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INVESTIGATION OF THE URANIUM CONTENT IN SEDIMENT AND SOIL SAMPLES FROM THE SANTOS AND SÃO VICENTE ESTUARY REGION, SP.

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ABSTRACT

In this work the uranium (U) content in sediment and soil samples collected near the Santos and São Vicente estuary was determined using the fission track registration technique (SSNTD). The sediment and soil samples after oven-dried and pulverized were prepared in the solution form. Around 10 µL of this solution was deposited on the plastic detector (PCLIGHT) and irradiated at the IEA-R1 (3.5 MW) nuclear reactor. After the irradiation and chemical etching of the plastic foils, the fission tracks were counted with a system consisting of an optical microscope together with a video camera and a PC computer. The U content in the analyzed samples ranged from 3.12 ± 0.55 to 18.3 ± 1.2 ppm for sediments and from 3.21 ± 0.63 to 11.5 ± 1.1 ppm for soils. These resultas were compared to other values reported in the literature for sediments and soils collected in environments similar to the ones studied in this work The average values for the U content obtained in this work are significatively higher (above twice) than the world mean and are in reazonable agreement with results found by other authors for sediments and soils from regions considered as polluted or with a high level of radioactivity.

1. INTRODUCTION

Uranium (U) is the heaviest chemical element of natural occurrence and can be found in food, soils, waters, sediments and living organisms in trace quantities (ppm). The techniques most usually employed to determine such small amount of U are: gamma spectroscopy, mass spectrometry, neutron activation analysis and nuclear fission track registration technique (SSNTD). [1]

Phosphate fertilizers applied to the agriculture soils usually contain high U content (up to hundred of ppm) due to natural occurrence of this element in phosphate rocks which are employed as phosphorous source in the production of these fertilizers. According to the origin and application form, the fertilizers can raise the occurrence level of U in the environment and so, increasing the exposition of human beings to the radiation produced by U and its progeny.

The most important Brazilian fertilizer industries are located at the Cubatão county, São Paulo state. They were installed near the Cubatão river basin and thus the pollutants materials discharged by them may be producing an U accumulation in waters, sediments and soils of the estuarine region of Santos and São Vicente. The presence of U in large scale in these environment compartments can induce its accumulation in living beings and consequently to represent a potential radiological risk to the population of these areas. In this way, the

knowledge of U concentration in sediments and soils is important not only to assess the contamination level but also, to understand the transference processes which have occurrence at different trophic levels of the feed chain.

This work aims to determine the U content in sediment and soil samples collected throughout the Santos and São Vicente estuary region using the fission track registration technique (SSNTD) in order to evaluate the contamination level to which the population is being exposed in that region.

2. MATERIALS AND METHODS

To determine the U concentration in sediment and soil samples it was employed the SSNTD technique in a polycarbonate plastic named PCLIGHT (1 mm thickness) produced by Policarbonatos do Brasil S/A.

The study area is located in southwest Brazil, São Paulo state, chich includes the counties of Santos, São Vicente, Guaruja e Cubatão, as can be seen in Fig. 1. The samples were collected either by dragging or manually with a stainless steel spoon, at a depth of 0 – 10 cm, in the period from 2007 to 2008. All the samples (around 500 g each one) were stored in plastic vials previously washed with HNO_3(2%) solution in order to eliminate possible U impurities.

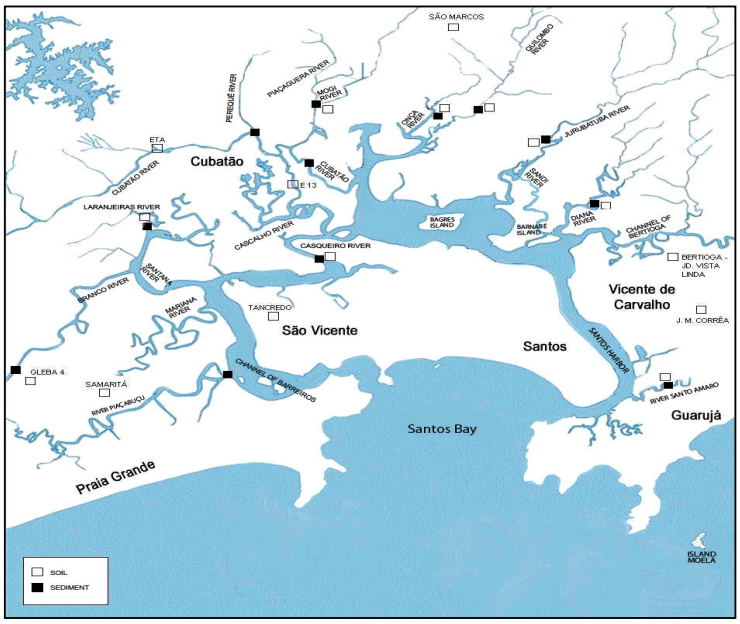

Figure 1. Selected sampling sites in the estuarine region of Santos and São Vicente

Inicially the samples were oven-dried, pulverized and submitted to a screening process using 63 μm plastic sieves. Following, the powder material was again oven-dried at 90 ^{o}C until a constant weight (± 1%) was obtained.

