ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN
2019 International Nuclear Atlantic Conference - INAC 2019
Santos, SP, Brazil, October 21-25, 2019

Agência Brasileira do ISBN
ISBN 978-85-99141-08-3
9 788599 141083

NATURAL RADIONUCLIDES IN SOIL PROFILES AND SEDIMENT CORES FROM JUNDIAI RESERVOIR, STATE OF SAO PAULO.

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ABSTRACT

The activity concentration of natural radionuclides in soils and sediments is dependent on many factors, such as the rock parental material, pedogenic and weathering processes, physical and chemical properties of the environment, anthropogenic sources, among other aspects. Naturally occurring radiation in the environment is mostly due to the decay of ^{238}U and ^{232}Th series; another important source of natural radiation is the radionuclide ^{40}K. Reservoirs are artificial systems made in order to stock riverine and rainwater to supply water to the population. There are few studies about the levels of natural radionuclides in reservoirs in both, international and national, literature. The objective of this paper was to evaluate the activity concentration of ^{238}U and ^{232}Th by Instrumental Neutron Activation Analysis and ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th and ^{40}K by gamma spectrometry in two soil profiles and three sediment cores collected in the catchment area of Jundiai reservoir, located in the state of São Paulo, Brazil. Principal component analysis was applied to verify the correlation of the activity concentrations of the natural radionuclides with physical and chemical properties of soil and sediment samples. In the soil profiles, the radionuclides that showed higher activity concentration when compared to the UNSCEAR values were ^{232}Th in the both profiles and ^{238}U only in one; for the sediment cores, the activity concentrations of ^{238}U and ^{232}Th were higher than the UNSCEAR values in all the samples analyzed and also for the radionuclide ^{226}Ra in two sediment cores.

1. INTRODUCTION

Ionizing radiation is characterized by electromagnetic waves and electrically charged particles which ionize other atoms. Natural radionuclides are formed by sources of ionizing radiation [1] and these elements can be founded in all types of ecosystems of the environment. Human and environmental exposure to natural radiation is an important subject for public health prevention, geologic characterization and radioecology [2]. The natural occurring radiation materials are part of the Earth rocks composition. These rocks undergo weathering and erosion processes and carried out radionuclides and other trace elements for soil composition. These elements can be transported, by water or wind, to a sedimentation watershed where occurs the deposition in the bottom of a lake, ocean, rivers, and reservoirs [3] and may be absorbed by biota, causing concern about the possible negative biological effects that the radiation can trigger in animals, plants or humans [4]. The use of fertilizers in soils can also increases the activity concentrations of radionuclides from the ^{238}U and ^{232}Th series, as well as the concentration of the natural radionuclide ^{40}K [1]. Hence, the major source of human exposure to radiation is the natural source, mostly due to the radionuclides ^{226}Ra, ^{210}Pb, ^{228}Th, ^{228}Ra present in both series, also ^{40}K. Another source of natural radiation

are the cosmogenic radionuclides, however its contribution to human exposure is lower. The external exposure is due to the gamma-ray emission and internally exposure occurs through inhalation or ingestion, including water consumption [2].

Reservoirs are constructed by river segmentation and its impacts are phenomena to study [5], including the fact that the natural radionuclides transportation and deposition are influenced by these modifications in the environment [4].

This paper had a purpose to evaluate the activity concentration of ^{238}U and ^{232}Th by neutron activation analysis, and ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th and ^{40}K by gamma spectrometry in soils profiles and sediment cores from Jundiai reservoir. The behavior of the natural radionuclides in the soil profiles and the sediment cores was studied using statistic correlation of soil and sediment physical-chemical properties, grain size, organic matter content and pH, with the radionuclide vertical distribution.

2. METHODOLOGY

2.1. Study area and sampling

The Jundiai reservoir is located at the southeast region of the state of Sao Paulo in Mogi das Cruzes county (23°40'S and 46°10'W), it is formed by river Biritiba-Mirim and Tietê waters, and has a drainage area of 111 km^2 and a flooded area about to 17 km^2 [6]**.** The local climate is classified as a temperate ocean climate in the Koppen system (Cfb), with annual average rainfall and temperature of 1582 mm and 17,6°C, respectively. The Upper Tietê water basin is responsible to supply millions of people in the Sao Paulo Metropolitan area. This area is characterized by intense agriculture, industrial activities [7], and the concentration of many pollutants that can affect the natural radionuclide concentrations.

Soil samples were collected vertically in two profiles located near to the reservoir shore and sampled each 10 cm. Sediment samples were collected in three points in the margin of the reservoir with 70-100 cm of the water column and sampled according to the morphology and lithology of the sediment; two of these sampling points of the sediment cores represent coordinates from the respective soil profile. A third sediment core was collected away from the location of the other soil profiles. The points were chosen according to the main lithology around the reservoir. Figure 1 presents the Jundiai reservoir and the lithology map [8] with the three sampling points.

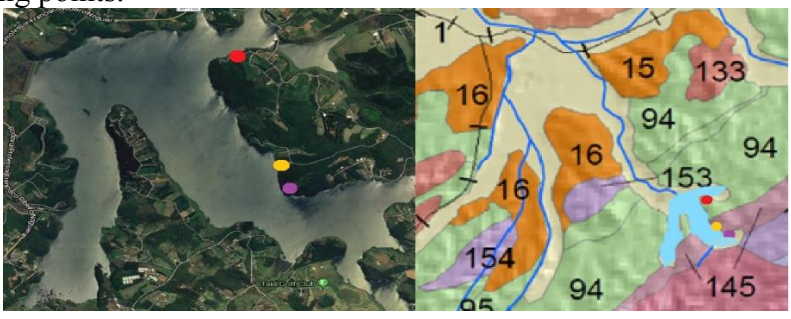

Figure 1 – Jundiai reservoir and the lithology map [8] with the three sampling points.

The lithology that represents the green area on the map (n°94) is composed by schist (point one – red point); the other lithology, indicated by the purple area on the map (n°145), is represented by orthogneiss complexes (metamorphic granitic rocks), which comprises the second (purple point) and third (yellow point) points of sampling.

