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DETERMINATION OF NATURAL RADIONUCLIDES, U, Th-232, Ra-226, Ra-228, Pb-210 AND K-40 IN SEDIMENTS FROM CANANÉIA-IGUAPE SYSTEM, BRAZIL

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ABSTRACT

The Cananéia-Iguape estuarine-lagoon complex, located in the south of São Paulo State, Brazil, is a protected area recognized by UNESCO as part of the Biosphere Reserve, due to its importance as a natural ecosystem. However, along the years, the mining activities in the region affected the river basin, to such an extent that contamination was observed for As, Cu, Pb and Zn. Since the mining activities can also enhance the levels of natural radioactivity in the sediments, this study aimed to determine the activity concentration of the natural radionuclides (K-40, U, Ra-226, Pb-210, Th-232 and Ra-228) in 34 bottom sediments samples collected in the Cananéia-Iguape system. The samples were measured by gamma spectrometry, using a HPGe for the determination of K-40, Ra-226, Pb-210 and Ra-228. The concentration of U and Th-232 was determined by instrumental neutron activation analysis. The activity concentration of K-40 varied from 119 ± 17 to 522 ± 74 Bq kg^{-1}; U-238 varied from 0.31 ± 0.05 to 5.8 ± 0.3 mg kg^{-1}; Ra-226 varied from 3.7 ± 0.3 to 43.3 ± 1.5 Bq kg^{-1}; Pb-210 varied from 5.8 ± 2.6 to 118 ± 12 Bq kg^{-1}; Th-232 varied from 0.67 ± 0.02 to 16.6 ± 0.4 mg kg^{-1} and Ra-228 varied from 3.5 ± 0.6 to 64.9 ± 2.4 Bq kg^{-1}. These results were compared with literature values for the region, indicating that they are the background of the region and no contamination was observed from NORM (Naturally Occurring Radioactive Material) industries.

1. INTRODUCTION

Due to its geological and physico-chemical characteristics, estuaries are considered environments extremely susceptible to contamination by metals and radionuclides. The mixture of seawater with river water modifies the physical-chemical characteristics of the estuary, providing the formation and deposition of particulate matter and associated contaminants, thus retaining sediments. The entrance of the contaminating elements in this system occurs mainly by the mining activity. Pollution of the marine environment from natural radionuclide discharges (U-238, Ra-226, Ra-228, Pb-210 and Th-232) can also pose a serious environmental problem [1].

The uranium is a primordial natural radionuclide found in nature at very low concentrations. The most abundant isotope of uranium is U-238, which is an alpha emitter with a half-life of 4.47×10^9 years. Due to its long half-life, uranium is distributed homogeneously in the water, depending mainly in the water salinity. It enters the ocean in oxidizing conditions, remaining

soluble, but this solubility is altered through the redox state of the medium, which occurs frequently in marine sediments, so the uranium is reduced, becoming insoluble [2].

The Ra-226 is an alpha emitter with relatively long half-life (1600 years), formed by the sequential radioactive decay of five radioactive isotopes: U-238→Th-234→ Pa→ U-234→Th-230→Ra-226. It has low affinity with the particulate material of the ocean. Since it belongs to the series of alkaline earth metals, its behaviour in the ocean is similar to that of Ca^{2+} and Ba^{2+} [1].

The Pb-210 (beta emitter with half-life of 22.3 years) is a natural radionuclide that can be found in nature, as a result of the decay of the U-238 natural series. The main source of this radionuclide in the marine environment is due to the emanation of Rn-222, which is released from the Earth's crust into the atmosphere resulting in the deposition of Pb-210 and Po-210, through fall-out and rain-out. The Pb-210 accumulates in sediments and marine organisms and fish, which is the final link in the aquatic food chain and an important source of food for man. The Pb-210 can also accumulate in the aquatic system due to discharges of phosphate industries, oil and gas extraction, as well as the burning of fossil fuels [3]. In these cases, these radionuclides are known as Technically Enhanced Natural Occurring Radioactive Material (TENORM).

The Th-232, as well as the U-238, is a primordial natural radionuclide, with a half-life of $1.39x10^{10}$ years. It has high natural abundance, with concentrations of the order of 10 ppm, and is the only natural thorium isotope. In mining, the main source of this element is the monazite deposits [4]. Because it has high reactivity with particulate materials, it is withdrawn quickly from the water column. The Th isotopes (Th-232, Th-230, Th-228, Th-227 and Th-234) are extremely particle-reactive in the marine environment, being the most commonly used radionuclides as ocean process tracer [5].

The Ra-228 is a decay product of the Th-232 radioactive series. It is a natural element with half-life of 5.75 years, found in all terrestrial sediments. According to Lapa [6], high concentrations of Ra-228, in general, are found near marine sediments and on the continental slope.

