# Effective dose assessment due to Águas de Lindóia water ingestion

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Abstract

Due to the growing consumption of mineral water, the concern with radiological implications has become a highlighted topic. Nevertheless, the radioactive parameters of this type of water should be well established to avoid radiological implications. In this paper, the mineral water of Águas de Lindóia balneary, in the Northeast of São Paulo state, Brazil, was evaluated for the content of the $^{238}$U and $^{232}$Th decay radionuclides series, the content of $^{40}$K and the concentration of trace and ultra-trace elements. The results showed that both radionuclide concentrations and the effective dose are below the established limits for water ingestion.

## 1. INTRODUCTION

The radionuclides from U and Th series are responsible for about 80% of the natural radiation exposure, together with the $^{40}$K (UNSCEAR, 2000). These primordial radionuclides are widely spread in the lithosphere, atmosphere and hydrosphere. The main route for their internal exposition is through ingestion. In the water, the radionuclides can be dissolved, as complexes, or bound to the particulate matter (Skwarzec et al., 2003).

The consumption of spring and mineral water is continuously growing worldwide and mineral water, with relatively high radioactive levels, has become a generalized practice for medicinal purposes (Komatina, 2004; Botezatu et al., 2007; Walencik et al., 2010). Nevertheless, this water consumption might become a crucial factor for the exposure to natural radionuclides, predominantly the members of the U and Th series. Due to the importance of water for human health, studies should be performed in order to verify whether they have low radioactivity levels (Canu et al., 2011). For natural mineral waters, the measurement of the naturally occurring radionuclide $^{40}$K, which represents about 0.12 % of natural potassium, is obligatory.

The recommended radioactivity levels for drinking water (WHO, 2011) are 0.5 Bq/L for the gross alpha and 1 Bq/L for the gross beta activity: the guideline levels are calculated for a water consumption rate of 2 L daily.

Águas de Lindóia, located in São Paulo State, Southwest of Brazil, is a well-known region where radioactive water is found and several spas offer therapeutic, cosmetic and anti-stress treatment. Águas de Lindóia waters had already been characterized for the long lived radio isotopes (Negrão, 2012), but data on a complete evaluation of the effective dose assessment are scarce. The objective of this study was to evaluate de effective dose due to ingestion of Águas de Lindóia waters due to the presence of $^{238}$U, $^{232}$Th, $^{226}$Ra, $^{228}$Ra, $^{210}$Pb and $^{40}$K. Due to the importance of the surrounding geochemical environment to the radioactive content of the water, trace elements content were also evaluated.

### 1.1 Studied Area

Águas de Lindóia city is located in the Northeast of São Paulo State, Brazil, as showed in Figure 1. In this region, fractured crystalline aquifers develop on discontinuities generated by rock fracturing. The climate of the area is subtropical wet, Cwf (Köppen classification) and the average annual rainfall is 1400 mm. The relief is moderate to high, with elevations ranging from 700 to 1100 m and a thick weathering cover varying from 10 to 70 m (Madrucci et al., 2008). The water circulation at Águas de Lindóia city leach migmatite, quartzite and milonite/quartzite rocks and its water is considered mineral due to the present radioactivity (Bonotto, 2014).

The samples analyzed in this study were collected in the Municipal of Águas de Lindóia Balneary, where people go for crenology therapy, such as for sore spots treatments, relaxing and moisturizers baths, skin disease treatment and also to drink the local “radioactive water”. In the balneary, the water from the springs named Madame Curie (MDCR) and Santa Filomena (STFL) is distributed by a pumping system to the whole balneary, pouring the water into secondary springs named Filomena (FLMN), Beleza (BLZ) and Emanatório (EMA).


Figura 1: Location of Águas de Lindóia city in the Northeast of São Paulo State, Brazil.

