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Natural radionuclides, ^{226}Ra, ^{228}Ra and ^{210}Pb, determined in mineral water springs from Parque das Águas de Caxambu, and assessment of the committed effective doses

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ABSTRACT

The increase of mineral water consumption and its medicinal use results in the necessity of characterization of these waters sources, once that water is a vital part of human diet. In the mineral waters, besides stable elements, responsible of the chemical composition, the presence of natural radionuclides from the ^{238}U, ^{232}Th, ^{235}U series and ^{40}K gives the radiation property. The incorporation of these radionuclides through the ingestion and external treatment of mineral waters are a very important point, due the ionizing radiation of these radionuclides are harmful to the organism. The largest mineral water park of the world is situated in Brazil, in the city of Caxambu, called "Parque das Águas de Caxambu". In this park are 12 fountains distributed in the park, also a tubular well of 60 meters of depth which regularly provide water spouts, geyser, and another spring located inside the Gloria Hotel. Therefore, the aim of this work was to evaluate the activity concentrations of the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in the mineral waters springs collected at the "Parque das Águas de Caxambu" and in the Gloria Hotel, as well as to estimate the committed effective doses due to the consumption of these waters. In six campaigns, the radionuclides with the highest concentrations were ^{226}Ra and ^{228}Ra in the springs D. Ernestina, Beleza and Venâncio. These springs also presented the highest values of the committed effective dose.

1. INTRODUCTION

According to the mineral summary of Departamento Nacional de Produção Mineral - DNPM [1], the consumption of mineral water have been increasing year by year, with a global consumption in 2014 6.2% greater than 2013 (which already had a consumption 7.0% greater than 2012),fact that reinforces the importance of the characterization and regulation of the mineral waters.

Mineral waters are defined as those that comes from natural springs or that are artificially collected with chemical composition or physical chemical properties which imbues them with medicinal action that distinguishes them from ordinary water [2]. There is another definition which separates natural from mineral water based on mineral concentration levels that is applied to bottled water; this threshold is defined by law [3].

Chemical composition of mineral water is the result of soil and water interaction and depends on the soil geology, because the chemical elements are in these waters through the leaching and dissolution process, according to Fig. 1 where the first step (A) represent the rainfall infiltration, the second step (B) the mineralization of this water and the last step (C) the replenishment of water in springs and wells as mineral water. However, another characteristic what came from these process is the natural radiation of natural radionuclides; in fact, all minerals contain radionuclides of natural origin [4].

These natural radionuclides, also called primordial radionuclides, are from ^{235}U, ^{238}U e ^{232}Th decay series and from before the formation of Earth. They can be found in water, soil and air and, together the cosmogenic radiation and ^{40}K, contribute with the major human radiation exposure. Also, the natural radiation is responsible for about 2/3 of committed effective dose in the population [5].

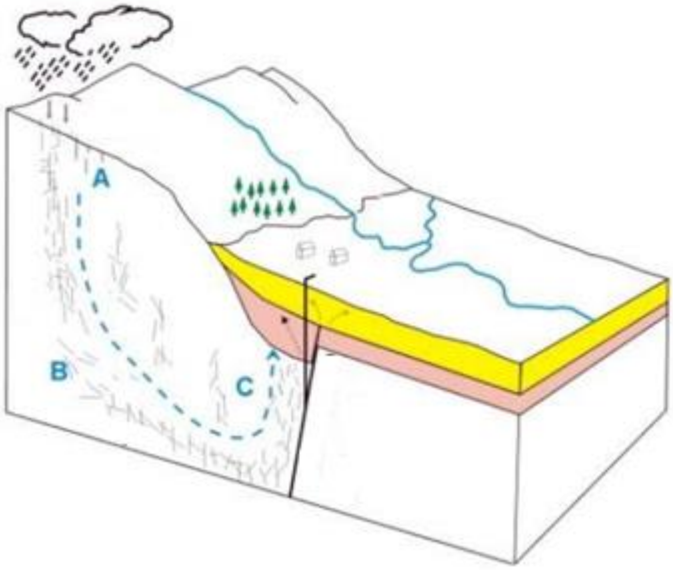

Figure 1: Water mineralization process.

Radon, radium and uranium isotopes are of great concern from the point of view of health risk due to its larger solubities; thorium isotopes, and radionuclides ^{210}Pb and ^{210}Po are also important in radiation dose, they have a particle-reactive behavior and except in specific cases where there is a high concentration of suspended organic material, they are at lower concentration levels than the previous ones [6][7][8].

In relation to the therapeutic practices based on the ingestion of water, immersion bath and medicinal mud, the natural radionuclides, when presents, are a major contribute to the internal and external irradiation of the individuals. Rn-222 is generally present in mineral waters in higher levels when compared to other radionuclides, it is often the most contributing to the effective dose in man and the risk of cancer arising from these activities [9].

Concentrations of ^{226}Ra and ^{228}Ra in mineral waters can reach values higher than 1.0 $Bq.L^{-1}$ and 0.1 $Bq.L^{-1}$, respectively, which are the standard values established to potable water consumption in Brazil according by Ministry of Health [10].

