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# DETERMINATION OF THE NATURAL RADIONUCLIDES $^{226}$Ra, $^{228}$Ra AND $^{210}$Pb ACTIVITY CONCENTRATIONS IN THE MINERAL WATERS FROM THE CITIES OF MONTE ALEGRE DO SUL AND SOCORRO, SP

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## ABSTRACT

The use of mineral water for medical treatment is widespread throughout the world, and several mineral water springs have considerable concentrations of natural radionuclides from the $^{238}$U and $^{232}$Th series. The estimate of probable adverse effects on human health that may occur because of the ingestion or inhalation of radioactive substances present in these waters is relevant in Radiological Protection. The objective of this study was to determine the activity concentrations of the radionuclides $^{226}$Ra, $^{228}$Ra and $^{210}$Pb in the mineral water springs of Monte Alegre do Sul and Socorro, cities of the Paulista Water Circuit, collected in the seasons of summer, autumn, winter and spring of 2018; these cities have several mineral water springs distributed in many parts of them. The activity concentrations for the mineral waters from Monte Alegre do Sul ranged for $^{226}$Ra from limit detection of 2.2 ± 0.2 mBq L$^{-1}$ to 23.0 ± 0.2 mBq L$^{-1}$, from limit detection of 3.7 ± 0.1 mBq L$^{-1}$ to 16.0 ± 0,8 mBq L$^{-1}$ for $^{228}$Ra and for $^{210}$Pb from the limit detection of 4.9 ± 0.4 mBq L$^{-1}$ to 58 ± 5 mBq L $^{-1}$; for Socorro ranged from limit detection of 2.2 ± 0.2 mBq L$^{-1}$ to 11.0 ± 0.9 mBq L$^{-1}$ for $^{226}$Ra, from limit detection of 3.7 ± 0.1 mBq L$^{-1}$ to 48 ± 3 mBq L$^{-1}$ for $^{228}$Ra and for $^{210}$Pb from limit detection of 4.9 ± 0.4 mBq L$^{-1}$ to 49 ± 4 mBq L $^{-1}$.

## 1. INTRODUCTION

The natural radioactivity present in groundwater systems is mostly due to the dissolved radioactive elements in water and the naturally occurring radioactive materials in the composition of the rocks. The water mineralization occurs when elements and radionuclides present in soil and rocks composition undergo to leaching and these elements are transported to the groundwater. The mineral waters are frequently used for human consumption, in thermal baths due to its therapeutic properties and in medicine, which increases the risk of internal and external exposure to radiation [1].

Mineral water, according to Decree Law No. 7.841 of 08.08.1945 is defined as: "Mineral waters are those from natural or artificially collected sources that have chemical composition or physicochemical properties distinct from common waters with characteristics that give them a medication action" [2].

According to the World Health Organization, the recommended effective dose level reference is 0,1 mSv.y$^{-1}$, therefore the radiological characterization of these waters is a relevant subject for public health prevention.

The most important source of natural radioactivity is from the natural radionuclides present in the $^{238}U$ and $^{232}Th$ decay series, including $^{226}Ra$ and $^{210}Pb$ from $^{238}U$ series, and $^{228}Ra$ from $^{232}Th$ series [3]. The radionuclides that represent more concern through water ingestion are the radium isotopes ($^{226}Ra$ and $^{228}Ra$) and radon ($^{222}Rn$); the high solubility of these radionuclides increases the activities concentrations in the water [4]. $^{210}Pb$ has a particle-reactive behavior and this radionuclide is normally associated to the organic matter fraction [5].

Some studies showed that mineral waters can have high concentrations of the natural radionuclides $^{226}Ra$ and $^{222}Rn$ originally dissolved when compared with natural waters. However, in relation to therapeutic practices based on water intake, immersion thermal baths and the use of medicinal muds, the radionuclides $^{210}Pb$ and $^{228}Ra$ when present are of relevant importance, since they contribute in large part to the internal and external irradiation of the individuals [6-7].

The objectives of this work were to determine the activities concentrations of $^{226}Ra$, $^{210}Pb$ and $^{228}Ra$ in mineral waters from the cities of Monte Alegre do Sul and Socorro, both located in the "Paulista Water Circuit" in the state of São Paulo. The seasonality influence was also studied to verify the correlation between the activity concentrations of the radionuclides with the different environmental processes that occur in which season of the year.