2.2. **Physical-chemical parameters**

2.2.1. Grain size analysis

Soil and sediment grain size analysis were performed by sieving 5 g of the samples and the particles were classified as sand (0,06 mm to 2 mm), silt (2 μm to 0,06 mm) and clay (<2 μm). Soil and sediment textures were classified according to the USDA-NRCS ternary diagram for soil texture.

2.2.2. Organic matter content – O.C

Soil and sediment organic matter contents were estimated by the loss-on-ignition method. The samples were dried at high temperatures in muffle furnace and the organic carbon volatilizes as CO_2. The content of organic matter was evaluated by gravimetric calculations based on mass loss; the samples were weighed before and after the heating at 500°C. This method provides only an estimate of the total organic carbon in samples; other compounds, such as carbonates and sulfates can be lost on the process [9].

2.2.3. Potential of hydrogen - pH

Potential of hydrogen-ion activity of soil samples was measured using a pH meter with 0,02 uncertain. The measurement was performed using potassium chloride (1 mol. L^{-1}) and calcium chloride (0,01 mol.L^{-1}) with a soil/extractor proportion of 1:5. The pH measured in calcium chloride solution represents the active acidity of soil; the solubility of elements and geochemical speciation are followed by active acidity of soil. The exchangeable soil acidity was measured using the solution of potassium chloride, and this compartment is correlated with the amount of exchangeable Al^{3+} adsorbed in clay minerals and humic substances present in the soil composition. The delta pH (ΔpH) was measured according to the expression (1) [10] and represents the electrical charge present in soil colloid.

$$\Delta pH = pH_{KCl} - pH_{CaCl_2} \quad (1)$$

Where:
ΔpH < 0; surface area of colloid is negative electrically charged (cation adsorption)
ΔpH > 0; surface area of colloid is positive electrically charged (anion adsorption)
ΔpH = 0; zero point of charge (ZPC)

2.3. **Instrumental Neutron Activation analysis (INAA)**

The activities concentration of ^{238}U and ^{232}Th were determined by instrumental neutron activation analysis. For the analysis, the aliquots of soil and sediment samples were mashed, using mortar and pestle, in 115 mesh (0,125 mm). Then, approximately 200 mg of samples and the reference materials *Lake Sediment – SL3* from IAEA, *Inorganic Marine Sediment – 2702* and *Montana Soil II* from NIST were irradiated in a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} at the IPEN Research Reactor IEA-R1 for a 6 h period.

The measurement process was performed by Gamma-ray Spectrometry, using a coaxial HPGe detector, Ortec, and associated electronics. The analysis of the spectrum was done with INTERWINNER 6.0 gamma-ray software to identify and discriminate the gamma-ray peaks.

2.4. **Gamma spectrometry**

The activity concentrations of the radionuclides ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, and ^{40}K were determined by Gamma-ray Spectrometry. Approximately 120g of the soil and 15g of the sediment samples were measured in a coaxial Be-layer HPGe detector with 25% relative efficiency, 2.09 keV resolution at 1.33 MeV and associated electronic devices, with a live counting time of 150 000s.The spectra were acquired by multichannel analyzer Ethernim and, for the analysis, WinnerGamma software was used (ORTEC. INTERWINNERTM 6.0 MCA). The associated uncertainty for one sigma confidence ranged from 10% to 40% from the obtained results. The detector was calibrated using IAEA 300 Standard Reference Material.

2.5. **Principal component analysis (PCA)**

Principal component analysis is a multivariate statistical method based on a linear distribution reduction of the variances in two principal components. It is useful for the simultaneous analysis of several variables and this technique shows which parameter has more statistical significance in the analysis; the *x* component represents more significance of variance that the *y* component [11]. This method was employed to establish correlations between the activities concentrations of the radionuclides and the physical-chemical parameters of soil and sediment samples.

3. RESULTS AND DISCUSSION

The soil profiles were named as JUSO and numbered according to the point of sampling (JUSO1 represents the soil profile sampling at point one and JUSO2 represents the soil profile sampling at point two). The sediment cores were named as JUSE and numbered according to the point of sampling as well as the soil profiles.

3.1. Soil

3.1.1. Physical-chemical parameters

Figure 2 presents the results obtained in the physical-chemical analysis for the two soil profiles. The first profile, JUSO 1, presented a higher content of organic matter than the second one. The mean contents of organic matter for JUSO 1 and JUSO 2 were 13% and 9%, respectively; the clay fraction was higher in JUSO 1. The mean contents of clay, silt and sand fractions for JUSO 1 were 45%, 5%, and 44%, respectively, which takes a sandy clay texture for this profile. The mean contents of clay, silt and sand fractions for JUSO 2 were 28%, 13%, and 55%, respectively, which takes a sandy clay loam texture for it.

For the potential of hydrogen-ion activity, the mean active pH (pH in $CaCl_2$) was 3,8 and 3,7 for the JUSO 1 and JUSO 2, respectively. In both profiles, the results of ΔpH presented positive values. Therefore, both types of soils are likely to anion adsorption in more significance over cation adsorption.

