

Mobility indices and doses from ^{210}Po and ^{210}Pb activity concentrations data in Brazilian spas groundwaters



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ABSTRACT

^{210}Po and ^{210}Pb activity concentrations in spas groundwaters occurring at São Paulo (SP) and Minas Gerais (MG) states, Brazil, have been reported in this paper with a dual purpose: to compare different indices for evaluating the radionuclides mobility into waters and to evaluate the drinking water quality from dose calculations. The waters (75 sampling points) are extensively used for drinking in public places, bottling and bathing purposes, among other. The samples were taken from springs and wells drilled at different aquifer systems inserted in Paraná and Southeastern Shield hydrogeological provinces. The WHO guideline reference value for ^{210}Pb and ^{210}Po of 0.1 Bq/L in drinking water was not reached for ^{210}Pb but the ^{210}Po levels were equal or above it in four spas groundwaters from MG State. The maximum WHO guidance dose level of 0.1 mSv/yr was also reached or surpassed in them. The ^{210}Pb “mobility index” taking into account the ratio of the weight of the dissolved ^{210}Pb per unit volume of solution to its weight per unit weight of the rock matrix yielded values in the range of 0.01–5.2 kg/m³. Another “mobility index” (Preference Ratio) expressing the ratio of ^{210}Pb and ^{238}U in the waters divided by the ratio of ^{210}Pb and ^{238}U in the rock matrices provided values between 0.004 and 7994. The $^{210}\text{Pb}/^{238}\text{U}$ activity ratios of some spas groundwaters suggested preferential ^{238}U transport relative to ^{210}Pb into the liquid phase, whereas the ratio of the ^{210}Pb to ^{238}U mobility indices indicated the opposite. Such finding showed a better usefulness of the mobility indices for evaluating processes affecting the radionuclides release into the liquid phase during the water/rock interactions.

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1. Introduction

^{210}Pb and ^{210}Po are progenies in the natural mass number $(4n+2)$ ^{238}U decay series that finishes at the stable ^{206}Pb , according to the sequence: ^{238}U (4.49 Ga, α) \rightarrow ^{234}Th (24.1 d, β^-) \rightarrow ^{234}Pa (1.18 min, β^-) \rightarrow ^{234}U (0.248 Ma, α) \rightarrow ^{230}Th (75.2 ka, α) \rightarrow ^{226}Ra (1622 a, α) \rightarrow ^{222}Rn (3.83 d, α) \rightarrow ^{218}Po (3.05 min, α) \rightarrow ^{214}Pb (26.8 min, β^-) \rightarrow ^{214}Bi (19.7 min, β^-) \rightarrow ^{214}Po (0.16 ms, α) \rightarrow ^{210}Pb (22.26 a, β^-) \rightarrow ^{210}Bi (5 d, β^-) \rightarrow ^{210}Po (138 d, α) \rightarrow ^{206}Pb . Like other ^{238}U -descendants, ^{210}Pb and ^{210}Po are produced continuously in minerals from rocks as uranium is an important radioelement contributing to the natural terrestrial radioactivity, concentrating preferentially in acid igneous rocks compared with intermediate, basic, and ultrabasic varieties (crustal average $\sim 2.5 \mu\text{g/g}$; Bowie and Plant, 1983).

Some ^{210}Pb and ^{210}Po atoms escape the rocks and soils to the surrounding fluid, such as groundwater during interactions between the liquid and solid phases. Both ^{210}Pb and ^{210}Po in water are well-documented radionuclides for health risk, as WHO (2011) proposed a guidance level of 0.1 Bq/L for their activity concentration in drinking water in order to not exceed the reference dose level of the committed effective dose equal to 0.1 mSv from 1 year's consumption. In terms of the decay sequence ^{210}Pb (22.26 a, β^-) \rightarrow ^{210}Bi (5 d, β^-) \rightarrow ^{210}Po (138 d, α) \rightarrow ..., both radionuclides ^{210}Pb and ^{210}Po are much more restrictive than ^{210}Bi for ingestion in drinking water, since a guideline level of 100 Bq/L has been proposed by WHO (2011) for ^{210}Bi .

Analyses of several natural waters have shown that ^{210}Po and ^{210}Pb occur at different levels, depending on factors like lithology, acidity, etc. For instance, high activity concentration values have been reported in brines, spring waters and groundwaters from sulfide-bearing aquifers at fairly acidic (pH < 5) conditions (e.g. Harada et al., 1989; Dickson and Herczeg, 1992). Overlapping terms such as “drinking water”, “tap water”, “naturally occurring water”,

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“thermal water”, “bottled water”, “potable water” and “mineral water” would be applicable to the waters considered in this study. However, such terms have strict scientific/regulator definitions in each country. Thus, they will be only mentioned as “spas groundwaters” in this paper.

