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ORIGINAL ARTICLE

Study of radon exposure, chemical and radiological characterization of spring mineral waters from Águas de Lindóia and Poços de Caldas, Brazil

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Abstract

Hydrothermal resources are used for health prevention and treatment worldwide based on drinking, bathing, and immersing in thermal mineral waters. In some places, ^{222}Rn inhalation is also present. In Brazil, several locations apply thermal and hydrotherapies integrated into the Unified Health System as in Águas de Lindóia and Thermas Antonio Carlos in Poços de Caldas Town. The effective dose due to ^{222}Rn inhalation by the public and balneary workers, as well as the chemical and radiological characterization for these spas were evaluated. ^{222}Rn activity concentration was measured by using CR-39, elemental water composition by neutron activation, and radionuclides, by gamma espectrometry. Results showed that the ^{222}Rn activity concentration varied from 21 to 71 Bq m^{-3} in the public areas of the balnearies and from 407 to 16,451 Bq m^{-3} in the closed springs. Effective doses varied from 0.01 to 0.02 mSv y^{-1} for the public, from 0.10 to 0.33 mSv y^{-1} for works and from 0.03 to 4.95 mSv y^{-1} for maintenance. No risk occurs for members of the public and workers due to radon inhalation, but care must be taken on behalf of the maintenance workers from Águas de Lindóia balneary. The water, for both balnearies, do not exceed the recommendation for drinking water for gross alpha and gross beta activities. Chemically, the water from Águas de Lindóia is classified as hypo saline and the water from Poços de Caldas, as low mineral content.

Keywords Radon · Spring water · Balneary · Effective dose · Spa therapy

Introduction

Human beings are constantly exposed to various sources of radiation. Excluding those arising from anthropogenic actions, natural radioactivity, due to all the sources of radiation received by man is, without a doubt, the most important. It is estimated that the average annual dose from natural sources is approximately 2.4 mSv y^{-1}. According to UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation), there are several types of radiation sources that contribute to the dose received by humans (UNSCEAR 2000). Terrestrial, cosmic and cosmogenic radiation are among them and the noble gas ^{222}Rn is the main contributor accounting for about 54% of the total dose received by humans.

Radon exposure in indoor environments occurs in homes, offices, underground places and warehouses (Xie et al. 2021). In external environments, radon and its decay products present low concentrations due to their continuous dispersion in the atmosphere. In closed environments, where traces of natural radionuclides are present, and ventilation and air renewal rates are normally reduced, their concentration may reach worrying levels (UNSCEAR 2000). In 2013, the Council of the European Union presented a document with guidelines for basic safety against the dangers arising from exposure to ionizing radiation including radon, the Euratom Basic Standards (Council Directive 2013).

On the other hand, radon therapy, the exposure to radon for therapeutic purposes, also has been used for the treatment

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of rheumatic diseases in countries with traditions of spa therapy (Annegret and Thomas 2013; Forestier et al. 2017, 2022; Kavasi et al. 2019; Tefner et al. 2023). Although there are some studies that demonstrate the effectiveness of using radon to treat some diseases (Yamaoka and Kataoka 2022), the importance of new and constant studies on the harmful effects that this radionuclide may cause to the respiratory tract is highlighted, mainly in bathhouses and spas, where indoor concentrations tend to be higher.

The use of hydrothermal resources for health prevention and treatment is widespread (Mooventhan and Nivethitha 2014; Jazani et al. 2023). These treatments are based on drinking water, bathing and immersing in thermal mineral waters and inhaling the gases present in the water, including ^{222}Rn. Thermal treatment causes a set of effects that are obtained due to the specific composition of the mineral-medicinal water supported by the effects derived from the thermal environment, the application of thermal techniques and also of other therapies. (Klim et al. 2016).

In Brazil several places use water as a therapeutic resource (Bonotto and Thomazini 2019; de Oliveira et al. 2022) and in Águas de Lindóia, in the state of São Paulo, and Poços de Caldas, in the state of Minas Gerais, municipalities, balneotherapy treatments are integrated into the Unified Health System (SUS), serving thousands of patients annually. In many of these places the water springs are considered radioactive and/or radiferous, highlighting the importance of a precise knowledge of the water composition, since benefit might be the result of a combination of different effects (mechanical, thermal and chemical composition) (Lv et al. 2021) and ^{222}Rn for workers and public exposure.

This work has the general objective of evaluating the effective dose received by workers and members of the public due to ^{222}Rn inhalation, who visits the municipal spa located in Águas de Lindóia town (MSAL), state of São Paulo, and the spa Thermas Antônio Carlos, located in Poços de Caldas town (TAC), state of Minas Gerais, as well as to chemically and radiologically characterize their water springs.

Materials and methods

Sampling

Measurements of ^{222}Rn in the air were carried out in the MSAL and TAC located in the States of São Paulo and Minas Gerais, respectively. These towns are renowned for their hydromineral hot springs with several spas that are known to provide complementary treatments.

