

# ASSESSMENT OF Ra-226, Ra-228, Pb-210 and Po-210 ACTIVITY CONCENTRATIONS AND INORGANIC CHEMISTRY COMPOSITION OF THE MINERAL WATERS OF AMPARO, SP

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## ABSTRACT

Significant concentrations of natural radionuclides dissolved can be found in mineral water springs, mainly radionuclides from the <sup>238</sup>U and <sup>232</sup>Th decay series that are used worldwide due to its therapeutic properties. The estimation of possible adverse effects on human health due to the ingestion or inhalation of radioactive substances present in these waters is a relevant factor in the context of Radiological Protection. The objective of this work was to evaluate the activity concentrations of the radionuclides <sup>226</sup>Ra, <sup>228</sup>Ra, <sup>210</sup>Pb and <sup>210</sup>Po in the mineral water springs of the city of Amparo in the seasons of summer, autumn, winter and spring of 2018 and the committed effective doses due to the consumption of these waters, and as well as, characterize its chemical composition. The city of Amparo has 11 springs distributed in many places of the city and belongs to the Paulista Water Circuit. The highest activity concentrations were obtained for the radionuclides <sup>228</sup>Ra and <sup>210</sup>Po and consequently the highest committed effective dose. Among the chemical elements analyzed, Al, Mn, and Pb presented the highest concentrations in all the mineral water springs.

## 1. INTRODUCTION

Water is fundamental for the human being life; since the Mesopotamian, Greek and Egyptian civilizations water was used to improve the quality of life of the population that built their cities near the lakes and rivers. The use of underground water to supply the populations was developed in the Brazilian Colonial Period (1500 – 1822) and during the First and Second Reign (1822 – 1840) using wells. However, only in 1907 there was the presentation of the Water Code Project, this decree establishes on the groundwater that “the owner of any land can appropriate himself through wells, galleries, etc..., of the waters that exist beneath the surface of its building, as long as it does not harm existing uses or derive or divert from its natural course, public or private water” [1][2].

According to Resolution RDC n°. 54 of June 15, 2000, natural mineral water is obtained directly from natural or artificially captured sources of underground origin, characterized by a defined and constant content of mineral salts (ionic composition). The water used for human consumption must be potable, intended for ingestion, preparation and production of food and personal hygiene, regardless of its origin. It must be treated and submitted to physical and

chemical process in order to meet the standards of potability which involves the set of values allowed as parameters of water quality for human consumption [3].

Mineral waters are originated from natural or artificially captured springs and have chemical composition or physical or physical-chemical properties other than ordinary waters [4]. These waters may have in their composition natural radioactivity derived from the radioactive elements dissolved in them and from the gases of some diffused radioactive elements of highly mineralized ground rocks. These radioactive elements may be carried away by underground currents, but not all of them can be determined in the emergence of the springs [5].

Many studies are carried out in regions of high natural radioactivity to verify the possible biological effects on human health from prolonged exposure to low doses of ionizing radiation, mainly due to the incorporation of natural radionuclides from the  $^{238}\text{U}$  and  $^{232}\text{Th}$  series that have relatively long half-lives. In some places, the levels of  $^{238}\text{U}$  and  $^{232}\text{Th}$  present in soil and mineral deposits are high and through physical and chemical mechanisms of dissolution and leaching these radionuclides pass into groundwater that can emerge with considerable activity from these elements [6-12].

Due to the fact that several mineral and/or thermal water springs contain relatively high concentrations of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  originally dissolved [13, 14] and are used worldwide because of their therapeutic properties, the estimation of the possible adverse effects on human health that may occur as a result of ingesting or inhaling radioactive substances in these waters is of great importance in the context of Radiological Protection [15-18].

The objectives of this work were to determine the activity concentration of the natural radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the mineral waters springs of the city of Amparo, and the district of Arcadas, SP, and assess the committed effective doses of these radionuclides due to the ingestion of these mineral waters, in addition to perform an inorganic chemical characterization determining the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb e Zn by Argon Plasma Optical Emission Spectrometry (ICP-OES).

## 2. METHODOLOGY

### 2.1. Study Area

The city of Amparo is one of the cities of the “Circuito das Águas Paulista”, along with the cities of Águas de Lindóia, Jaguariúna, Lindóia, Monte Alegre do Sul, Pedreira, Serra Negra and Socorro, Fig. 1. Located at 658 m above sea level and area of 447,2 km<sup>2</sup> it has maximum temperatures have of 32°C and minimum of 12°C, being February the warmest month and July the coldest month. Amparo have intense rains between the months of December and March and low rainfall between June and August, and a population of 65.829 residents [19].

The city has a hydrographic system with springs and streams whose waters drain in the course of the Camaducaia river and the city is known as “Portal das Cidades das Águas” [20].

Amparo has springs managed by “Sistema Autônomo de Água e Esgotos de Amparo – SAAE” and springs prevention of spouts, located in many addresses of the city. The springs managed by SAAE are denominated: Nossa Senhora do Amparo, São Benedito, Santa Rita de Cássia, São Vicente de Paulo, São Roque (disabled), Santa Luzia, São José (Floresta Atlético Clube owner), Nossa Senhora da Aparecida e Coqueiros, these last two are located in district of Arcadas, 11km far from the Amparo downtown .