1.1. Brief History of Cananéia-Iguape system

The estuarine-lagoon complex of Cananéia-Iguape, located on the south coast of the State of São Paulo, is a region of lacustrine canals, presenting coastal lagoons and traces of estuaries. It is part of the Cananéia-Iguape-Paranaguá Environmental Protection Area, recognized by UNESCO as part of the Biosphere Reserve, due to its importance as a natural environment and traditional cultures. Even after the end of activities of metallurgy and mining activities in 1996, the environmental contamination, such as lead and arsenic, persists until today. The soil and sediment contamination occurred mainly due to emission of metals into the atmosphere and deposition of particulates.

Between 1827 and 1852, took place the opening of a canal, known as Valo Grande, with the intention of benefiting the local economy, facilitating the landing of goods that descended the river in boats in the port of Iguape. This channel, that connected the Ribeira de Iguape River with the Mar Pequeno, was done without evaluation of the environmental and social impacts,

causing the passage of sediments to the internal part of the estuary, making navigation difficult and contributing to the enhancement of some elements in the estuarine-lagoon complex of Cananéia-Iguape [7]. Soon after its construction, the Valo Grande channel was about 4.4 meters wide and 2.0 meters deep; currently it is approximately 300 meters wide and 7 meters deep, due to the strength of the waters of the Ribeira de Iguape River [8]. The waters diverted from the river, loaded with muddy sediments, caused a great sedimentation, thus making the Port of Iguape unfeasible.

From 1945 to 1995, the installation "Plumbum Mineração e Metalurgia S.A" operated in Adrianople (Paraná). During this period, the mill processed approximately three million tons of lead ore, without control over the environmental impacts generated. From 1945 to 1991, all solid waste generated by "Plumbum Mineração e Metalurgia S.A" was dumped directly into the Ribeira de Iguape River, without any treatment. Even after the end of activities of mining and metallurgy in 1996, the environmental contamination of soil and sediment was a serious problem, mainly due to the emission of lead and arsenic to the atmosphere and deposition of particulates [9].

2. OBJECTIVES

The aim of this work is to determine the concentrations of natural radionuclides U, Th-232, Ra-226, Ra-228, Pb-210 and K-40 in sediments of the estuarine-lagoon complex of Cananéia-Iguape.

3. BEHAVIOR OF SEDIMENTS AND DYNAMICS OF STUARIAN SYSTEMS

3.1. Guiding values of quality of sediments

The adsorption or desorption of chemical elements in aquatic environment depends on several factors, such as sediment granulometry, solubility, pH, etc. To evaluate the quality of the sediment, the environmental agencies of each country elaborate Quality Guidelines for sediment, which associate the adverse effects of the pollutant on biota, through a survey of the mortality rate of organisms with the concentration range of a pollutant [10].

The concentration of radionuclides in sediment can be analyzed by comparing values found in the study area with natural values, which are called background.

In Brazil, there is still no specific law for the quality of sediment, except CONAMA Resolution 344/04, which establishes guidelines and techniques for the evaluation of dredged material [10].

Many products or chemicals are released into the ecosystem every day naturally or by anthropogenic activities, and can be made available in aquatic ecosystems in the form of particulate matter. These compounds are deposited in superficial sediment layers in which contaminants concentrate over time [11]. The sediments act as a file of environmental changes over time [12]. The sediments are one of the most important constituents of an aquatic ecosystem, because they support life, generate a diversity of ecosystems and represent a significant source of nutrients for aquatic organisms [13].

The analysis of adverse biological effects in aquatic systems determines the quality guidelines of sediment and scientific benchmarks. These parameters are derived from toxicological information according to the formal protocol specified by the Canadian Council of Ministers of the Environment [14]. The CONSELHO NACIONAL DO MEIO AMBIENTE (CONAMA) determines a set of general guidelines and methods to evaluate the dredged material in Brazilian jurisdictional waters, in the Conama Resolution Nº 344 of March 25, 2004 [15].

The Estuarine-Lagoon Complex Iguape-Cananéia (latitudes 24°40'S and 25°05'S and longitudes 47°25'W and 48°10'W) is located in the sub-unit south of the coast of the State of São Paulo and borders the State of Paraná (Figure 1). This region is part of the Cananéia-Iguape-Paranaguá Environmental Protection Area and is recognized by UNESCO as part of the Biosphere Reserve, due to its importance as a natural environment and traditional cultures. It is a region composed of a group of islands near the continent, being: Cananéia, Cardoso, Ilha Comprida and Iguape, the latter an artificial island that emerged from the opening of the Valo Grande Canal, in the city of Iguape – northern part of the system. These islands are bathed by canals that interconnect with each other with the Atlantic Ocean through the bars of Arapira and Trapandé (near the city of Cananéia) and Icapara and Ribeira (near the city of Iguape). The Island of Cananéia is separated from the mainland by a canal called Mar de Cubatão, or Mar de Dentro and separated from Ilha Comprida by Mar de Cananéia, or otherwise known as Mar de Fora. Baía de Trapandé interconnects these two canals in the southern portion of the system.