## 2. METHODOLOGY

### 2.1 Study Area

The cities of Monte Alegre do Sul and Socorro are part of the "Paulista Water Circuit", located in the northeast region of the state of Sao Paulo. This circuit is also formed by the cities Águas de Lindóia, Amparo, Holambra, Jaquariúna, Pedreira, Lindóia and Serra Negra.

The city of Monte Alegre do Sul (22º40'55" S and 46º40'51" W) is located in the Mantiqueira Sierra and has the mineral water springs Bom Jesus, Bica, Balneário Municipal, Paulo Lemos Girardelli, and Índia. The city of Socorro (22º35'29" S and 46º31'44" O), which is also located in the Mantiqueira Sierra, has the mineral water springs Pompéia 1, Pompéia 2, Lions, Calafiori, Juventude Dr. Maneco, Mar del Plata, Vitório Fávaro, Santo Seti e Cristo.

Both cities have hydromineral resorts with crystal clear waters and a lot of tourists visit the cities for that reason [8].

The cities are in an area which is composed by orthogneiss complexes of the sub-alkaline granitic series and portions of migmatites gneisses. This geological environment is characterized by faults and fractures which is associated with a good hydrogeological potential represented by an irregular fissure aquifer. However, this good hydrological potential is also associated with high risks of groundwater contamination and pollution due to the features of these rocks [9].

Figure 1 presents the map of the Paulista Water Circuit with the cities Monte Alegre do Sul and Socorro, and the study area lithology.

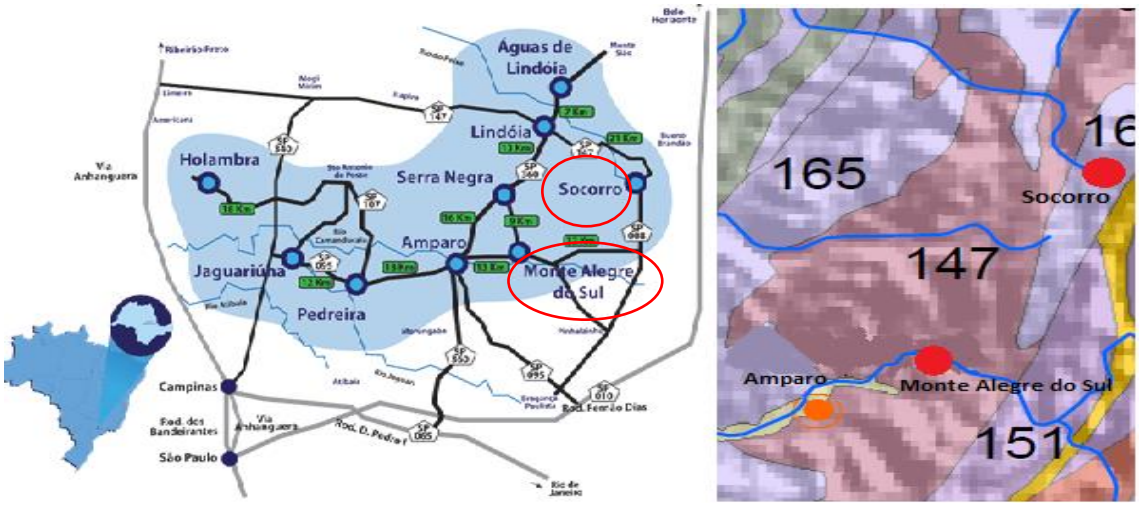


**Figure 1: Map of the Paulista Water Circuit with the cities Monte Alegre do Sul and Socorro, and the study area lithology**
http://www.rotadasaguas.com.br/circuito-das-aguas-paulista/mapa-circuito-das-aguas-paulistas-sp-rota-das-aguas-2/

## 2.2 Sampling

The mineral water samples were collected during a period of 12 months, in summer, fall, winter and spring seasons of 2018. From each mineral water spring were collected 15L of mineral water for the radiochemical analysis of $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$; it was also collected a sample of potable water in each sampling of mineral water. The collected samples were acidified with 50% $HNO_3$ in order to maintain the pH ≤ 2,0 to avoid adsorption of the radionuclides to the polyethylene flask [10].