## 2. METHODS

For $^{226}Ra$, $^{228}Ra$ and $^{210}Pb$ determination, the following procedures were adopted. Carries of $Ba^{2+}$ and $Pb^{2+}$ were added to 2 L of water samples. The solutions were treated with citric acid, for iron and lead complexation. Sulfuric acid was added so that $^{226,228}Ra^{2+}$ and $^{210}Pb^{2+}$ had co-precipitation as $Ba(Ra)SO_4$ and $PbSO_4$. The precipitate was dissolved with NTA (nitrilotriacetic acid) and 6M NaOH was added. Solutions of $(NH_4)_2SO_4$ and glacial acetic acid were added to the precipitate $Ba(Ra)SO_4$, leaving $Pb^{2+}$ in solution. The precipitate was separated in two steps of centrifugation, dissolved with EDTA (ethylenediaminetetraacetic acid) and, again, precipitated as $Ba(Ra)SO_4$, which was filtered in Millipore filter and stored for counting. Counting was performed after 21 days of precipitation. The solution containing $Pb^{2+}$ was treated with 1M $NaS_2$ to precipitate PbS. The precipitate was centrifuged, dissolved in $HNO_3$ and filtered to separate the precipitated sulfur. The addiction of 30% $Na_2CrO_4$ precipitated $PbCrO_4$ that was filtered in Millipore filter and stored for counting. Counting was performed after 10 days of precipitation. Counts were made in a gas flow proportional detector of low background, Berthold, model Lb 770 (BERTHOLD TECHNOLOGIES GmbH & Co. KG, Germany), for 200 minutes. The procedure was taken from Leonardo et al. (2014). Quality control of results is guaranteed by the laboratory participation in periodic international inter comparison programs.

For uranium, thorium, potassium and other trace elements determination, neutron activation analysis was applied. For this determination, 1 L of the water samples was evaporated to approximately 20 mL. From this concentrated sample, 1mL was taken and transferred to a paper filter sheet and dried under an infrared lamp. Synthetic standards were, also, prepared by pipetting convenient aliquots of standard solutions (SPEX Certiprep Inc., USA), onto paper filter sheets. The samples and synthetic standards were irradiated for 8 h, for the determination of the long life nuclides, with half-life higher than several hours. For the determination of short life nuclides, less than three hours, the irradiation time was set at 20 seconds. All the irradiations were performed in the IEA-R1 nuclear reactor at IPEN (Nuclear and Energetic Research Institute, São Paulo, Brasil), under a thermal neutron flux of 1 to 5 x $10^{12}$ n $cm^{-2}$ $s^{-1}$. The counting was done at different time frames by Gamma Spectrometry, using an EG&G Ortec Ge High pure Gamma Spectrometer detector (AMETEK Inc., USA) and associated electronics, with a resolution of 0.88 keV and 1.90 keV for $^{57}Co$ and $^{60}Co$, respectively. The analysis of the data was done by using in-house gamma ray software, VISPECT program, to identify the gamma-ray peaks. Table 1 shows the determined elements, the radioisotope formed in the neutron activation, the energy of the transition lines used in the activity determination and the half-life of each determined nuclide.

For quality control of the measurements, a sample of high pure water was spiked with standard solutions (SPEX Certiprep Inc., USA) of the same elements being determined and another sample of high pure water (blank) was prepared and analyzed, following the same procedure as the water samples.

Table 1: Determined elements, formed radioisotopes, transition line energy and half-life of the determined nuclides.

| Element | Radioisotope | E (keV) | Half-life |
|---|---|---|---|
| Ba | $^{131}Ba$ | 496.3 | 11.8 days |
| Br | $^{82}Br$ | 554.3 e 776.5 | 35.3 hours |
| Ca | $^{47}Sc$ | 159.4 | 3.4 days |
| Ce | $^{141}Ce$ | 145.44 | 32.5 days |
| Co | $^{60}Co$ | 1173.2 e 1332.5 | 5.3 years |
| Cu | $^{66}Cu$ | 1039 | 5.1 minuts |
| Cr | $^{51}Cr$ | 320.1 | 27.7 days |
| Cs | $^{134}Cs$ | 795.8 | 2.1 years |
| Eu | $^{152}Eu$ | 121.8 e 1408 | 13.3 years |
| Fe | $^{59}Fe$ | 1099.2 e 1291.6 | 44.5 days |
| Hf | $^{181}Hf$ | 482.2 | 42.4 days |
| La | $^{140}La$ | 328.8 e 1596.2 | 40.3 hours |
| Lu | $^{177}Lu$ | 208.4 | 6.7 days |
| Mg | $^{27}Mg$ | 843.8 e 1014.4 | 9.5 minuts |
| Mn | $^{56}Mn$ | 846.8 e 1810.7 | 2.6 hours |
| Na | $^{24}Na$ | 1368.6 | 14.9 hours |
| Rb | $^{86}Rb$ | 1076.6 | 18.7 days |
| Sc | $^{46}Sc$ | 889.3 | 83.8 days |
| Sm | $^{153}Sm$ | 103.2 | 46.3 hours |
| Ta | $^{182}Ta$ | 1221.4 | 114.5 days |
| Th | $^{233}Pa$ | 312.0 | 27 days |
| V | $^{52}V$ | 1434.1 | 3.8 minuts |
| Yb | $^{169}Yb$ | 177.2 e 197.9 | 32.0 days |
| Zn | $^{65}Zn$ | 1115.6 | 243.9 days |
| Zr | $^{95}Zr$ | 724.2 e 756.7 | 64.0 days |