It is a region of subtropical climate, whose average annual air temperature is 21.4 °C, being in February the highest monthly average with 25.2 °C and in July the lowest with 17.8 °C. The rain is related to the seasons, with rainy summers and dry winters. The average annual precipitation is greater than 2.200 mm, being the rainy period from December to April and the driest period from May to November [16].

The South and North sectors of this Complex are subject to different anthropogenic pressures, of different origins. Historically in the northern region, the pollution caused by mining activities dating from the early 17th century, and two centuries later there was an intensification of exploration in relation to Pb, with the backdrop of the First World War. This fact was first observed by [17], when the presence of metals such as Zn, Fe, Cu and Pd was identified in the sediment analysis, with Pb present in the water at levels up to 730 times higher than the recommended maximum limit for the preservation of aquatic life. In relation to the sediment, the content of 2.560 $\mu g\ g^{-1}$, was recorded, surpassing in some 164 times the established limit, thus qualifying the environment as highly polluted [18]. Mahiques [9] carried out a historical survey of 150 years of the anthropic contribution of metals in the Cananéia-Iguape system, evidencing several levels of contamination. Therefore, the study of the availability of metals in the region, the estimation of its available fraction and its sediment remobilization behavior has become a priority. More recently, [19] evaluated the availability of Cu, Pb and Zn metals in sediments of the Cananéia-Iguape system, by means of its association with the main sediment components. They concluded that the content of Pb exceeded the natural levels in several sampling sites, suggesting the need to monitor its bioavailability

In the literature, several studies on the concentration of radionuclides in the Cananéia-Iguape system are found. Saito [20] carried out environmental studies of radionuclides (Pb-210, Ra-

226, Po-210 and Cs-137) in the Cananéia-Iguape coastal system, on the southern coast of the State of São Paulo. The author verified the great influence of River Ribeira de Iguape and found the highest levels in the Valo Grande canal.

Saito et al. [21] studied the levels of Pb-210 and Po-210 in sediments, waters and bio-indicators in the Cananéia-Iguape estuary and concluded that the concentrations of Pb-210 and Po-210 in sediment cores collected in the Cananéia-Iguape estuary reflect the influence of the Ribeira de Iguape River and the possible impact of agriculture.

Saito et al. [22] studied a recent sedimentation model in the Cananéia-Iguape Estuary and observed that the higher levels of metals measured in sediments are due to the mining activities already in place.

Armelin et al. [23] determined values of metals and other elements in the estuarine-lagoon system of Cananéia-Iguape, by means of the instrumental neutron activation technique. The results acquired were associated with the anthropic processes due to the opening of the Valo Grande Canal and also due to the mining activity of the region.

Jesus et al. [24] studied groundwater in the assessment of environmental and health risks in Cananéia, Iguape and Ilha Comprida. The highest concentrations of Ra-226 and Ra-228 were obtained in the groundwater in Ilha Comprida.

Amorim [11] evaluated the concentration of metals and other elements of interest in sediment samples from Santos (São Vicente) and Cananéia estuaries. The author verified that the concentration values of the analyzed metals are below the limits established by CONAMA legislation 344/2004.

Ribeiro et al. [25] studied the distribution of radionuclides in sediments of the Cananéia-Iguape Estuarine Complex and found a correlation between radionuclide levels and several sediment parameters. They concluded that the levels are within the range expected for a southern hemisphere coastal system.

Saito et al. [26] determined Ra-226 and Pb-210 by gamma spectrometry in marine sediments of the southern coast of São Paulo (Cananéia-Iguape, where values ranged from 19.8 to 122.5 Bq kg^{-1} for Pb-210 and 5.1 to 15.1 Bq kg^{-1} for Ra-226).

Figure 1: Satellite image of the Cananéia-Iguape Estuarine-Lagoon Complex (Google Earth).

4. MATERIALS AND METHODS

4.1. Collection of the superficial sediment in the Estuarine-Lagoon Complex of Cananéia-Iguape

The samples were collected on 11 and 19 September 2013, in the winter period. Surface sediments were sampled using a van veen stainless steel bottom catcher, with an area of 0.05m^2, where aliquots of about 5 cm of the superficial layer of the sediment were collected, in each of the stations where the water column was collected. The sediments were stored in plastic pots and remained frozen at -20 °C from the date of collection until June 20, 2016, when they were placed under greenhouse protection at 60 °C for drying. After obtaining a constant mass, the sediments were slightly disaggregated (were not macerated so that there was no destruction of larger granules such as carbonates and plant material). Figure 2 shows the map containing the position of the collection stations at the Canaréia-Iguape estuarine-lagoon complex and table 1 shows the identification and location of the samples and respective masses available.