## 2.3 $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$ determination

The analyzes were performed in duplicate, with the mineral water samples from each spring that were concentrated from 2 L to 1 L. As an initial step of the methodology stable Ba and Pb carriers and $H_2SO_4$ (3 mol $L^{-1}$) were added under heating and stirring for precipitation of $(BaRaPb)SO_4$, followed by dissolution with nitrilotriacetic acid (NTA) at alkaline pH and re-precipitated in acid pH with sulfate.

The precipitate containing $^{226}Ra$ and $^{228}Ra$ was dissolved with EDTA, re-precipitated with sulfate in acid pH as $Ba(^{226,228}Ra)SO_4$ and filtered. In the supernatant that contain $^{210}Pb$, NaS was added to precipitate PbS and the precipitated was dissolved with 50% $HNO_3$ for the final precipitation as $^{210}PbCrO_4$ with a solution of sodium chromate.

The $^{226}Ra$ and $^{228}Ra$ concentrations were determined by gross alpha and beta counting of the $Ba(Ra)SO_4$ precipitate and the $^{210}Pb$ concentration through its decay product, $^{210}Bi$, by measuring the gross beta activity of the $PbCrO_4$ precipitate. Both radionuclides were determined in a low background gas flow proportional detector Berthold, model LB770-2. For the methodology validation, the reference materials Pacific Ocean Sediment 367 and Irish Sea Sediment 385, both from IAEA were analyzed yielding results in agreement with the certified values [11]. The detection limits - DL for the studied radionuclides determined by gross alpha and beta methodology were 2.2 mBq $L^{-1}$ for $^{226}Ra$, 3.7 mBq $L^{-1}$ for $^{228}Ra$ and 4.9 mBq $L^{-1}$ for $^{210}Pb$ [12].

## 3. RESULTS AND DISCUSSION

In Table 1 are presented the activity concentrations of the natural radionuclides $^{226}$Ra, $^{228}$Ra and $^{210}$Pb, mBq L$^{-1}$, determined in summer, fall, winter and spring seasons of 2018 in the mineral springs of the cities Monte Alegre do Sul and Socorro.

For the city of Monte Alegre do Sul the mineral water activity concentrations ranged for $^{228}$Ra from DL to 16 ± 0.8 mBq L$^{-1}$, for $^{226}$Ra from DL to 23 ± 0.2 mBq L$^{-1}$ and for $^{210}$Pb from DL to 58 ± 5 mBq L$^{-1}$; the highest activity concentration determined was for $^{210}$Pb in most of the mineral water springs of this city.

For the city of Socorro the mineral waters activity concentrations ranged for the radionuclide $^{228}$Ra from DL to 48 ± 3 mBq L$^{-1}$, for $^{226}$Ra from DL to 11 ± 0.9 mBq L$^{-1}$ and for $^{210}$Pb from DL to 49 ± 4 mBq L$^{-1}$, besides of $^{210}$Pb had presented the highest activity concentrations in the mineral waters of Socorro, the radionuclide $^{228}$Ra also presented high activity concentrations when compared with $^{226}$Ra in the majority of the samples.

Figure 2 presents the mean activity concentrations of the studied radionuclides for both cities. In this Figure is possible to observe that the highest activity concentrations were obtained for the radionuclide $^{210}$Pb in almost all springs of both cities and the spring Paulo Lemos presented the highest activity concentration of $^{210}$Pb. On the other hand, the Santo Seti spring presented the highest activity concentrations for the natural radionuclides $^{226}$Ra and $^{228}$Ra.

Comparing the activity concentrations of the two cities, Socorro presented for all radionuclides higher concentrations when compared with Monte Alegre do Sul in the most springs.