## 3.RESULTS AND DISCUSSION

Table 2 shows the activity concentrations of $^{226}Ra$, $^{228}Ra$, $^{210}Pb$, $^{238}U$, in mBq/L, and $^{40}K$, in Bq/L, determined in water samples, as well as, literature values for comparison. It was observed that for the U-series the nuclides $^{226}Ra$ and $^{238}U$ tend to present concentrations in the same order of magnitude while the activity concentration of $^{210}Pb$ is higher than that observed for its precursors, mainly due to its formation through $^{222}Rn$ decay. The radioactive minerals contained in the surrounding rocks escapes constantly by process such as alpha recoil during the $^{226}Ra$ decay or diffusion from microfractures, providing radon to the spring waters (Sakoda et al., 2008; Vinson et al., 2009). This $^{222}Ra$ will decay with a half-life of 3.8 days and in confined environments such as groundwater will give rise to the $^{210}Pb$ content.

Compared to literature values, the activity concentrations of Águas de Lindóia balneary samples are in the same range of those found by Labidi et al. (2010) in samples from Tunisia, for mineral water. Nevertheless, these authors reported much higher values for radium isotopes in therapeutic waters. High values of Ra-isotopes were, also, found by Joksić et al. (2005) in mineral waters from South Serbia.

Table 2: Activity concentrations of the determined radionuclides, in the Águas de Lindóia balneary samples and in the literature values.

| | U-238 | Ra-226 | Pb-210 | Ra-228 | K-40 |
|---|---|---|---|---|---|
| | mBq/L | mBq/L | mBq/L | mBq/L | Bq/L |
| MDCR | 2.04 ±0.01 | 8.5 ±0.4 | 22 ±1 | 17 ±2 | 0.016 ±0.006 |
| STFL | ND | 9.3 ±0.8 | 29 ±1 | 16.5 ±0.9 | ND |
| BLZ | 5 ±1 | 3.0 ±0.3 | 14.2 ±0.1 | 7 ±1 | ND |
| FLMN | 11 ±2 | 5.1 ±0.1 | 51.3 ±0.4 | 11 ±1 | 0.13 ±0.09 |
| EMA | 5 ±1 | 7.9 ±0.3 | 30.4 ±0.5 | 19 ±2 | 0.08 ±0.03 |
| | | Labidi et al. (2010) | | | |
| Mineral water | 3.3-22.5 | 2-67 | | 2-30.2 | |
| Therapeutic water | 1.23-41.6 | 157-1160 | | 108-406 | |
| | | Joksić et al. (2005) | | | |
| Mineral water | 2.2-3.8 | 92-2200 | | 608.5 | |
| | | Nieri Neto and Mazzilli (1998) | | | |
| Mineral water | | | 5.9-587 | | |

Nieri Neto and Mazzilli (1998) presented the $^{210}$Pb activity concentration for ten mineral water springs in Brazil. Comparing the activity concentration of this nuclide found in Águas de Lindóia samples with those reported by the latter authors, the values are in agreement, except for two springs highly mineralized.

It is also worth noting that none of the samples from Águas de Lindóia exceeded the recommended values for radioactivity levels in drinking water (WHO, 2011). If those values were not exceeded, then the dose contribution due to water ingestion is less than 5% of the average annual dose attributable to radiation of natural origin.

Table 3 shows the effective dose calculated for each determined radionuclide and the total dose due to the ingestion of 2 L of water. The total dose varied from 11 to 32 µSv/y, both values in the secondary springs, where people take water for drinking. The level recommended by the World Health Organization of the effective dose due to water consumption is 0.1mSv/year (WHO, 2011). The total dose, considering any of the springs sampled, are well below this limit.