In MSAL, samplings were carried out in the bath house, places where the concentration of radon in the air was significantly high considering the level of exposure to workers and also the places frequented by members of the public for treatment and/or recreation. In total, six sampling points were analyzed for ^{222}Rn activity concentration in the air, namely: Filomena spring, Currie spring, São Roque spring, São Roque emanatory, men's and women's bathrooms. All spring sources are covered by masonry rooms and public access is not allowed. São Roque spring feeds the emanatory where people can rest and breathe its vapors. In the bathrooms, the water from the Filomena spring feeds the bathtubs used for therapeutic immersion baths.

In TAC, four points were chosen for sampling. In this balneary, the existing three spring sources, named Chiquinha, Mariquinha and Pedro Botelho, were piped and direct contact with the water only occurs through the three taps of each one. All the sources are also enclosed in a masonry room without public access. Two points were sampled inside this room and two inside the men's and women's bathrooms of the main balneary building.

In both balnearies, water samples were also collected for chemical and radiological characterization.

Detection of ^{222}Rn in the air

There are several known methods that are used to determine the radon concentration in the air (Nastro et al. 2018; Abojassim 2020). These methods are classified as instantaneous or continuous, and are subsequently divided into two detection techniques, active and passive. In the active detection technique, through mechanical pumping, a sample containing several liters of ambient air is collected, passes through a filter, and then is analyzed. In the passive detection technique, the detector is left at the study site for a predetermined period, chosen according to the expected radon activity concentration. For environmental studies, the exposure time generally last for three months. Lower periods are chosen for places with expected high ^{222}Rn concentration. After the exposure period, the detectors are subsequently analyzed.

Nuclear solid-state track detectors (SSNTDs) are solid materials that present damage on the surface when exposed to a defined radiation (Rana 2018). Among the commercially available track detectors, the CR-39® was chosen because it presents better optical quality since it is transparent, and it allows a contrast between the produced track and the plastic body itself. Therefore, in this work, we opted for the passive detection technique, using solid nuclear track detectors of the CR-39® type.

After exposure of the CR-39®, the detectors underwent a chemical attack with potassium hydroxide solution, 30% (w/v), for 5.5 h at 80 °C. The tracks in the detector were observed using a ZEISS Axiolmager light microscope for a transmitted light model, with an increase of 10. The equipment was connected to a video camera Zeiss ICC-1 (Karl Zeiss AG, Oberkochen, Germany), connected to a microcomputer with a HP 29-inch monitor. Radon-222 concentration was calculated according to Eq. 1 (Mayya et al. 1998), taking the density of tracks (tracks cm^{-2}), the exposure time, and the calibration factor that relates the track density on the surface of the detector and the concentration of radon:

$$C_{Rn} = \frac{D}{k \cdot t_{ef}} \quad (1)$$

In the equation C_{Rn} is the ^{222}Rn activity concentration in Bq m^{-3}; k is the calibration factor (tracks cm^{-2} per Bq m^{-3} d^{-1}); D is the net track density (discounting the density relative to background radiation in the detectors; tracks cm^{-2}); and t, the exposure time (d).

The calibration factor was obtained experimentally by exposing the SSNTDs to a known ^{222}Rn concentration generated by a calibrated source of ^{226}Ra. In this case, the value was 0.0672 tracks cm^{-2} per Bq m^{-3} d^{-1}.

Chemical and radiological water characterization

For chemical characterization, Instrumental neutron activation analysis (INAA) (Greenberg et al. 2011) was used to search for the elements As, Ba, Br, Co, Cr, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sb, Sc, Se, Ta, Ti, Th, U, V, Zn and Zr, and for the elements Cd, Cu, Ni and Pb, graphite furnace atomic absorption spectrometry (GF-AAS) (Silva et al. 2022) was used.

For INAA, approximately 100 g of water samples were weighed in a 250 mL glass beaker for evaporation on a hot plate at a temperature of 40 °C until almost completely dry. The remaining volume was pipetted into polypropylene pots with a capacity of approximately 2 mL and allowed to dry under infrared light. Then, the pots were packed with transparent adhesive tape, and in aluminium foil for long irradiation (8 h) and thin cellulose paper for short irradiation (20 s). For long irradiation, the samples were placed in an aluminium capsule and for short irradiation, the samples were placed in high purity polyethylene capsules. For concentration determination, synthetic standards from Spex Certiprep with known concentrations were used. The standards were also pipetted into polypropylene pots and allowed to dry under infrared light.

All samples and standards were irradiated in the IEA-R1 Nuclear Research Reactor at IPEN/CNEN-SP under a flux of thermal neutrons (average energy of 0.025 eV) of 1 to 5×10^{12} cm^{-2} s^{-1}. Two series of irradiation were carried out according to the decay time of each radionuclide of interest formed in the sample, known as long irradiation and short irradiation. The activity concentrations of radionuclides in the samples were measured using an EG & Ortec hyperpure germanium detector, model GEM20190-P.