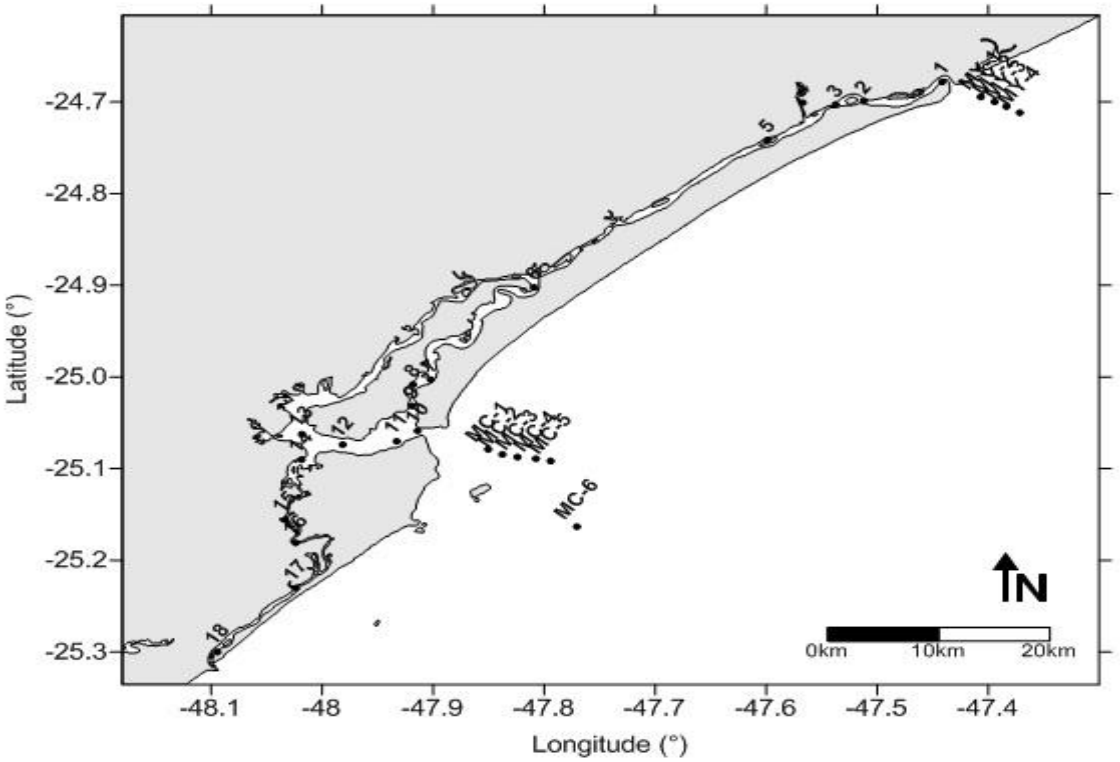

Figure 2: Location of sampling points.

Table 1: Identification of samples, location and respective masses available

LOCATION	POINT	MASS (g)
Rio Ribeira de Iguape (North region)	R1	215
	R2	140
	R3	160
	R4	90
	R5	400
	R6	170
Mar adjacente to the north of the complex (North region)	MY1	75
	MY2	210
	MY3	160
	MY4	80
Mar Pequeno/Iguape (North region)	1	220
	2	290
	3	110
	4	325
	4 A	410
	5	275
	Pedra do Tombo	125
Mar de Cananéia/Baía de Trapandé (South region)	7	175
	8	200
	9	420
	10	370
	11	250
	12	355
Canal de Ararapira (South region)	13	115
	14	335
	15	95
	16	150
	17	390
	18	140
Mar adjacente ao sul do complexo (South region)	MC1	250
	MC2	205
	MC3	340
	MC4	210
	MC5	365

4.2. Determination of K-40, Ra-226, Pb-210 and Ra-228 in the sediment samples

The sediment samples were oven dried at 60°C until constant mass, sieved at 60 meshes and packed in polyethylene flasks with capacity of 100 mL, named F-100. The samples were sealed in the F-100 container and stored for 30 days to allow the equilibrium between Ra-226 and its decay products. Some samples were measured on smaller container, with a maximum capacity of 15g, when the available mass was not sufficient to fill the F-100 container.