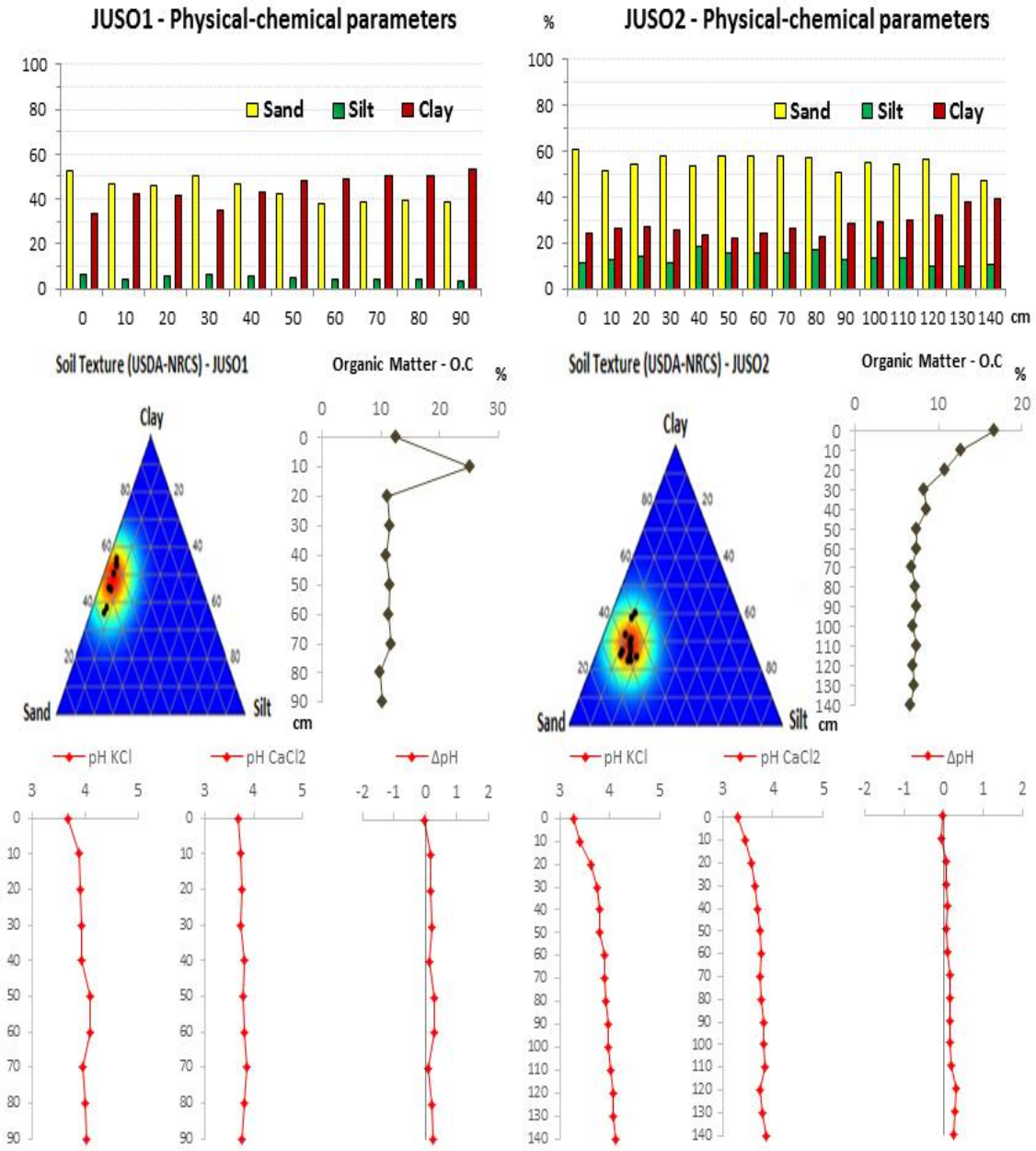

Figure 2- Physical-chemical parameters for the soil profiles JUSO 1 and JUSO 2

3.1.2. Activities concentrations of the natural radionuclides

Figures 3 and 4 present the results obtained for the activities concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{228}Ra, ^{228}Th, and ^{40}K, in $Bq.kg^{-1}$, in the function of the depth (cm), for JUSO 1 and JUSO 2. In both profiles, the activity concentration of the radionuclide ^{232}Th presented higher values when compared to UNSCEAR* values. The mean activity concentrations for ^{232}Th in JUSO 1 and JUSO 2 were 90 $Bq.kg^{-1}$ and 60 $Bq.kg^{-1}$, respectively. According to UNSCEAR, the mean activity concentration of ^{232}Th in global soils is 30 $Bq.kg^{-1}$. The values obtained in this work are not an anomaly, because the values from UNSCEAR were obtained

* *United Nations Scientific Committee on the Effects of Atomic Radiation*

by various types of soils and different types of lithology around the Earth. The radionuclides ^{226}Ra, ^{228}Ra, and ^{40}K presented levels in the range of the activity concentration for these radionuclides in global soils. The mean activity concentration of ^{238}U presented slightly higher values than the UNSCEAR values for JUSO 1. The mean activity concentration of ^{238}U obtained in this profile was 37 Bq.kg^{-1}, and the mean level in global soils is 35 Bq.kg^{-1}. The activity concentration of ^{40}K was slightly higher in the second profile, and a possible explanation to this is the fact that felsic granitic rocks present in the lithology of JUSO 2 have high amounts of stable K, what increases the activity concentration of the radioactive isotope.