Crenotherapy, one of the mainly ways of mineral water is used, is the medicinal use of these water as a health treatment complement. This practice, also known as balneology, appeared in Brazil with the Portuguese colonization and it is common in cities with thermal parks, applied as immersion baths, steam room, water intake and inhalation [11][12].

Therefore, the crenotherapy practice and the fact that in many places of the world these waters are the exclusive source of potable water in their diet make aware of the necessity, in the radioprotection vision, of dose studies and the presumable effects in the human health [13][14].

In termal parks as Caxambu's park, the waters are used as health therapy, as diuretic waters, cathartic waters and anti-inflammatory waters. Though there is few studies conducted about natural radioactivity in Caxambu, such as the study performed by Negrão 2012 [15] at Parque das Águas of Caxambu, which determined relevant activity concentrations of ^{226}Ra and ^{228}Ra in some springs. In the author's work, the committed effective doses were calculated and exceed in almost all springs the WHO recommended level of 0.1 mSv.a^{-1}.

Thus, studies of the committed effective dose in the mineral water consumption and its use for health treatment related to the activity concentrations of radionuclides are very widespread for mineral water parks and bottled drinking waters[16][17][9].

Therefore, the aim of this work was to evaluate the activity concentrations of the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb in mineral waters springs collected in the "Parque das Águas de Caxambu" and in the Gloria Hotel, as well as to estimate the committed effective doses due to the consumption of these waters.

2. EXPERIMENTAL

2.1. Study Area

The study was performed at Caxambu, Minas Gerais, one of the cities of "Circuito das Águas" Fig.2, where exists one of the most famous places by the large mineral water consumption and crenotherapy, in cities of Baependi, Cambuquira, Campanha, Carmo de Minas, Caxambu, Conceição do Rio Verde, Lambari, Maria da Fé, Soledade de Minas and Três Corações. These cities composse the "Circuito das Águas", FIG. 2, located among São Paulo, Rio de Janeiro e Minas Gerais.

Parque das Águas of Caxambu, the largest mineral water park in the world, has 12 springs: Leopoldina, Beleza, Duque de Saxe, Princesa Isabel and Conde D'Eu, Dom Pedro, Viotti with two taps (1 and 2), Venâncio, Mayrink I, II and III and Ernestina Guedes and also a 60 m deep geyser.

The springs of this park were discovered around 1814 and became famous and known due to the "miracle cures" reported by the first people that used these springs with medicinal purposes (Prefeitura Municipal de Caxambu, 1998). The first mineral water well was built in 1884, Dom Pedro and Princesa Isabel springs; in 1885 Viotti, Beleza and Conde D'Eu springs; in 1891 Dona Leopoldina, Duque de Saxe and Mayrink; in 1935-39 Venâncio and Ernestina Guedes in 1958. Nowadays, the waters of Mayrink I, II and III are botlled and sold in Brazil. Also, in front to the park are a ferruginous spring inside the Hotel Glória[18].