**Figure 1: City of Amparo in “Circuito das Águas Paulista”**

<http://www.rotadasaguas.com.br/circuito-das-aguas-paulista/mapa-circuito-das-aguas-paulistas-sp-rota-das-aguas-2/>

The geological context of Amparo denominated the springs of the “Circuito das Águas Paulista” as gneiss Amparo, this metamorphic complex is delimited to east by the granite massif of Socorro. The gneiss Amparo is represented, primarily of quartz, hornblende, diopside and biotite [21].

## 2.2 Sampling

The mineral water samples were collected during a period of 12 months, in summer, autumn, winter and spring seasons of 2018. From each mineral water spring were collected 15L of mineral water for the radiochemical analysis of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  and for the inorganic chemical characterization; it was also collected a sample of potable water in each sampling of mineral water.

In each collection were evaluated *in situ* the water temperature and in the laboratory the water pH and conductivity. The collected samples were acidified with 50%  $\text{HNO}_3$  in order to maintain the  $\text{pH} \leq 2,0$  to avoid adsorption of the radionuclides to the polyethylene flask [22].

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

The radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  were precipitated with  $\text{H}_2\text{SO}_4$  3 mol  $\text{L}^{-1}$ , followed by dissolution with nitrilotriacetic acid (NTA) at alkaline pH and re-precipitated in acid pH with sulfate. The precipitate containing  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  was separated, dissolved with EDTA, re-precipitated with sulfate in acid pH as  $\text{Ba}(\text{}^{226,228}\text{Ra})\text{SO}_4$  and filtered. In the supernatant that contain  $^{210}\text{Pb}$ , NaS was added to precipitate  $\text{PbS}$ ; this precipitated was dissolved with 50%  $\text{HNO}_3$  for the final precipitation as  $^{210}\text{PbCrO}_4$  with a solution of sodium chromate. The  $^{226}\text{Ra}$

and  $^{228}\text{Ra}$  concentrations were determined by gross alpha and beta counting of the  $\text{Ba}(\text{Ra})\text{SO}_4$  precipitate and the  $^{210}\text{Pb}$  concentration through its decay product,  $^{210}\text{Bi}$ , by measuring the gross beta activity of the  $\text{PbCrO}_4$  precipitate. Both precipitates were measured in a low background gas flow proportional detector, Berthold model LB 770 “10 Channel Low-Level Counter” [23].

## 2.4 $^{210}\text{Po}$ determination

The radionuclide  $^{210}\text{Po}$  was determined with the addition of  $^{209}\text{Po}$  tracer and subsequently pH adjusted with the 25%  $\text{NH}_4\text{OH}$ . The solution was heated at a controlled temperature of  $80^\circ\text{C}$ , under stirring to occur the spontaneous deposition of  $^{210}\text{Po}$  on a copper disk for 4 hours. After deposition, the supernatant was discarded, and the copper disk was washed. The radionuclides  $^{209}\text{Po}$  and  $^{210}\text{Po}$  were measured on Alpha Analyst spectrometer, Canberra.

## 2.5 Experimental procedure of optical emission spectrometry with argon plasma (ICP-OES)

For the ICP-OES procedure, samples from the summer and winter 2018 seasons were separated. Three consecutive readings of each sample were taken to analyze the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Zn. The determination of the elements was performed by calibrating the equipment with standard multi-element solution and obtaining a calibration curve for each element to determine the Minimum Quantification Limit (MQL) of the methodology (Table 1).

**Table 1: Minimum Quantification Limit (MQL) values of the ICP-OES methodology.**

Elements	MQL	Curve Error	Unit
Al	0.05	0.01720	mg/kg
As	0.005	0.00108	mg/kg
Ba	0.05	0.00486	mg/kg
Ca	10.143	0.50900	mg/L
Cd	0.043	0.01150	mg/kg
Cr	0.01	0.00282	mg/kg
Fe	0.05	0.00712	mg/kg
K	0.055	0.12900	mg/kg
Mg	0.201	0.32300	mg/kg
Mn	0.01	0.00272	mg/kg
Na	6.756	2.44000	mg/L
Ni	0.01	0.00265	mg/kg
Pb	0.008	0.00628	mg/kg
Zn	0.021	0.00519	mg/kg

## 2.6 Committed effective dose

The committed effective doses due to the ingestion of mineral waters containing the radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  were calculated, for individuals up to 15 years old and for adults according to the expression (1) [24]:

$$H_e \dot{=} C_n \cdot I \cdot FCD_e \quad (1)$$

Where:

$H_e$  = committed effective dose, in  $mSv \cdot y^{-1}$ ;

$C_n$  = activity concentration of radionuclide  $n$  in water, in  $Bq \cdot L^{-1}$ ;