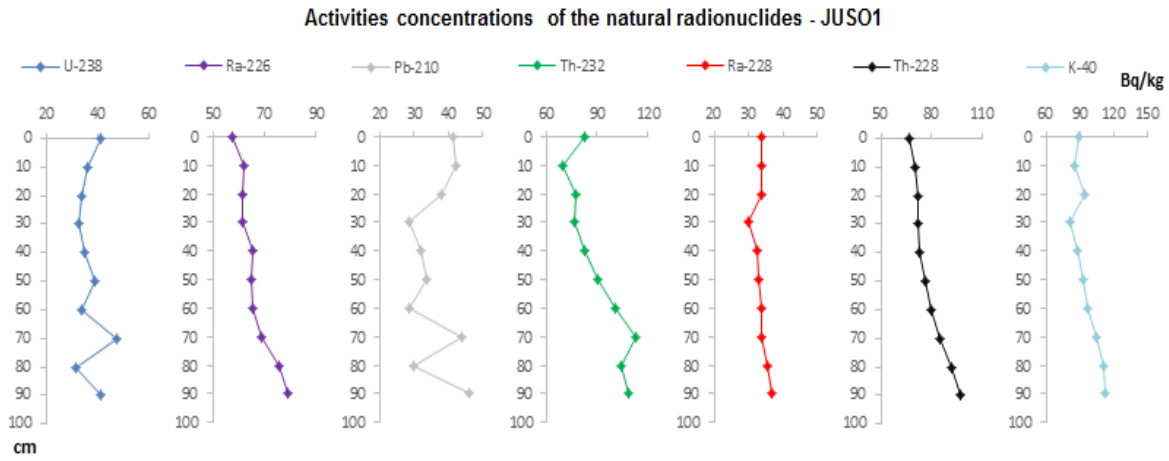

Figure 3 – Activity concentrations of the natural radionuclides in JUSO 1

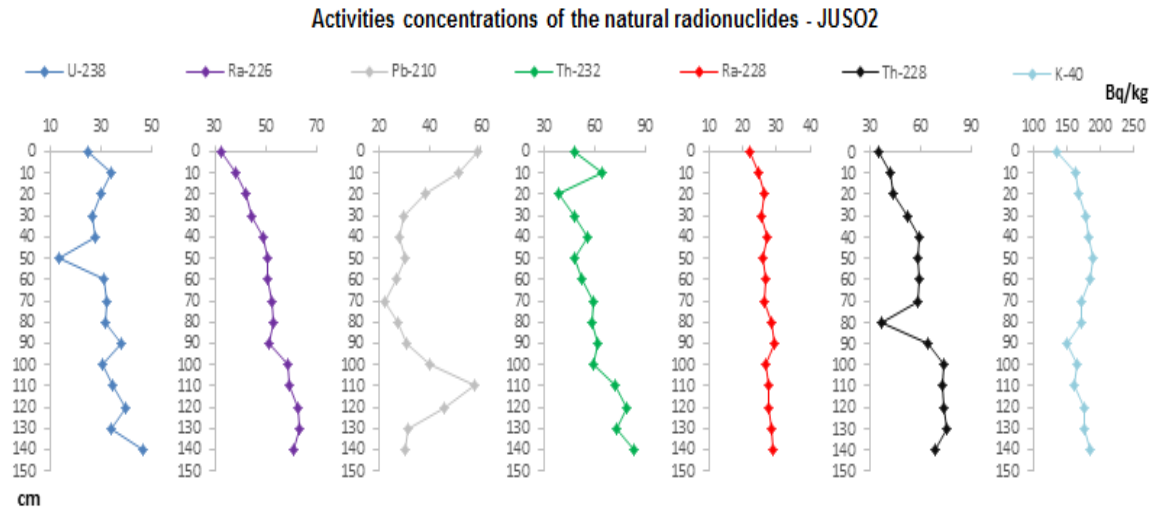

Figure 4 – Activity concentrations of the natural radionuclides in JUSO 2

The mean activity concentrations of ^{210}Pb obtained in JUSO 1 and JUSO 2 were 35 Bq.kg^{-1} and 37 Bq.kg^{-1}, respectively. In both profiles, the levels of this radionuclide were higher in the surface, probably due to ^{222}Rn decay and subsequently precipitation as ^{210}Pb.

3.1.3. Principal component analysis (PCA)

Figures 5 and 6 present the results obtained in PCA between the activity concentrations of the natural radionuclides and the soil physical-chemical parameters.