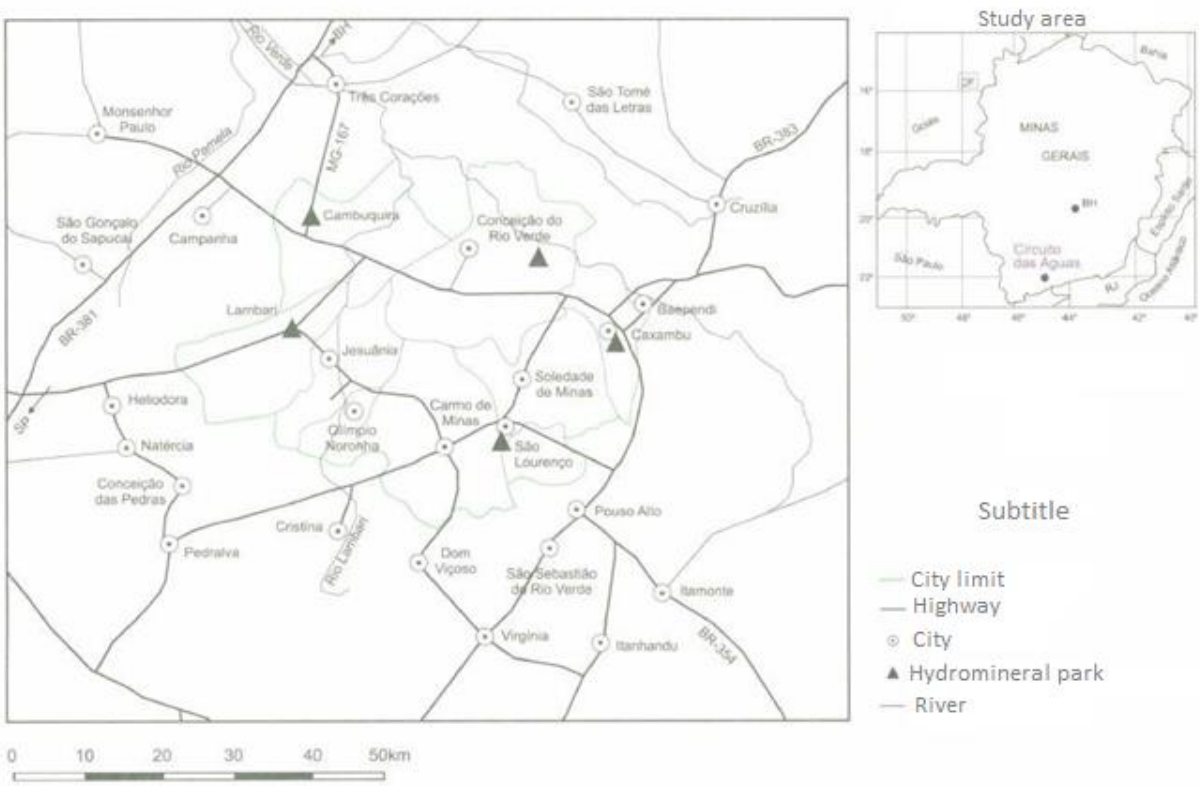

FIG. 2 – “Circuito das águas” of Minas Gerais.

The weather in the region is classified as humid temperate with dry winter and temperate Summer, with average temperature between 18° and 19°C, being the Summer the rainy season and Winter the drier. However in high altitudes there is no winter drought [19].

The geologic substrate in Caxambu is compound by meta-sediment from Andrelândia group. In south-west of the city, the occurrence of schist is predominant but also there are some spots of quartzite. The underground waters source are from sandstones, clay and conglomerate of Mezozoic-Cenozoic age and these waters are from different typologies, but are mainly of meteoric origin, also having some paleo infiltrates waters, from metamorphic and diagenetic origins [19].

2.2. Sampling

The water samples was collected every three months in one and half year in 12 springs of mineral water for free use of the park, one spring located at Hotel Glória, one from the bathhouse and one sample from the city supply to measure the background radiation. Ten liters of each sample was collected for the radiochemistry method.

In each quarterly sampling was evaluated some physical chemical parameters, as the pH measured in the laboratory, and temperature “in situ”.

At the moment of sampling, was added HNO_3 50% in water to maintain the pH ≤ 2.0 to avoid the radionuclides adsorption in the polyethylene bottle [20].

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

To determine the activity concentration of ^{226}Ra, ^{228}Ra and ^{210}Pb was used the gross alpha and beta measurement in a low background gas flow proportional detector, Berthold model LB 770 was used. [21]

The method was validated by an intercomparison program that is managed by Institute of Radiation Protection and Dosimetry – IRD; a sample with the interest radionuclide with a known concentration is sent to laboratory to evaluate the accuracy and precision of the method. The results obtained was in the range required, validating the methodology.

The radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb were precipitated with 3 mol.L^{-1} H_2SO_4, followed by dissolution with nitrilotriacetic acid (NTA) at an alkaline pH and re-precipitation in acid pH with sulfate. The precipitate containing ^{226}Ra and ^{228}Ra was separated, dissolved with EDTA, re-precipitated with sulfate in acid pH and filtered. For the ^{210}Pb in the supernatant, NaS was added to precipitate PbS. This precipitated was dissolved with HNO_3 50% for the final precipitation as $^{210}PbCrO_4$ with a solution of sodium chromate. Ra-226 and ^{228}Ra concentration were determined by gross alpha and beta counting, respectively, of the Ba(^{226,228}Ra)SO_4 precipitate and the ^{210}Pb was measured based on its decay product ^{210}Bi by measuring the gross beta activity of the $^{210}PbCrO_4$ precipitate. For the measurement a low background gas flow proportional detector, Berthold model LB 770, was used [21].

3. RESULTS AND DISCUSSION

The values of pH and temperature, except for the fall 2015 sampling that these values were not measured, are show in Table 1. The pH of the mineral waters samples ranged from 5.35 to 7.29, which classified the majority of the samples as acid or neutral. For the temperature, the values ranged from 22°C to 29°C; waters with a temperature below 25°C are classified as cold waters, meanwhile those between 25°C and 33°C as hypothermal waters. [2] Only geyser, Hotel Glória and Venâncio springs were classified as hypothermal in all samplings.

The values obtained for de activity concentrations in each season and for each spring were meaningly different, indicating that, despite these springs were located close to each other; the lithology of Caxambu has a high influence in the mineral water activity concentrations for the natural radionuclides analyzed in this work. Nevertheless, according to CPRM (1998) [19], besides the soil composition influence, the depth of the well and also the interaction time between water and soil until the mineral water outcrop in the surface, is another important factor.

For a better interpretation of the activity concentration values, the results obtained were plotted in graphs by season to visualize the different results during the seasons, FIG. 3 and FIG. 4.