$I$  = water intake rate, in  $L \cdot y^{-1}$  ( $730 L \cdot y^{-1}$ );

$FCD_e$  = committed effective dose conversion factor for ingestion of radionuclide  $n$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 pH and Temperature

The pH values were measured in the laboratory after the collections and the temperature *in situ* for each season of each collection, as shown in Table 2:

**Table 2: pH and temperature values of mineral water samples collected in 2018.**

SPRINGS	Summer		Autumn		Winter		Spring	
	pH	Temp.(°C)	pH	Temp.(°C)	pH	Temp.(°C)	pH	Temp.(°C)
São Benedito	6.29	22	5.49	***	5.92	21	5.62	21
Nossa Sra. Amparo	5.83	21	5.55	***	6.05	18	5.68	21
Sta. Rita de Cássia	5.81	22	5.68	***	6.21	20	5.81	22
Vicente de Paulo	5.96	23	5.59	***	6.06	21	5.70	22
Marcellino Marchi	-	-	-	***	6.16	***	5.93	***
Potable Water	5.52	25	6.08	***	6.53	22	6.03	24
São José	5.97	24	5.53	***	6.06	24	5.72	23
Sta. Luzia	6.31	24	6.02	***	6.37	19	6.06	22
Nossa Sra. Aparecida	6.12	25	5.85	***	6.27	20	6.80	22
Coqueiros	6.18	25	5.97	***	6.30	22	6.21	22
Bica	4.66	25	4.31	***	4.84	23	4.45	23

-not collected    \*\*\*not measured

The temperature of the springs ranged from 18°C to 25°C and, according to the Mineral Water Code [4] the springs with temperatures below 25°C are characterized as cold springs and values ranging from 25°C to 33°C are classified as hypothermic. Therefore, the mineral waters of the city of Amparo can be classified as cold.

The pH of the samples varied from 4.31 to 6.80 and, according to the Resolution n°12 of March 1978 [25], the water for private consumption from springs, or in other words, that come from natural springs and that emerge naturally on the soil surface should have pH between 4 and 10. The pH values obtained in this work for the mineral waters studied are within the range of this Resolution and can be used for private consumption. The acidic characteristic of groundwater, as is the case of the springs of Arcades spout, can be the result of rapid transit time in the aquifer and, because it presents a smaller quantity of dissolved solids. For waters with higher pH, as in the case of the spring Nossa Senhora da Aparecida, also located in the district of Arcadas, which presented a higher quantity of dissolved solids, it should probably have a longer transit time in the aquifer [26].

### 3.2 Electrical conductivity

The conductivity of waters is related to ionic concentrations and may indicate the presence of existing salts. The conductivity value increases according to dissolved solids in mineral waters [27]. Table 3 shows the values of electrical conductivity and the values ranged from 101  $\mu\text{S cm}^{-1}$  to 378  $\mu\text{S cm}^{-1}$ . For the potable water, the values ranged from 84  $\mu\text{S cm}^{-1}$  to 129  $\mu\text{S cm}^{-1}$  during the four seasons of the year.

Table 3: Electrical conductivity, in  $\mu\text{S cm}^{-1}$

SPRINGS	Summer	Autumn	Winter	Spring
	$\mu\text{S/cm}$	$\mu\text{S/cm}$	$\mu\text{S/cm}$	$\mu\text{S/cm}$
São Benedito	184	186	201	203
Nossa Sra. Amparo	179	181	175	185
Sta. Rita de Cássia	124	137	148	147
Vicente de Paulo	204	212	223	215
Marcellino Marchi	-	-	378	358
Potable Water	84	129	109	90
São José	243	263	274	277
Sta. Luzia	135	144	146	147
Nossa Sra. Aparecid	101	114	124	118
Coqueiros	117	112	119	118
Bica	205	229	242	232

-not collected

The conductivity values are lower in the summer, rainy period, due to the increase in the ion dilution factor [28], with a variation of 84  $\mu\text{S cm}^{-1}$  for the potable water and 243  $\mu\text{S cm}^{-1}$  for the São José spring and, higher in the dry, winter period, with a variation of 109  $\mu\text{S cm}^{-1}$  for potable water and 378  $\mu\text{S cm}^{-1}$  for the Marcellino Marchi spring, the latter was collected only in winter and spring.

Natural waters have conductivity values between 10  $\mu\text{S cm}^{-1}$  and 100  $\mu\text{S cm}^{-1}$  [29]. For the mineral water spring of the city of Amparo, only the potable water fits the parameters of the Health Surveillance Secretariat, except for the autumn season.

### 3.3 Optical emission spectrometry with argon plasma (ICP-OES)

Tables 4 and 5 show the concentration values of the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn, in  $\text{mg L}^{-1}$ , for the mineral waters collected in the city of Amparo and Arcadas district, respectively, and also the Maximum Allowable Values – MPV, for potable water established by the Ministry of Health, Ordinance n° 2914 (2011), in the summer season 2018. The values were separated, between the waters of Amparo and the waters of the Arcadas district, to better assess possible differences in concentrations of the elements analyzed between the two regions, in periods of rain and drought.

