Determination of uranium and thorium in sediments from Cananéia-Iguape system, Brazil

Luiz Flávio Lopes Teixeira[1] · Barbara Paci Mazzilli[1]

Abstract

The Cananéia-Iguape system is a complex of lagoon and estuarine channels located in the south of state of São Paulo. This system received the waters of Ribeira de Iguape River, after the construction of a channel in 1852, which changed its original characteristic. This study evaluated the uranium and thorium concentrations in superficial bottom sediments samples from this system by spectrophotometric determination. The mean uranium concentration found was 2.9 mg kg^{-1} and 6.6 mg kg^{-1} for thorium. Geo-accumulation index classified the sediments as "unpolluted to moderately polluted". Statistical analysis showed that uranium and thorium presented a non-homogeneous behavior along the system.

Keywords Uranium · Thorium · Sediment · Cananeia-Iguape · Spectrophotometry

Introduction

The Cananéia-Iguape system is located in the extreme south area of the state of São Paulo (between latitudes 24°40′S and 25°05′S, longitudes 47°25′W and 48°00′W), bordering the state of Paraná, Brazil. Covering 100 km in length, this system is composed of channels around the Cananéia Island, Cardoso Island, Comprida Island and the city of Iguape (Fig. 1). This system is classified as subtropical climate, presenting around 87% relative humidity and an annual rainfall of more than 2248 mm, with rainy season between December and April and dry season from May to November. This region was recognized as a Biosphere Reserve by UNESCO (The United Nations Educational, Scientific and Cultural Organization) in 1991 [1].

During the period from 1827 to 1852, the Valo Grande channel was built. This artificial channel created an inexpensive and easy route to transport the agricultural production from Vale do Ribeira do Iguape to the main port of the region. This channel allowed the drainage of the Ribeira do Iguape River in the Cananéia-Iguape system, altering the physical–chemical characteristics of the system [1].

Due to intense mining activity (e.g. lead, zinc) until the mid-1990 on the Vale do Ribeira region, [1] many studies have been carried out to verify contamination by metals along the Ribeira do Iguape River and in the Cananéia-Iguape system [2–5]. These studies pointed out that the concentration of arsenic, copper, lead and zinc has increased because of the activities of mining and metallurgical industries along the Ribeira do Iguape River.

However, there are few studies about natural and artificial radionuclides concentration in this region [6–10]; these studies determined the activities of ^{137}Cs, ^{210}Pb, ^{40}K, ^{226}Ra, thorium and uranium in superficial bottom sediments and sediments profiles from Cananéia-Iguape system and others nearby systems. Armelin [9] determined the uranium and thorium concentration in a sediment core from the region, finding an abrupt decrease of the concentration through the core, which indicates an anthropic impact. Amorim [10] calculated the Geo-accumulation index (IGeo) and enrichment factor (EF) of uranium and thorium for sediments of the system, indicating a possible anthropogenic interference. These natural radionuclides uranium and thorium can be found in radioactive equilibrium with their decay products in several compartments of the environment, such as rocks, soil and water. The mining activity can eventually concentrate these radionuclides during the chemical process, in the final product, byproducts and even in waste. These radionuclide enriched materials are known as naturally occurring radioactive material (NORM). Therefore, the evaluation

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Fig. 1 Location of study area—Cananéia-Iguape system
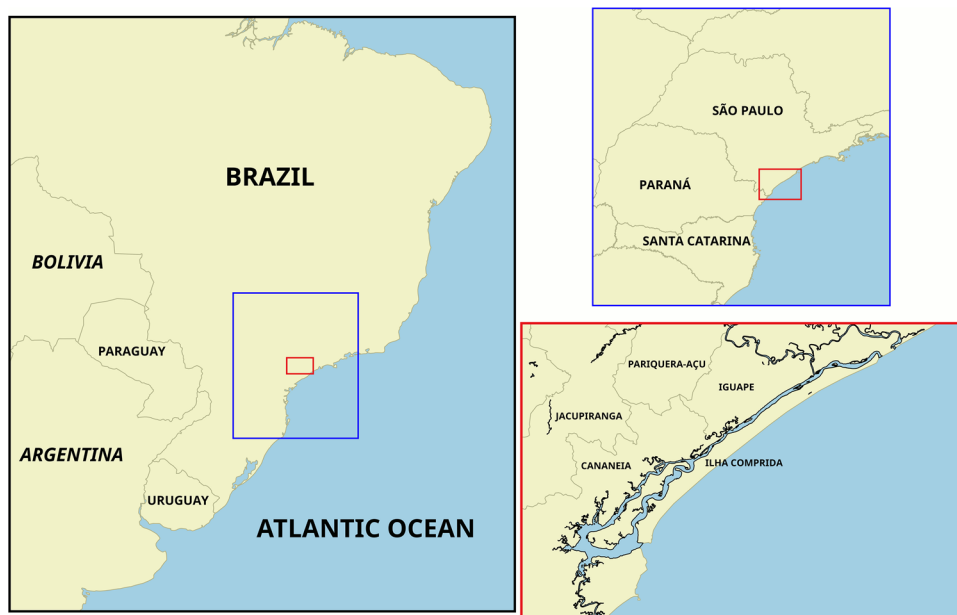
of environmental radionuclide concentrations is one of the most important ways to check the anthropogenic interference. One way to evaluate contamination on waterbodies is the quantification of radionuclides in the sediment. The uranium and thorium that could be present on NORM tends to aggregate in the sediment by adsorption and precipitation, increasing the natural radionuclide concentrations in the environment.