For GF-AAS analysis, before carrying out the measurements of Cd, Cu, Ni and Pb, dilutions of these elements were prepared from stock solutions and 0.2% (v/v) HNO_3 (Merck), used as a diluent, were used for construction of the calibration curve. Samples were acidified with 0.2% (v/v) HNO_3 and no other treatment was necessary prior to the measurement. A GF-AAS equipment model AANALYST 800 from Perkin Elmer was used.

The pH of the water was measured directly from the gallons in which it was stored after collection using a Quimis brand bench pH meter, model Q400AS. For total solid dissolved, 100 mL of water was totally dried in a furnace oven at 180 °C and weighted in an analytical balance of 0.1 mg of precision.

The determination of the cooling kinetics was carried out following the procedure adapted from Pozo et al., (2013). For this analysis, 80 g of water was placed in a closed lid Teflon® container measuring approximately 75 cm^3, then heated to 60 °C, placed in a water bath at 37 °C and observed every two minutes for cooling until the temperature stabilized. The cooling time from 47 °C to 37 °C was also measured as this is the temperature range normally applied in the patient's bath.

The activity concentration of radionuclides was determined only for the men's bath water samples. For ^{226}Ra, ^{228}Ra and ^{210}Pb, 1 mL of Pb^{2+} and 1 mL of Ba^{2+} carriers, both with a concentration of 20 mg mL^{-1}; 10 mL of 1 mol L^{-1} citric acid were added to the samples and placed on a hot plate with a magnetic stirrer. Subsequently, seven drops of methyl red were added. Concentrated ammonium hydroxide (NH_4OH) was used to neutralize the solution. The sample was then left to heat and 50 mL of 3 mol L^{-1} sulfuric acid (H_2SO_4) was added. The solution was left to rest for 24 h to form the sulfate precipitate. In the sequence, the precipitate was filtered in vacuum suction, using cellulose filters measuring 47 mm × 0.45 µm. Finally, the filters were dried in an oven at a temperature between 50 °C and 60 °C and put in a desiccator prior to the measurements by gamma spectrometry. Chemical recovery was determined by adding ^{233}Ba tracer in the beginning of the process.

As complementary measurements for water characterization, the pH, total dissolved solids and cooling kinetics were also measured.

^{222}Rn inhalation dose assessment

To determine the effective dose due to radon inhalation in the spas studied, the procedures prescribed by ICRP 89 form the International Commission on Radiological Protection (ICRP 2002) were used, adopting the epidemiological assessment method, using Eq. 2.

$$E = C \times I \times t \times FCD \tag{2}$$

where:

In the Eq. 2, E is the effective dose due to inhalation of ^{222}Rn in mSv y^{-1}; C is the activity concentration of ^{222}Rn in the air in Bq m^{-3}; I is the average annual breathing rate of the reference man of 1.2 m^3 h^{-1}; t is the exposure time in h y^{-1}; and FCD is the dose conversion factor for radon inhalation (2.46×10^{-6} mSv Bq^{-1}) (ICRP 1993).

Results

^{222}Rn concentration

In Tables 1 and 2, the activity concentrations of ^{222}Rn in the air measured in the MSAL and in TAC are presented. All the results are presented at a confidence level of 95%. In MSAL four measurement campaigns were done, from April 2016 to December 2017. In TAC the measurement campaigns occurred from March 2017 to March 2018.

It can be seen in MSAL, that in the places with public access, the ^{222}Rn concentrations in the air tend to be lower during summer and autumn seasons. Inside the spring rooms, except for the campaigns of 2016, when lower activity concentrations were measured, a pattern cannot be stated for the other three campaigns.

In TAC, as the water does not have direct contact with the air, unless the taps were opened, the ^{222}Rn activity concentration is low even in the closed room where the springs are located, and just a little bit higher than in the bathrooms.

^{222}Rn Inhalation dose assessment

According to these values, the estimation of the effective dose due to ^{222}Rn inhalation was calculated, based on the reference man (ICRP 2002).

In order to carry out the most realistic dosimetric assessment for the places with public access, three different scenarios were defined for calculating the effective dose. The distinction occurs in the exposure time (h y^{-1}) of each bathhouse employee or user in the location studied. Table 3 presents a description of the scenarios evaluated.

Table 2 ^{222}Rn concentrations in the air in the Thermas Antônio Carlos (TAC) spa

^{222}Rn concentrations in air (Bq m^{-3})			
Measured point	Mar–Jul/2017 Autumn	Jul–Oct/2017 Winter	Oct–Mar/2018 Spring/summer
Women's Bath	55 ± 3	53 ± 4	35 ± 3
Men's Bath	70 ± 4	[b]	35 ± 3
Point 1[a]	145 ± 5	156 ± 4	119 ± 7
Point 2[a]	77 ± 6	71 1	51 ± 1

[a] Inside the room containing the piped springs

[b] Lost detector (the detector was taken away from the point it was installed)

In the Tables 4 and 5 the inhalation dose is presented, according to the three stated scenarios. In the same way as the ^{222}Rn activity concentration, in MSAL, the effective dose due to inhalation is lower in summer and autumn seasons in the places with public access (1st and 3rd Scenarios) and in the 2rd scenario, a correlation with season is not observed. Considering the doses obtained for TAC, no trend can be observed in relation to the seasons.