Table 1: pH and temperature values of each season campaigns

Springs	Spring 2015		Summer 2016		Fall 2016		Winter 2016		Spring 2016	
	pH	Temp. (°C)	pH	Temp. (°C)	pH	Temp. (°C)	pH	Temp. (°C)	pH	Temp. (°C)
Mayrink 1	5.86	25	5.35	27	-	23	5.57	24	5.51	25
Mayrink 2	5.88	25.5	5.41	27	-	25	5.43	24	5.47	24
Mayrink 3	6.01	25	5.45	27	-	24	5.41	23	5.45	26
D. Isabel	6.67	24	6.12	27	-	23	6.13	23.5	6.27	24
Ernestina	6.81	24	6.29	27	-	23.5	6.35	23	6.57	25
Balneário	7.00	27	6.78	25	-	13	6.72	22	6.67	26
Pousada	-	-	6.49	-	-	24	7.23	13	7.00	25
D. Pedro	6.24	25	5.64	27	-	23	5.59	24	5.72	25
Viotti 1	6.01	25	5.38	27	-	24	5.40	24	5.45	25
Viotti 2	5.83	24.5	5.38	23	-	24	5.35	24	5.50	25
Geiser	7.29	27	7.28	27	-	25	7.18	25	7.13	27
D. Leopoldina	6.44	24	5.88	27	-	22	5.90	24	6.00	24
Hotel Glória	6.41	26	5.96	27	-	-	-	-	6.07	26
Beleza	6.83	24.5	6.48	28	-	24	6.45	23	6.64	25
Venâncio	6.79	26	6.34	29	-	25	6.56	25	6.57	26
D. de Saxe	6.88	24.5	6.23	27	-	23	6.32	24	6.37	25

- **Not measured**

It was possible to identify a higher concentration of ^{226}Ra in comparison to ^{210}Pb in almost all samples, mainly in Ernestina, Beleza and Venâncio springs that presented the highest values of activity concentration of these radionuclides. The geyser also showed high values of activity concentration if compared to the others springs, but it should be evaluated apart, because it is only for external use and it is unrecommended for ingestion.

In six sampling among fall 2015 and spring 2016, the values of ^{226}Ra varied from 73 ± 3 mBq.L^{-1}to 6088 ± 584 mBq.L^{-1}, from 34 ± 4 mBq.L^{-1} to 6019 ± 542 mBq.L^{-1} for ^{228}Ra and from 23 ± 1 mBq.L^{-1} to 365 ± 33 mBq.L^{-1} for ^{210}Pb. The highest values were obtained for ^{228}Ra and ^{226}Ra, geyser spring in fall 2015, 8777 ± 834 mBq.L^{-1} and 3491 ± 78 mBq.L^{-1}, respectively, and for ^{210}Pb are in spring 2015, 539 ± 48 mBq.L^{-1}.

When the activity concentrations of ^{226}Ra were compared with the maximum values of the Brazilian regulamentation of 1 Bq.L^{-1} for gross alpha, it can be observed that the springs D. Ernestina, Beleza and Venâncio exceed this maximum value in almost all sampling and D. Isabel spring in one sampling. For ^{228}Ra the results of activity concentration were compared with the maximum value of the same regulamentation for gross beta of 0.1 Bq.L^{-1} and it was also observed that almost all springs exceed this maximum, except in some samplings for Viotti 1, Viotti 2 and D. Isabel springs. [10]

However, almost all springs also exceeded the maximum value extended by United States Environmental Protection Agency (USEPA) of 185 mBq.L^{-1} for the sum of ^{226}Ra and ^{228}Ra concentrations [22].