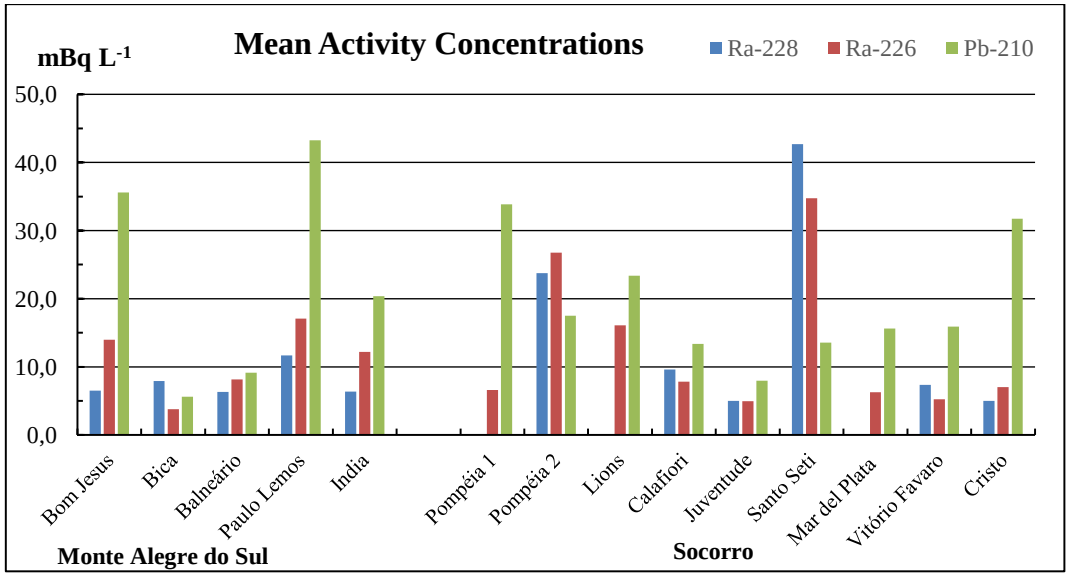


**Figure 2: Mean activity concentrations, mBq L$^{-1}$, of the radionuclides $^{226}$Ra, $^{228}$Ra and $^{210}$Pb in the mineral water springs of the cities of Monte Alegre do Sul and Socorro**

**Table 1: $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$, mBq $L^{-1}$, activity concentrations of the mineral water springs for the cities of Monte Alegre do Sul and Socorro in summer, fall, winter and spring of 2018**

**Monte Alegre do Sul**

| | Summer | | | Fall | | | Winter | | | Spring | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Spring** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** |
| **Bom Jesus** | 7.3 0.5 | 9.3 1.1 | 20.0 1.0 | < DL | 22.7 0.3 | 37.3 0.9 | 6.0 0.3 | 6.0 0.2 | 47 2 | 6.1 0.3 | 18 2 | 38 2 |
| **Bica** | 4.8 0.5 | < DL | 6.8 0.9 | 11.0 0.5 | 3.8 0.2 | 4.4 0.5 | < DL | < DL | < DL | < DL | < DL | < DL |
| **Balneário** | 6.3 0.3 | 4.1 0.1 | 8.7 0.1 | < DL | 11 1 | 10.8 0.7 | < DL | 9.7 1.3 | 8.0 0.7 | < DL | 8 1 | < DL |
| **Paulo Lemos** | 6.0 0.3 | 19 1 | 59 3 | 9 0.4 | 17 2 | 31 3 | 16 0.8 | 18 1 | 49.9 0.5 | 16 0.8 | 15 1 | 33 3 |
| **India** | < DL | 10.0 0.5 | 11.5 0.1 | 7.0 0.3 | 10 1 | 19.9 0.7 | 7.0 0.4 | 23 0.2 | 35 2 | 7.4 0.4 | 5.5 0.4 | 15 1 |
| **Potable Water** | 6.0 0.3 | 8 1 | < DL | 13 0.7 | 4.1 0.4 | < DL | < DL | 4.0 0.2 | < DL | < DL | 5.0 0.2 | 7.2 0.6 |