For the mineral waters of the city of Amparo, the highest concentration was for the element Na,  $17.402 \pm 0.002 \text{ mg L}^{-1}$ , and the lowest concentrations were <MQL for the elements As, Cd, Cr, Mn and Pb, in summer. For the Arcadas district mineral waters, the highest

concentration was for the element Ca,  $8.45 \pm 0.06 \text{ mg L}^{-1}$  and the lowest concentrations were <MQL for the elements As, Cd, Mn and Pb, in summer. For the springs in the city of Amparo, the Al and Pb elements exceeded the concentration values above the MPV in the springs Vicente de Paulo, São José, Santa Luzia, São Benedito, Sta. Rita de Cássia. For the mineral waters of the Arcadas district springs, only the Al element had the concentration value above the MPV.

The Ordinance No. 2914 (2011) provides the MPV for total water hardness up to  $500 \text{ mg L}^{-1}$ . Therefore, it can be observed that the values of total hardness of the springs varied from  $15.51 \pm 0.26 \text{ mg L}^{-1}$  to  $78.8565 \pm 0.00001 \text{ mg L}^{-1}$  for the springs of the city of Amparo in summer, being the spring with the highest total hardness value of  $78.8565 \pm 0.00001 \text{ mg L}^{-1}$ , São José and, for the district of Arcadas, varied from  $36.24 \pm 0.04 \text{ mg L}^{-1}$  to  $46.69 \pm 0.06 \text{ mg L}^{-1}$ , with values of total hardness within the MPV for all springs.

**Table 4: Concentrations of the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn,  $\text{mg L}^{-1}$ , in the mineral waters of the city of Amparo, summer 2018.**

Elements	Vicente de Paulo	São José	Santa Luzia	Nossa Sra. Amparo	São Benedito	Sta. Rita de Cássia	Potable Water	MPV
	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L}$
Al	$0.232 \pm 0.003$	$0.262 \pm 0.003$	$0.213 \pm 0.002$	$0.148 \pm 0.001$	$0.333 \pm 0.002$	$0.275 \pm 0.002$	$0.404 \pm 0.002$	0.200
As	<MQL	$0.0011 \pm 0.0001$	<MQL	<MQL	<MQL	<MQL	<MQL	0.010
Ba	$0.129 \pm 0.0003$	$0.179 \pm 0.002$	$0.0479 \pm 0.0006$	$0.1705 \pm 0.0006$	$0.241 \pm 0.002$	$0.0696 \pm 0.0004$	$0.0393 \pm 0.0001$	0.700
Ca	$15.16 \pm 0.03$	$16.4 \pm 0.1$	$11.4 \pm 0.2$	$13.08 \pm 0.09$	$13.7 \pm 0.02$	$6.0 \pm 0.06$	$4.07 \pm 0.01$	-
Cd	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	0.005
Cr	<MQL	$0.00589 \pm 0.00002$	<MQL	<MQL	$0.0070 \pm 0.0001$	<MQL	<MQL	0.050
Fe	$0.0449 \pm 0.0002$	$0.0285 \pm 0.0002$	$0.0270 \pm 0.0003$	$0.01233 \pm 0.00005$	$0.0688 \pm 0.0001$	$0.0586 \pm 0.0003$	$0.145 \pm 0.002$	2.400
K	$2.281 \pm 0.004$	$3.509 \pm 0.004$	$1.7660 \pm 0.0006$	$1.760 \pm 0.002$	$3.5620 \pm 0.0009$	$1.419 \pm 0.001$	$2.015 \pm 0.003$	-
Mg	$4.139 \pm 0.001$	$9.147 \pm 0.003$	$4.377 \pm 0.002$	$2.35 \pm 0.01$	$2.4820 \pm 0.0007$	$2.21 \pm 0.01$	$1.296 \pm 0.003$	-
Mn	<MQL	<MQL	$0.00278 \pm 0.00005$	$0.00470 \pm 0.00001$	<MQL	$0.001826 \pm 0.000008$	$0.00568 \pm 0.00002$	0.400
Na	$9.334 \pm 0.005$	$16.75 \pm 0.01$	$10.375 \pm 0.007$	$9.79 \pm 0.04$	$17.402 \pm 0.002$	$9.66 \pm 0.06$	$2.010 \pm 0.006$	200
Ni	$0.0535 \pm 0.0007$	$0.0584 \pm 0.0002$	$0.074 \pm 0.001$	$0.043 \pm 0.001$	$0.059 \pm 0.002$	$0.041 \pm 0.001$	$0.0103 \pm 0.0003$	0.070
Pb	<MQL	$0.0116 \pm 0.0005$	<MQL	<MQL	$0.0117 \pm 0.0003$	<MQL	<MQL	0.010
Zn	$0.00956 \pm 0.00006$	$0.0136 \pm 0.0001$	$0.0142 \pm 0.0001$	$0.0410 \pm 0.0003$	$0.0486 \pm 0.0003$	$0.0149 \pm 0.0001$	$0.0132 \pm 0.0001$	5.000
Total Hardness	$54.95 \pm 0.96$	$78.68565 \pm 0.00001$	$46.533 \pm 0.130$	$42.38 \pm 0.01$	$44.4758 \pm 0.0001$	$24.10 \pm 0.11$	$15.51 \pm 0.26$	500.000