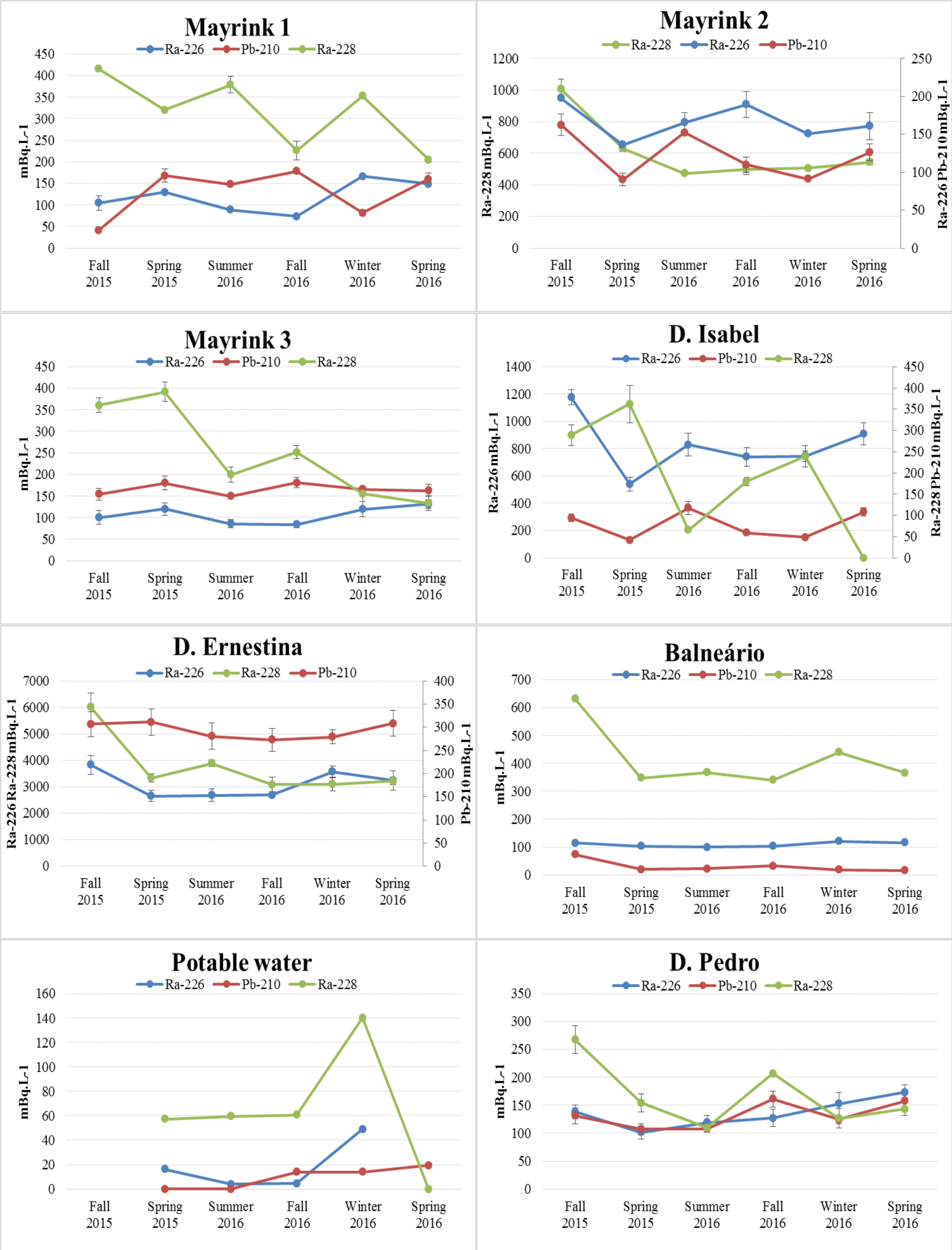

Figure 3: ^{226}Ra, ^{228}Ra and ^{210}Pb activity concentration by season in mBq.L^{-1} for the springs in each sampling