Economic reasons have favored their commercialization in Brazil (SEBRAE, 2012) and elsewhere (e.g. Van der Aa, 2003). Their use in Brazil is not recent due to arrival of European immigrants, mainly from Portugal, reaching the spas a maximum number in the 1930s and 1950s, chiefly at São Paulo (SP) and Minas Gerais (MG) states (Mourão, 1992). The Brazilian Code of Mineral Waters (BCMWW) was established in the 1940s, under French influence (DFPM, 1966). Bonotto (2014) reported dissolved ^{222}Rn (radon) and ^{220}Rn (thoron) data in 75 spas groundwaters from SP and MG states, classifying them according to the BCMWW guidelines. The same monitoring points were also analyzed by Bonotto (2015, 2017) for the isotopes of radium (^{226}Ra and ^{228}Ra) and uranium (^{238}U and ^{234}U) in order to investigate their relative mobilities. Other Brazilian groundwater sources were also analyzed for ^{226}Ra , ^{228}Ra , ^{210}Po and ^{210}Pb (Bonotto et al., 2009; Oliveira et al., 2001; Godoy et al., 2001).

This paper reports a novel ^{210}Pb and ^{210}Po activity concentration database in spas groundwaters from southeast Brazil for comparing different radionuclides mobility indices, as well to evaluate their radiological quality for ingestion from dose calculations. The investigation is justified by their increased consumption in Brazil (CPRM, 2012) and by the fact that both, ^{210}Pb and ^{210}Po in waters, are well-documented radionuclides for health risk.

2. Materials and methods

The groundwater samples (75) in this study were taken from springs and wells from 14 spas located in SP and MG states (Fig. 1) at various geological contexts: Águas de São Pedro (3), Águas da Prata (7), Águas de Lindóia (7), Serra Negra (8), Lindóia (2), Termas de Ibirá (5), Águas de Santa Bárbara (1), Lambari (6), São Lourenço (8), Cambuquira (6), Caxambu (10), Poços de Caldas (6), Pocinhos do Rio Verde (4) and Araxá (2). The groundwater samples (1–26 L) were from different aquifer systems in the Paraná and Southeastern Shield hydrogeological provinces as reported by Bonotto (2014). They corresponded to the same springs and wells analyzed in terms of physico-chemical parameters, major constituents, radium isotopes (^{226}Ra and ^{228}Ra) and dissolved gases (^{222}Rn , ^{220}Rn , O_2 , CO_2 , S^{2-}). The codes adopted by Bonotto (2014, 2015, 2016, 2017) for their identification will be also used in this paper.

Different methods have been used for characterizing ^{210}Pb and ^{210}Po in waters, for instance, γ -rays spectrometry with HPGe detector, gas-flow proportional counting, liquid scintillation counting, ICP-MS technique, electrochemical separation or measurement of the α -particles (energy = 5.3 MeV) emitted by ^{210}Po (Ivanovich and Harmon, 1992; Godoy and Godoy, 2006; etc.). In this study, the theoretical approach described by Bonotto et al. (2009) was adopted for generating the ^{210}Pb and ^{210}Po activity concentration data. Because ^{210}Bi grows into equilibrium with ^{210}Pb in about 25 days, a good approximation of the relationship between the ^{210}Po and ^{210}Pb activity concentrations after sampling (separation from the interaction with the host rock in the aquifer) is to wait at least a time (t_1) of about 20–30 days (several half-lives of ^{210}Bi) after sampling, extract ^{210}Po and measure its activity concentration. Then, the following equation (Froehlich, 2008) expresses the ^{210}Po and ^{210}Pb activity concentrations:

$$A_{Po}(t_1) = A_{Pb} + (A_{Poi} - A_{Pb}) \exp(-\lambda_1 t_1) \quad (1)$$

where: A stands for activity concentration of the respective

radionuclide and λ_1 is the decay constant of ^{210}Po . In order to avoid assumptions based on the condition of radioactive equilibrium to determine both radionuclide concentrations, a second groundwater sample from the same site was again analyzed by the same procedure, implying in another equation for a different time (t_2) that would permit unequivocally determine the two unknowns A_{Poi} and A_{Pb} ($=A_{Pbi}$, the initial ^{210}Pb activity concentration), i.e.:

$$A_{Po}(t_2) = A_{Pb} + (A_{Poi} - A_{Pb}) \exp(-\lambda_1 t_2) \quad (2)$$

Such an approach was applied for the groundwater samples collected in duplicate (75), despite the time consuming of the analysis and costly laboratorial procedures. However, under the usual time scale of laboratorial experiments like one year, the decrease of the initial ^{210}Po activity (A_{Poi}) is high (84%) and, therefore, the ^{210}Po activity concentration measured at instant t in eqs. (1) and (2) is mainly related to the ^{210}Pb activity concentration. Consequently, the initial ^{210}Pb activity concentration may be found from measured ^{210}Po activity concentration according to the simplified equation (A_{Poi} is disregarded in eqs. (1) and (2)):

$$A_{Po}(t) = A_{Pb} - A_{Pb} \exp(-\lambda_1 t) \quad (3)$$

where: A is the activity concentration of the respective radionuclide, λ_1 is the ^{210}Po decay constant, and t is the time elapsed between the sample collection and counting date. The results obtained from applying simplified eq. (3) were compared with those using eqs. (1) and (2).