Chemical and radiological water characterization

The pH, total solid content and cooling kinetics in the water of MSAL and TAC, are presented in Figs. 1, 2, and 3. In MSAL, the therapeutic hot baths are prepared by mixing cold and hot water, to get a temperature of about 40 °C. Both types of water were collected for analysis.

In TAC, the highest dose values are observed for the workers according to the 1st scenario.

MSAL water presented a pH relatively close to neutral varying from almost 7–8 for all its springs, while the three springs from TAC have a more alkaline value, close to 10.

Table 1 ^{222}Rn concentrations in the air in the municipal spa of Águas de Lindóia (MSAL)

^{222}Rn concentrations in air (Bq m^{-3})				
Measured point	Apr–Jul/2016 Autumn	Feb–Jul/2017 Summer/autumn	Jul-Oct/2017 Winter	Oct–Dec/2017 Spring
Women's bath	35 ± 5	26 ± 1	78 ± 16	49 ± 7
Men's bath	38 ± 5	27 ± 1	58 ± 4	71 ± 5
São roque emanatory	27 ± 4	21 ± 1	56 ± 6	51 ± 8
Filomena[a]	605 ± 45	11,966 ± 298	8992 ± 936	8814 ± 918
Curie[a]	449 ± 27	11,371 ± 207	13,192 ± 1300	12,142 ± 257
São Roque[a]	407 ± 36	16,451 ± 298	8456 ± 446	14,745 ± 2125

[a] Springs

Table 3 Scenarios used to calculate the effective dose caused by inhaling ^{222}Rn in the air of both resorts

Scenario	t (h y^{-1})	Justification
1st scenario—common worker[a] (bath)	1590	Working hours of 5.5 h per day × 6 days × 50 weeks per year
2nd scenario—common worker[a] (maintenance)	96	Working hours of 8 h per month × 12 months per year
3rd scenario—regular visitor to the thermal baths	99	Bath user for 0.33 h per day × 6 days × 50 weeks per year

[a] Supposing common workers excluded from the classification of IOE (occupationally exposed individual). 5.5 h per day is mean time the works spent inside the bathroom areas according their personal communication

Table 4 ^{222}Rn inhalation dose in Águas de Lindóia balneary according to the three stated scenarios

^{222}Rn inhalation dose (mSv y^{-1})[a]				
Measured point	Apr–Jul/2016 Autumn	Feb–Jul/2017 Summer/autumn	Jul–Oct/2017 Winter	Oct–Dec/2017 Spring
1st scenario				
Women's bath	0.17	0.12	0.37	0.24
Men's bath	0.18	0.13	0.28	0.34
Emanatory São Roque	0.13	0.10	0.27	0.24
2nd scenario				
Filomena	0.18	3.60	2.70	2.65
Curie	0.16	3.40	3.95	3.65
São Roque	0.12	4.95	2.55	4.45
3rd scenario				
Women's bath	0.01	0.01	0.02	0.01
Men's bath	0.01	0.01	0.02	0.02
Emanatory São Roque	0.01	0.01	0.02	0.02

[a] Doses calculated based on the exposure time shown in Table 3, i.e., 1590 h y^{-1} in the 1st scenario, 96 h y^{-1} in the 2nd scenario, and 99 h y^{-1} in the 3rd scenario

Table 5 Effective doses due to ^{222}Rn inhalation in Thermas Antônio Carlos, Poços de Caldas, according to the three stated scenarios

1st scenario			
^{222}Rn inhalation dose (mSv y^{-1})			
Measured point	Mar–Jul/2017 Autumn	Jul–Oct/2017 Winter	Oct–Mar/2018 Spring/summer
Women's bath	0.26	0.25	0.17
Men's bath	0.33	[b]	0.17
2nd scenario			
	1º Campanha	2º Campanha	3º Campanha
Point 1[a]	0.09	0.09	0.07
Point 2[a]	0.05	0.04	0.03
3rd scenario			
	1º Campanha	2º Campanha	3º Campanha
Women's bath	0.02	0.02	0.01
Men's bath	0.02	[b]	0.01

[a] Inside the room containing the piped springs

[b] Lost detector (the detector was taken away from the point it was installed)