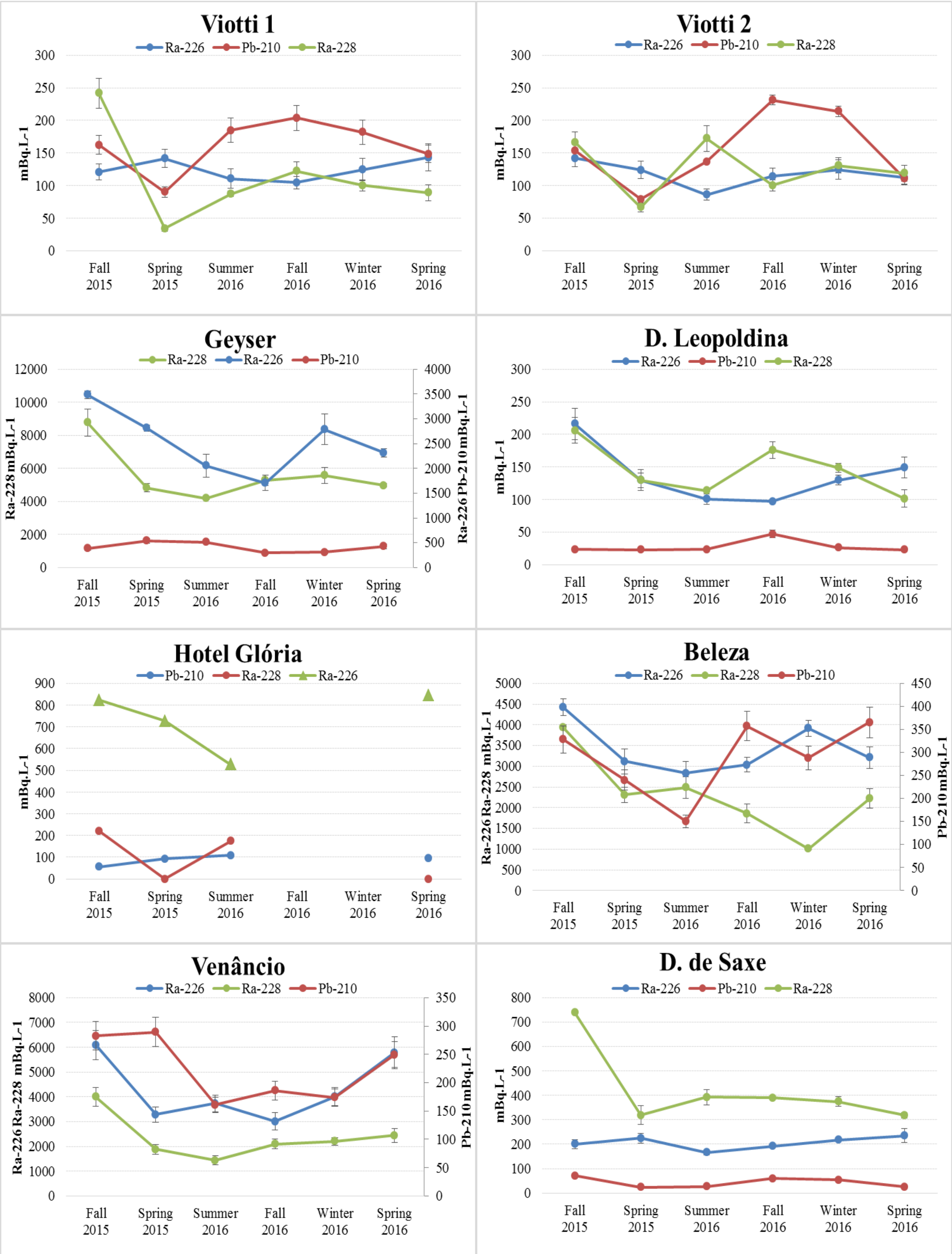

Figure 4: ^{226}Ra, ^{228}Ra and ^{210}Pb activity concentration by season in mBq.L^{-1} for the springs in each sampling.

The committed effective doses was evaluated for all springs and are present in FIG. 5, 6, 7, 8, 9 and 10; except for the geyser spring, that is recommended only for external use of the water. For this work, the public was separated in two groups: until 15 years old (He^1) and adult (He^2), using different dose conversion factor for each group, according to CNEN - 3.01/001:2011; this criterion allows a greater range of the people. [23]

The committed effective dose results for the public until 15 years old varied from 0.080 ± 0.005 $mSv.y^{-1}$ to 6.665 ± 0.639 $mSv.y^{-1}$ for ^{226}Ra, from 0.14 ± 0.016 $mSv.y^{-1}$ to 25.044 ± 2.253 $mSv.y^{-1}$ for ^{228}Ra and from 0.060 $mSv.y^{-1}$ to 0.959 ± 0.086 $mSv.y^{-1}$ for ^{210}Pb. For the adult public, the committed effective dose results varied from 0.018 ± 0.001 $mSv.y^{-1}$ to 1.244 ± 0.012 $mSv.y^{-1}$ for ^{226}Ra, from 0.017± 0.002 $mSv.y^{-1}$ to 3.031± 0.272 $mSv.y^{-1}$ for ^{228}Ra and from 0.011 ± 0.001 $mSv.y^{-1}$ to 0.179 ± 0.016 $mSv.y^{-1}$ for ^{210}Pb.

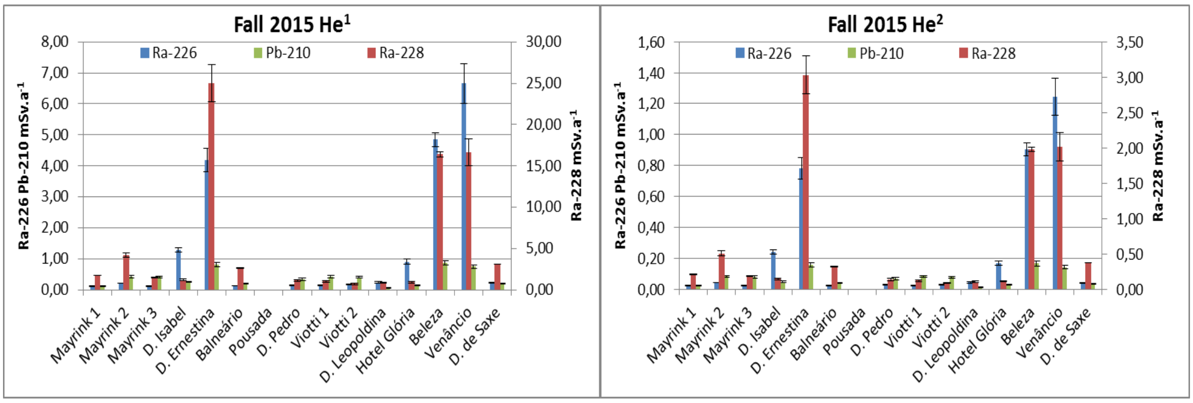

Figure 5: Committed effective dose results of ^{228}Ra, ^{226}Ra and ^{210}Pb in fall 2015 sampling for the public until 15 years old (He^1) and adult (He^2).

