



Natural radionuclides in surface soils from Biritiba-Mirim reservoir, state of São Paulo, Brazil.

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1. Introduction

Soils are complex systems developed by the weathering of the rocks and structured in horizons by pedogenic processes. The solid soil phase composition is characterized by the presence of minerals, clay minerals, and organic matter, whereas the soil liquid solution is a phase that has complex chemical interactions and plays an important role in the fixation of trace elements and radionuclides [1]. Natural radionuclides are widely distributed in many different minerals, and they are transferred to the soil composition by chemical weathering, however, human interference, mainly associated with agricultural activities and industrial emissions, can increase the activity concentrations of the radionuclides from the ²³⁸U and ²³²Th decay series and ⁴⁰K in surface soils [2]. The *Biritiba-Mirim* reservoir (23°36'S 46°05'W) is located at the Upper Tiete water basin, which is responsible for water supply in the *São Paulo* Metropolitan area [3]. Few studies aimed at the analysis of natural radionuclides in surrounding soils of the Brazilian water supply reservoirs, including the reservoirs of the Upper Tiete water basin. Some of this research is part of studies developed by the *Laboratório de Radiometria Ambiental* from the *Instituto de Pesquisas Energéticas e Nucleares (LRA-IPEN)* and aimed the evaluation of natural radionuclides activities concentrations in soils and sediments of the neighboring reservoirs (*Ponte Nova, Jundiá and Taiacupeba*) [4,5,6]. In international literature is possible to find some latest studies that have evaluated the levels of natural radionuclides in soils, however, most of them are focused on the analysis of recognized contaminated areas (e.g. mining activities or nuclear industry operations) [7,2].

The anthropogenic inputs of naturally occurrence radioactive materials should be managed to prevent risks either to humans or the biota [2], especially in disturbed environments, such as artificial water reservoirs. The main objective of this paper was to evaluate the activity concentrations of ²³⁸U, ²³²Th, ²²⁸Ra, ²²⁸Th, ²²⁶Ra and ⁴⁰K in surface soils from the *Biritiba-Mirim* reservoir. Moreover, this study aimed to verify the influence of soil physical-chemical parameters (clay, silt, and sand contents, pH, organic matter, cation exchangeable capacity, and total porosity), the lithological composition, and the land use on the activity concentrations of the natural radionuclides.

2. Methodology

Surface soil samples (0-20cm) were collected in the wet period (November/2022) in 12 points, chosen according to the local lithology and land use, on the shore of *Biritiba-Mirim* reservoir (Figure 1). In the laboratory, samples were air-dried and passed through a 10 mesh (2.00 mm) sieve. Afterward, the samples were homogenized, and one quarter was taken as the aliquot for the natural radionuclides determination. Soil grain size analysis, potential of hydrogen (pH), and total porosity (TP) were determined following the *EMBRAPA* soil chemical analysis manual [8]. Soil organic matter (OM) and cation exchange capacity (CEC) were analyzed using loss-on-ignition, and exchangeable metallic cations/exchangeable acidity methods, respectively [9,10]. The activity concentrations of ²³⁸U and ²³²Th were evaluated using Instrumental Neutron

Activation Analysis (INAA), through the comparative method with certified reference materials (CRM): Lake Sediment (SL3) from International Atomic Energy Agency (IAEA), Inorganic Marine Sediment (2702) and Montana Soil II from National Institute of Standards and Technology (NIST). Approximately 200 mg of samples and CRM were irradiated for 6h at the IPEN Research Reactor IEA-R1, with thermal neutron flux of 10^{12} n.cm⁻¹, and the concentrations were measured by gamma-ray spectrometry, using a coaxial HPGe detector, ORTEC. The activity concentrations of ²²⁸Ra (²²⁸Ac, 911 keV), ²²⁸Th (average of ²¹²Pb, 238 keV, and ²¹²Bi, 727 keV), ²²⁶Ra (average of ²¹⁴Pb, 352keV, and ²¹⁴Bi, 609 keV) and ⁴⁰K (1460keV) were evaluated by gamma-ray spectrometry. Approximately 100g of the soil samples were measured in a coaxial Be-layer HPGe detector after 30 days of the sample preparation (pulverization in 115 mesh) and sealing. The calculations were performed using gamma-ray software ORTEC INTERWINNER™ 6.0 [5].

Data analysis was used for the discussion of the results: Shapiro-Wilk test of normality; two-way ANOVA to verify the influence of the lithology and land use on the activity concentrations of the natural radionuclides; Principal Components of Analysis (PCA) to check statistical similarities between soil physical-chemical parameters and the natural radionuclides activity concentrations. All statistical analyses were conducted using IBM SPSS Statistics 26.