The duplicated groundwater samples were stored in polyethylene flasks, filtered through 0.45 μm Millipore membrane, acidified to $\text{pH} \approx 2$ with 8M HCl, and a known amount (133.2 mBq) of ^{209}Po spike (α -particles emitting radionuclide, energy = 4.9 MeV; Karraker et al., 1951) was added to each one in order to assess ^{210}Po recovery. About 500 mg of FeCl_3 was also added to them, and ^{210}Po plus ^{210}Pb co-precipitated with $\text{Fe}(\text{OH})_3$ by increasing the pH to 7–8 through addition of concentrated NH_4OH solution. The precipitated was recovered, dissolved in 8M HCl and Fe^{3+} was extracted into an equal volume of isopropyl ether. Then, it was added 5 mL of 20% hydroxylamine hydrochloride and 2 mL of 25% sodium citrate solution to the acid solution containing ^{210}Po and ^{210}Pb , being the pH adjusted to 2 with concentrated ammonia solution (Flynn, 1968). Polonium was subsequently plated onto a copper disc (1-in diameter) suspended in the solution placed on a hot plate magnetic stirrer, which was heated to 85–90 $^\circ\text{C}$, and stirred during 75–90 min with a Teflon stirrer. Then, the disc was removed, washed with demineralized water, dried in a heating lamp, and inserted in an evacuated chamber for α -counting.

The α -particles were counted by conventional alpha spectroscopy with four 450 mm^2 area, 100 μm depletion depth, 26 keV resolution PIPS detectors that were coupled to EG&G ORTEC multichannel buffer. The MAESTRO software provided 1024 channels to plot the alpha spectrum containing the ^{209}Po and ^{210}Po peaks. The system was calibrated in energy through a radioactive source prepared at the Centre de Faibles Radioactivités, CNRS-CEA, Gif-sur-Yvette, France, that contained 0.91 Bq of ^{238}U (α -particles energy = 4.2 MeV), 0.91 Bq of ^{234}U (α -particles energy = 4.8 MeV), and 0.17 Bq of ^{232}U (α -particles energy = 5.3 MeV) (Lederer et al., 1967). The ^{209}Po peak (energy = 4.9 MeV) situated close to that of ^{234}U and the ^{210}Po peak in the ^{232}U channel region. The isotope dilution technique was used to generate the ^{210}Po activity concentration values from ^{209}Po and ^{210}Po peaks, whose statistical uncertainty was generally between 5 and 10%, within 1 σ standard deviation.