The activity concentration of Ra-226, Ra-228 and Pb-210 in the sediment samples was performed by gamma spectrometry, by using a Hyperpure Germanium detector - HPGe. The radionuclide Ra-226 was determined after 30 days, taking the average value of the photo peaks of their decay products: Pb-214 (295.21 keV and 351.92 keV) and Bi-214 (609.31 keV and 1120.30 keV). The Ra-228 was determined by measuring the peak intensity of 911.07 keV and 969.11 keV of Ac-228. The Pb-210 was measured by the 46.50 keV photo peak. For

the Pb-210 the calculation of self-absorption correction was done using the method described by [27], due to attenuation of low energy gamma radiation by the sample itself.

The gamma spectrum obtained were analyzed with the Interwinner program and the concentration determined from the knowledge of the peak area, the background radiation for the considered transition range, the mass of the sample, the efficiency of the detector and the counting time. The samples were then counted on a GX2518 Hyperpure Germanium detector of 25% relative efficiency, from CANBERRA, with associated electronics, for 250,000 seconds. The quality control of the equipment used is carried out three times per year, participating in a Proficiency Test organized by "Instituto de Radioproteção e Dosimetria" IRD / CNEN.

The determination of the background radiation of the system was carried out using the same counting geometry of the samples that is F-100 container filled with water, measured for 500.000 seconds.

The concentration of Ra-226, Ra-228 and Pb-210 in the sediment samples obtained by gamma spectrometry was calculated by the equation:

$$C = \frac{N - N_0}{T \cdot \eta \cdot \gamma \cdot m}$$

where:

C: concentration in Bq kg^{-1};
N: sample count (cps);
N_0: background radiation count (cps);
T: measurement time (s);
η: counting efficiency (cps dps^{-1});
γ: photo peak intensity;
m: sample mass (kg).

Gamma spectrometry is a non-destructive technique that can present problems when low energy radionuclides are analyzed. In this case, the low energy photons present little penetration power and can interact with the sample itself and, consequently, self-absorption must be considered so that the activity measured at the detector corresponds to the actual activity.

The correction of the self-absorption consists in the determination of the attenuated transmission, by placing a centralized Pb-210 source on the container lid containing the samples and on the container lid containing water.

The self-absorption factor was calculated according to the equation:

$$A/O = \frac{\ln(T/I)}{(T/I - 1)}$$

where:

A: corrected activity (Bq kg^{-1});

O: measured activity (Bq kg^{-1}).

In the presented equation, T and I are the intensities attenuated through the sample and recipient containing water, respectively. The attenuated intensity (T) is defined as the difference between the sample measurement, with and without the Pb source. The same applies to the attenuated intensity (I), in relation to the measurement of the water sample.

The sensitivity of the gamma spectrometry technique, for a given gamma transition, was represented by the minimum detectable concentration (MDC), and the model used for the calculation was [28], as shown in the following equation:

$$MDC = 4.66 \frac{\sqrt{BG}}{Ef \,.V \,.t.I\gamma}$$

where:

MDC: detectable minimum concentration (Bq kg^{-1});

BG: net area of background radiation for the considered range transition (counts);

V: sample volume (kg);

t: counting time (s);

Ef: counting efficiency for the considered transition energy range

(cps dps^{-1});

Iγ: absolute intensity of the transition range considered (%);

4.66: number that express an associated confidence level of 95%.

4.3. Determination of U and Th-232 in sediment samples

The neutron activation analysis was used for the determination of U and Th. The experimental procedure consisted of irradiating 200 mg of sediment samples and standard reference materials (Soil-5, BEN and BRP-1) in the nuclear research reactor IEA-R1 of the Instituto de Pesquisas Energéticas e Nucleares (IPEN), at a neutron flux of 5.10^{12} n $cm^{-2}s^{-1}$, for a period of 8 hours. The concentration of U and Th was measured, using a Hyperpure Germanium detector (HPGe), from Canberra. Two series of counts were undertaken: 7 days after irradiation and the second one after 24–30 days of decay. The counting time was 3600 seconds.

5. RESULTS AND DISCUSSION

The results obtained for the concentration of the radionuclides in the sediment samples are presented in Table 2.

Table 2: Concentration of U and Th-232 (mg kg^{-1}) and K-40, Pb-210, Ra-226 and Ra-228 (Bq kg^{-1}) in sediment samples

