Sequential Determination of U and Th Decay Series in Santana Cave, Southwest Brazil

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Abstract. *Parque Estadual Turístico do Alto Ribeira* (PETAR) is located in the South-western part of São Paulo State, in the Ribeira Valley. In this national state park a large number of caves are found, which are among the most visited of the country. These caves, located in a karstic zone, are characterized by the presence of carbonaceous rocks frequently fractured and collapsed. Although, carbonates (dolomites and calcitic rocks) usually have low U content, this element can be found in the structure of the surrounding rocks. This paper aims to determine ^{238}U, ^{234}U, ^{226}Ra and ^{210}Pb concentration in samples of rock, soil, river water and sediment, in Santana cave. The radionuclide ^{238}U was determined by alpha spectrometry using a surface barrier detector. ^{226}Ra and ^{210}Pb were determined by measuring the gross alpha and beta activity on a gas flow proportional counter.

Keywords: Radionuclides, Santana Cave, carbonate rock.
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1. INTRODUCTION AND METHODOLOGY

The *Parque Estadual Turístico do Alto Ribeira* (PETAR) is located in Iporanga, South-western part of São Paulo State, 350km far from São Paulo City and approximately 100 km from the Atlantic coast, in the Ribeira Valley. In this national state park a large number of caves are found, which are among the most visited of the country. Caves located in karstic zones are characterized by the presence of carbonaceous rocks frequently fractured and collapsed. Although, carbonates (dolomites and calcitic rocks) usually have low U and Th content, these elements can be found in the structure of the surrounding rocks. PETAR accounts for more than 250 caves. For this study, Santana Cave was chosen since it is the most visited one. It is crossed by a river, Roncador, from which four water samples were collected: one up stream (1), two inside (2 and 3) and one downstream the cave (4). One water sample was also collected from a travertine inside Santana cave (TRV). The water sampling was carried out every season in order to verify correlation with seasonal variation. In one campaign sediment samples were collected in Roncador River in the same point as the water.

Santana Cave has an extension of 5040 m and is formed by several galleries, some of than are open for public visitation. Rock samples were collected in four galleries: Torres, Cristo, Descanso and Flores. Soil samples were collected in all galleries except for Flores.

A sequential method was applied for the determination of ^{238}U, ^{226}Ra and ^{210}Pb by using ion exchange resins and gravimetric radiochemistry separation. Alpha spectrometry and gross alpha and beta counting were used for the measurement of the activity concentrations[1, 2].

2. RESULTS AND DISCUSSION

Table 1 shows the results for the activity concentration of ^{238}U, ^{226}Ra and ^{210}Pb in the water samples collected in Roncador River. Uranium content in water showed a wide range of variation in concentration in different time periods of collection. Collections made in the rainy period (spring and summer) presented values that are much smaller than the value presented for the same point in the dry period (fall and winter) showing a clear seasonal variation. The travertine sample collected in summer presented a value that is one order of magnitude higher than the other points.

TABLE 1 – Activity concentrations of U, mBq L^{-1}, in the Roncador River water and travertine samples

	Spring	Summer	Fall	Winter
		^{238}U (mBq L^{-1})		
U1	ND	0.37±0.06	561±53	200±18
U2	2.8±0.4	1.5±0.1	560±56	387±22
U3	26±2	1.2±0.1	ND	117±10
U4	6.7±0.9	0.92±0.08	562±49	ND
UTRV	ND	21.7±0.4	354±20	790±60
		^{226}Ra (mBq L^{-1})		
Ra1	< 1,9	8.9±1	3.9±0.3	3.70.2
Ra2	< 2,9	7.7±0.5	ND	3.50.8
Ra3	< 1,7	7.3±1	4.3±1	ND
Ra4	3.3±0.2	5.5±1	3.0±0.6	< 2.8
RaTRV	ND	5.6±1	5±1	6.1±0.3
		^{210}Pb (mBq L^{-1})		
Pb1	6.8±0.4	18±2	6.0±0.1	12.9±0.2
Pb2	4.5±1	18.0±0.3	ND	13.6±3
Pb3	4.2±1	12.0±0.7	12.5±1	ND
Pb4	10±1	11.7±0.4	10.3±1.5	13.8±1.1
PbTRV	ND	17±2	11.1±0.7	10.2±0.7

Values for activity concentration of U found in literature[3, 4, 5] varies from 0,08 to 919 mBq L^{-1}. In the samples analyzed in this study its concentration varies from 0,34 $mBqL^{-1}$ to 790 $mBqL^{-1}$. The great variation observed for U concentration in the water samples possibly can be explained due to the concentration factor once in the dry

season the water level is much smaller than the level observed in the rainy period and higher concentration of carbonate ions can be present rising the complexation effect over uranium.