A known mass of about 40 mg dry weight from each powder sample was treated with acqua-regia solution (1 HCl:3 HNO_3), at a temperature around 115 ^{o}C, during 6 hours, in a digestor system. The resulting residue was diluted to a total volume of 25 mL. Aliquots of 10 μL of this solution were deposited on the plastic detector surface(1.2 cm^2 area) together with 5 μL of a Cyastat detergent solution (5%, Cytec Industrias) and evaporated under an infrared lamp (250 W) at an approximated temperature of 75 ^{o}C. The Cyastat detergent solution works as an eletrostatic neutralizer reducing the droplet surface tension and making possible to obtain a better homogeneity for the deposit. All the resulting deposits of non – volatile constituents were covered with an extremely thin collodion film (about 20 $\mu g/cm^2$) in order to protect them against humity and contamination. [1]

A standard soil sample having a known uranium content was prepared, in the same way as described for the sample solution, to be used as neutron flux monitoring during the irradiations.

All the plastic films, containning the sediment, soil and U standard samples were piled inside an aluminum rabbit (22 mm diameter by 70 mm height) usually employed for irradiations at IPEN-IEA-R1 (3.5 MW) pool type research nuclear reactor [1]. In order to get a better neutron flux monitoring during irradiations it was employed 10 U standard deposits distributed in two sets of five deposits, where one of them was placed at the upper and the other at the lower side relative to the sample deposits set.

The aluminum rabbit was placed near the reactor core for irradiation at a position EIRA 24B where the thermal neutron flux was about $1.2x10^{13}$ $n/cm^2.s$. The irradiation time employed for all samples was about 3 min.

After irradiations, chemical etching of the plastic detectors was carried out at 60 ^{o}C, for a time period of 60 min, in a NaOH (6N) solution. In these chemical etching conditions the fission tracks produced in the detectors presented the best visibility level in a optical microscope. The fission tracks were counted using a system consisting of binocular optical microscope, at a magnification of 400x, together with a video camera and a PC computer [2]. For each sample it was scanned at least 4 plastic films and the final result was calculated by the average of the values obtained in the fission tracks counting.

3. RESULTS AND DISCUSSION

The precision (reproducibility) and accuracy of the method employed in this work were determined using sediment and soil standard reference materials from the International Atomic Energy Agency (IAEA). These reference materials were prepared in the same way as described for the sediment and soil samples. The results obtained are reported in Table 1 and as it can be seen, within the experimental uncertainties, the values are in reasonable agreement.

Table 1. Results obtained for the precision and accuracy of the method employed in this work.

Reference Samples	U Experimental Result (ppm)	U Certified Value (ppm)	Precision	Accuracy
IAEA-SOIL 375	2.14 ± 0.38	1.86 ± 0.19	18%	15%
IAEA-SEDIMENT 314	49 ± 11	56.8 ± 3.9	22%	14%

The average values found in this work for U content in sediment and soil samples from the Santos and São Vicente estuarine region are listed in Table 2. The total uncertainties reported in this table are the standard deviation (SD) of the average value obtained for 5 deposits analysis of each sample.

Table 2: Average uranium contents (± 1 SD) obtained in this work for sediment and soil samples from Santos e São Vicente region.

Sediment Sampling Location	U in Sediment Samples (ppm)	Soil Sampling Location	U in Soil Samples (ppm)
Onça River	18. 3 ± 1.2	Tancredo	11.5 ± 1.1
Branco River	8.5 ± 1.0	Quilombo River	10.89 ± 0.83
Quilombo River	8.0 ± 1.0	Diana River	10.24 ± 0.94
Mogi River	7.04 ± 0.82	Onça River	9.76 ± 0.73
Diana River	6.42 ± 0.64	J. São Marcos	8.8 ± 2.3
Laranjeiras River	5.63 ± 0.96	Sto Amaro River	8.3 ± 1.5
Cubatão River	4.63 ± 0.68	Jurubatuba River	7.1 ± 1.5
Perequê River	4.61 ± 0.46	Mogi River	6.40 ± 0.68
Jurubatuba River	3.80 ± 0.72	Cubatão – E_{13}	6.13 ± 0.85
Casqueiro River	3.61 ± 0.72	J. M. Corrêa	5.9 ± 1.5
Piaçabuçu River	3.30 ± 0.50	Casqueiro River	4.79 ± 0.71
Sto Amaro River	3.12 ± 0.55	Gleba 4	4.12 ± 0.91
		Jardim Vista Linda	4.07 ± 0.57
		Cubatão – ETA	3.97 ± 0.42
		Laranjeiras River	3.68 ± 0.57
		Samaritá	3.21 ± 0.63
Total Average	**6.4 ± 4.2**	**Total Average**	**6.8 ± 2.8**