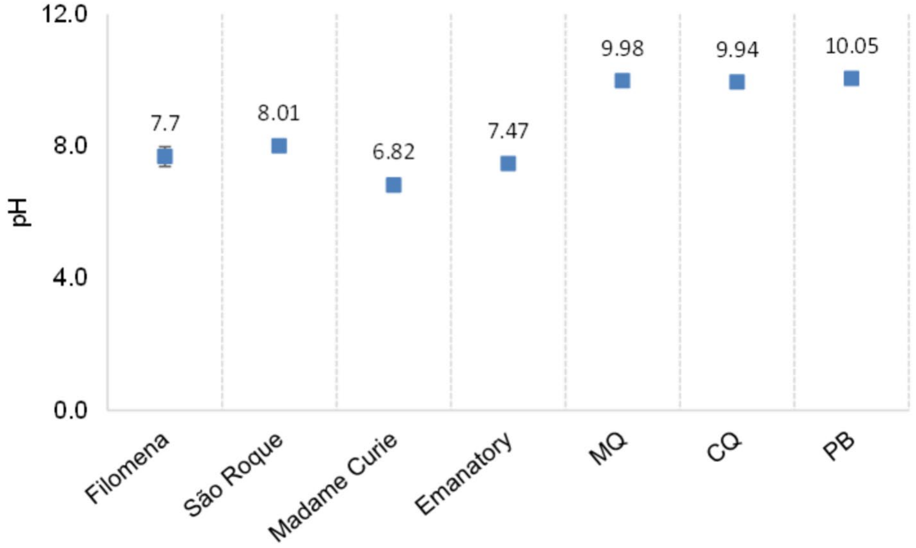

Fig. 1 pH values obtained for the water samples from Águas de Lindóia and Poços de Caldas. MQ, CQ, and PB stands for Mariquinha, Chiquinha and Pedro Botelho springs, respectively

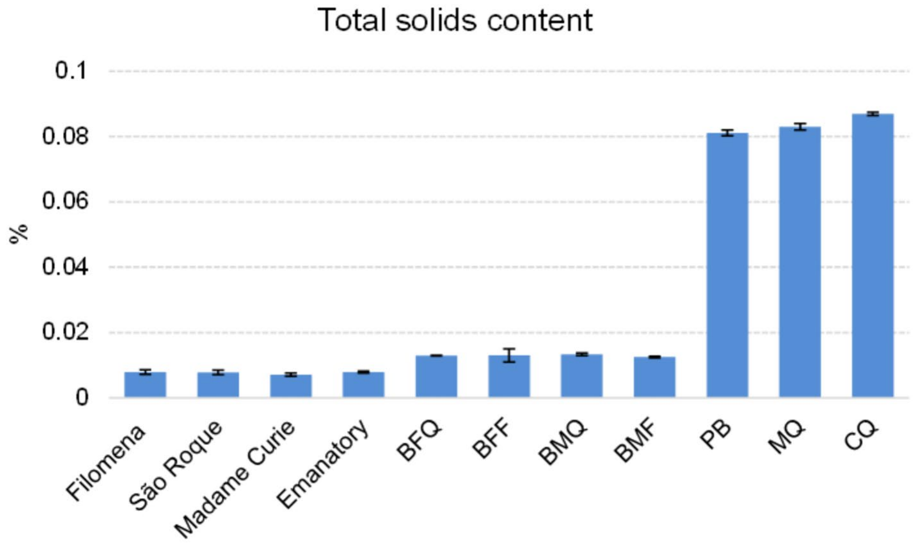

Fig. 2 Total solid content values obtained for the water samples from Águas de Lindóia and Poços de Caldas. CMB, CWB, HMB, and HWB stands for cold men's bathroom, cold women's bathroom, hot men's bathroom, and hot women's bathroom, respectively and MQ, CQ, and PB stands for Mariquinha, Chiquinha and Pedro Botelho springs, respectively

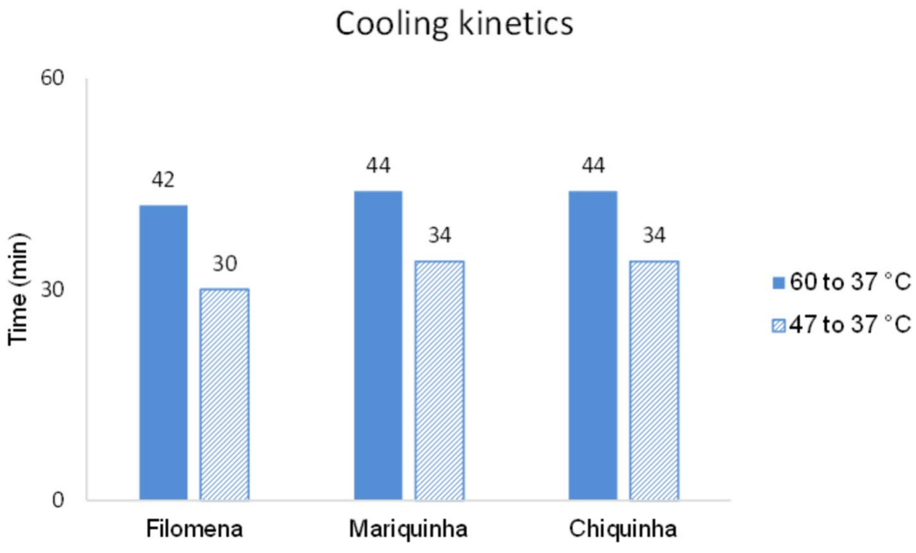

Fig. 3 Cooling kinetics values obtained for the water samples from Poços de Caldas

Low total solid content is observed for the MSAL water compared to that from TAC. The cooling kinetics, done only for the TAC water samples showed an almost constant time in both experiments.