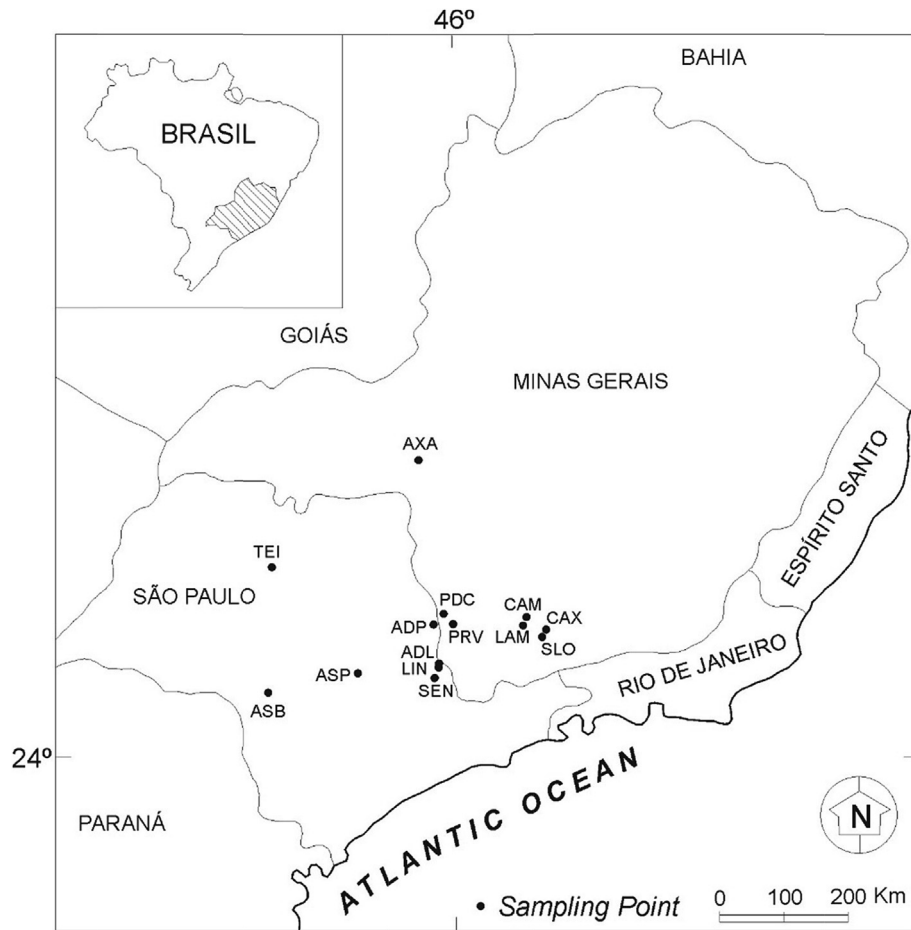


Fig. 1. Sketch map of the research region in Brazil and location of the groundwater sampling points in the following spas of São Paulo and Minas Gerais states: ASP = Águas de São Pedro, ADL = Águas de Lindóia, SEN = Serra Negra, LIN = Lindóia, TEI = Termas de Ibirá, ASB = Águas de Santa Bárbara, ADP = Águas da Prata, PDC = Poços de Caldas, PRV = Pocinhos do Rio Verde, LAM = Lambari, SLO = São Lourenço, CAM = Cambuquira, CAX = Caxambu, AXA = Araxá.

3. Results and discussion

Each measured ^{210}Po activity concentration from eqs. (1) and (2) [$A_{Po}(t_1)$ and $A_{Po}(t_2)$] is not the initial ^{210}Po activity concentration in the groundwater sample (A_{Po_i}), but it is a value produced from two opposite processes: a) ^{210}Po decrease according to its decay

constant of 0.005 days^{-1} ; b) ^{210}Po ingrowth from its grandparent ^{210}Pb that decays more slowly (decay constant of $8.55 \times 10^{-5} \text{ days}^{-1}$). The time elapsed between the sampling and counting date was from 25 to 2776 days, the initial ^{210}Po activity values were within the range of 0.09–401.5 mBq/L, and the ^{210}Pb activity concentration varied between 0.07 and 54.8 mBq/L, as shown in the

Table 1

Statistical evaluation of the data obtained for the activity concentrations of ^{210}Po and ^{210}Pb in spas groundwaters from southeastern Brazil.

Range of ^{210}Po activity conc. (mBq/L)	Average activity conc. (mBq/L)	Frequency	Frequency percentage (%)	Cumulative percentage (%)
0.06–0.2	0.09	4	5.3	5.3
0.2–0.9	0.4	9	12.0	17.3
0.9–3.8	1.5	11	14.7	32.0
3.8–15.2	6.0	27	36.0	68.0
15.2–61.7	24.4	19	25.3	93.3
61.7–250.2	99.0	4	5.4	98.7
250.22–1015.23	401.5	1	1.3	100.0
Range of ^{210}Pb activity conc. (mBq/L)	Average activity conc. (mBq/L)	Frequency	Frequency percentage (%)	Cumulative percentage (%)
0.05–0.1	0.07	2	2.7	2.7
0.1–0.4	0.2	9	12.0	14.7
0.4–1.3	0.6	12	16.0	30.7
1.3–4.0	2.0	14	18.7	49.4
4.0–12.0	6.0	20	26.6	76.0
12.0–36.4	18.1	16	21.3	97.3
36.4–110.6	54.8	2	2.7	100.0