According to Table 2 one can see that the mean U contents in soils and sediments from the estuarine region of Santos and São Vicente are approximately equals, within the calculated uncertainties (±1 SD). However, for the majority of the areas the U content is above the world mean concentration reported by UNSCEAR [3] as being about 3.0 ppm (or 35 Bq/Kg for ^{238}U isotope).

Several authors have determined U concentration in environment samples employing gamma spectroscopy techniques and the results were, usually, reported in Bq/Kg for the ^{238}U isotope. In order to be possible a comparison of the present results with those reported by other authors, the average values were converted in equivalent activity for ^{238}U isotope. These values were calculated using a conversion factor of 1.0 ppm = 12,35 Bq/Kg, adopting an isotopic abundance of 99.27% and half-life of $4.468x10^9$ y for ^{238}U . [4]

The interval obtained in ^{238}U equivalent activity for all sediment and soil samples from the Santos and São Vicente region is listed in Table 3 together with the results reported in literature for similar samples and the world mean value for U in soils.

Table 3: Comparison of ^{238}U equivalent activity interval for soil and sediment samples from Santos and São Vicente region with values reported for other areas of the world.

Country – Region	Sampling Locations	Results ^{238}U (Bq/Kg)	Reference
Brazil-Santos (SP)	Mangle Area-Sediment and Soil	38.5 – 226	This work
Greece-Milos Island	Volcanic Origin Area-Sediment	29 – 110	[5[
Greece-Milos Island	Volcanic Origin Area-Soil	21 – 187	[5]
Portugal-Central Region	Contaminated Rivers-Sediment	129 – 952	[6]
China-Xiazhuang	Near Uranium Ore Field-Soil	40.2 – 442	[7]
Malasya-Selangor, Perak	Rcycling Pond-Efflent Sediment	61.2 – 472.3	[8]
Madagascar-Antsirabe	High Radioactivity Area-Soil	22 – 765	[9]
Italy-Padua	Thermal Waters SPA-Sediment	42 – 70	[10]
Turquey-Kestanbol	Granite Area-Soil	82.3 – 167.0	[11]
Spain-Extremadura	Contaminated River-Sediment	77 – 6401	[12]
India-Kangra	County Area-Soil	9.26 – 25.4	[13]
Kuwait - Kuwait Bay	Marine Área-Sediment	21.4 – 24.0	[14]
Kenyan-Bombasa	Marine Area-Sediment	11.9 – 22.8	[15]
Nigéria-Ibadan	Near Road Area-Soil	10.2 – 40.7	[16]
Algeria-Algiers Bay	Marine Area-Sediment	10.8 – 25.0	[17]
Turkey–Firtina Valley	Volcanic Origin Area-Sediment	16 – 113	[18]
Turkey-Istanbul	Near City Area-Soil	2.63 – 58.98	[19]
Albânia- Butrint Lagoon	Lagoon Area-Sediment	8 – 27	[20]
France-Several Rivers	Not Polluted Rivers-Sediment	9 – 62	[21]
Worldwide mean	Soils	35	[3]

As can be seen in Table3, the values obtained in this work compare suitably with the intervals found by others authors for sediments and soils which were considered as polluted or having high natural radioactivity and are much higher than those found for samples supposed to be not polluted or having normal radioactivity levels. Compared to the worldwide average concentration in soils, the present results are in general significatively higher (on average more than twice) indicating a possible accumulation of U in Santos and São Vicente estuary which may due to geochemical processes and/or emission from Cubatão county industries, mainly, residues from the fertilizer manufacturers.

3. CONCLUSIONS

The average U content values obtained in this work for sediment and soil samples from the Santos and São Vicente estuarine region were approximately equal within the experimental uncertainties, indicating that there is not a preferential route of U transference. However, the results found are significatively above (more than twice) the world mean for soil and so, uranium accumulation may be occurring by emission from the Cubatão county industries and/or by natural geochemical processes in the region.

The present U content interval determined in terms of ^{238}U equivalent activity for sediment and soil samples is, according to the results reported in the literature, compatible with those found for areas considered as polluted or with high level of natural radioactivity.

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