-not provided

**Table 5: Concentrations of the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn,  $\text{mg L}^{-1}$ , in the mineral waters of the district of Arcadas, in summer 2018.**

Elements	Coqueiros	Nossa Sra. Aparecida	MPV
	$\text{mg/L} \pm \text{DP}$	$\text{mg/L} \pm \text{DP}$	$\text{mg/L}$
Al	$0.420 \pm 0.005$	$0.226 \pm 0.003$	0.200
As	<MQL	<MQL	0.010
Ba	$0.179 \pm 0.001$	$0.1346 \pm 0.0007$	0.700
Ca	$8.45 \pm 0.06$	$6.98 \pm 0.03$	-
Cd	<MQL	<MQL	0.005
Cr	$0.00798 \pm 0.00008$	$0.0061 \pm 0.0001$	0.050
Fe	$0.0976 \pm 0.0007$	$0.0413 \pm 0.0004$	2.400
K	$3.668 \pm 0.002$	$2.629 \pm 0.002$	-
Mg	$6.193 \pm 0.006$	$4.562 \pm 0.001$	-
Mn	$0.00132 \pm 0.00001$	<MQL	0.400
Na	$6.23 \pm 0.04$	$4.76 \pm 0.04$	200
Ni	$0.047 \pm 0.001$	$0.0373 \pm 0.0005$	0.070
Pb	<MQL	<MQL	0.010
Zn	$0.0318 \pm 0.0003$	$0.01309 \pm 0.00008$	5.000
Total Hardness	$46.69 \pm 0.06$	$36.24 \pm 0.04$	500.000

-not provided

Tables 6 and 7 present the concentration values of the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn, in mg L<sup>-1</sup>, of the mineral waters collected in the city of Amparo and Arcadas district, respectively, in the winter season of 2018. For the mineral water springs of the city of Amparo, the highest concentration value was for the element Na, 24.142 ± 0.005 mg L<sup>-1</sup> in the spring Vicente de Paulo, and the lowest concentrations were <MQL for the elements As, Cd, Cr, Mn and Pb.

For the Arcadas district mineral water springs, the highest concentration was for the element Ca, 8.11 ± 0.04 mg L<sup>-1</sup> in the Coqueiros spring, the lowest concentrations were <MQL for the elements As and Cd and only the spring Coqueiros presented a concentration value of Al above the MPV. For the springs in the city of Amparo, the elements with concentrations above the MPV were Al, Mn, Ni and Pb.

**Table 6: Concentrations of the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn, mg L<sup>-1</sup>, in the mineral waters of the city of Amparo, collected in winter 2018.**

Elements	Vicente Paulo	São José	Santa Luzia	Nossa Sra. Amparo	São Benedito	Sta. Rita de cásia	Potable Water	MPV
	mg/L ± DP	mg/L ± DP	mg/L ± DP	mg/L ± DP	mg/L ± DP	mg/L ± DP	mg/L ± DP	mg/L
Al	0.303 ± 0.005	0.262 ± 0.003	0.151 ± 0.003	0.209 ± 0.003	0.333 ± 0.002	0.220 ± 0.003	0.135 ± 0.001	0.200
As	0.0018 ± 0.0001	0.0011 ± 0.0001	< MQL	< MQL	< MQL	< MQL	< MQL	0.010
Ba	0.184 ± 0.001	0.179 ± 0.002	0.0337 ± 0.0002	0.179 ± 0.002	0.241 ± 0.002	0.0922 ± 0.0007	0.0446 ± 0.0001	0.700
Ca	22.68 ± 0.02	16.4 ± 0.1	7.32 ± 0.06	12.6 ± 0.1	13.7 ± 0.02	9.58 ± 0.09	5.912 ± 0.007	-
Cd	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL	< MQL	0.005
Cr	0.00386 ± 0.00002	0.00589 ± 0.00002	0.00163 ± 0.00003	0.00167 ± 0.00003	0.0070 ± 0.0001	< MQL	< MQL	0.050
Fe	0.0293 ± 0.0002	0.0285 ± 0.0002	0.013627 ± 0.000004	0.03337 ± 0.00009	0.0688 ± 0.0001	0.03709 ± 0.00009	0.1380 ± 0.0006	2.400
K	3.631 ± 0.003	3.509 ± 0.004	1.79 ± 0.06	2.968 ± 0.005	3.5620 ± 0.0009	1.9870 ± 0.0004	3.734 ± 0.003	-
Mg	5.973 ± 0.005	9.147 ± 0.003	2.30 ± 0.01	3.082 ± 0.006	2.4820 ± 0.0007	3.526 ± 0.003	5.43 ± 0.03	-
Mn	0.001108 ± 0.000004	< MQL	< MQL	0.00133 ± 0.00001	< MQL	0.00119 ± 0.00001	1.832 ± 0.003	0.400
Na	24.142 ± 0.005	16.75 ± 0.01	17.8 ± 0.5	11.44 ± 0.06	17.402 ± 0.002	6.787 ± 0.005	5.33 ± 0.02	200
Ni	0.083 ± 0.001	0.0584 ± 0.0002	0.0538 ± 0.0008	0.0487 ± 0.0005	0.059 ± 0.002	0.058 ± 0.001	0.0165 ± 0.0003	0.070
Pb	0.0178 ± 0.0004	0.0116 ± 0.0005	0.0103 ± 0.0003	0.01424 ± 0.00008	0.0117 ± 0.0003	< MQL	< MQL	0.010
Zn	0.0313 ± 0.0003	0.0136 ± 0.0001	0.01240 ± 0.00003	0.0173 ± 0.0001	0.0486 ± 0.0003	0.085 ± 0.001	0.0190 ± 0.0001	5.000
Total Hardness	81.309 ± 0.009	78.6856 ± 0.0001	27.776 ± 0.013	44.19 ± 0.01	44.4758 ± 0.0001	38.47 ± 0.11	37.15 ± 0.20	500.000