**Socorro**

| **Spring** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** | **$^{228}Ra$-SD** | **$^{226}Ra$-SD** | **$^{210}Pb$-SD** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Pompéia 1** | < DL | 6.0 0.3 | 39 1 | < DL | 8 1 | 30 1 | < DL | 6.0 0.3 | 23 1 | < DL | < DL | 44 1 |
| **Pompéia 2** | 11 0.6 | 10 1 | 23 2 | 6.0 0.3 | 8 1 | 22 2 | 3.9 0.1 | 8.0 0.4 | 12 1 | 39 2 | 8.1 0.4 | 13 3 |
| **Lions** | < DL | 7 1 | 49 4 | < DL | 4.3 0.2 | 6.5 0.4 | < DL | < DL | < DL | < DL | 37 2 | 15 2 |
| **Calafiori** | < DL | 11.0 0.9 | 11 1 | 9.6 0.5 | 6 1 | 21 1 | < DL | 7.0 0.4 | 12 1 | < DL | < DL | 9 1 |
| **Juventude** | 5.0 0.8 | 6.5 0.6 | 5.0 0.8 | < DL | 4.2 0.4 | 10.9 0.6 | < DL | < DL | 8 1 | < DL | 4.2 0.4 | < DL |
| **Santo Seti** | - | - | - | 32 2 | 37 2 | 9.7 0.6 | 48 3 | 34 2 | 20 2 | 48 2 | 34 2 | 11 1 |
| **Mar del Plata** | < DL | 6.7 0.8 | 8.9 0.5 | < DL | 7.4 0.3 | < DL | < DL | 4.7 0.2 | 28 2 | < DL | < DL | 10 1 |
| **Vitório Favaro** | < DL | 4.8 0.9 | 8.6 0.2 | 14.0 0.7 | 6.2 0.2 | 23.3 0.5 | 4.0 0.2 | 5.7 0.4 | < DL | 4.0 0.2 | < DL | 13 1 |
| **Cristo** | - | - | - | 5.0 0.3 | 7.6 0.3 | 44 2 | < DL | 6.4 0.4 | 20 1 | < DL | < DL | 17 2 |
| **Potable water** | 7.0 0.3 | 6.6 0.3 | < DL | 8.0 0.4 | < DL | < DL | < DL | 4.20 0.01 | < DL | < DL | < DL | < DL |

- not collected
DL: detection limit

The Ministry of Health [13] established the maximum permissible values – MPV to potable water of 1.0 Bq $L^{-1}$ for the radionuclide $^{226}Ra$ and 0.1 Bq $L^{-1}$ for the radionuclides $^{228}Ra$ and $^{210}Pb$; for the three radionuclides studied in this work none exceeded the established limit of Ministry of Health.

In Figures 3 and 4 the mean activity concentrations, mBq $L^{-1}$, of the radionuclides $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$ by rainy and dry season are presented, respectively, for the mineral water springs of the cities of Monte Alegre do Sul and Socorro.

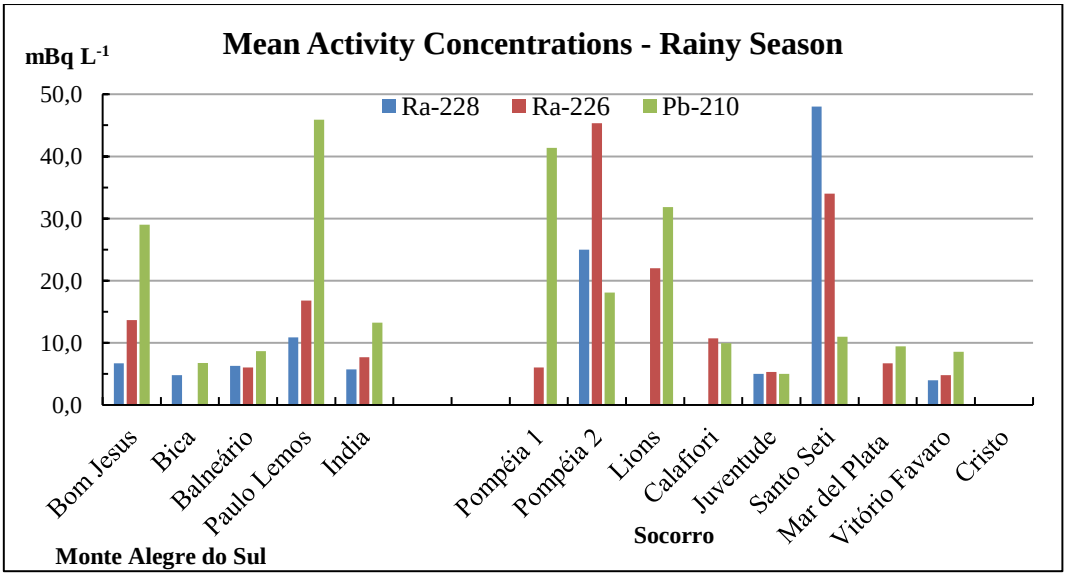


**Figure 3: Mean activity concentrations, mBq $L^{-1}$, in the rainy season of the radionuclides $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$ in the mineral water springs of the cities of Monte Alegre do Sul and Socorro**

