location, near the coastal line, it is also an important industrial area, where phosphate fertilizer plants, petrol refineries, and chemical and steel industries are present. Such human activities contribute to the enhancement of elemental composition in sediments and, in some cases, also increase the radionuclide concentrations, the so called Technologically Enhanced Natural Occurring Radioactive Materials – TENORM.[2] The contamination of land and sediments by TENORM is of major concern.[3–5] Measurement of radionuclide concentrations along the river-estuary-ocean transects has also been used to obtain information on the weathering process, transport mechanism, and geochemistry from land to sea as well as to identify pollution sources.[6–8]

In the eighties, Cubatão city was internationally known as one of the most polluted cities of the world. Since then, government efforts have been made to minimize the effects of the amount of pollution discharged in the region due to its intense industrial activities. Several papers have been published concerning the anthropogenic contamination in sediments from this region,[9–11] especially in Cubatão River. However, few data are found in the literature concerning the increase of radioactivity due to anthropogenic activities.

Experimental

The activity concentration of radionuclides from U and Th series was determined in five sediment samples from Cubatão River. Samples were collected manually with PVC cores, 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 determination of Th and U. Samples of approximately 150 mg were irradiated for 16 hours at a neutron flux of 10^{12} $n\cdot cm^{-2}\cdot s^{-1}$, at the research reactor IEA-R1, of Instituto de Pesquisas Energéticas e Nucleares (IPEN). Two series of counting were made: the first after one-week decay (for U determination) and the second, after 15–20 days (for Th determination). 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 determined elements was calculated by comparing the activities of the sediment samples with that of standard reference material (Buffalo River Sediment, NIST SRM 2704) and reference material with recommended values (Soil-7, IAEA). The precision of the method, expressed in relative standard deviation, was less than 10% for U and Th analyzed in SRM 2704 and Soil-7 for ten replicates.

Activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb were measured by gamma-spectrometry. Samples were packed in polyethylene containers and sealed for about four weeks prior to measurements in order to ensure that equilibrium has been reached between ^{226}Ra and its

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* E-mail: mazzilli@ipen.br

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decay products of short half-life, ^{214}Bi at 295 keV and 352 keV and ^{214}Pb at 609 keV. 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 the WinnerGamma program.[12]

^{226}Ra activities were determined by taking the mean activity of three separate photopeaks 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 keV and 968.90 keV gamma-ray peaks from ^{228}Ac.

^{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 elsewhere.[13]

The accuracy of the method is periodically checked by analyzing standard samples supplied by the Instituto de Radioproteção e Dosimetria (IRD) in an inter-comparison program.

For the determination of ^{234}U/^{238}U ratio, samples were measured by alpha-spectrometry. For the determination of isotopic ratio of the same nuclide by alpha-spectrometry, the counting statistics is the only source of error, once the analyzed nuclides are subjected to the same chemical treatment, they have the same chemical recovery, counting efficiency and, as they are in the same stainless disc, the same counting time. Approximately 1.0 g sample was completely dissolved with strong acids, co-precipitated with iron hydroxide, purified in AG-X 1 chromatographic resin and electroplated in a stainless steel disc. Alpha-activities were determined in a surface barrier alpha spectrometer.

In order to understand better the behavior of the radionuclides in the sediments, contents of organic carbon (OC) was determined by titration with dichromate and the concentrations of Al, Ca, Cr, Cu, Fe, Hg, Li, Ni, Pb, Mg and Mn were determined by Lakefield Geosol Laboratory. Sediment samples were digested with strong acids and the concentrations were determined by atomic absorption spectrometry. All elements, except Hg, were analyzed in the flame mode. Mercury was determined by cold vapour technique with an automatic hydride generator.[14]

Results and discussion

The activity concentration for natural uranium (U), ^{238}U, Th, ^{226}Ra, ^{228}Ra and ^{210}Pb for the samples collected in Cubatão River are shown in Table 1. In Table 2 the results obtained for organic carbon (OC) and for the concentrations of Al, Ca, Cr, Cu, Fe, Hg, Li, Ni, Pb, Mg and Mn are presented.