The chemical compositions of water from TAC and MSAL springs are shown in Table 6. The elements Co, Cr, Cu, K, and Th were below the detection limit in all of the samples and Na was the element in higher quantity. Comparing the water from both localities it can be seen that MSAL has the lower content of all the analyzed elements and TAC samples presented higher salinity.

In samples from both, MSAL and TAC, the activity concentration of ^{210}Pb was below the detection limit. The activity concentrations measured for ^{226}Ra, ^{228}Ra and ^{228}Th are shown in Table 7.

In MSLA the activity concentration of ^{228}Ra was below the detection limit while the activity concentrations for ^{228}Th and ^{226}Ra were higher than those found in TAC spring water. Results for MSLA are in good agreement with previous reports by Silva et al. (2016).

Table 7 Activity concentrations of ^{228}Ra, ^{228}Th, and ^{226}Ra in Águas de Lindóia (MSAL) and Poços de Caldas (TAC) balnearies

	MSLA mBq L^{-1}	TAC
^{228}Ra	< DL	24 ± 11
^{228}Th	59 ± 17	5 ± 2
^{226}Ra	63 ± 13	13 ± 2

Discussion

Concentration levels of ^{222}Rn and the effective dose

The World Health Organization (WHO) establishes that national authorities should set a reference level of annual average residential radon concentration in 100 Bq m^{-3}, and should not exceed 300 Bq m^{-3} depending on regional circumstances (Harrison and Marsh 2020) and Brazil follows these guidelines.

Table 6 Element concentrations in water samples from Poços de Caldas and Águas de Lindóia in μg L^{-1}, except for Na^{a} in mg L^{-1}

Sample	Na^{a}	As	Ba	Br	Ca	Cd	Cl	Cs
CQ	18.1 ± 0.2	< DL	< DL	20 ± 6	< DL	< DL	471 ± 6	1.10 ± 0.04
MQ	7.79 ± 0.02	12.6 ± 0.2	132 ± 9	19 ± 3	120 ± 5	0.47 ± 0.01	795 ± 9	< DL
PB	14.67 ± 0.07	2.3 ± 0.3	< DL	32 ± 2	0.10 ± 0.04	< DL	1075 ± 7	0.78 ± 0.05
FILOMENA	4.32 ± 0.09	< DL	< DL	7.30 ± 0.04	< DL	0.06 ± 0.01	< DL	< DL
CWB	0.596 ± 0.005	< DL	102 ± 33	7.9 ± 0.6	1.28 ± 0.04	0.012 ± 0.005	< DL	< DL
HWB	0.954 ± 0.009	< DL	< DL	7.5 ± 0.7	0.73 ± 0.02	< DL	< DL	< DL
CMB	0.861 ± 0.007	< DL	200 ± 108	11 ± 1	1.34 ± 0.05	< DL	< DL	< DL
HMB	0.596 ± 0.005	< DL	122 ± 41	8.3 ± 0.7	1.43 ± 0.06	< DL	< DL	< DL

Sample	Fe	Hf	Mn	Ni	Pb	Rb	Sb	Sc
CQ	0.30 ± 0.01	0.05 ± 0.01	< DL	< DL	< DL	37 ± 1	0.53 ± 0.04	0.003 ± 0.002
MQ	0.062 ± 0.005	1.07 ± 0.03	10 ± 2	< DL	< DL	1469 ± 107	< DL	1.0 ± 0.2
PB	0.073 ± 0.004	0.11 ± 0.02	< DL	< DL	< DL	35 ± 1	0.62 ± 0.05	< DL
FILOMENA	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
CWB	< DL	< DL	< DL	< DL	4.5 ± 0.3	< DL	< DL	< DL
HWB	< DL	< DL	< DL	< DL	5.2 ± 0.7	< DL	< DL	< DL
CMB	< DL	< DL	< DL	2.87 ± 0.08	3.85 ± 0.09	< DL	< DL	0.002 ± 0.001
HMB	< DL	< DL	< DL	< DL	9.7 ± 0.2	< DL	< DL	0.003 ± 0.001

Amostra	Ta	Ti	U	Zn
CQ	< DL	< DL	< DL	< DL
MQ	8.07 ± 0.09	< DL	< DL	70 ± 1
PB	< DL	490 ± 269	0.4 ± 0.1	14.2 ± 0.6
FILOMENA	< DL	< DL	< DL	< DL
CWB	0.0412 ± 0.0003	< DL	< DL	15.2 ± 1.9
HWB	< DL	< DL	< DL	153 ± 82
CMB	0.45 ± 0.04	< DL	< DL	10.9 ± 0.7
HMB	0.45 ± 0.04	< DL	< DL	< DL