Amostra	K-40	U	Ra-226	Pb-210	Th-232	Ra-228
R1	405 ± 18	1.28 ± 0.10	6.6 ± 0.4	<6.5	6.80 ± 0.21	8.1 ± 0.8
R2	420 ± 19	0.61 ± 0.04	14.1 ± 0.6	<7.6	3.04 ± 0.10	17.0 ± 1.0
R3	480 ± 21	0.56 ± 0.04	8.5 ± 0.4	<6.7	2.11 ± 0.07	10.0 ± 0.8
R4	ND	1.73 ± 0.11	12.7 ±1.8	<11.1	9.64 ± 0.32	15.0 ± 2.0
R6	416 ± 19	3.31 ± 0.37	12,9 ± 0.5	10.1 ± 3.1	16.29 ± 0.53	19.7 ± 1.1
#1	207 ± 10	1.43 ± 0.08	5.4 ± 0.3	<5.9	3.31 ± 0.16	6.0 ±0.7
#2	499 ± 23	1.4 ± 0.1	19.0 ± 0.8	29.7 ± 4.1	5.17 ± 0.24	27.1 ± 1.4
#3	ND	0.67 ± 0.06	13.0 ± 1.7	7.3 ± 4.7	1.48 ± 0.03	11.5 ± 1.8
#4A	308 ± 14	2.63 ± 0.16	9.6 ± 0.4	11.4 ± 2.8	8.93 ± 0.30	13.1 ± 0.8
#4	355 ± 16	0.73 ± 0.04	6.4 ± 0.4	<7.3	1.59 ± 0.06	8.2 ± 0.7
#5	182 ± 9	0.96 ± 0.05	6.2 ± 0.4	<6.2	2.43 ± 0.08	6.3 ± 0.7
#6	166 ± 8	0.49 ± 0.05	7.0 ± 0.4	5.8 ± 2.6	1.34 ± 0.05	7.4 ± 0.7
#7	407 ± 58	1.22 ± 0.11	16.4 ± 0.8	99.8 ± 10.3	6.10 ± 0.20	23.9 ± 1.7
#8	384 ± 55	2.75 ± 0.20	15.9 ± 0.7	70.5 ± 7.6	7.66 ± 0.25	22.8 ± 1.6
#9	187 ± 9	0.49 ± 0.06	9.9 ± 0.4	12.9 ± 2.8	1.80 ± 0.06	8.1 ± 0.7
#10	194 ± 28	0.37 ± 0.04	3.7 ± 0.3	8.2 ± 2.4	0.79 ± 0.04	4.2 ± 0.6
#11	297 ± 14	0.74 ± 0.09	11.9 ± 0.5	11.9 ± 3.0	4.98 ± 0.23	14.5 ± 1.0
#12	303 ± 43	1.15 ± 0.08	8.7 ± 0.5	50.8 ± 5.7	3.37 ± 0.11	11.4 ± 1.0
#13	498 ± 23	1.65 ± 0.16	16.6 ± 0.7	88.7 ± 8.0	6.05 ± 0.23	25.3 ± 1.4
#14	380 ± 17	1.43 ± 0.11	11.0 ± 0.5	27.5 ± 4.1	3.31 ± 0.11	13.5 ± 0.9
#15	ND	2.76 ± 0.24	25.7 ± 2.5	27.4 ± 5.5	9.36 ± 0.30	34.8 ± 3.3
#16	241 ± 12	4.51 ± 0.31	14.6 ± 0.6	43.6 ± 4.8	4.23 ± 0.14	16.0 ± 1.1
#17	133 ± 8	0.62 ± 0.08	7.5 ± 0.4	17.9 ± 4.5	1.19 ± 0.03	5.8 ± 0.8
#18	220 ± 11	0.31 ± 0.05	5.0 ± 0.3	6.4 ± 2.5	0.67 ± 0.02	3.5 ± 0.6
MY1	ND	0.94 ± 0.08	15.1 ± 1.9	6.9 ± 5.2	3.48 ± 0.13	18.1 ± 2.3
MY2	408 ± 19	2.65 ± 0.28	23.9 ± 0.9	62.6 ± 6.2	16.14 ± 0.37	38.9 ± 1.7
MY3	343 ± 16	3.42 ± 0.28	43.3 ± 1.5	54.8 ± 5.8	16.19 ± 0.37	64.9 ± 2.4
MY4	ND	2.03 ± 0.20	29.5 ± 2.6	56.3 ± 7.9	10.98 ± 0.35	45.2 ± 4.0
MC1	119 ± 17	0.92 ± 0.07	17.9 ± 0.8	17.8 ± 3.2	3.89 ± 0.13	27.3 ± 1.6
MC2	434 ± 20	3.49 ± 0.40	18.4 ± 0.7	63.7 ± 6.1	14.39 ± 0.45	24.1 ± 1.3
MC3	207 ± 30	1.20 ± 0.08	11.9 ± 0.6	53.2 ± 5.9	4.91 ± 0.16	13.9 ± 1.1
MC4	133 ± 19	0.81 ± 0.08	6.3 ± 0.4	15.6 ± 2.8	3.85 ± 0.14	6.9 ± 0.7
MC5	186 ± 9	1.48 ± 0.16	13.7 ± 0.6	26.3 ± 3.8	5.64 ± 0.13	18.8 ± 1.0
P. TOMBO	522 ± 74	5.83 ± 0.26	33.6 ± 1.5	118 ± 12.2	16.56 ± 0.42	61.0 ± 3.6

ND = Not Determined.