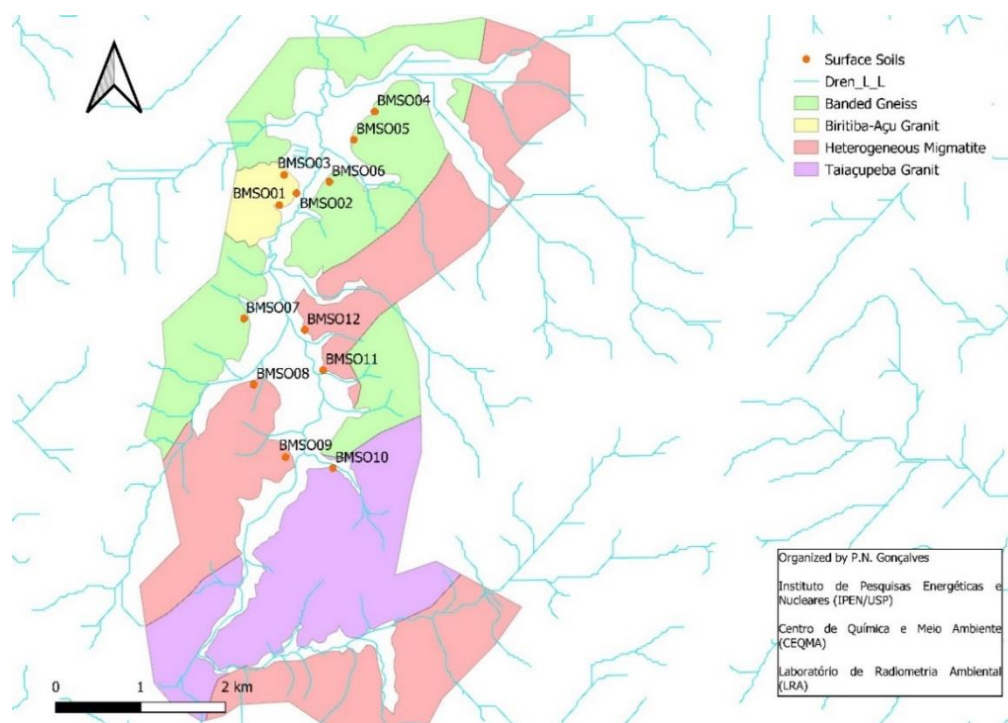


Figure 1: Sampling information and Biritiba-Mirim reservoir lithology.

3. Results and Discussion

The results of the activity concentrations (Bq.kg⁻¹) of the natural radionuclides on the surface soils from the Biritiba-Mirim reservoir, as well as information about the land use, descriptive statistics, comparison with local research and the mean levels of the activity concentrations of the radionuclides reported by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), and data analysis is shown on table 1. The activity concentrations of ²³⁸U and ²³²Th have exceeded the mean levels reported by UNSCEAR and were slightly above the local reports in most of the samples analyzed. The activity concentrations of ²²⁸Th, ²²⁸Ra, ²²⁶Ra, and ⁴⁰K remained moderately similar to respective comparisons. Data analysis has shown that only ²³²Th is influenced by the effects of local lithology and land use, and all radionuclides analyzed have followed the normal distribution, accrediting this data for the ANOVA analysis.

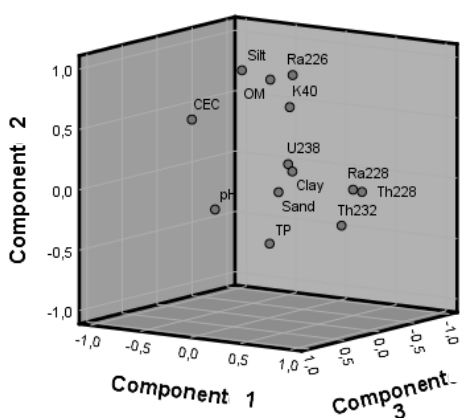
Table I: Activity concentrations (Bq.kg⁻¹) of ²³⁸U, ²³²Th, ²²⁸Th, ²²⁸Ra, ²²⁶Ra, and ⁴⁰K, descriptive statistics and comparisons, and data analysis of the surface soils from the Biritiba-Mirim reservoir.