[a] mg L^{-1}, < DL = lower than detection limit. MQ, CQ, and PB stands for Mariquinha, Chiquinha and Pedro Botelho springs, respectively

In the public spaces of MSAL, the ^{222}Rn activity concentrations in the air varied from 21 ± 1 to 78 ± 16 Bq m^{-3} and in TAC, from 35 ± 3 to 70 ± 4 Bq m^{-3}. Values that are lower than the recommended ones. Worldwide, the ^{222}Rn levels vary from tens to thousands as can be seen in Table 8. In work places, in which public access is not allowed, the ^{222}Rn activity concentrations were almost the same as the public spaces for the reasons cited above, varying from 51 ± 1 to 156 ± 4 for TAC. In MSAL, the fact that the springs are located in closed small brickwork rooms with low air exchange, and no public access, allows ^{222}Rn to accumulate up to levels in the order of thousands Bq m^{-3} varying from 407 ± 36 to 16,451 ± 298 Bq m^{-3}.

UNSCEAR (2000) establishes that from the 2.3 mSv annually received from natural radiation, 1.32 mSv is due to radon. In both balnearies, the effective dose for members of the public that eventually visit for leisure or treatment are the same, varying from 0.01 to 0.02 mSv y^{-1}, corresponding up to 1.5% of the dose due to the mean value of radon inhalation anywhere. In the proposed scenarios of this study, two worker categories were stated: the ones that work inside bath places (1st scenario) and the ones working in the maintenance of the springs (3rd scenario). For the workers of the 1st scenario, the effective dose may vary from 0.10 to 0.37 mSv y^{-1} in MSAL and from 0.17 to 0.33 mSv y^{-1} in TAC, corresponding up to 28%, calculated with the highest dose, of the mean dose due to radon inhalation. For workers of the 3rd scenario, in TAC the effective dose is lower than that received by the ones of the 1st scenario, varying from 0.03 to 0.09, corresponding up to 6.8% of the mean dose due to radon inhalation, on the other hand, for MSAL, the dose may be higher than the global average, considering all sources. Nevertheless, it is unlikely that a worker spends such time on maintenance work inside the spring rooms. Otherwise, they should be considered occupationally exposed workers.

Water chemical and radiological characterization

The health effects of hydrotherapy are generally related to the thermal, mechanical, and chemical water properties, either alone or as mixed effects (An et al. 2019), although the mechanisms of action are not well understood. These properties vary in a wide range depending on the geological characteristics of the water spring as can be seen in Table 9. The pH of MSAL springs varied from 6.82 to 8.01, mainly neutral to mild alkaline, and from TAC was almost constant, around 10, alkaline, for the three springs. It is considered that alkaline spring waters have a positive effect on various skin and gynecological diseases. Temperatures measured directly in the spring may reach up to 95 °C (Table 9), although most of the studies on heat application

Table 8 Activity concentration of ^{222}Rn in air of spas in different regions and effective dose for inhalation for public individuals and workers

	^{222}Rn in air (Bq m^{-3})	Effective dose (mSv y^{-1})	Target	References
Italy	38 ± 9–430 ± 84	0.51 ± 0.12–5.8 ± 1.1	Workers	La Verde et al. (2022)
Venezuela	54,000	4	Public	Horvath et al. (2000)
Serbia	0.14 ± 0.03–2.81 ± 0.15	0.45 ± 0.04–4.7 ± 0.3	Public	Nikolov et al. (2012)
Croatia	17.3 ± 10.3–91.0 ± 8.0	0.27	Workers	Radolić et al. (2005)
Portugal	73–4335	1.21–31.21	Workers	Silva et al. (2016)
Hungary	1980 ± 1260–4290 ± 510	8–34.8	Workers	Szerbin (1996)
Iran	1880–2450	0.031–0.098	Public	Adelikhah et al. (2020)
V4[a]	15–279			Mullerová et al. (2016)
China	220 ± 130–720 ± 140			Song et al. (2011)

[a] Czech Republic, Hungary, Poland and Slovakia

Table 9 Temperature, pH and total solid content found in spring water from different countries

Location	Temperature (°C)	pH	Total solid (mg L^{-1})	References
Algeria	29.4–69.1	6.31–7.90	532–56,751	Zemour et al. (2023)
Indonesia	36–46	5–7		Nugraha et al. (2023)
Poland	12–16	7.62–7.72		Pawlik-Sobecka et al. (2021)
Spain	5–39.2	7.13–9.70		Moreno et al. (2018)
Pakistan	18–98	7.4–8.7	391–636	Ullah et al. (2022)
Spain	15–51.9		638–14,790	Dueñas et al. (1998)
China	40–80		240–5800	Song et al. (2005)
Serbia	14.4–95	6.5–9.0	100–6200	Tanasković et al. (2012)
Ecuador	18–61	4.96–8.30	166.9–8970	Carrera-Villacrés et al. (2015)

used temperatures of about 40 °C (Krafft et al. 2023), as the adopted protocol in both MSAL and TAC.