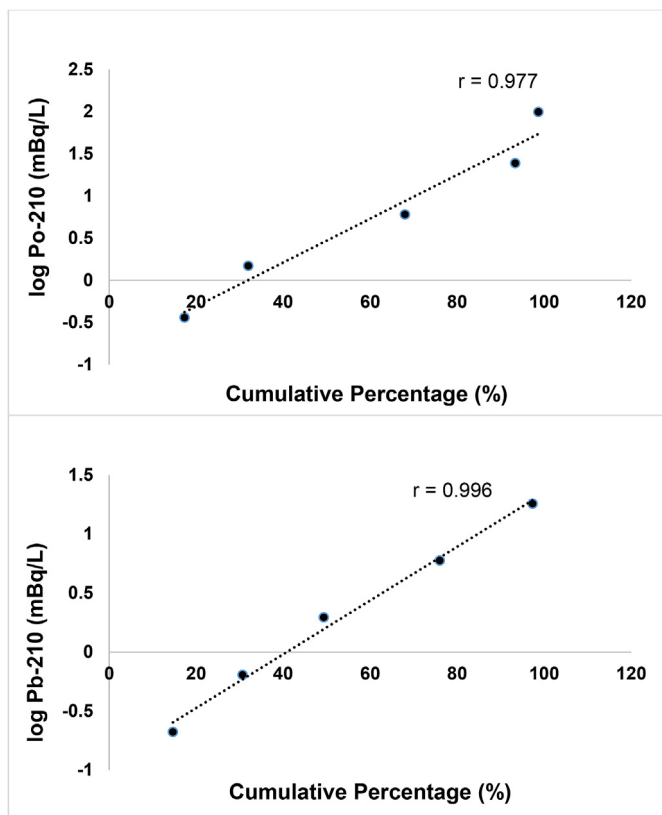


Fig. 2. The logarithm of the average activity concentration of ^{210}Po and ^{210}Pb in the spas groundwaters from southeastern Brazil.

following [Supplementary material](#) related to this article.

The whole data set for the ^{210}Po and ^{210}Pb activity concentrations was submitted to a statistical treatment, considering class intervals arranged in geometric progression, due to the great variability of the values obtained ([Table 1](#)). Lognormal distributions were found ([Fig. 2](#)) as also reported by [Bonotto \(2014, 2015, 2017\)](#) for other radionuclides (^{222}Rn , ^{226}Ra , ^{238}U and ^{234}U) in the same spas groundwaters. The median, modal, and mean values were, respectively: $^{210}\text{Po} = 2.9, 14.9$, and 6.6 mBq/L ; $^{210}\text{Pb} = 2.6, 8.3$, and 4.7 mBq/L .

The use of eq. (3) to the spas groundwaters whose time elapsed between the sampling and counting was higher than 140 days yielded 12.6 mBq/L for the average ^{210}Pb activity concentration. Its application for GAS groundwaters provided a mean value ~ 6 times lower (2 mBq/L) ([Bonotto et al., 2009](#)) due to the presence of lithologies less enriched in natural radionuclides in the Paraná basin. It is important emphasize that such ^{210}Pb activity concentration data represent maximum values as the use of eq. (3) implies on a frequent source of errors because it does not take into account the contribution of the initial ^{210}Po levels to the measured ^{210}Po activity concentration. The following [Supplementary material](#) related to this article shows the estimated ^{210}Pb activity concentrations from the use of eq. (3).

[Fig. 3](#) plots the ^{210}Pb activity concentrations reported in S1 (eqs. (1) and (2)) and S2 (eq. (3)). Several water sources fit the equiline, however, many of them indicate that eq. (3) yields ^{210}Pb values higher than those evaluated from the use of eqs. (1) and (2). In these cases, there is failure on the premise of disregarding the initial ^{210}Po activity on the measured ^{210}Po activity concentration value. As a consequence, the overestimation of the ^{210}Pb activity concentration may cause false decision on the evaluation of the

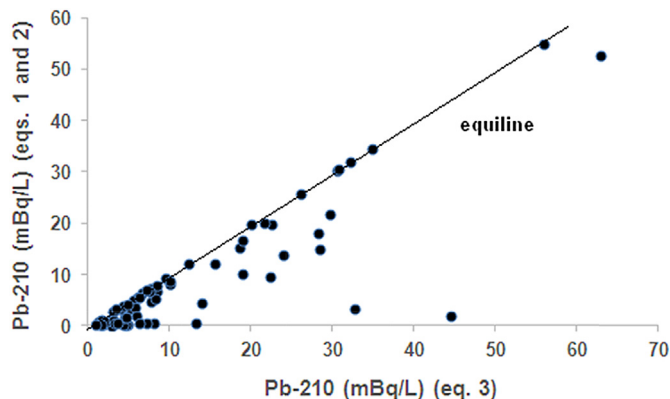


Fig. 3. The ^{210}Pb activity concentrations determined by eqs. (1) and (2) plotted against the ^{210}Pb activity concentrations estimated by eq. (3).

drinking water quality due to the presence of dissolved ^{210}Pb . For instance, it may be pointed out the need of bores sealing or the closure of taps exploiting springs whose waters were previously available for human consumption. Therefore, eqs. (1) and (2) are recommended for providing the ^{210}Po and ^{210}Pb activity concentrations data, despite the time consuming of the analysis in duplicate and costly laboratorial tasks. Such procedure implies on avoiding occasional inconvenient decision for members of the public.