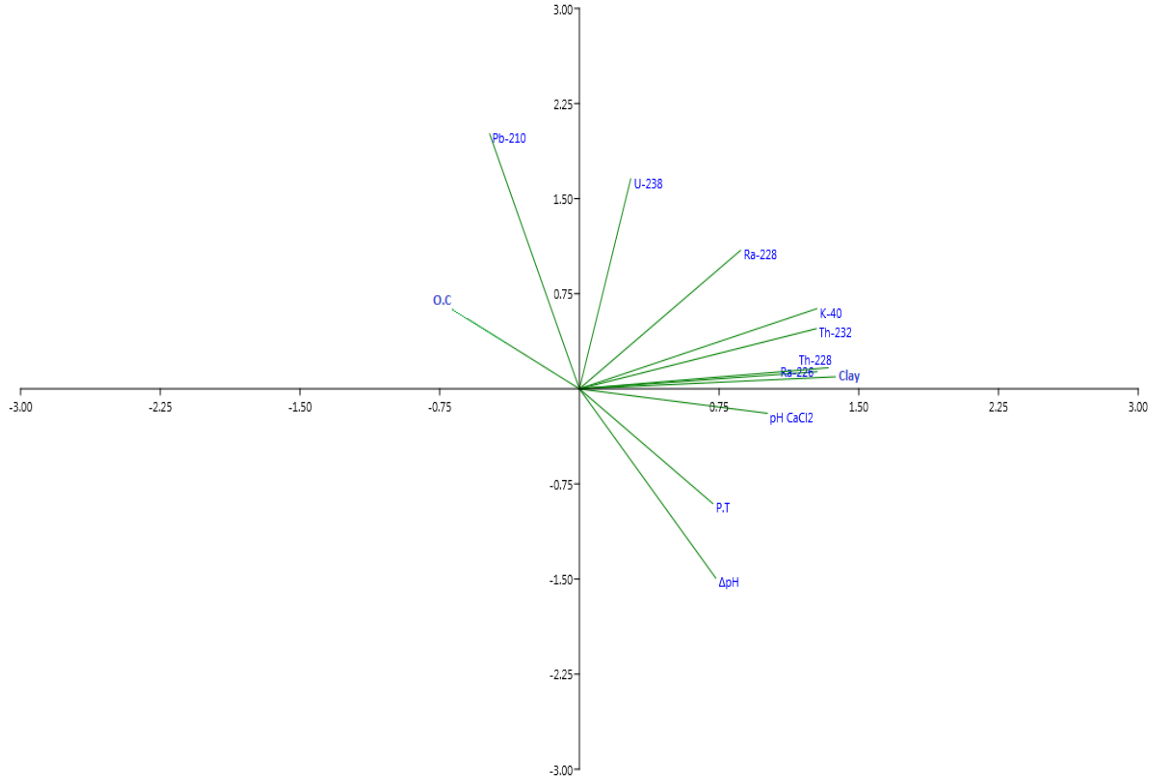

Figure 5 – PCA for JUSO 1

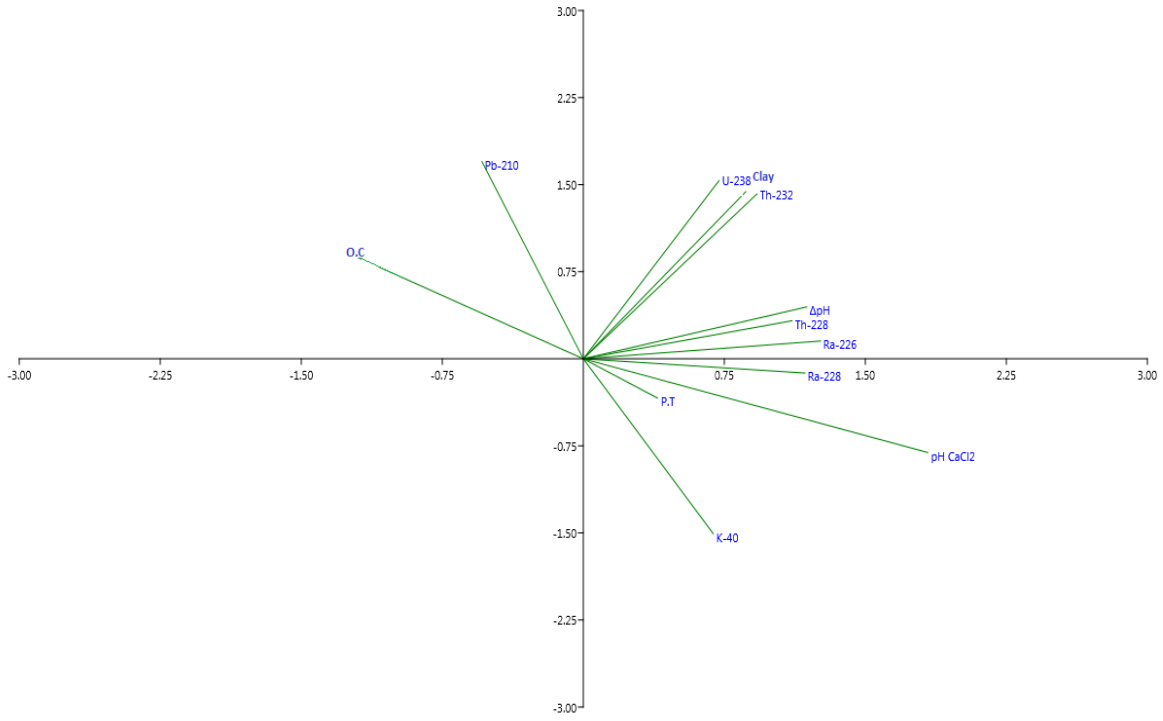

Figure 6 – PCA for JUSO 2

In both soil profiles, the results of PCA showed that the parameters which represented more significance for the availability of the radionuclides in the soil profile were the amount of clay fraction and the pH of active acidity (pH in $CaCl_2$). Data from literature [12] show that the rise of soil alkalinity provides an increase in soil cation exchange capacity (CEC), which could explain this strong association. The chemical behavior of the radionuclides looks like metals behavior, and metals, normally, forms cationic compounds in the environment.

In the *y* coordinate, the organic matter showed good association with ^{210}Pb, however, this correlation represents less significance over the correlations in the *x* coordinate. For JUSO 1 the ΔpH parameter presented a negative association with the activity concentration of ^{210}Pb.

The radium isotopes, ^{228}Ra and ^{226}Ra, were strongly associated with the clay fraction and the thorium isotopes (^{232}Th and ^{228}Th) showed an inverse correlation with the content of organic matter. Thorium becomes readily more soluble when it complex with the organic chelates [13] present in high amount in the soil surface, hence, the element could possibly leach to the depths of the profile, where the contents of organic matter are low.

3.2. Sediment

3.2.1. Physical-chemical parameters

Figures 7 and 8 present the results obtained in the physical-chemical analysis for the three sediment cores. JUSE 1 presented a higher content of organic matter than the others.