-not provided

**Table 7: Concentrations of the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn, in mg L<sup>-1</sup>, in the mineral waters of the city of Amparo, collected in winter 2018.**

Elements	Coqueiros	Nossa Sra. Aparecida	MPV
	mg/L ± DP	mg/L ± DP	mg/L
Al	0.401 ± 0.002	0.1457 ± 0.0006	0.200
As	< MQL	< MQL	0.010
Ba	0.156 ± 0.002	0.146 ± 0.001	0.700
Ca	8.11 ± 0.04	7.66 ± 0.04	-
Cd	< MQL	< MQL	0.005
Cr	0.0108 ± 0.0001	0.0089 ± 0.0001	0.050
Fe	0.205 ± 0.002	0.0511 ± 0.0002	2.400
K	3.3 ± 0.1	3.61 ± 0.002	-
Mg	4.0 ± 0.1	5.43 ± 0.03	-
Mn	0.00197 ± 0.00003	0.001826 ± 0.000008	0.400
Na	7.11 ± 0.09	6.22 ± 0.01	200
Ni	0.0488 ± 0.0009	0.0454 ± 0.0009	0.070
Pb	0.0094 ± 0.0003	0.0076 ± 0.0003	0.010
Zn	0.0204 ± 0.0002	0.01884 ± 0.00005	5.000
Total Hardness	36.75 ± 0.06	41.52 ± 0.03	500.000

-not provided

The values of total hardness of the mineral water springs of the city of Amparo ranged from  $27.776 \pm 0.013 \text{ mg L}^{-1}$  to  $81.309 \pm 0.009 \text{ mg L}^{-1}$  and for Arcadas from  $36.75 \pm 0.06 \text{ mg L}^{-1}$  to  $41.52 \pm 0.03 \text{ mg L}^{-1}$ , values within the MPV and the springs. The values of water hardness of the mineral water of the city of Amparo and the district of Arcadas can be classified as very soft water ( $70 \text{ mg L}^{-1}$ ) to soft water ( $7\text{-}140 \text{ m L}^{-1}$ ) [30].

### 3.4 $^{226}\text{Ra}$ , $^{228}\text{Ra}$ , $^{210}\text{Pb}$ and $^{210}\text{Po}$ concentrations

Fig. 1, 2, 3 and 4 present the activity concentrations of the radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , in  $\text{mBq L}^{-1}$ , respectively, for each collection of mineral water in the four seasons of 2018. The Lower Limit of Detection (LLD) values for the radionuclides determined are:  $2.2 \text{ mBq L}^{-1}$  for  $^{226}\text{Ra}$ ;  $3.7 \text{ mBq L}^{-1}$  for  $^{228}\text{Ra}$ ;  $4.9 \text{ mBq L}^{-1}$  for  $^{210}\text{Pb}$  and  $3.3 \text{ mBq L}^{-1}$  for  $^{210}\text{Po}$ .