The objective of this study was to evaluate the concentration of uranium and thorium in the superficial bottom sediment from Cananeia-Iguape system, checking if there is a possible NORM contamination on the system and establishing the background concentration of these two radionuclides.

Experimental

Study area and sampling

Superficial bottom sediment samples from Cananéia-Iguape system were collected by Instituto de Oceanografia da Universidade de São Paulo (IOUSP) in March 2011. Twenty-eight samples were collected with a Van Veen sampler [1]; Fig. 2 presents the sampling collection location. The samples were digested using a microwave and then analyzed for uranium and thorium determination; for each determination 0.5 g was used.

Acid digestion of samples in microwave

0.5 g of each sample was digested in the microwave CEM MARS 5 with MARSXpress vessels; 6 mL of concentrated

HNO_3, 0.5 mL of 40% HF and 4 mL of deionized water were added to the vessel. The first microwave digestion cycle was performed with heating ramp until 175 °C for 15 min and hold this temperature for 10 min. Afterwards, it was added to the vessel 1 mL of 40% (v/v) H_2O_2, 2 mL of concentrated HNO_3 and a microwave digestion cycle, described above, was performed again; these steps were performed twice. The final solution was transferred to a polytetrafluoroethylene beaker and heated in a hot plate until almost total dryness. Drops of concentrated HNO_3 and 40% (v/v) H_2O_2 were added to the beaker and heated until almost total dryness; these steps were performed three times. Finally, 5 mL of concentrated HNO_3 and super pure water were added to the beaker until reach the final volume of 20 mL [11, 12]. All the chemicals used were ACS grade.

Thorium determination methodology [12–16]

The digested sample was transferred to a separatory funnel and 5 mL of 4% (m/v) boric acid, 10 mL of 0.1 mol L^{-1} trioctylphosphine oxide (TOPO) and 1 mL of concentrated HNO_3 were added. The funnel was shaken for 30 s and after 10 min the aqueous phase was discarded. 10 mL of 1 mol L^{-1} HNO_3 (containing 0.3% (m/v) urea) were added to the funnel. The funnel was shaken for 30 s and after 20 min the aqueous phase was discarded; 8 mL of 5% (m/v) oxalic acid were added to the funnel and it was shaken for 30 s. After 20 min the aqueous phase was collected in a 25 mL volumetric flask for the thorium determination. The remaining phase in the funnel was washed with 10 mL of concentrated HCl and the aqueous phase was collected in the volumetric flask; 5 mL of 10% (m/v) ascorbic acid were added
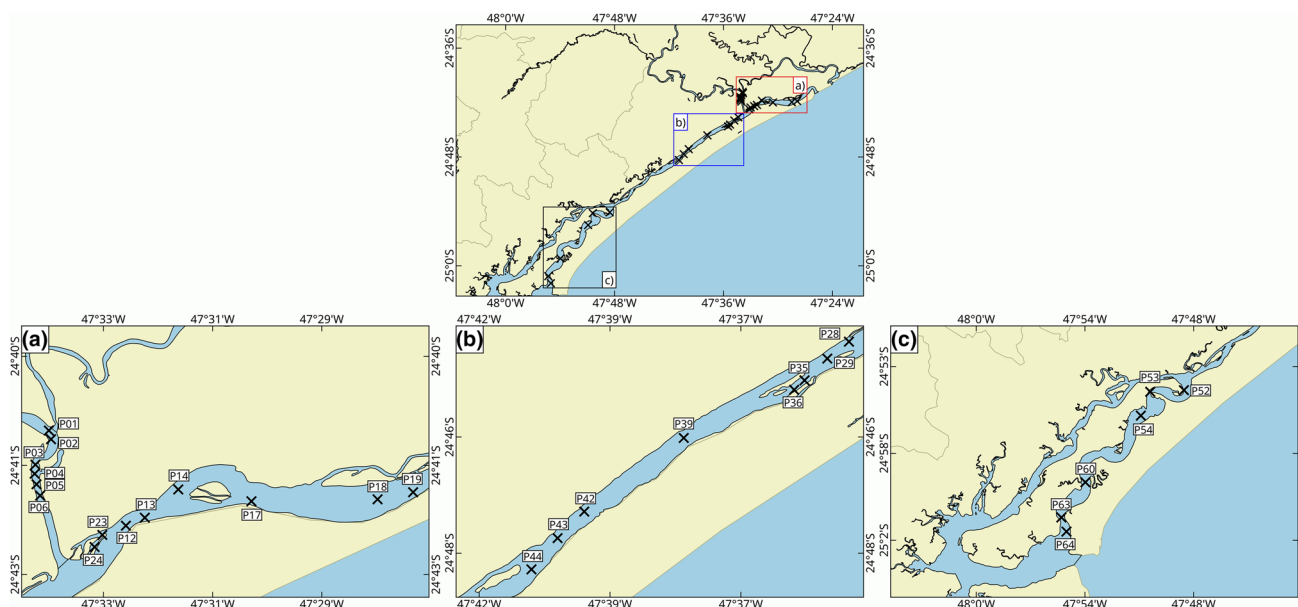
Fig. 2 Location of the superficial bottom sediment samples collected in the Cananéia-Iguape system

to the volumetric flask. After 2 min 1 mL of 0.06% (m/v) Arsenazo III was added to the volumetric flask. Super pure water was added to the volumetric flask until 25 mL. Figure 3 presents the flow chart of the method described. The final solution from the volumetric flask was analyzed for thorium determination using SHIMADZU UVmini-1240 spectrophotometer at wavelength 665 nm.