The concentration of natural uranium ranged from 89 to 154 Bq·kg^{-1}. These values are higher than that observed for the mean of the upper continental crust (36 Bq·kg^{-1}), soil (22 Bq·kg^{-1}) and shale (40 Bq·kg^{-1}).[15] The concentration of thorium varied from 66 to 98 Bq·kg^{-1}. As for U, the ^{232}Th is also higher when compared with the upper continental crust (37 Bq·kg^{-1}) and shale (54 Bq·kg^{-1}).[15] It is worth to emphasize that there are no available data on these concentrations for sediments in the near shore region in Brazil.

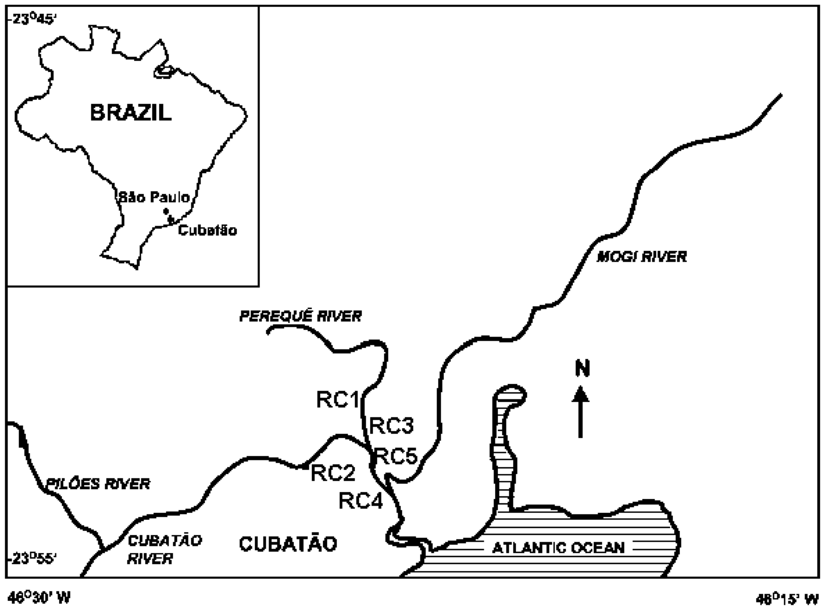

Fig. 1. Cubatão River and location of sampling points (modified from FURLAN et al.)[1]

Figure 2 shows the results of the cluster analysis applied to radioactive and stables elements. As can be seen, three groups were formed: (A) Mn, Ca, Pb, Cu, ^{210}Pb and Fe; (B) Mg, Li, Al, Ni, and OC and (C) ^{226}Ra, ^{228}Ra, U, Th and Hg. Group A accounts for Mn and Fe oxy-hydroxide elements. Group B accounts for the granulometric characteristics of the sediments, as the elements that were linked together are generally associated to silt and clay fractions.[16] Group C grouped together radioactive elements and Hg. This result could be due to the influence of anthropogenic activities in this region. Anomalous concentrations for Hg in the sediments of Cubatão River have been reported, related to industrial activities.[9,17] The observed association between this element and the radionuclides indicates that the relatively high concentrations are due to Technologically Enhanced Natural Occurring Radioactive Materials – TENORM. An anthropogenic origin can be also attributed to the concentration of ^{210}Pb. The concentration of this nuclide is almost constant along Santos and São Vicente estuary due to diffuse sources of ^{222}Rn that exist in the region.[14] Once ^{210}Pb is formed by the decay of its gaseous precursor in the U-series, it is incorporated in the sediments and is associated to iron oxy-hydroxide minerals.[18]

The ^{234}U/^{238}U, ^{226}Ra/^{238}U, ^{210}Pb/^{238}U, ^{228}Ra/Th, ^{228}Ra/^{226}Ra and Th/^{228}U isotopic ratios were calculated and the results are shown in Table 3.

In spite of the chemical differences between Th and U, their concentration ratio is almost constant in the majority of minerals forming rocks with a mean value of 4.[19] In the analyzed sediments this ratio varied from 3.7 to 5.0 indicating some enrichment of Th related to U.