3.1. The variability of the ^{210}Po and ^{210}Pb activity concentrations

[Bonotto \(2014, 2015, 2016, 2017\)](#) reported data for the following parameters in these spas groundwaters: temperature, pH, electrical conductivity, redox potential Eh, dissolved gases (O_2 , CO_2 , H_2S), dry residue ($\sim \text{TDS}$, total dissolved solids), alkalinity (bicarbonate, carbonate, hydroxide), major cations (Na , K , Ca , Mg), major anions (sulfate, chloride, nitrate, fluoride, phosphate), silica, iron (total Fe, Fe^{2+}), and radionuclides (^{222}Rn , ^{220}Rn , ^{226}Ra , ^{228}Ra , ^{238}U , ^{234}U). Statistical tests of correlation were realized among such parameters and the ^{210}Po and ^{210}Pb activity concentrations reported in S1, but none significant value was found. This also happened in other contexts, for instance, in Nordic drinking water from 328 wells ([Isam Salih et al., 2002](#)) and in GAS groundwater from 77 wells ([Bonotto et al., 2009](#)).

This indicates the complexity of the processes involving the transfer of both radionuclides ^{210}Pb and ^{210}Po into the liquid phase after their production in the minerals occurring in the various lithologies. Microscopic, geochemical and other factors very difficult or impossible to measure practically have been pointed out by authors like [Rama and Moore \(1984\)](#), [Clever \(1985\)](#), [Krishnaswami and Seidemann \(1988\)](#), [Harada et al. \(1989\)](#) and [Semkow \(1990\)](#) in order to justify such absence of correlations. Some of them could explain the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio range from 0.003 (BOI) to 434.7 (BRU) (S1) that is much more pronounced than the ratios 0.03–0.43 as reported by [Bonotto et al. \(2009\)](#) in GAS groundwaters, whose lithologies are less diverse than those of this study.

Such factors certainly affect the $^{210}\text{Pb}/^{226}\text{Ra}$, $^{210}\text{Po}/^{226}\text{Ra}$, $^{210}\text{Pb}/^{222}\text{Rn}$, $^{210}\text{Po}/^{222}\text{Rn}$, $^{210}\text{Pb}/^{238}\text{U}$ and $^{210}\text{Po}/^{238}\text{U}$ activity ratios of the spas groundwaters. ^{222}Rn activity concentration data reported by [Bonotto \(2014\)](#) allows calculate values between 2×10^{-6} and 0.05 for the $^{210}\text{Pb}/^{222}\text{Rn}$ activity ratio and from 1×10^{-6} to 0.3 for the $^{210}\text{Po}/^{222}\text{Rn}$ activity ratio. These large deviations from the radioactive equilibrium condition are compatible with the high mobility of ^{222}Rn due to its gaseous nature.

The $^{210}\text{Pb}/^{226}\text{Ra}$, $^{210}\text{Po}/^{226}\text{Ra}$, $^{210}\text{Pb}/^{238}\text{U}$ and $^{210}\text{Po}/^{238}\text{U}$ activity

Table 2

Activity ratios of $^{210}\text{Pb}/^{226}\text{Ra}$, $^{210}\text{Po}/^{226}\text{Ra}$, $^{210}\text{Pb}/^{238}\text{U}$ and $^{210}\text{Po}/^{238}\text{U}$ in spas groundwaters from southeastern Brazil. The data for ^{226}Ra and ^{238}U provide from Bonotto (2015, 2017). Uncertainties ± 10 –15% at 1σ standard deviation based on Poisson counting statistics and error propagation theorem (Young, 1962).