Uranium determination methodology [12–15]

The digested sample was transferred to a separatory funnel, 10 mL of Complexing Solution A (660 g/L aluminum nitrate, 26.7 g/L tartaric acid and 11.2 g/L ethylenediamine tetraacetic acid (EDTA)) and 10 mL of 10% (m/v) tributyl phosphate (TBP) were added. The funnel was shaken for 1 min and after 20 min the aqueous phase was discarded; 10 mL of 50% (v/v) HCl were added to the funnel. The funnel was shaken for 1 min and after 20 min the aqueous phase was discarded; 10 mL of Complexing Solution B (500 g/L ammonium nitrate, 1 g/L EDTA, 1 g/L in HNO_3 Cyclohexylenedinitrilotetraacetic acid (CDTA)) were added to the funnel. That was shaken for 1 min and after 20 min the aqueous phase was discarded. 10 mL of a solution of 0.006% Arsenazo III in pH 3 sodium acetate-acetic acid buffer
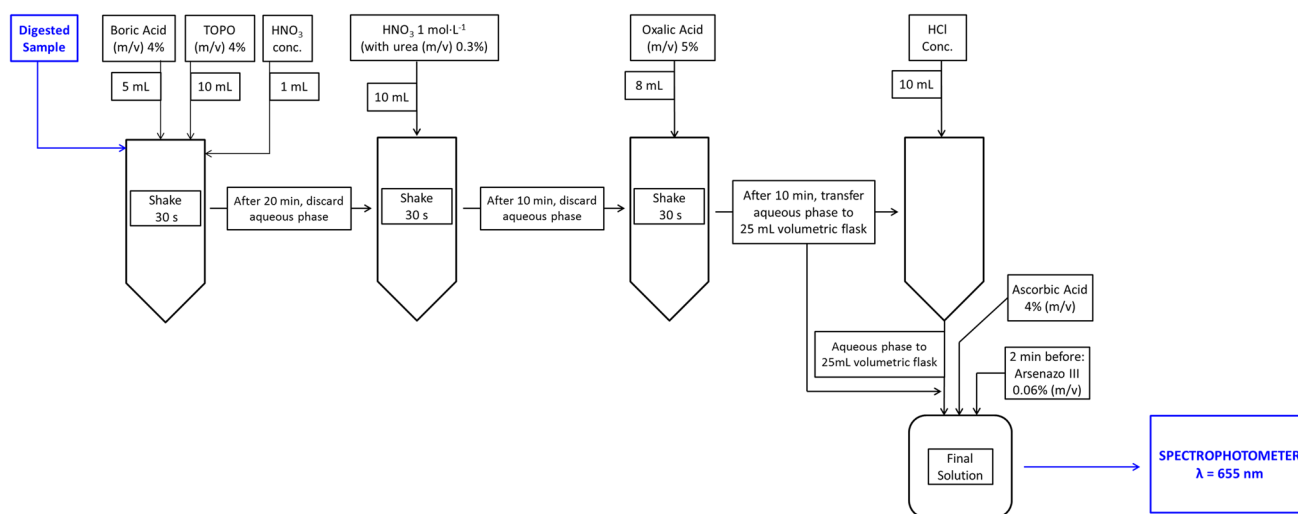

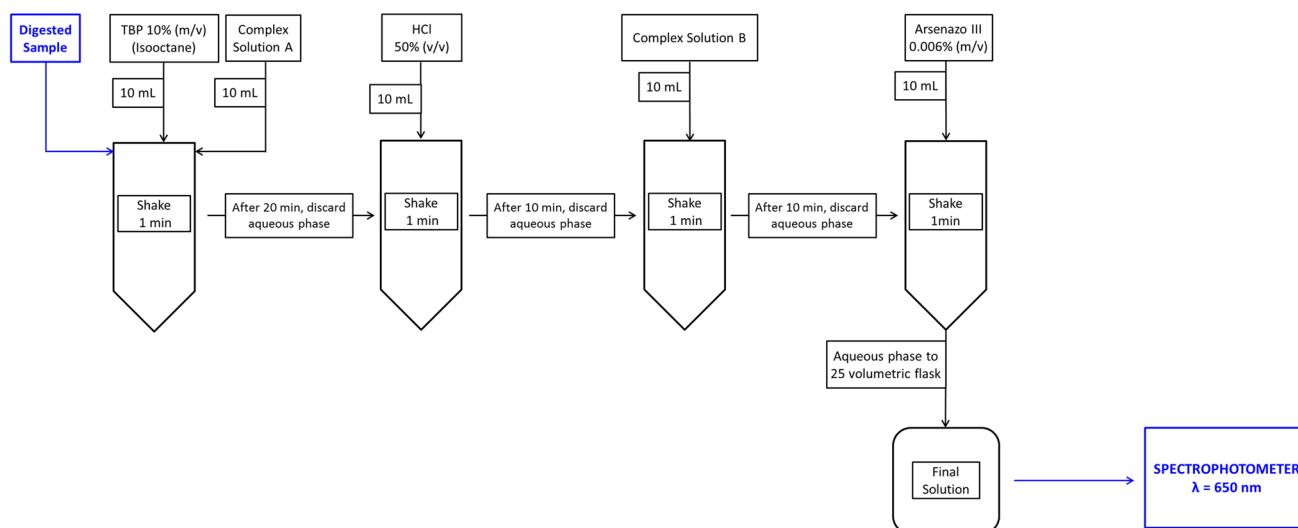**Fig. 3** Flow chart of thorium determination methodology