Also, depending on the geological basement, the total solid content may vary to a great extent and the water may be classified from very low mineral content to rich in mineral salts (Astel 2016). Most of the spring waters may present as main inorganic constituents chloride, sulfur, sulfate, carbonate, bicarbonate, calcium, magnesium, sodium, potassium, iron, and silicon (Fernández-González et al. 2013). The total solid content observed in MSAL, below 20 mg L^{-1}, indicates that it can be classified as hypo saline water and, as shown in Table 6 its main inorganic constituents are Na and Ca. The Zn content observed in the bathroom water from MSAL may probably have originated from the water pipes that take it to the bathtub.

The water from TAC presented a total solid content, below 100 mg L^{-1}, that classify it as low mineral content, its main inorganic constituents being Na, Br, Ca, Cl, Fe and Rb (Table 6) besides sulfur, that was not determined in this work.

In hydrothermal treatments, the water temperature produces different effects (Mooventhan and Nivethitha 2014). Also, the water thermal conductivity is related to the salinity (Gámiz et al. 2009). In therapies using hot water the time for water cooling is expected to be kept longer than the recommended bath time, generally 20 min. The cooling kinetics experiment done with TAC water showed that cooling water takes more than 40 min to go from 60 to 37 °C and more than 30 min to go from 47 to 37 °C. The temperature of 37 °C was kept constant in the measurements because it is approximately the regular body temperature.

Concerning the radionuclides, the Brazilian legislation follows the WHO (2011) recommendation for drinking water of 0.5 Bq L^{-1} for gross alpha and 1 Bq L^{-1} for gross beta. There is no regulation for radionuclides activity concentrations for therapeutic uses of spring water, but considering the potability guidance, the water of both MSAL and TAC is well below the limits. Compared with the activity concentrations presented by Bonotto (2019), who determined the activity concentrations in 75 different spring sources, finding variations from 41 to 2912.8 mBq L^{-1} for ^{226}Ra, from 3.4 to 3899.1 mBq L^{-1} for ^{228}Ra, and from 0.14 to 54.83 mBq L^{-1} for ^{210}Pb it can be concluded that the values obtained in this work are in good agreement with those reported.

Conclusions

Águas de Lindóia and Poços de Caldas municipalities water balnearies used as a therapeutic resource in Brazil were evaluated for the dose of radiation received by workers and members of the public due to ^{222}Rn inhalation and chemically and radiologically characterized. Both balnearies are supplied by different spring sources.

In MSAL and TAC, radon activity concentration in the air is below 100 Bq m^{-3} in the public environments where treatment takes place. In the sealed spring sources of MSAL, this concentration may reach values as high as 16,400 Bq m^{-3} while in TAC, where the spring sources are not directly exposed to the air, ^{222}Rn activity concentrations did not exceed the intervention limits.

Effective dose due to ^{222}Rn inhalation for members of the public visiting the balnearies for leisure or treatment are about 1.5% of the average inhalation dose due to radon in outdoor environments. For workers, working in the bath areas, the effective dose may reach up to 28% of the mean dose due to outdoor radon inhalation. For maintenance workers in TAC the effective dose is lower than that received by the ones working in the bath areas, corresponding up to 6.8% of the mean inhalation dose due to radon. On the other hand, for MSAL, the inhalation dose may be higher than the global average, considering all sources, in the considered scenario and it is recommended that those workers spend the shortest possible time in this activity and ventilate the area before entering.

The TAC water is more alkaline, with a pH of around 10, with a higher salinity than that from MSAL, a pH around neutral, and hyposaline, with total solid content below 20 mg L^{-1} mainly due to Na and Ca presence. In TAC, the main inorganic constituents are Na, Br, Ca, Cl, Fe and Rb, besides sulfur, not determined in this work but noticeable due to the strong sulfur smell in the water.

The determined activity concentrations of ^{226}Ra and ^{228}Ra indicate that the waters from MSAL and TAC do not exceed the recommendation for drinking water of 0.5 Bq L^{-1} and 1 Bq L^{-1} for gross alpha and gross beta, respectively and are in good agreement with literature reported previous values.

Author contributions G.L.R. Worked with radon measurements M.P.C. Worked with dose calculations B.P.C. Contributed with the organization of the research as adviser of G.L.C in his master degree J.K.T Made the water phisical chemical and elementar analysis in the water samples N.S.O. Analysed the radionuclides in water samples D.A.S contributed with the sampling in Águas de Lindóia J.M.O.M contributed with the sampling in Poços de Caldas.

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Declarations

Competing interests The authors declare no competing interests.

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