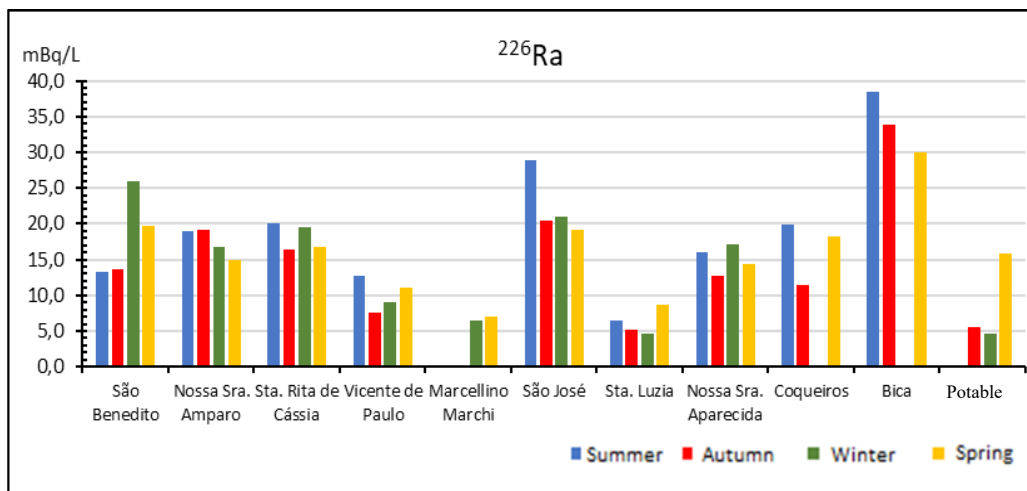


Figure 1:  $^{226}\text{Ra}$  concentration,  $\text{mBq L}^{-1}$

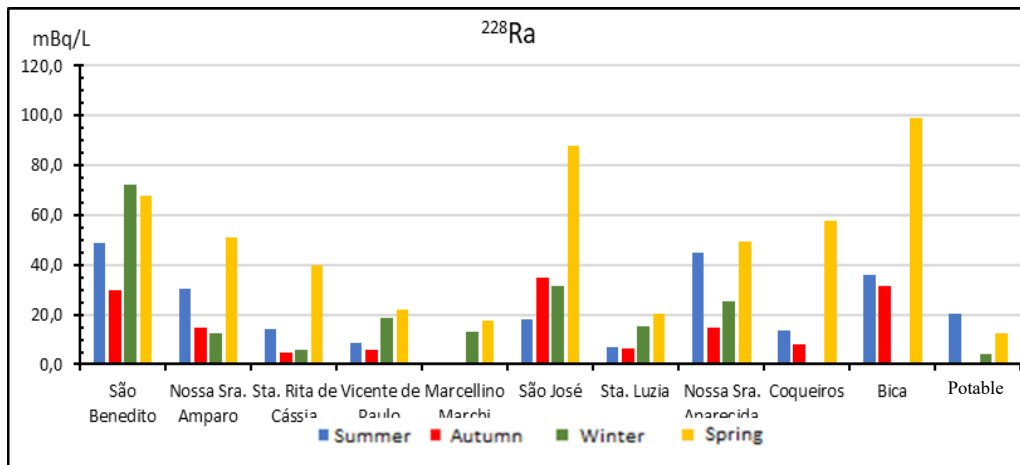


Figure 2:  $^{228}\text{Ra}$  concentration,  $\text{mBq L}^{-1}$ .

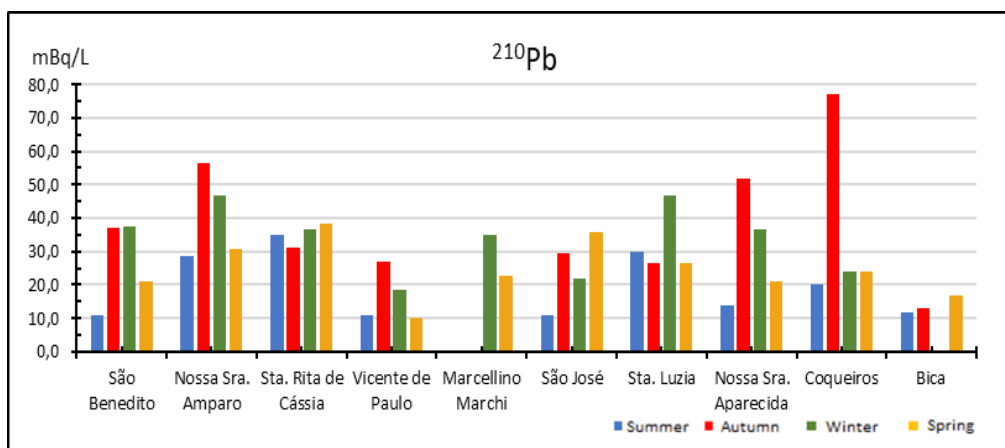


Figure 3: Radionuclide concentration  $^{210}\text{Pb}$  in mBq L<sup>-1</sup>.