Radium-226 in natural water is derived mainly by the interaction between the water and radium-bearing materials, such as rocks, soil and ore deposits due to its great solubility[6, 7]. In surface water, radium concentrations[8] generally range from 0.01 to 0.1 Bq L^{-1}. In the analyzed samples ^{226}Ra concentrations varied from < 1.7 to 8.9 mBq L^{-1}. These values are lower than that presented for Southeastern region of Brazil and worldwide as registered in literature[9]. These low values can indicate that water is leaching rocky layers depleted in radium due to its great solubility.

^{210}Pb is supplied to body waters from atmospheric input, run-off and the "in situ" decay of ^{226}Ra its precursor in the water column. Lead mobility in water depends on the pH, hardness, sulfate and carbonate ion concentration and the presence of organic complexation agents[10]. Santana Cave samples presented activity concentrations for ^{210}Pb varying form 4.2 to 18 mBq L^{-1}. As for ^{226}Ra, these values are lower than that the mean values of the region. As ^{210}Pb is a daughter of ^{226}Ra in the U series the low content of radiogenic lead probably is related to low content of its father.

Both, ^{226}Ra and ^{210}Pb, showed no seasonal variation. The great difference presented between U and its nuclides daughters in fall and winter times deserve further investigations.

For sediment, soil and rock results are presented in Table 2. It can be seen that the rock concentrations are smaller than the ones observed in soil.

TABLE 2 – Activity concentrations of ^{238}U, ^{226}Ra and ^{210}Pb, in Bq kg^{-1}, in soil, rock and sediment samples

	^{238}U	^{226}Ra	^{210}Pb	
		Soil		Location
SSD	68± 2	ND	ND	Descanso Gallery
SLST	29± 1	ND	ND	Torres Gallery
SSC	15,7± 0,5	68±7	70± 7	Cristo Gallery
		Rock		
RSF	2,9±0,1	16±2	55± 5	Flores Gallery
SC	17,6± 0,6	40±4	53± 5	Cristo Gallery
		Sediment		
sed1	17,8± 0,6	52±5	67± 7	upstream
sed2	10,4± 0,3	51±5	42± 4	Inside cave
sed3	5,7± 0,2	38±4	42± 4	Inside cave
sed4	9,8± 0,3	25±3	36± 4	downstream
sed5	7,9± 0,2	53±5	31± 3	downstream

Considering ^{238}U concentrations, rock samples from Santana Cave are in the range registered for in literature for pure carbonate spelothems. Soil samples present higher concentrations for Descanso and Torres Galleries. This fact is probably due to the contribution of detritic material. In the sample collected in the Cristo Gallery the concentrations is almost the same as that observed for rock samples indicating no

contribution of supergene material. In the Flores Gallery there's no unconsolidated material forming soil.

The activity concentrations of ^{226}Ra and ^{210}Pb in soil were greater than that presented for rock samples and the same considerations made for U could be applied.

The greater ^{238}U and ^{210}Pb concentration in sediment was obtained in the samples collected before water entrance and became smaller as water runs through the cave. A possible explanation could be the fact that inside the cave the water became enriched in dissolved carbonate ions that raise the complexation effect.

3. CONCLUSIONS

It was observed that uranium concentrations in water samples present seasonal variations while ^{226}Ra and ^{210}Pb are almost constant over the different seasons. The concentration of the radionuclides analyzed in this study in rock and soil samples indicates detritic contribution since higher values was found in the most visited galleries. Sediment analysis indicates that the complexation by carbonate ions is an important factor controlling U and Pb concentrations.

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