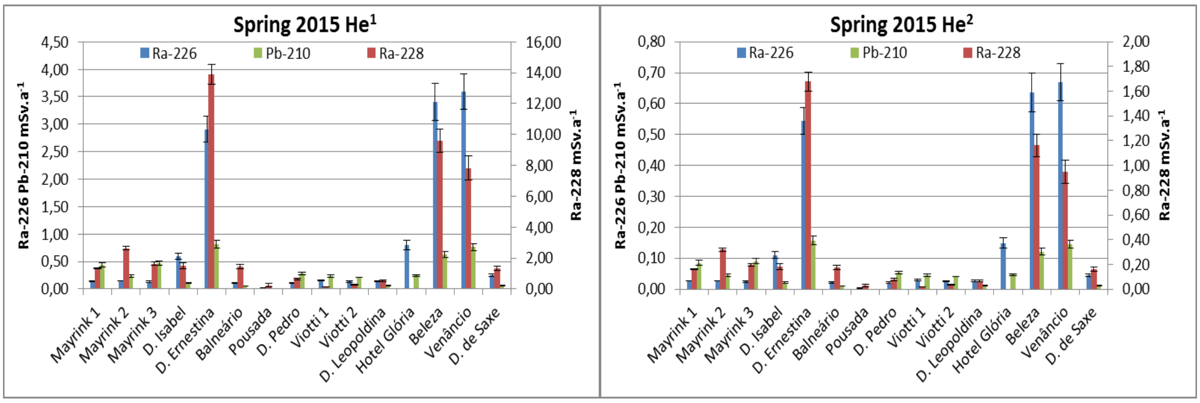

Figure 6: Committed effective dose results of ^{228}Ra, ^{226}Ra and ^{210}Pb in spring 2015 sampling for the public until 15 years old (He^1) and adult (He^2).

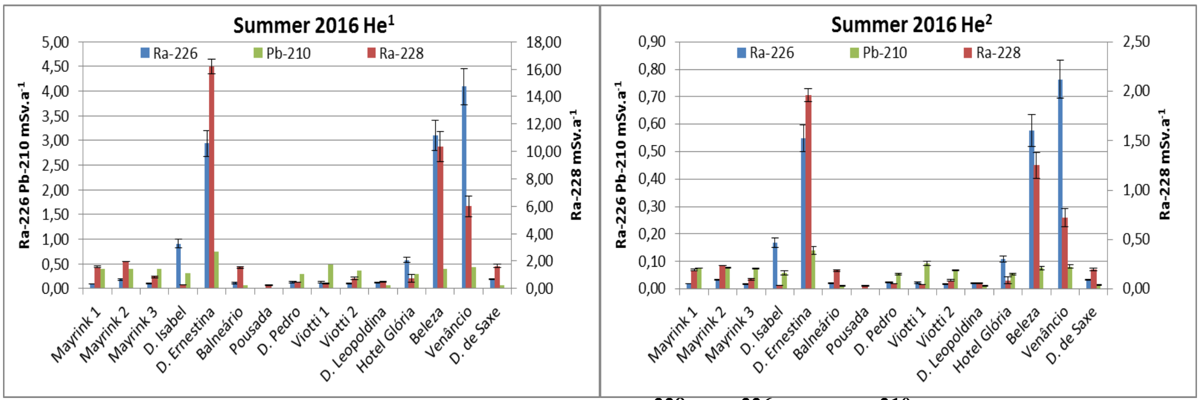

Figure 7: Committed effective dose results of ^{228}Ra, ^{226}Ra and ^{210}Pb in summer 2016 sampling for the public until 15 years old (He^1) and adult (He^2).

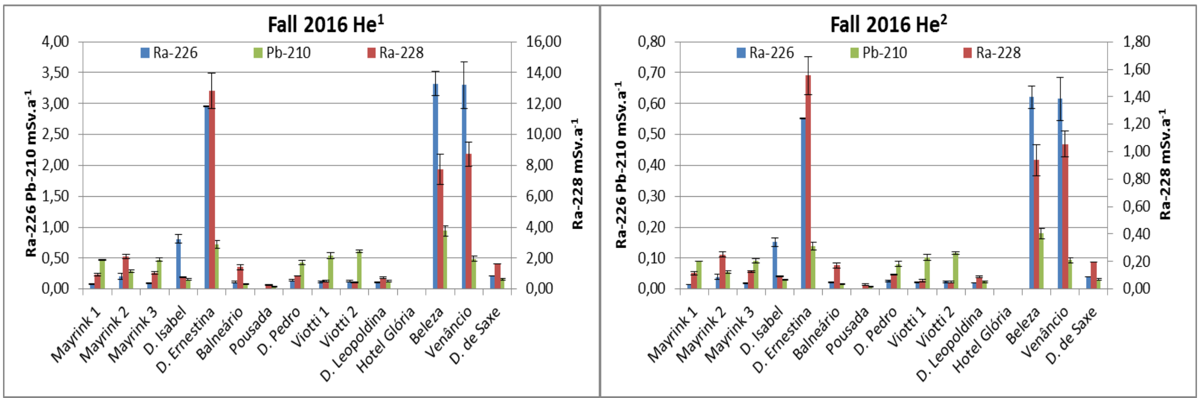

Figure 8: Committed effective dose results of ^{228}Ra, ^{226}Ra and ^{210}Pb in fall 2016 sampling for the public until 15 years old (He^1) and adult (He^2).