From the results of table 2, it can be seen that the activity concentration of K-40 ranged from 119 ± 17 to 522 ± 74 Bq kg^{-1}; U ranged from 0.31 ± 0.05 to 5.8 ± 0.3 mg kg^{-1}; Ra-226 ranged from 3.7 ± 0.3 to 43.3 ± 1.5 Bq kg^{-1}; Pb-210 ranged from 5.8 ± 2.6 to 118 ± 12 Bq kg^{-1}; Th-232 ranged from 0.67 ± 0.02 to 16.6 ± 0.4 mg kg^{-1} and Ra-228 ranged from 3.5 ± 0.6 to 64.9 ± 2.4 Bq kg^{-1}. It was observed that the sediment collected in Pedra do Tombo presented the highest concentration of radionuclides, except for Ra-226 and Ra-228. Table 3 presents the results obtained in the present study and literature data for the Cananéia-Iguape region.

Table 3: Literature data for radionuclides concentration in the region of Cananéia-Iguape

	Author	**U (mg kg^{-1})**	**Ra-226 (Bq $kg^{-1)}$**	**Pb-210 (Bq kg^{-1})**	**Th (mg kg^{-1})**	**Ra-228 (Bq kg^{-1})**
This work	-	0.31 – 5.8	3.7 – 43.3	5.8 – 118	0.67 – 16.6	3.5 – 64.9
Coastal system of Cananéia-Iguape	[20]	-	4.1 – 28.5	6.1 – 167.5	-	-
Cananéia-Iguape Estuary	[22]	-	-	6.1 – 167	-	-
Cananéia-Iguape Estuarine	[26]	-	-	14.3 – 122.5	-	2.3 – 15.2

A Box Plot was used to analyze radionuclide concentration distribution throughout the system studied (Figure 3). This method allows the visualization in a single graph of the dispersion of analytical results through averages arithmetic, median and standard deviation. It is verified that the Pb-210 was the radionuclide that presented greater dispersion of the results, probably due to the fact that Pb-210 may have its origin by the decay of Rn-222 from the atmosphere, besides the decay of U-238 present in the sediment itself. Radionuclides Ra-226 and Ra-228 showed similar behavior, which was expected, because although they have different origin, they are alkaline earth elements with the same chemical properties. The uranium and thorium also exhibit similar chemical behavior, presenting low dispersion. The results obtained in the present work for the concentration of U and Th was compared with mean values of world concentration WEDEPOHL [29]. The radionuclides studied were also compared with data from UNSCEAR [30], and the values obtained in the present work are below the world mean values.