Sample code	$^{210}\text{Pb}/^{226}\text{Ra}$	$^{210}\text{Pb}/^{238}\text{U}$	$^{210}\text{Po}/^{226}\text{Ra}$	$^{210}\text{Po}/^{238}\text{U}$
ALS	0.002	1.3	0.06	38.8
GIO	0.0008	0.06	0.1	11
JUV	0.01	0.6	0.06	3
PLA	0.007	0.3	0.04	1.9
POL	0.004	0.1	0.006	0.2
VIT	0.001	0.03	0.04	0.9
BOI	0.5	30.7	0.001	0.09
PTA	0.003	0.6	0.02	4.4
VIL	0.006	0.8	0.02	2.5
PDE	0.04	60.9	0.004	7
SIL	0.05	7.5	0.002	0.3
FIL	0.006	0.4	0.03	2.5
BEL	0.06	2.6	0.02	0.9
SRE	0.04	3.5	0.002	0.2
COM	0.006	1.5	0.0004	0.1
LIN	0.01	4.7	0.1	59.3
CUR	0.008	3.9	0.04	18.5
SJO	0.02	69.4	0.008	31.2
SCA	0.03	46.3	0.02	32.7
ITA	0.2	137.8	0.006	3.6
SLU	0.003	7.6	0.5	1228
SAT	0.2	310.1	0.5	771
BRU	0.0006	0.6	0.3	254
LAN	0.004	41.5	0.07	691
SAA	0.3	266.8	0.001	1.2
SBE	0.06	10.8	0.05	8.3
BIO	0.02	42	0.006	12.7
JOR	0.01	4.1	0.2	98.3
ADB	0.002	0.04	0.3	6.7
CGO	0.0007	0.01	0.05	0.9
SRC	0.03	2.4	0.04	3.2
SEI	0.02	13.2	0.03	19.7
BMU	0.004	0.005	0.07	0.09
LA1	0.002	2.2	0.1	141
LA2	0.01	4.1	0.009	3.2
LA3	0.05	79.1	0.06	91
LA4	0.008	36.8	0.04	192
LA5	0.2	37.4	0.007	1.1
LA6	0.02	4.5	0.005	0.9
SL7	0.005	2.3	0.01	5.2
SL5	0.01	6.6	0.003	1.3
SL6	0.01	4.2	0.002	0.4
SL3	0.02	8.4	0.005	2.2
SL4	0.002	0.9	0.03	14.2
SL1	0.008	5.6	0.02	11.9
SL10	0.01	35	0.002	5.4
SL9	0.003	0.3	0.03	3.6
ROR	0.002	2.5	0.08	108
REW	0.02	40.3	0.01	21.3
CAF	0.02	81.8	0.009	38.4
FEP	0.2	254.8	0.001	1.7
MAR	0.1	198.3	0.001	2.6
SLI	0.02	26.4	0.02	31
GFL	0.01	24.5	0.007	15
VEN	0.0005	6	0.05	633
MAY	0.03	154.9	0.2	1036
EGU	0.02	74.1	0.001	4.6
VIO	0.03	38.5	0.4	478
DPE	0.2	105.5	0.09	56
BZA	0.0007	2.8	0.1	542
DXE	0.04	32.5	0.008	7.4
LEO	0.03	0.6	0.2	3.7
ISA	0.02	66.4	0.02	86.5
QUI	0.01	1.5	0.02	3.1
NOV	0.05	27.4	0.06	36.1
MAC	0.005	2.2	0.2	79.1
SIN	0.1	20.3	0.8	137.6
FRA	0.0007	0.06	0.05	4.8
PEB	0.004	6.2	0.01	18.8
RIV	0.1	150.8	0.2	230
SMA	0.04	108.4	0.2	483

Table 2 (continued)

Sample code	$^{210}\text{Pb}/^{226}\text{Ra}$	$^{210}\text{Pb}/^{238}\text{U}$	$^{210}\text{Po}/^{226}\text{Ra}$	$^{210}\text{Po}/^{238}\text{U}$
SJO	0.04	9.2	0.04	8
AMO	0.04	704	1.1	17513
DBJ	0.07	13	0.02	3.9
AJU	0.04	16.4	0.03	10.5

ratios as determined from data reported by Bonotto (2015, 2017) are shown in Table 2. These ratios also show deviation from the radioactive equilibrium condition like reported in S1 for the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios and mentioned for the $^{210}\text{Pb}/^{222}\text{Rn}$ and $^{210}\text{Po}/^{222}\text{Rn}$ ratios. The ratios $^{210}\text{Pb}/^{226}\text{Ra}$ are always lower than unity, indicating ^{210}Pb depletion in the waters relatively to its ancestor ^{226}Ra . Except for one groundwater sample (AMO), the same happened for the ratios $^{210}\text{Po}/^{226}\text{Ra}$ that evidenced ^{210}Po depletion in solution relatively to ^{226}Ra . However, the ratios $^{210}\text{Pb}/^{238}\text{U}$ and $^{210}\text{Po}/^{238}\text{U}$ pointed out non-systematic trend of values lower than unity as they were much higher than 1 in many cases. One possible explanation for such finding could be related to the uranium behavior that is an element very sensible to redox conditions, tending to migrate in oxidized environments and precipitate in reduced zones (Langmuir, 1978; Ivanovich and Harmon, 1992), differently from radium, lead and polonium that do not exhibit such tendency.

3.2. Radionuclides mobility indices

The acquired database allows compare different indices sometimes used in the literature for characterizing the heavy metals and radionuclides transfer into the waters. The distribution coefficient (constant), K_D , expresses the partitioning of a particular chemical species between the solid and liquid phases of the porous medium (Borovec, 1981):

$$K_D = m_a V / m_s m \quad (4)$$

where: V/m is the liquid/solid ratio (V is the liquid volume and m is the solid weight), m_a and m_s are amounts of the chemical species adsorbed and remaining in solution, respectively. Such a parameter (in cm^3/g , m^3/kg or dimensionless for diluted water) has been also named as geochemical enrichment factor (Szalay, 1964), enrichment factor (Langmuir, 1978), or adsorption coefficient (AAEC, 1983).

Bonotto (1998, 2015, 2017) adopted another “mobility index” (in g/cm^3 or kg/m^3) for evaluating the radionuclides solubility. It is the reciprocal of the above mentioned indices, corresponding to the ratio of the weight of the dissolved radionuclide per unit volume of solution to its weight per unit weight of the rock matrix. Its numerator and denominator tell us about the liquid and solid phases, respectively. It may be written as $m_{210} = (^{210}\text{Pb})_{\text{water}} / (^{210}\text{Pb})_{\text{rock}}$ in order to express the ^{210}Pb solubility in this study.