Fig. 4 Flow chart of uranium determination methodology
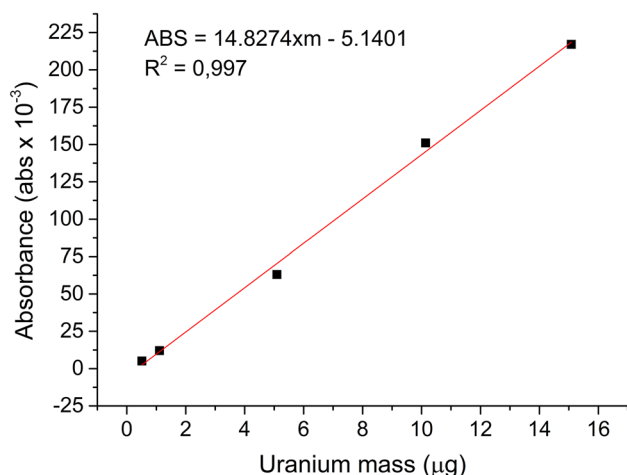

Fig. 5 Calibration curve for uranium

Fig. 6 Calibration curve for thorium

solution was added to the funnel. The funnel was shaken, and the aqueous phase was collected in a flask. Figure 4 presents the flow chart of the method described. The final solution from the flask was analyzed using SHIMADZU UVmini-1240 spectrophotometer at wavelength 650 nm.

Calibration curve and method validation

Uranium and thorium stock solutions were prepared diluting the SPECSOL uranium standard solution (1004 kg mg^{-1}) and SPECSOL thorium standard solution (996 kg mg^{-1}). The calibration curve for each radionuclide methodology was built by the analysis of 5 different dilutions from the uranium and thorium stock solutions prepared. Figs. 5, 6 present the calibration curve, the coefficient of determination
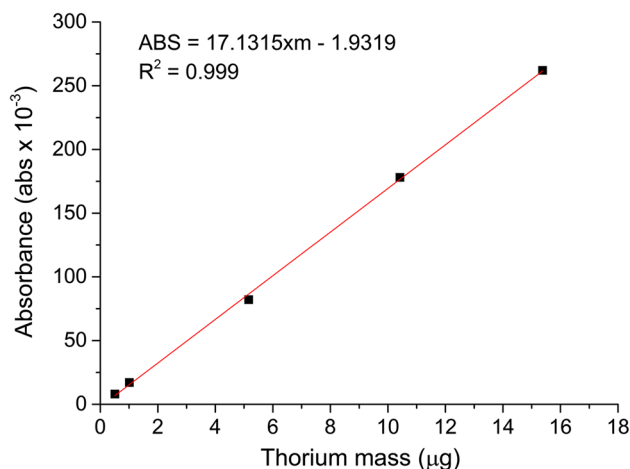
(R^2) and the calculated linear equation for uranium and thorium, respectively, methodologies.

The limit of detection (LOD) and limit of quantification (LOQ) were determined by the analysis of seven blank (super pure water) samples [17], and the results are shown in Table 1.

Table 1 LOD and LOQ for U and Th

	Uranium determination (mg kg^{-1})	Thorium determination (mg kg^{-1})
LOD	0.98	0.61
LOQ	1.11	0.81

Table 2 Results of CRM SL-1 analysis, accuracy and precision of the methodology for uranium determination

Present work (mg kg^{-1})				CRM SL-1 certificate(mg kg^{-1})	
Mean	Standarad deviation	Accuracy (Z-score)	Precision (RSD)	Mean	Standard deviation
4.32	0.08	0.52	1.8%	4.02	0.58

Table 3 Results of CRM SL-3 analysis, accuracy and precision of the methodology for thorium determination

Present work (mg kg^{-1})				CRM SL-3 certificate (mg kg^{-1})	
Mean	Standarad deviation	Accuracy (Z-score)	Precision (RSD)	Mean	Standard deviation
6.31	0.26	− 0.67	4.0%	7.02	1.06

The methodologies employed were validated by the criteria of accuracy and precision using Certified Reference Materials (CRM) SL-1 for uranium determination, and SL-3 for thorium determination. Both CRM are lake sediment from the International Atomic Energy Agency (IAEA). The accuracy was evaluated by the Z-score and precision by relative standard deviation (RSD) [17]. The results of a triplicate analysis of each methodology are shown in Table 2 for uranium and in Table 3 for thorium.

Results and discussion

Determination of U and Th in the superficial bottom sediments

Table 4 and Fig. 7 present the obtained concentration for uranium and thorium and Fig. 8 the distributions of these radionuclides through the Cananéia-Iguape system.