Table 3: Effective dose, in µSv/y, due to the water ingestion.

| | U-238 | Ra-226 | Pb-210 | Ra-228 | K-40 | Total |
|---|---|---|---|---|---|---|
| | µSv/y | | | | | |
| MDCR | 0.0655 ±0.0002 | 1.74 ±0.09 | 10.9 ±0.5 | 8.5 ±1.0 | 0.07 ±0.03 | 21.2 |
| STFL | - | 1.9 ±0.2 | 14.5 ±0.6 | 8.1 ±0.4 | - | 24.5 |
| BLZ | 0.17 ±0.03 | 0.61 ±0.07 | 7.04 ±0.06 | 3.2 ±0.5 | - | 11.0 |
| FLMN | 0.35 ±0.05 | 1.04 ±0.03 | 25.5 ±0.2 | 5.2 ±0.6 | 0.6 ±0.4 | 32.6 |
| EMA | 0.16 ±0.03 | 1.61 ±0.06 | 15.1 ±0.3 | 9.2 ±0.9 | 0.4 ±0.1 | 26.5 |

Table 4 shows the results obtained by neutron activation analysis. The first column (SW) presents the concentrations of the spiked water while the second, the determined concentrations that were obtained following the analysis procedure. Good agreement between the theoretic and measured values was obtained for the majority of the elements. As for Br, Na, Mg, Cr and Mn, the relative errors were below 20%, indicating good precision considering the ultra-trace levels determined. A blank procedure (BLK) using high pure water was also performed and the results are also shown in Table 4.

It is possible to observe that among the elements present in microgram levels, calcium shows the highest amount in the water samples followed by Br, Na and Mg, while iron and barium presented the lowest concentrations. Calcium was, also, the element with the highest variation, with concentrations varying from 8 to 120 µg $g^{-1}$. Among the elements present in nanogram levels, zinc was that with the highest concentration. In all the samples, the Th concentration was below the detection limit of 73 ng $g^{-1}$.

Custer analysis for the normalized results was applied in order to evaluate the similarity among the elements distribution. As it can be seen in Figure 2, two main groups were formed. Group 1 was composed by the elements Ca, Zn and $^{210}$Pb. These elements are among the ones with higher concentrations. Group 2A comprises the elements with high solubility, Ra-isotopes and alkaline earth metals associated to Mn and Mg. Finally, group 2B is composed by the transition and rare earth elements, which are less soluble. It can, also, be

observed that the radioactive elements are mainly linked to the groups 1 and 2A.

Table 4: Concentration of trace elements, determined in the water samples by neutron activation analysis.

| | SW | MSW | | BLK | | MDCR | | STFL | | BLZ | | FLMN | | EMA | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | ppm | | | | | | | |
| Ba | 0.42 | 0.57 | ±0.03 | < 0.04 | | 0.061 | ±0.004 | 0.137 | ±0.009 | 0.129 | ±0.006 | 0.18 | ±0.01 | 0.2 | ±0.1 |
| Ca | 20 | 17 | ±3 | < 0.01 | | 51 | ±7 | 1.3 | ±0.3 | 8 | ±2 | 8 | ±1 | 121 | ±63 |
| Br | 52 | 35.0 | ±0.5 | 0.96 | ±0.05 | 2.55 | ±0.02 | 5.0 | ±0.1 | 1.92 | ±0.04 | 5.7 | ±0.1 | 3.1 | ±0.6 |
| Fe | 1 | 1.04 | ±0.02 | 0.016 | ±0.002 | 0.025 | ±0.005 | 0.022 | ±0.007 | 0.103 | ±0.003 | <0.006 | | 0.021 | ±0.004 |
| K | - | ND | | ND | | 0.5 | ±0.2 | ND | | ND | | 4.0 | ±3.0 | 2.6 | ±0.8 |
| Na | 1 | 1.63 | ±0.04 | 0.35 | ±0.01 | 0.947 | | 2.28 | ±0.06 | 1.43 | ±0.03 | 1.32 | ±0.03 | 2.5 | ±0.9 |
| Mg | 0.52 | 0.75 | ±0.06 | 0.14 | ±0.02 | 1.31 | 0.06 | 2.89 | ±0.09 | 4.0 | ±0.1 | 5.7 | ±0.1 | 4 | ±2 |
| | | | | | | | | ppb | | | | | | | |
| Co | 2.6 | 2.27 | ±0.04 | 0.106 | ±0.005 | 0.57 | ±0.02 | 0.07 | ±0.01 | 0.136 | ±0.005 | 0.097 | ±0.009 | 0.82 | ±0.01 |
| Cs | 2.6 | 2.2 | ±0.2 | 0.18 | ±0.02 | <0.007 | | 0.13 | ±0.02 | 0.20 | ±0.02 | 0.21 | ±0.02 | 0.07 | ±0.01 |
| Eu | 1 | 1.098 | ±0.041 | 0.029 | ±0.003 | 0.040 | ±0.005 | <0.0015 | | 0.039 | ±0.003 | 0.040 | ±0.007 | 0.023 | ±0.004 |
| La | 26.1 | 24.98 | ±0.49 | 0.09 | ±0.02 | 0.05 | ±0.00 | 0.13 | ±0.02 | 0.10 | ±0.01 | 0.14 | ±0.03 | 0.04 | ±0.02 |
| Lu | 1 | 0.97 | ±0.05 | 0.007 | ±0.001 | <0.0012 | | 0.011 | ±0.003 | 0.006 | ±0.001 | 0.012 | ±0.003 | <0.0012 | |
| Rb | 52 | 59 | ±3 | 0.5 | ±0.1 | < 3.0 | | < 3.0 | | 3.5 | ±0.2 | < 3.0 | | 6.1 | ±0.4 |
| Sc | 1 | 0.701 | ±0.005 | 0.0017 | ±0.0003 | <0.0003 | | <0.0003 | | 0.0030 | ±0.0003 | 0.0017 | ±0.0005 | <0.0003 | |
| Se | 52 | 59.9 | ±0.7 | < 1 | | < 1 | | < 1 | | 0.48 | ±0.11 | < 1 | | 0.19 | ±0.03 |
| U | 26.3 | 27 | ±2 | 0.24 | ±0.04 | 0.08 | ±0.02 | < 0.0016 | | 0.21 | ±0.04 | 0.43 | ±0.06 | 0.20 | ±0.04 |
| Zn | 104 | 135 | ±5 | 15.0 | ±0.6 | 42.3 | ±0.9 | 23 | ±1 | 29 | ±1 | 12.3 | ±0.7 | 34.5 | ±0.9 |
| V | - | - | | < 0.3 | | 0.3 | ±0.2 | < 0.3 | | 0.18 | ±0.03 | 0.98 | ±0.06 | 0.6 | ±0.3 |
| Mn | 52 | 87 | ±2 | 0.69 | ±0.06 | 0.14 | ±0.05 | 3.1 | ±0.3 | 7.7 | ±0.2 | 0.58 | ±0.07 | 0.24 | ±0.03 |