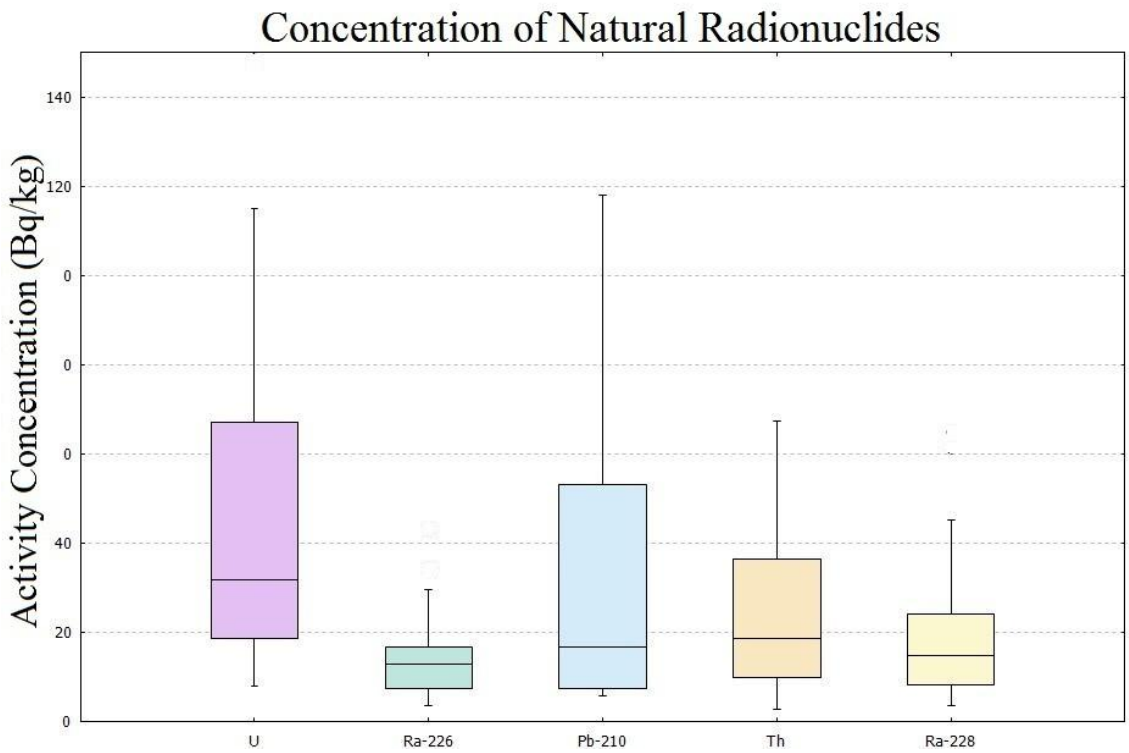

Figure 3: Mean concentration of radionuclides in the surface sediment samples in the Cananéia-Iguape estuarine-lagoon complex.

Cluster Analysis or hierarchical cluster analysis is a Multivariate Statistics procedure that groups objects into homogeneous groups called clusters. It is a mathematical technique that aims to present classification structures in the obtained data. The figure 4 shows the result of the cluster analysis of the concentration of radionuclides (U, Ra-226, Pb-210, Th-232 and Ra-228 and K-40) in all samples analyzed.

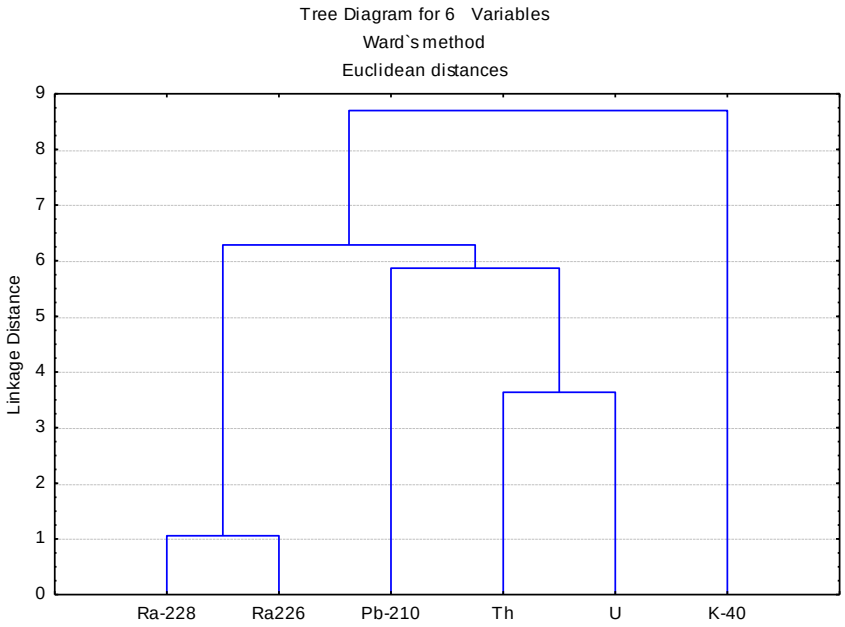

Figure 4: cluster analysis of the concentration of radionuclides in all samples analyzed.

The Ra-226 and Ra-228 formed a separate group. This behavior was expected, as they have similar chemical behavior, although the radionuclides are of different decay series (Ra-226 from the U-238 series and Ra-228 from the Th-232 series). The radionuclides Ra-226 and Ra-228 are from the alkaline earth family and, therefore, have chemical behavior similar to barium.

The U and Th also formed a separate group. Uranium is more soluble than thorium, having four oxidation states in aqueous solution (3^+, 4^+, 5^+ and 6^+). The most unstable oxidation states are respectively 3^+ and 5^+, unlike 4^+, which is stable, being easily oxidized by the oxygen of the air. The transport of uranium occurs mainly by rainwater and fluvial waters, and is deposited in estuarine regions, incorporating in the sediments. The thorium has only one oxidation state in aqueous solution, being stable in oxidation state 4^+. This element is transported to the aquatic system mainly as detrital material, thus contributing to a greater composition in the sediments.

CONCLUSIONS

In this work, 34 samples of sediments collected in six sectors of the Cananéia-Iguape estuarine-lagoon complex were analyzed: Ribeira de Iguape River, Mar Adjacente to the north of the complex, Mar Pequeno/Iguape, Mar of Cananéia/Baía of Tranpadé, Canal de Ararapira and Mar Adjacente to the south of the complex. In these profiles the concentrations of natural radionuclides of the series of U-238 and Th-232 and K-40 were determined. It was verified that the sample Pedra do Tombo has higher concentration of radionuclides, except for Ra-226 and Ra-228.

Comparing the results with values from the literature it is concluded that the values are of the same order of magnitude and therefore, can be considered as reference values for the region.

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