The mean uranium concentration in the superficial bottom sediment samples was 2.9 mg kg^{-1} (standard deviation (SD): 1.2 mg·kg^{-1}), and the results varied from 1.3 ± 0.4 to 5.8 ± 0.4 mg kg^{-1}, excluding the samples P04, P05, P18 and P28 which presented concentration below LOQ. The mean thorium concentration of the superficial bottom sediment samples was 6.6 mg kg^{-1} (SD: 3.8 mg kg^{-1}), and the results varied from 0.82 ± 0.38 to 12.1 ± 0.4 mg kg^{-1}, excluding the samples P13, P24 and P29 which presented concentration below LOQ. These results are in good agreement with those obtained by Wedepohl [18], for the upper continental crust (2.5 mg kg^{-1} for uranium and 10.3 mg kg^{-1} for thorium).

Table 4 Uranium and thorium concentration in the superficial bottom sediment samples from Cananéia-Iguape system

Samples	Uranium concentration (mg kg^{-1})	Thorium concentration (mg kg^{-1})
P01	2.0 ± 0.4	12.1 ± 0.4
P02	1.8 ± 0.5	12.1 ± 0.4
P03	5.0 ± 0.8	0.9 ± 0.4
P04	LQ (< 1.11)	2.8 ± 0.2
P05	LQ (< 1.11)	0.8 ± 0.4
P06	1.3 ± 0.4	3.3 ± 0.2
P12	2.6 ± 0.4	4.5 ± 0.4
P13	1.4 ± 0.5	LQ (< 0.81)
P14	1.3 ± 0.4	2.5 ± 0.4
P17	3.0 ± 0.4	11.1 ± 0.3
P18	LQ (< 1.11)	2.7 ± 0.2
P19	2.9 ± 0.4	7.7 ± 0.3
P23	3.8 ± 0.4	5.3 ± 0.2
P24	2.3 ± 0.4	LQ (< 0.81)
P28	LQ (< 1.11)	3.6 ± 0.2
P29	1.9 ± 0.4	LQ (< 0.81)
P35	2.6 ± 0.4	6.2 ± 0.2
P36	3.6 ± 0.4	10.5 ± 0.3
P39	3.8 ± 0.8	4.5 ± 0.4
P42	4.5 ± 0.4	10.1 ± 0.3
P43	4.1 ± 0.4	10.7 ± 0.3
P44	3.6 ± 0.4	11.4 ± 0.3
P52	2.7 ± 0.4	5.9 ± 0.2
P53	3.3 ± 0.4	8.6 ± 0.3
P54	2.3 ± 0.4	5.0 ± 0.2
P60	2.3 ± 0.4	8.1 ± 0.4
P63	5.8 ± 0.4	12.0 ± 0.4
P64	2.6 ± 0.4	2.1 ± 0.2

The results of this study were compared with results from the literature for sediments from Cananéia-Iguape system (Amorim [10], Armelin [9], Perreira [6]) and for sediments from Santos-Cubatão system (Amorim [10] and Damatto [19]). Figure 9 presents a comparison between the results of this study and those from literature. The U and Th concentration obtained are in good agreement with data from literature.

Fig. 7 Uranium (**a**) and thorium (**b**) concentration in the superficial bottom sediment samples from Cananéia-Iguape system
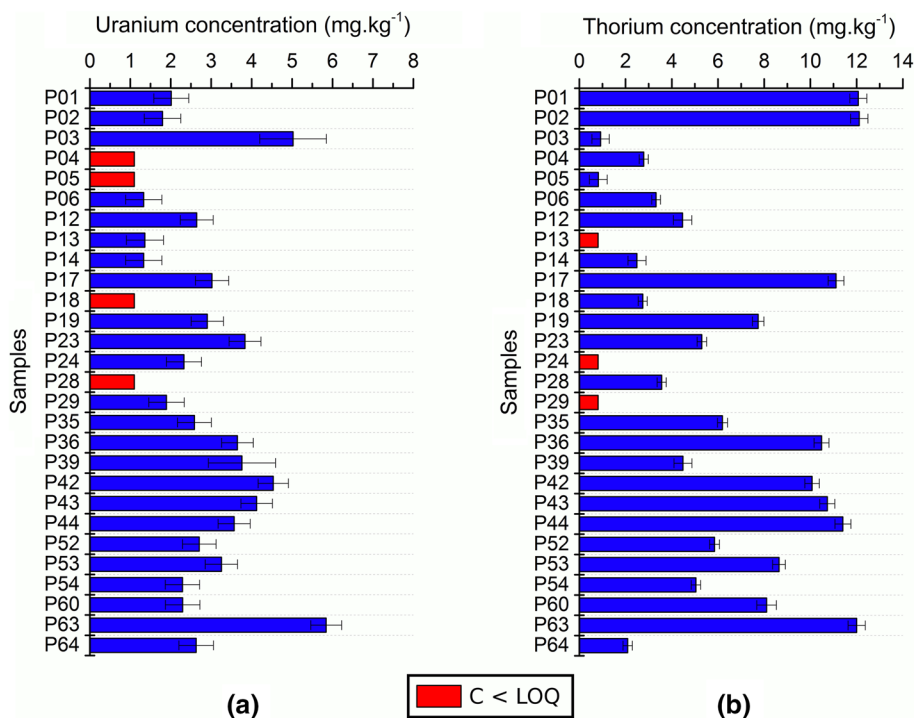
Geo-accumulation index (IGeo)

IGeo [19] was calculated using the concentration of uranium and thorium from UCC [18] as background values. Figure 10 shows the IGeo calculated for the uranium and thorium.