Sample	Land use	²³⁸ U	²³² Th	²²⁸ Th	²²⁸ Ra	²²⁶ Ra	⁴⁰ K
BMSO01	Large vegetation cover	77 ± 5	120 ± 3	85 ± 10	75 ± 5	53 ± 5	237 ± 17
BMSO02	Large vegetation cover	59 ± 3	89 ± 2	62 ± 10	65 ± 4	43 ± 4	201 ± 15
BMSO03	Agricultural land	88 ± 5	177 ± 5	140 ± 14	125 ± 8	51 ± 5	413 ± 25
BMSO04	Small and medium vegetation cover	74 ± 4	99 ± 3	67 ± 8	64 ± 4	44 ± 4	97 ± 9
BMSO05	Small and medium vegetation cover	53 ± 3	104 ± 3	69 ± 11	60 ± 5	40 ± 5	106 ± 15
BMSO06	Agricultural land	95 ± 5	145 ± 4	80 ± 9	77 ± 5	44 ± 4	143 ± 11
BMSO07	Agricultural land	69 ± 9	136 ± 5	97 ± 10	80 ± 5	38 ± 3	115 ± 10
BMSO08	Agricultural land	49 ± 6	105 ± 4	97 ± 13	83 ± 6	43 ± 5	65 ± 13
BMSO09	Agricultural land	59 ± 8	104 ± 4	70 ± 8	67 ± 4	38 ± 3	108 ± 9
BMSO10	Agricultural land	69 ± 10	147 ± 5	90 ± 10	82 ± 5	28 ± 3	187 ± 15
BMSO11	Small and medium vegetation cover	79 ± 9	210 ± 8	128 ± 13	115 ± 7	30 ± 3	139 ± 13
BMSO12	Large vegetation cover	88 ± 10	101 ± 4	59 ± 7	52 ± 4	37 ± 7	259 ± 18
Descriptive statistics and comparisons							
Mean	-	71,6	128	86,9	78,7	40,7	173
St. deviation	-	4,2	11	7,3	6,3	2,1	28
Amplitude	-	49-95	89-210	59-140	52-125	29-53	65-413
UNSCEAR [11]	-	35	30	not reported	11-64	11-60	140-850
Jundiai [5]	-	25-41	49-83	35-70	22-34	32-62	85-163
Ponte Nova [4]	-	30-68	15-155	30-175	25-140	25-50	50-190
Taiacupeba [6]	-	29-62	53-100	54-111	54-93	34-64	184-417
Data analysis							
Shapiro-Wilk ρ	-	.814	.065	.113	.073	0.743	.058
ANOVA Litho. ρ	-	.944	.020*	.137	.072	.479	.280
ANOVA Land ρ	-	.781	.008*	.093	.057	.748	.718

* p<0,05 rejects the null hypothesis, suggesting that the lithology and land use have statistical effect on the ²³²Th activity concentrations.

The results of the PCA and soil physical-chemical parameters are shown in figures 2a and 2b, respectively. The figure 2b of is displayed in two axes; the principal axis (on the left) represents values in percentage and includes sand, clay, silt, and TP; the secondary axis (on the right) represents CEC, pH, and OM.

(2a)



(2b)

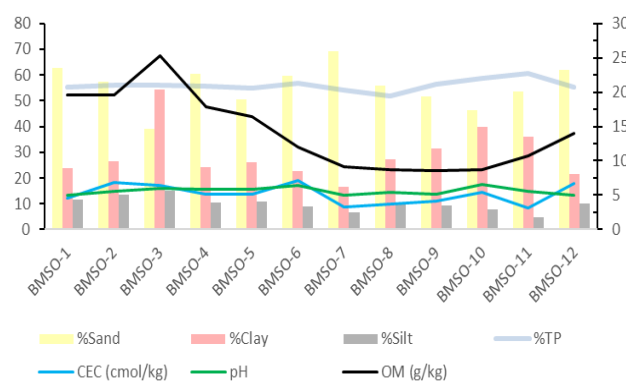


Figure 2: Results of the Principal Components of Analysis (2a) and Soil physical-chemical parameters (2b).

The figure 2b) presents the PCA results; three principal components of analysis can be observed, and represents a cumulative variance of 78%, using the Varimax rotation method with Kaiser normalization. The

results showed a strong correlation between ^{238}U and clay content, whereas ^{226}Ra and ^{40}K were associated with CEC, OM, and silt. The radionuclides from the ^{232}Th decay series (^{228}Ra and ^{228}Th) have a strong association with the principal component and stayed away from the other parameters, suggesting that the lithology, the land use, or the decay processes are controlling more significantly the activity concentrations of these radionuclides. The different associations between the two isotopes of radium reinforce this statement. The isotope ^{226}Ra from the ^{238}U decay series, despite having the same geochemical behavior that ^{228}Ra , is associated with other components.

4. Conclusions

The achievements of this study pointed to consistent results of ^{40}K , ^{226}Ra , ^{228}Ra and ^{228}Th in comparison with UNSCEAR mean values and local data, however, the activity concentrations of ^{238}U and, mostly ^{232}Th , were higher than these references and need further investigation. The findings of this research will be complemented with the dry period (August/2023) analysis, wherein the same work will be performed to verify the influence of the seasonality on the activity concentrations of the natural radionuclides analyzed.

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