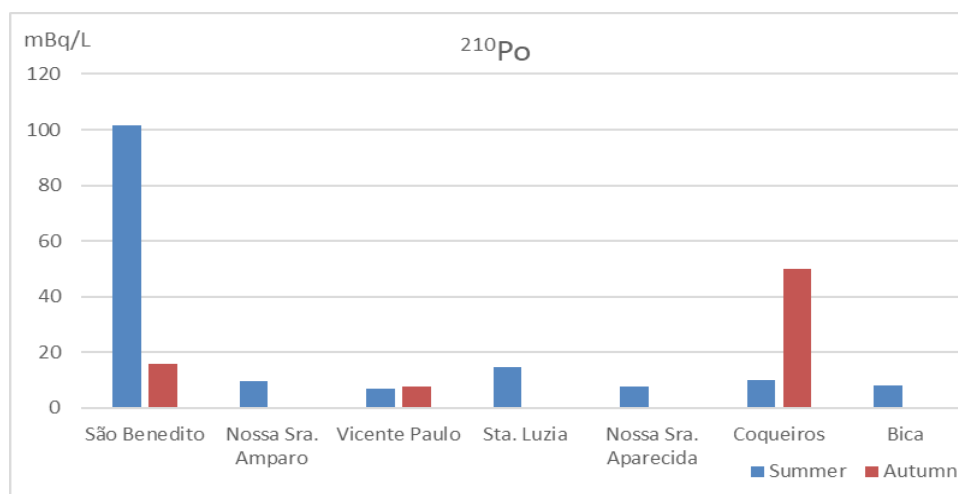


Figure 4: Radionuclide concentration  $^{210}\text{Po}$  in mBq L<sup>-1</sup>

The concentrations of  $^{226}\text{Ra}$  ranged from  $4.65 \pm 0.14$  mBq L<sup>-1</sup> to  $39 \pm 7$  mBq L<sup>-1</sup>;  $^{228}\text{Ra}$  from  $4.91 \pm 0.55$  mBq L<sup>-1</sup> to  $99 \pm 2$  mBq L<sup>-1</sup> and  $^{210}\text{Pb}$  from  $10.0 \pm 0.9$  mBq L<sup>-1</sup> to  $57 \pm 5$  mBq L<sup>-1</sup>. For  $^{210}\text{Po}$  only 7 springs were analyzed in summer: São Benedito, Nossa Senhor do Amparo, Vicente Paulo, Nossa Senhora Aparecida, Coqueiros and Bica and only 3 springs were analyzed in autumn: São Benedito, Vicente Paulo and Coqueiros, and the concentration ranged from  $7.0 \pm 0.6$  mBq L<sup>-1</sup> to  $101 \pm 11$  mBq L<sup>-1</sup>.

The maximum permissible values – MPV established to potable water by Ministry of Health [3] for the radionuclides  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are  $1.0$  Bq L<sup>-1</sup> and  $0.1$  Bq L<sup>-1</sup>, respectively, and for  $^{210}\text{Pb}$  and  $^{210}\text{Po}$   $0.1$  Bq L<sup>-1</sup>. It was observed that for the radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  the activity concentration values were below of these MPV in all collections, for both cities of study. However, for the radionuclides  $^{210}\text{Po}$  the activity concentrations determined in the present work presented values above the established by Ministry of Health [3].

### 3.5 Committed effective dose

The committed effective dose, in  $\text{mSv y}^{-1}$ , to the whole body was calculated for the radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  concentrations for individuals up to the age of 15 y and for adults, and in Table 8 are presented the range values.

**Table 8: Range values of committed effective dose for radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  for individuals up to the age of 15 y and adults.**

Radionuclide	He <sup>1</sup> <15 years old (mSv/year)	He <sup>2</sup> adult (mSv/year)
$^{226}\text{Ra}$	0.0051 to 0.096	0.001 to 0.0004
$^{228}\text{Ra}$	0.0190 to 0.3829	0.0012 to 0.0246
$^{210}\text{Pb}$	0.0150 to 0.0671	0.0050 to 0.0388
$^{210}\text{Po}$	0.0081 to 0.1185	0.0061 to 0.0889

The values of dose limit for individuals up to 15 years of age, for the radionuclides  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  were within the maximum dose limit value of  $0.1 \text{ mSv y}^{-1}$  [8] established, the radionuclides  $^{228}\text{Ra}$  and  $^{210}\text{Po}$  had the dose level values above the maximum allowed value.

The values of dose limit for individuals from the adult public, for the radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  of all mineral water springs were within the dose limit values established [3], for the radionuclides  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  are  $1.0 \text{ Bq L}^{-1}$  and  $0.1 \text{ Bq L}^{-1}$ , respectively, and for  $^{210}\text{Pb}$  and  $^{210}\text{Po}$   $0.1 \text{ Bq L}^{-1}$ , during the four seasons of 2018.

## 4. CONCLUSIONS

The present work determine the activity concentration of the natural radionuclides  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the mineral waters springs of the city of Amparo, and the district of Arcadas, SP, and assess the committed effective doses of these radionuclides due to the ingestion of these mineral waters, in addition to perform an inorganic chemical characterization determining the elements Al, As, Ba, Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb e Zn.

The highest activity concentrations determined in all mineral water springs were for the radionuclides  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  in the majority of the springs, therefore these results were below of the MPV, established to potable water by Ministry of Health [3], in all collections, for both cities of study city of Amparo and the district of Arcadas. For the results of the committed effective doses only the radionuclide  $^{228}\text{Ra}$  and  $^{210}\text{Po}$  had the level values above the MPV for individuals up to 15 years of age for the city of Amparo. For the radionuclides  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  the results were within the MPV. For the individuals from the adult public all values were within the MPV for the studied radionuclides.

Among the chemical elements analyzed the elements Ca and Na presented the highest concentrations in the majority of the mineral samples studied and also several elements presented values below the Minimum Quantification Limit.

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