The uranium IGeo values classifies 21% of the samples (P03, P23, P42, P43, P63 and P39) as "unpolluted to moderately polluted" and 79% of the samples as "unpolluted" [19]. For thorium, the IGeo values classifies all samples as "unpolluted" [19]. These results indicate that the region is not contaminated by NORM.

Statistical analysis

Statistical analyses were performed with the results of uranium and thorium concentration determined in this study combined with the parameters obtained by Tramonte [1] in the same superficial bottom sediment samples: Total Organic Carbon (TOC), sand fraction (%Sand), silt fraction (%Silt), clay fraction (%Clay), and concentration (mg kg^{-1}) of copper, lead and zinc.

A correlation matrix was made for all the parameters and the results of Pearson coefficient (ρ) are shown in the Table 5.

The correlation matrix presents a weak positive correlation (> 0.3) of uranium concentration with thorium concentration, silt fraction and clay fraction. Thorium concentration presents a weak positive correlation with uranium, copper, lead, zinc, clay fraction and silt fraction. The sand fraction presents a negative correlation with all the parameters studied, confirming the affinity between the elements studied and the fine fraction and TOC.

Principal component analysis (PCA) was performed using the correlation matrix. Table 6 shows the correlation coefficient and the variance calculated for each principal component (PC). It can be seen that the principal components PC1 and PC2 are responsible for 70.64% of the total variance, indicating that other PCs are irrelevant in this study. The PC1 shows a higher positive correlation coefficient with silt fraction, and a positive correlation coefficient with clay fraction, uranium, thorium, copper, lead, zinc and TOC. The PC1 only presents a negative correlation coefficient with the sand fraction. The PC2 shows a higher positive correlation coefficient with lead concentration, and a positive correlation coefficient with sand fraction, cooper, zinc and TOC. The correlation between the parameters studied are shown in the Biplot graph, Fig. 11, where it is possible to observe that the silt fraction, clay fraction, uranium and thorium concentration are grouped on the quarter quadrant; TOC, copper, lead and zinc concentration are grouped on the first quadrant, and the sand fraction is isolated on the third quadrant.

Cluster analysis was performed in two different ways: one to evaluate how the parameters interact among them in all superficial bottom sediment samples, and the second one to group the superficial bottom sediment samples in which the parameters present similar behavior. Both analyses were performed applying the Ward's method for hierarchical cluster analysis with evaluation of similarity by Euclidean distance.
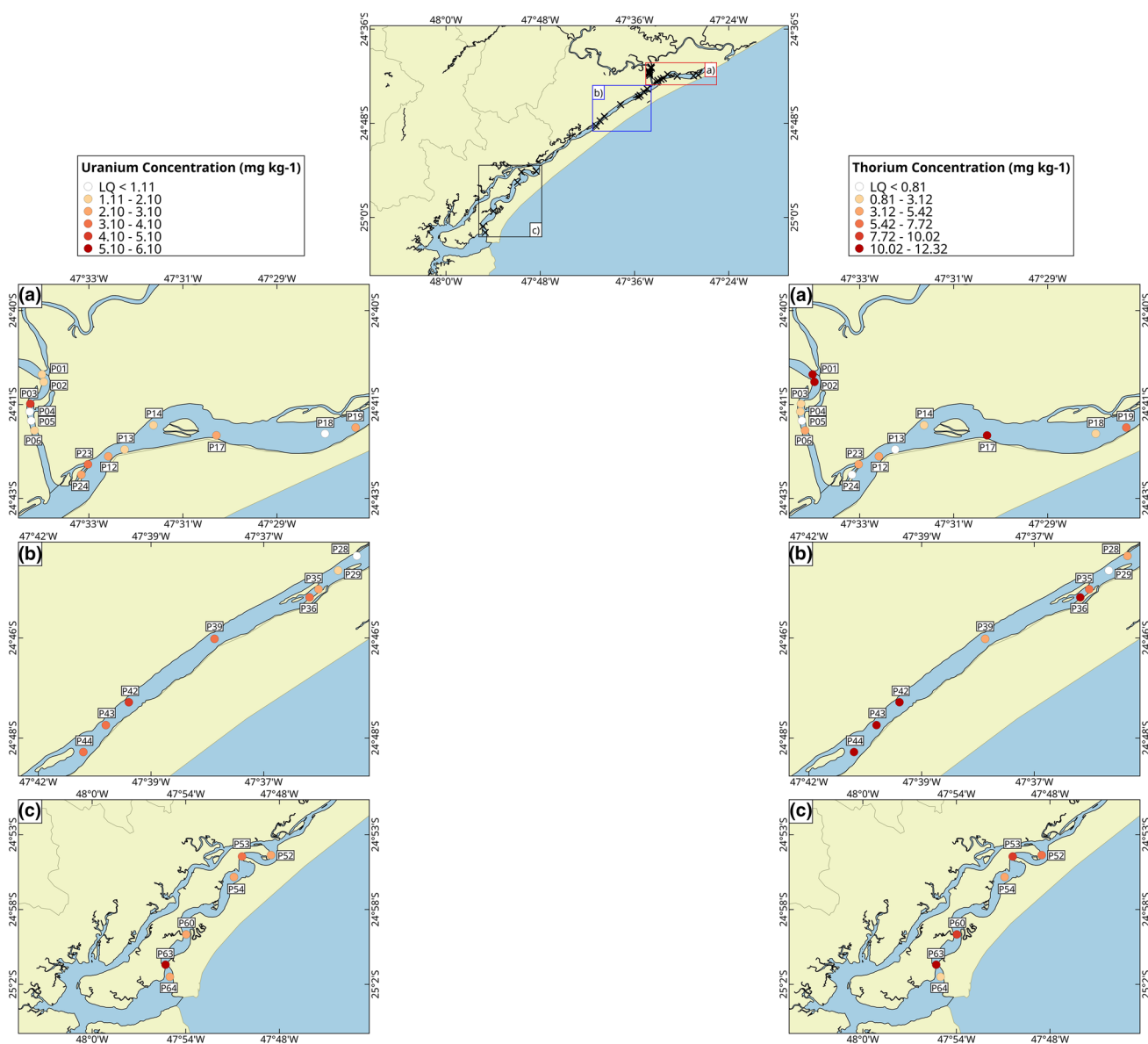
Fig. 8 Uranium and thorium concentration distribution through the Cananéia-Iguape system