In reducing environments, uranium occurs as U(IV), and is practically immobile due to the extreme insoluble compounds. Under oxidizing conditions, U(IV) is oxidized to U(VI), which greatly enhances its solubility. U(VI) forms uranyl ion complexes that are highly stable. Uranium is reduced by organic material, i.e., carbonaceous or bituminous shales and lignites,[20] reduced by Fe (producing Fe oxides), reduced by sulphide,[21] or adsorbed onto mineral surfaces or organic matter. The uranium concentration in natural waters and in sediments is primarily controlled by sorption and desorption processes.[22,23] Between pH 5 and 8.5 sorption occurs on organic matter, Fe and Mn oxy-hydroxides and clays.

Radium chemistry is relatively simple. This element presents only one valence state (+II) and it behaves in the same way as the other alkaline earth elements. The Ra^{2+} ion is moderately soluble in natural waters and its solubility rises with salinity. In surficial processes, equilibrium with its parent ^{238}U may not be reached because of the selective leaching of radium.[20]

In surficial water environments, the ^{234}U/^{238}U activity ratio is generally higher than the unity due to the interaction processes between water and sediments.[24,25] It can be seen, that this ratio is equal to unity in the analyzed samples. This fact can be explained by the reducing conditions observed in Cubatão River,[26] which is responsible for re-precipitation of the ^{234}U and its incorporation in the sediments.

Table 1. Activity concentration and combined uncertainties, obtained by propagation of error (in Bq·kg^{-1}) for the analyzed radionuclides in the sediment samples of Cubatão River

Sample	U*	^{238}U	^{226}Ra	^{210}Pb	Th	^{228}Ra
RC1	113 ± 7	55 ± 3	42 ± 2	56 ± 9	66 ± 3	64 ± 4
RC2	89 ± 6	43 ± 3	39 ± 2	68 ± 9	71 ± 3	59 ± 3
RC3	109 ± 7	53 ± 3	42 ± 2	72 ± 10	80 ± 4	68 ± 27
RC4	154 ± 16	75 ± 8	46 ± 2	40 ± 8	98 ± 5	74 ± 4
RC5	108 ± 8	53 ± 4	37 ± 14	62 ± 9	77 ± 4	65 ± 4

* Natural uranium.

Table 2. Concentration of elements analyzed in the sediment samples of Cubatão River

Sample	Cr	Cu	Li	Ni	Pb	Zn	Al	Mg	Ca	Mn	Hg,	O.C.,
	mg·kg^{-1}						%				μg·kg^{-1}	%
RC1	72	35	22	32	26	126	9.5	1.1	0.4	0.06	71	2.9
RC2	69	43	18	29	34	131	8.9	1.1	0.5	0.10	74	1.9
RC3	56	36	17	27	27	96	7.4	0.9	0.5	0.09	84	1.4
RC4	56	30	22	27	23	109	7.0	1.1	0.4	0.06	143	1.2
RC5	64	37	16	33	24	94	7.8	0.9	0.3	0.05	94	1.6

O.C.: Organic carbon.
Analysis was done in Lakefield Geosol Laboratory.
Quality control of the results is obtained by participating in inter-comparison programs.