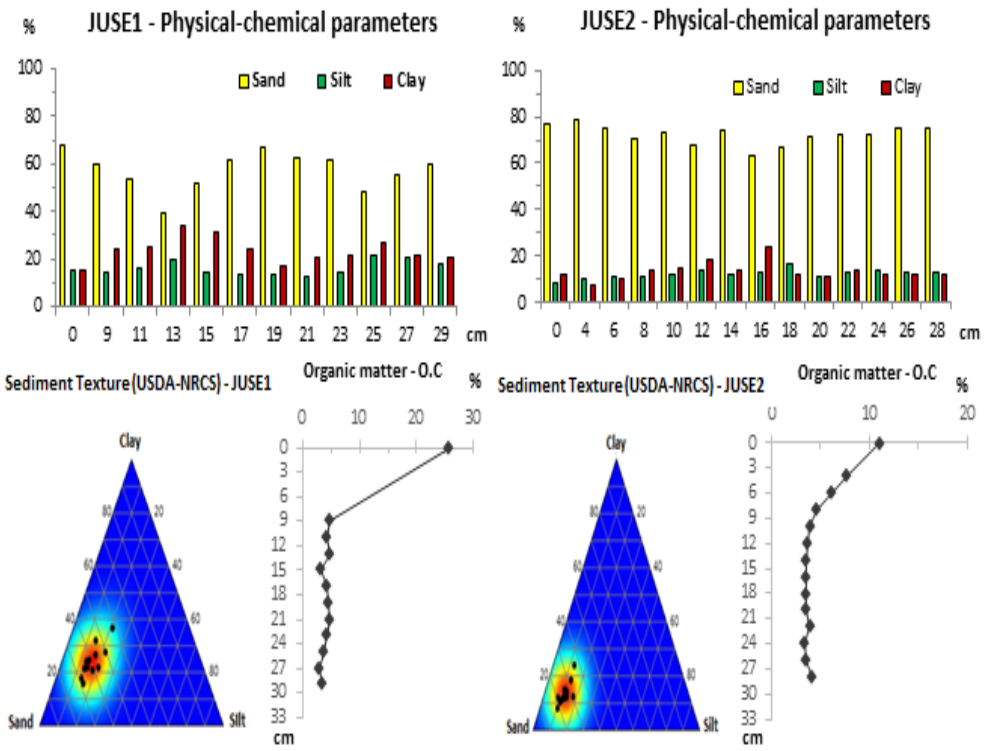

Figure 7- Physical-chemical parameters for JUSE 1 and JUSE 2

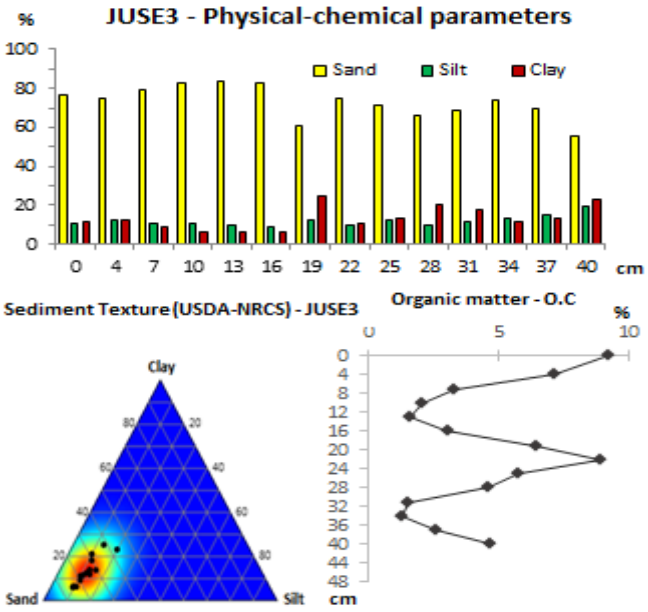

Figure 8- Physical-chemical parameters for JUSE 3

The mean content of organic matter in JUSE 1, JUSE 2 and JUSE 3 was 6%, 5%, and 4%, respectively. The mean contents of clay, silt and sand fractions for JUSE 1 were 23%, 16%, and 57%, respectively, which takes a sandy clay loam texture for this core. The mean contents of clay, silt and sand fractions for JUSE 2 were 13%, 12%, and 73%, respectively, which takes a sandy loam texture for it and for JUSE 3, the mean contents of clay, silt and sand fractions were 13%, 12%, and 73%, respectively, and the texture was classified as sandy loam.

3.2.1. Activities concentrations of the natural radionuclides

Figures 9, 10 and 11 present the results obtained for the activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{228}Ra, ^{228}Th, and ^{40}K, in $Bq.kg^{-1}$, in the function of the depth (cm), for the three sediment cores.