Figure 12 shows the cluster analysis dendrogram of each parameter in all superficial bottom sediment samples; with the formation of three distinct groups: group A is formed by the silt fraction, clay fraction, uranium and thorium, group B is formed by copper, lead, zinc and TOC, and group C formed by the sand fraction. The result obtained in the cluster analysis is in good agreement with the ones obtained in the PCA. It is interesting to note that both cluster analysis and PCA show that uranium and thorium have more affinity with the silt and clay fraction than with TOC, which implies that the grain size of the sample is more important than the TOC.

Figure 13 shows the cluster analysis dendrogram grouping the superficial bottom sediments samples with similar behavior, where it is possible identifies three groups. The group A is formed by the samples P01, P02, P23, P29, P42, P44, P53 and P60, and that one have the higher concentration of copper, lead, thorium and zinc. The group B is formed by the samples P03, P05, P12, P13, P17, P24, P28, P35, P36, P39, P43, P54 and P63, and samples that have the higher concentration of uranium and TOC. The group C is formed by the samples P04, P06, P14, P18, P19, P52 and P64, which have the higher sand fraction.

Figure 14 presents the distribution of these three groups along the Cananéia-Iguape system; and it is possible to
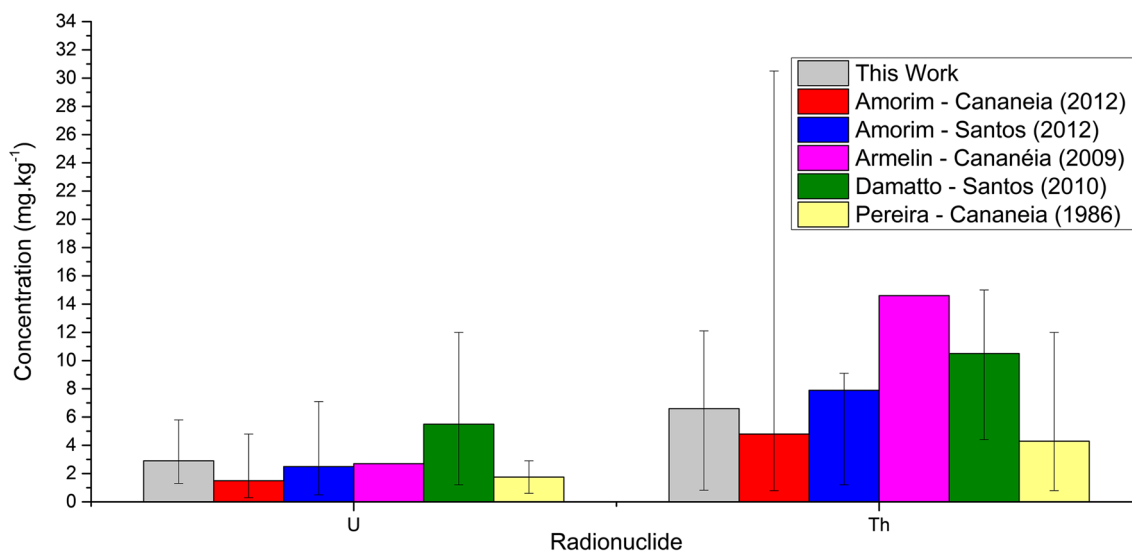
Fig. 9 Comparison of radionuclide concentration (mean, maximum and minimum) determined in sediments samples in this study and in the literature. **a** Uranium concentration; **b** Thorium concentration