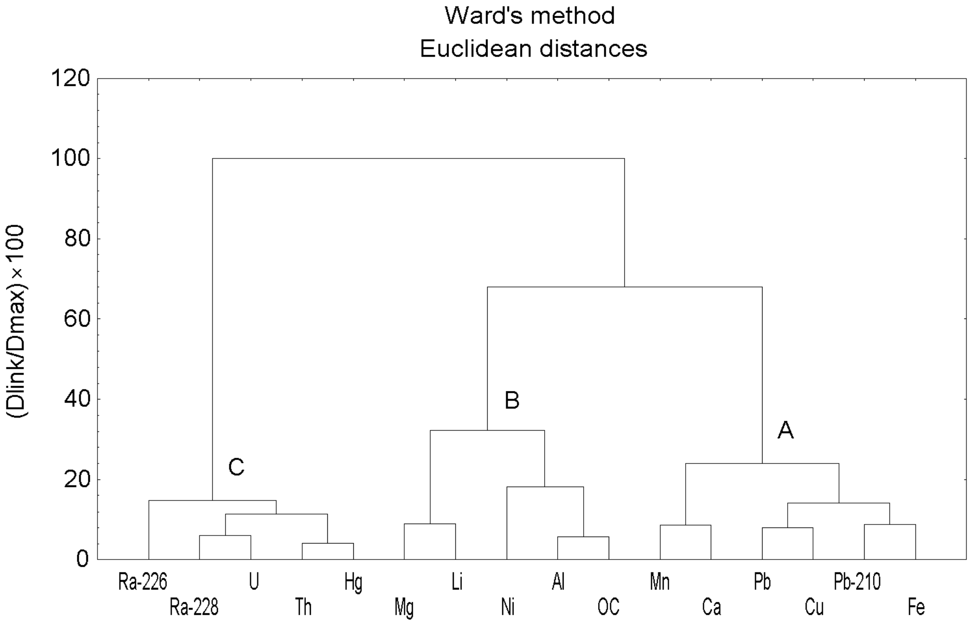

Fig. 2. Cluster analysis applied for the Cubatão River sediment samples

Table 3. Isotopic ratios and combined uncertainties for the determined nuclides

Sample	$^{234}U/^{238}U$	$^{226}Ra/^{238}U$	$^{210}Pb/^{238}U$	$^{228}Ra/Th$	$^{228}Ra/^{226}Ra$	$Th/^{238}U$
RC1	1.02 ± 0.03	0.76 ± 0.06	1.0 ± 0.2	0.97 ± 0.07	1.5 ± 0.1	1.2 ± 0.1
RC2	1.04 ± 0.04	0.90 ± 0.08	1.6 ± 0.2	0.83 ± 0.05	1.5 ± 0.1	1.6 ± 0.1
RC3	1.07 ± 0.05	0.79 ± 0.06	1.4 ± 0.2	0.86 ± 0.07	1.6 ± 0.1	1.5 ± 0.1
RC4	1.07 ± 0.09	0.62 ± 0.07	0.5 ± 0.1	0.76 ± 0.06	1.6 ± 0.1	1.3 ± 0.2
RC5	1.0 ± 0.1	0.70 ± 0.07	1.2 ± 0.2	0.84 ± 0.07	1.7 ± 0.1	1.5 ± 0.1

The pattern observed for the $^{226}Ra/^{238}U$ and $^{228}Ra/Th$ reflects the solubility of Ra isotopes related to ^{238}U and Th. The $^{210}Pb/^{238}U$ is higher than one in three samples. Considering that ^{210}Pb is generated by the decay of ^{226}Ra in the U-series, this enrichment indicates an amount of unsupported ^{210}Pb caused by the local radon sources (steel plant, phosphate fertilizer plants, phosphogypsum piles). The $^{228}Ra/^{226}Ra$ and $Th/^{238}U$ activity ratios reflect the fact that Cubatão River sediments are enriched in Th related to U isotopes.

Conclusions

The activity concentration of U, ^{238}U, Th, ^{226}Ra, ^{228}Ra and ^{210}Pb was measured in five sediment samples collected in Cubatão River in 2000. Cluster analysis applied to radioactive and stable elements showed the formation of three distinct groups. Group A (Mn, Ca, Pb, Cu, ^{210}Pb and Fe) accounts for Mn and Fe oxy-hydroxide elements; Group B (Mg, Li, Al, Ni, and OC) accounts for the granulometric characteristics of the sediments and in Group C (^{226}Ra, ^{228}Ra, U, Th and Hg), the radioactive elements and Hg were grouped together. The analyzed radionuclides present a distribution similar to Hg, which is an element known as a widespread pollutant of the region. An anthropogenic origin can be also attributed to the concentration of ^{210}Pb and the concentration of this nuclide is almost constant along Santos and São Vicente estuary due to diffuse sources of ^{222}Rn that exist in the region. The presence of a steel plant, phosphate fertilizer plant and the phosphogypsum piles are among the human activities present in the region that can cause an increase in the concentrations of radionuclides. The obtained isotopic ratios indicate a reducing environment for Cubatão River. The sediments showed enrichment in Th series nuclides related to U series nuclides.

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