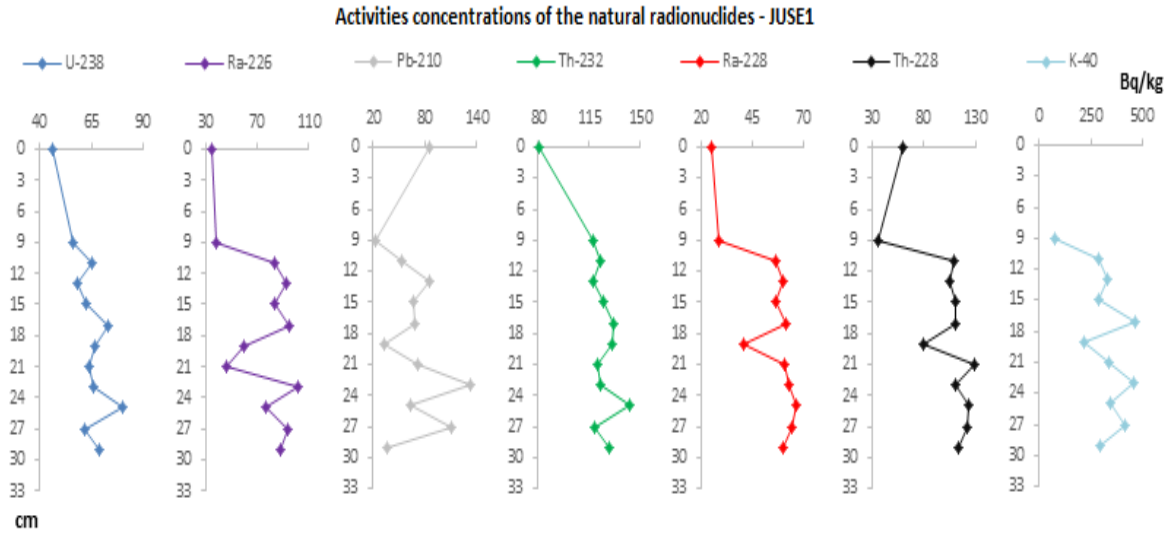

Figure 9 – Activity concentrations of the natural radionuclides in JUSE 1

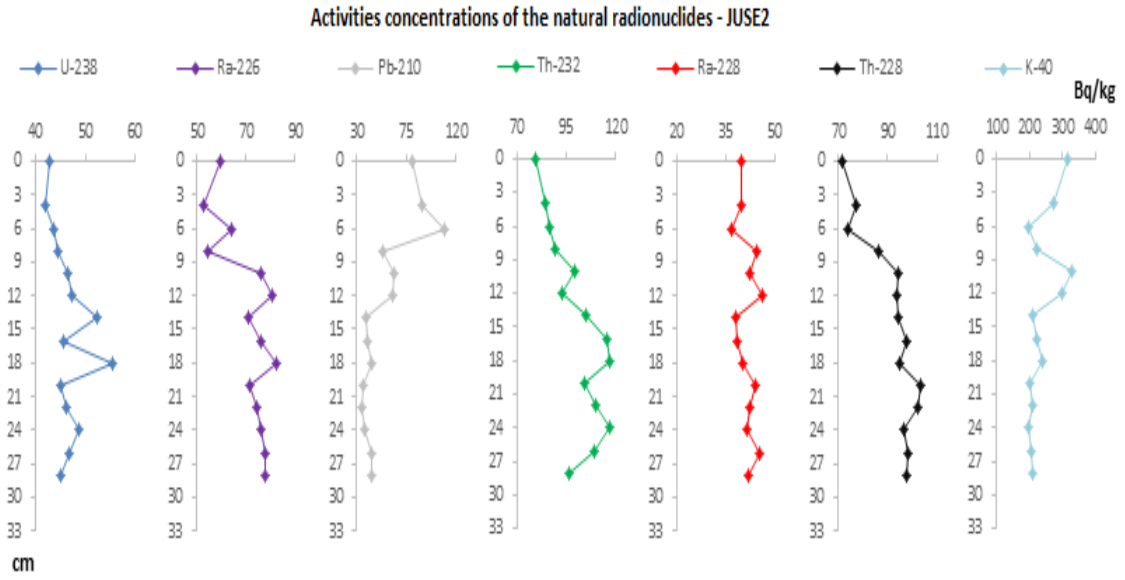

Figure 10 – Activity concentrations of the natural radionuclides in JUSE 2

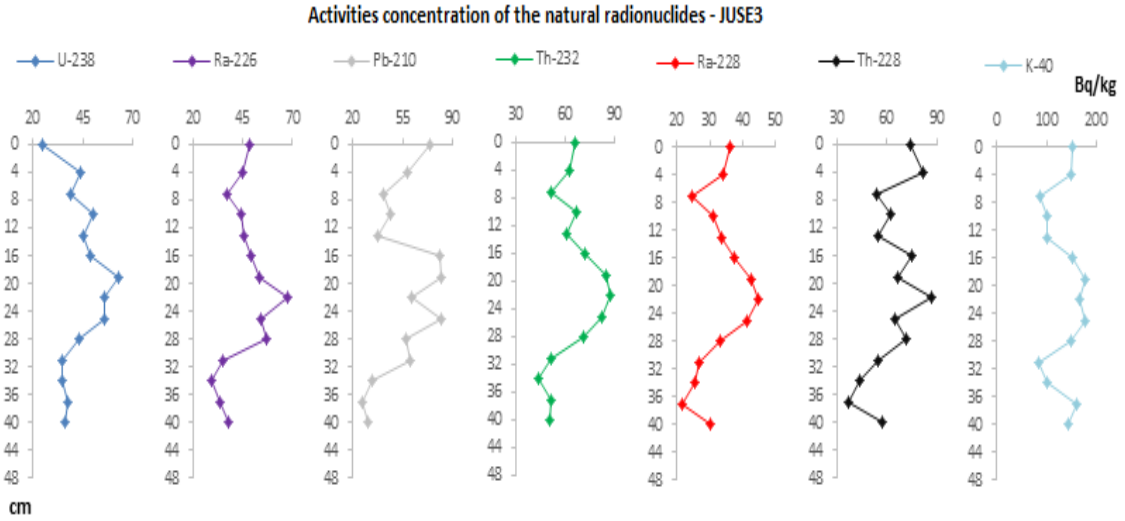

Figure 11 – Activity concentrations of the natural radionuclides in JUSE 3

The mean activity concentrations of the radionuclides ^{238}U and ^{232}Th were higher than the UNSCEAR values in the three sediment cores. The mean activity concentrations of ^{238}U in JUSE 1, JUSE 2 and JUSE 3 were 64 $Bq.kg^{-1}$, 47 $Bq.kg^{-1}$, and 44 $Bq.kg^{-1}$, respectively. For ^{232}Th, the mean activity concentrations obtained in JUSE 1, JUSE 2 and JUSE 3 were 122 $Bq.kg^{-1}$, 100 $Bq.kg^{-1}$, and 64 $Bq.kg^{-1}$, respectively. Another radionuclide that showed higher levels when compared to UNSCEAR values was ^{226}Ra; its values were higher in JUSE 1 and JUSE 2, and the mean activity concentrations obtained were 74 $Bq.kg^{-1}$ and 71 $Bq.kg^{-1}$, respectively. According to UNSCEAR, the variation of activity concentration for ^{226}Ra in global soils is between 17 $Bq.kg^{-1}$ to 60 $Bq.kg^{-1}$; these were unexpected results due to the high amount of sand in the sediment cores and because the radium retention would be impaired in these conditions. The activities concentrations of ^{40}K showed high variations through the depths of the first and third sediment cores, and it is probably due to the high

solubility of the potassium isotope, what it possibly takes a non-uniform distribution for this radionuclide.

The activity concentrations of ^{210}Pb presented high variations in JUSE 1 and JUSE 3 and this variation could be associated with the variations of dry periods in the region of Sao Paulo after the construction of the Jundiai reservoir. The dry period has a strong influence in the flooded area of the reservoir and when marginal sediment gets exposed to air, the radon gas (^{222}Rn) emanates and decays to a several short half-life radionuclides until ^{210}Pb that is carried out by the rain water.

3.2.2. Principal component analysis (PCA)

Figures 12, 13 and 14 present the results obtained in PCA between the activity concentrations of the natural radionuclides and the sediment physical-chemical parameters for JUSE 1, JUSE 2 and JUSE 3, respectively.