Fig. 10 Geo-accumulation index (IGeo) [19] of superficial bottom sediments samples from Cananéia-Iguape system. **a** Uranium concentration; **b** Thorium concentration
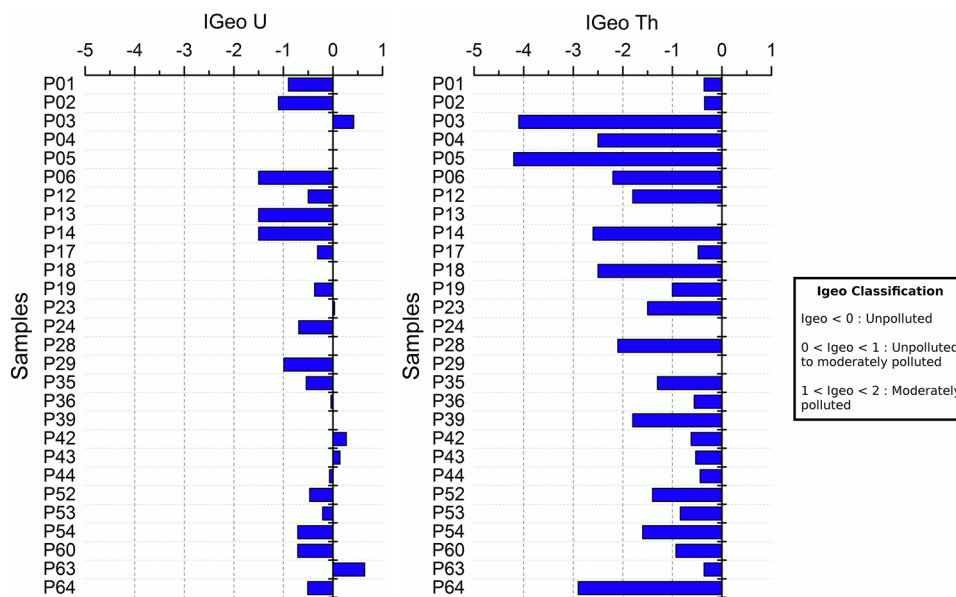

Table 5 Pearson's correlation matrix

	U	Th	TOC	%Sand	%Silt	%Clay	Cu	Pb	Zn
U	1	0.478	0.178	−0.347	0.334	0.353	0.017	−0.043	0.104
Th	0.478	1	0.192	−0.433	0.441	0.365	0.308	0.438	0.356
TOC	0.178	0.192	1	−0.345	0.380	0.193	0.436	0.212	0.474
%Sand	−0.347	−0.433	−0.345	1	−0.992	−0.920	−0.458	−0.346	−0.441
%Silt	0.334	0.441	0.380	−0.992	1	0.865	0.472	0.380	0.466
%Clay	0.353	0.365	0.193	−0.920	0.865	1	0.364	0.198	0.316
Cu	0.017	0.308	0.436	−0.458	0.472	0.364	1	0.767	0.979
Pb	−0.043	0.438	0.212	−0.346	0.380	0.198	0.767	1	0.786
Zn	0.104	0.356	0.474	−0.441	0.466	0.316	0.979	0.786	1

Table 6 Correlation coefficients of principal components and variance percentage

	PC1	PC2	PC3	PC4
U	0.173	− 0.402	0.614	0.163
Th	0.282	− 0.117	0.605	− 0.279
TOC	0.241	0.113	0.057	0.868
%Sand	− 0.406	0.298	0.275	0.043
%Silt	0.410	− 0.265	− 0.255	− 0.016
%Clay	0.354	− 0.373	− 0.309	− 0.124
Cu	0.370	0.409	− 0.052	0.004
Pb	0.313	0.425	0.105	− 0.349
Zn	0.374	0.407	0.056	0.046
% Variance	50.47	20.17	11.30	9.57

Fig. 13 Cluster analysis dendrogram: superficial bottom sediments samples with similar behavior

Fig. 11 Principal component analysis: Biplot graph
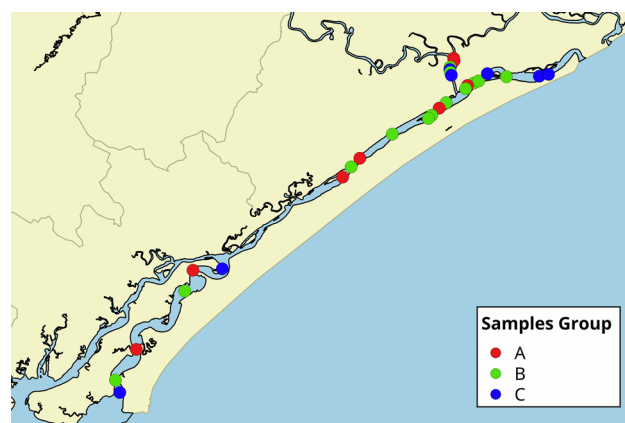
Fig. 14 Sample group distribution

verify that there is not a specific group that stays together in a specific area through the entire system. This heterogeneous distribution of the groups proves the complexity of the system.

Conclusions

The acid digestion of the sediment followed by the uranium and thorium determination by the spectrophotometric method gave good results for the analysis of 0.5 g of sediment samples, presenting LOD of 0.98 mg kg^{-1} and LOQ of 1.11 mg kg^{-1} for uranium and for thorium LOD of 0.61 mg kg^{-1} and LOQ of 0.81 mg kg^{-1}.

The results obtained for the sediment samples from the Cananéia-Iguape system presented an average uranium concentration of 2.9 mg kg^{-1} (SD: 1.2 mg kg^{-1}) and average thorium concentration of 6.6 mg kg^{-1} (SD: 3.8 mg kg^{-1}).

**Fig. 12** Cluster analysis dendrogram: parameters interaction in all parameters

These results are in agreement with previous studies performed in the same location. The geo-accumulation index classifies 21% of the sediments as "unpolluted to moderately polluted" and 79% as "unpolluted" for uranium. For thorium all the sediments were classified as "unpolluted". It can be concluded that the region is not affected by NORM activities and the results obtained for U and Th represent the background concentration of the region.

The statistical analyses identified the affinity of uranium and thorium with the silt and clay fraction and the complexity of the system studied.

Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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