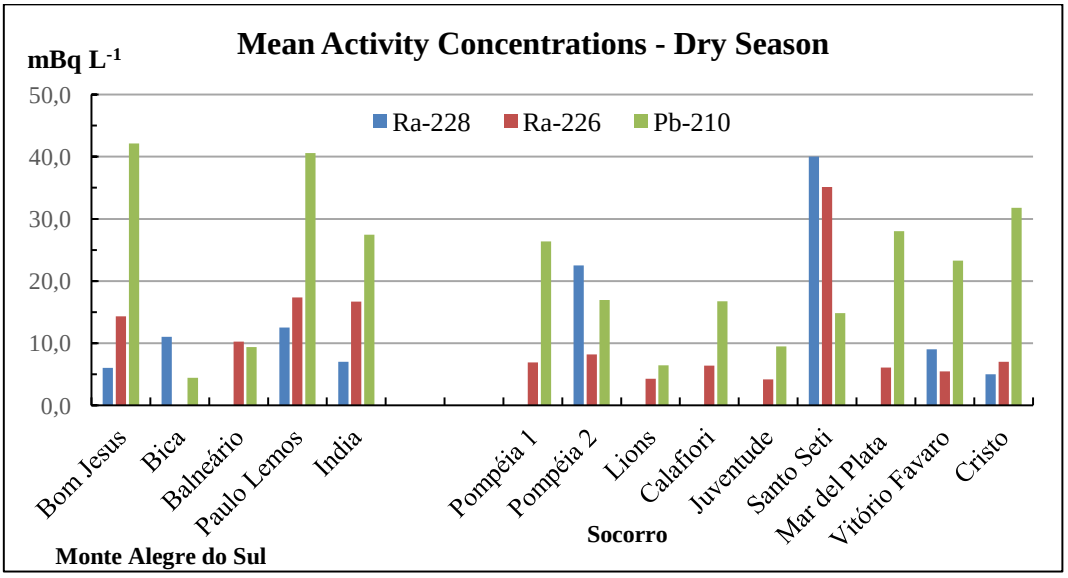


**Figure 4: Mean activity concentrations, mBq $L^{-1}$, in the dry season of the radionuclides $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$ in the mineral water springs of the cities of Monte Alegre do Sul and Socorro**

For the mineral waters from Monte Alegre do Sul it is possible to observe that the highest activity concentrations were obtained in the dry season for the most radionuclides studied and springs. The same was observed for the city of Socorro, although the Cristo spring had presented values of activity concentrations only in the dry season for the three radionuclides studied and the springs Pompéia 1, Pompéia 2, Lions and Santo Seti presented the highest activity concentrations in the rainy season. In general, for both cities, the highest activity concentrations were obtained in the dry season.

Analyzing each radionuclide separately, the same behavior was observed for the most springs of the city of Monte Alegre do Sul higher values of activity concentrations in the dry season and for the city of Socorro only for the springs Calafiori, Juventude and Santo Seti for $^{210}$Pb, and Mar del Plata Vitório Favaro and Cristo.

The potable water for both cities, presented activity concentrations close to the DL values of the methodology used in the radionuclides determination and also results slightly higher in the dry season.

## CONCLUSION

The present work determined the activity concentration of the natural radionuclides $^{226}$Ra, $^{228}$Ra and $^{210}$Pb in the mineral water springs of the city of Monte Alegre do Sul and Socorro, cities that belong to Paulista Water Circuit, located in the state of São Paulo.

The highest activity concentrations were obtained for the radionuclide $^{210}$Pb in almost all springs of both cities and the activity concentrations determined in the mineral water spring from the city of Socorro presented higher activity concentrations than Monte Alegre do Sul, mainly for the radionuclides $^{228}$Ra and $^{226}$Ra.

The concentrations obtained of the natural radionuclides $^{228}$Ra, $^{226}$Ra and $^{210}$Pb in the mineral waters of the cities Monte Alegre do Sul and Socorro did not exceed the limits established by the Ministry of Health.

Comparing the results obtained for the natural radionuclides studied, for both cities, the highest activity concentrations were obtained in the rainy season.

This paper presented the first results of the radionuclides $^{228}$Ra, $^{226}$Ra and $^{210}$Pb activity concentrations in mineral waters from two cities that belongs to the Paulista Water Circuit, Monte Alegre do Sul and Socorro, and these results can contribute for the assessment of the committed effective dose due to the ingestion of these mineral waters.

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