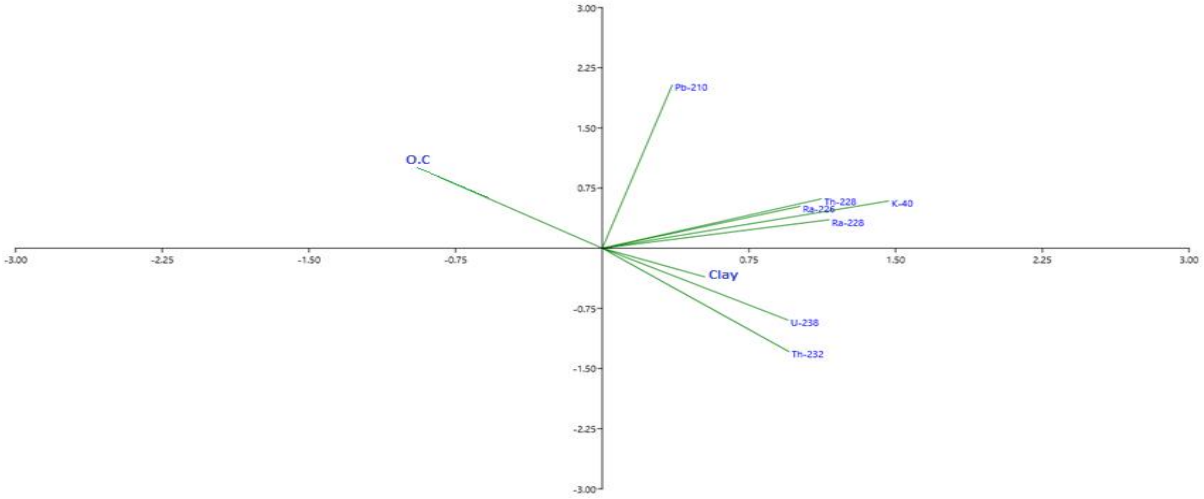

Figure 12 – PCA for JUSE 1

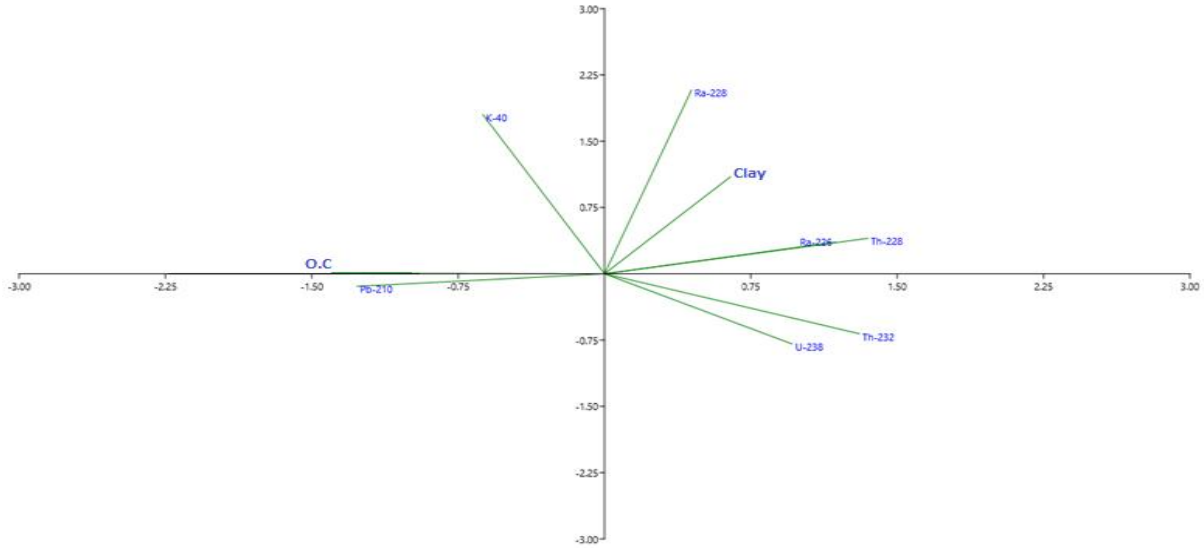

Figure 13 – PCA for JUSE 2

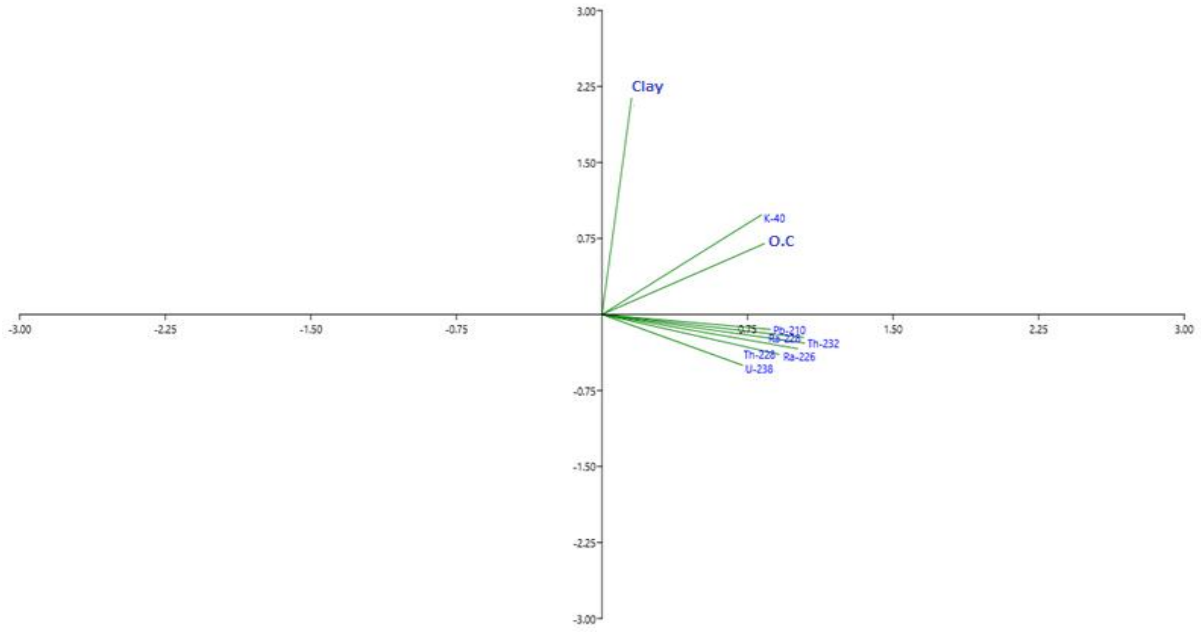

Figure 14 – PCA for JUSE 3

In general, the organic matter contents presented more statistical significance over the clay fraction for the availability of the natural radionuclides in the sediment cores. However, in JUSE 1 and JUSE 2, this association was negative. In these two cores, the amount of clay showed an insignificant association with the activity concentrations of the natural radionuclides. Other factors in the environment, such as physical-chemical parameters of the reservoir water, could be inducing the distribution of the radionuclides in the sediments. Therefore, a more detailed research is needed for a complete understanding of these radionuclides behavior in this specific environment.

4. CONCLUSIONS

The present work evaluated the activity concentrations of the natural radionuclides from ^{238}U and ^{232}Th series and ^{40}K in soil profiles and sediment cores collected in Jundiai reservoir; some natural radionuclides presented the results in higher activity concentration than UNSCEAR values. In the soil profiles, the activity concentration of ^{232}Th presented higher levels when compared to the levels in global soils. In the sediment cores, the activity concentrations of ^{232}Th and ^{238}U were also higher, however, only the activity concentrations of radium isotopes demand more detailed research and investigation. These values were higher than expected and the high contents of sand in sediment cores would impair the radium retention, despite both radium isotopes are soluble. Therefore, the amount of these isotopes in the precipitate phase at the bottom of the lake would be low.

The principal component analysis performed to verify the behavior of the natural radionuclides showed good associations of activity concentrations with soil pH and clay fraction in the soil profiles. In the sediment cores, other parameters need to be evaluated to explain the availability of the natural radionuclides.

ACKNOWLEDGMENTS

This paper was supported by *Comissão Nacional de Energia Nuclear* (CNEN) and *Instituto de Pesquisas Energéticas e Nucleares* (IPEN).

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