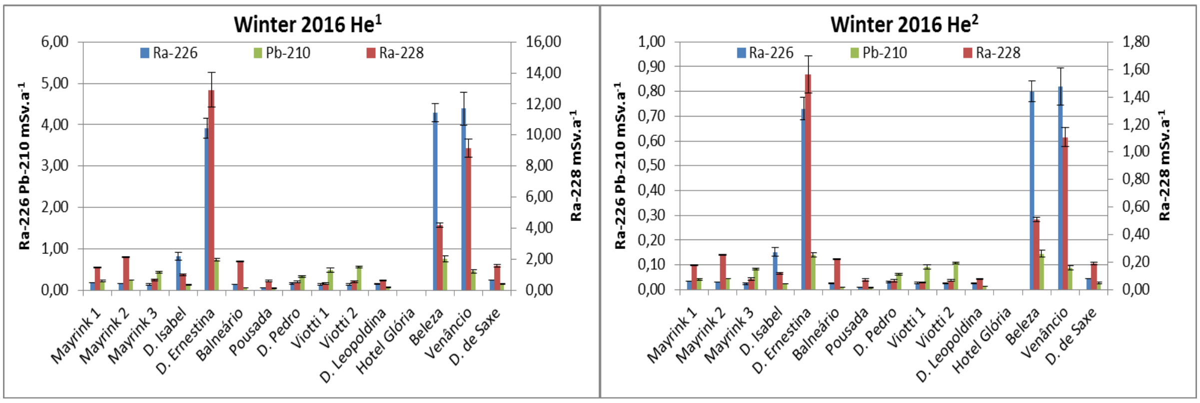

Figure 9: Committed effective dose results of ^{228}Ra, ^{226}Ra and ^{210}Pb in winter 2016 sampling for the public until 15 years old (He^1) and adult (He^2).

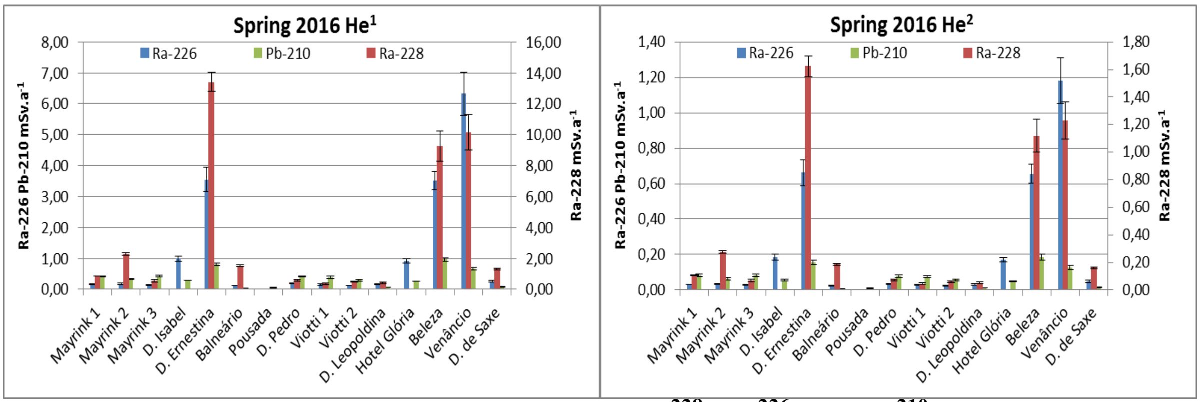

Figure 10: Committed effective dose results of ^{228}Ra, ^{226}Ra and ^{210}Pb in Spring 2016 sampling for the public until 15 years old (He[1]) and adult (He[2]).

For public until 15 years old, the maximum value of committed effective dose established by World Health Organization – WHO of 0.1 mSv.y^{-1} [8] was exceed in all six campaigns for the radionuclides ^{228}Ra, ^{226}Ra and ^{210}Pb in almost all samples, reaching values much higher than that established by WHO. Ra-228 was responsible for the highest doses of these radionuclides.

For adult public, only D. Ernestina, Beleza and Venâncio exceed the maximum value established by WHO for the radionuclide ^{210}Pb, while for ^{228}Ra and ^{226}Ra only some samples exceed this value.

Even though, D. Ernestina, Beleza and Venâncio springs are outliers in all committed effective dose results for public until 15 years old and adult public.

4. CONCLUSION

The results presented in the present work indicate that the radionuclide with the highest activity concentration value was ^{228}Ra, followed by ^{226}Ra and ^{210}Pb, D. Ernestina, Beleza and Venâncio springs were the springs that showed the highest value.

The results of committed effective dose for the public until 15 years old is the most affected by ingestion of the water of the Caxambu's park, because for this public, almost all springs exceed the maximum value established by WHO of 0.1 mSv.y^{-1} for the three radionuclides analyzed.

However, the adult public also presented values above the established by WHO and the springs that make the highest contribution to the total committed effective dose was D. Ernestina, Beleza and Venâncio.

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