ND = not determined.

The dissimilarity observed between $^{210}$Pb and Ra-isotopes indicate that their amount in the water must be due to different mechanisms. While radium is mainly leached from the bedrocks, $^{210}$Pb can, also, be formed by the $^{222}$Rn exhalation to water and air from the crystalline fractured surrounding rocks. As the balneary springs are confined, the formed $^{210}$Pb can be reincorporated to the water.

## 4. CONCLUSIONS

The activity concentrations and effective dose of the water springs from Águas de Lindóia balneary presented values lower than those found in the literature for mineral and therapeutic water. The radionuclides distribution showed the following allocation of their activity concentration, $^{40}$K > $^{210}$Pb > $^{228}$Ra > $^{226}$Ra > $^{238}$U > $^{232}$Th. Lead-210 is the nuclide that mostly contributes to the total dose from water ingestion. The total effective dose due to the Águas de Lindóia water ingestion determined in these samples, considering a 2 L daily consumption, accounts for 23% of the established dose limit by WHO, of 0.1 µSv/y. Neutron activation analysis results indicated that earth alkaline elements are the major ions present in the water and that the majority of the other ions are present in ultra-trace levels. Multivariate statistical analysis suggested that the radionuclide water incorporation should follow different mechanisms: leaching from the surrounding rocks and exhalation of $^{222}$Rn.

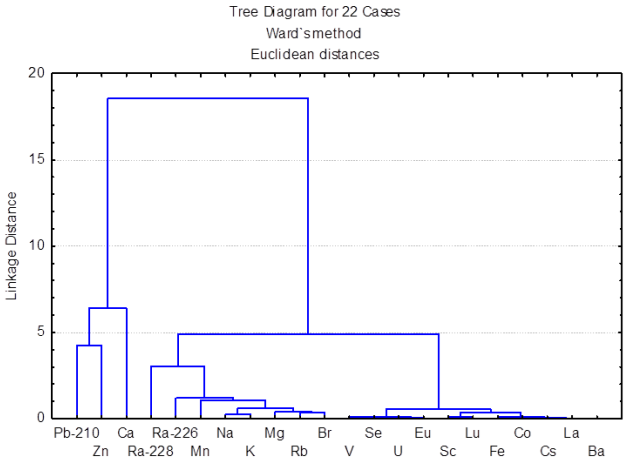


Figure 2: Dendrogram obtained for the elements measured in the water samples.

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