Different rock types exhibit variable ^{210}Pb levels due to their variable mineral constituents. This is typical in the study area where occurs leaching of sandstones, siltstones, limestones, basalts, diabases, migmatites, milonites, quartzites, phonolites, nepheline syenites, volcanic tuffs, gneisses, granites, schists and carbonatites, among others. The mean ^{210}Pb activity concentration in rocks from the major geological domains is: Paraná basin (SP) (Bonotto and Lima, 2006) = 12.5 mBq/g; Poços de Caldas intrusive complex (SP/MG) (Matamet, 2016) = 7.5 mBq/g; crystalline basement (SP) (Sabaris and Bonotto, 2010) = 6.7 mBq/g; Alto Paranaíba igneous Province (MG) (this paper) = 100 mBq/g; southeastern shield (MG) (average of all lithologies) = 12.5 mBq/g. Table 3 reports the m_{210} values estimated from all available data, which are in the range of

Table 3Mobility indices of ^{210}Pb and ^{238}U in spas groundwaters from southeastern Brazil. The data for ^{238}U provide from Bonotto (2017).

Sample code	m_{210}^a (kg/m ³)	m_{238}^b (kg/m ³)	$P_{\text{Pb/U}}^c$	Sample code	m_{210}^a (kg/m ³)	m_{238}^b (kg/m ³)	$P_{\text{Pb/U}}^c$
ALS	0.03	0.02	1	LA6	0.63	0.09	7
GIO	0.02	0.40	0.05	SL7	0.13	0.04	3
JUV	0.08	0.16	0.50	SL5	0.26	0.03	10
PLA	0.13	0.20	0.66	SL6	0.46	0.07	6
POL	0.13	0.50	0.26	SL3	0.66	0.05	12
VIT	0.06	0.86	0.06	SL4	0.04	0.03	1
BOI	4.05	0.07	61	SL1	0.17	0.02	8
PTA	0.03	0.02	1	SL10	0.70	0.01	52
VIL	0.66	0.44	1	SL9	0.05	0.10	0.48
PDE	0.97	0.008	121	ROR	0.05	0.01	4
SIL	0.98	0.005	194	REW	0.32	0.005	60
FIL	0.10	0.009	11	CAF	0.33	0.003	122
BEL	1.03	0.02	68	FEP	2.45	0.006	380
SRE	0.84	0.009	89	MAR	1.59	0.005	296
COM	0.43	0.01	38	SLI	0.25	0.006	39
LIN	0.52	0.004	122	GFL	1.22	0.03	36
CUR	0.15	0.001	101	VEN	0.02	0.003	9
SJO	0.52	0.0003	1789	MAY	1.12	0.005	231
SCA	0.83	0.0007	1194	EGU	4.39	0.04	110
ITA	5.17	0.001	3552	VIO	0.77	0.01	57
SLU	0.06	0.0003	196	DPE	4.22	0.03	157
SAT	3.26	0.0004	7994	BZA	0.16	0.04	4
BRU	0.01	0.0007	15	DXE	1.61	0.03	48
LAN	0.12	0.0001	1070	LEO	0.37	0.39	0.94
SAA	4.80	0.0007	6877	ISA	1.33	0.01	99
SBE	1.82	0.006	280	QUI	0.44	0.15	3
BIO	0.44	0.0004	1082	NOV	1.35	0.02	54
JOR	0.08	0.02	3	MAC	0.07	0.02	4
ADB	0.01	0.40	0.04	SIN	2.00	0.05	40
CGO	0.01	1.10	0.01	FRA	0.02	0.17	0.13
SRC	0.28	0.14	2	PEB	0.21	0.02	12
SEI	0.26	0.02	11	RIV	2.41	0.008	300
BMU	0.02	5.66	0.004	SMA	0.72	0.003	216
LA1	0.04	0.01	3	SJO	0.91	0.05	18
LA2	0.40	0.07	6	AMO	0.94	0.0007	1400
LA3	1.58	0.01	118	DBJ	0.26	0.01	21
LA4	0.29	0.005	55	AJU	0.12	0.004	26
LA5	0.75	0.01	56				

^a $m_{210} = (^{210}\text{Pb})_{\text{water}} / (^{210}\text{Pb})_{\text{rock}}$.^b $m_{238} = (^{238}\text{U})_{\text{water}} / (^{238}\text{U})_{\text{rock}}$.^c $P_{\text{Pb/U}} = (^{210}\text{Pb}/^{238}\text{U})_{\text{water}} / (^{210}\text{Pb}/^{238}\text{U})_{\text{rock}}$.

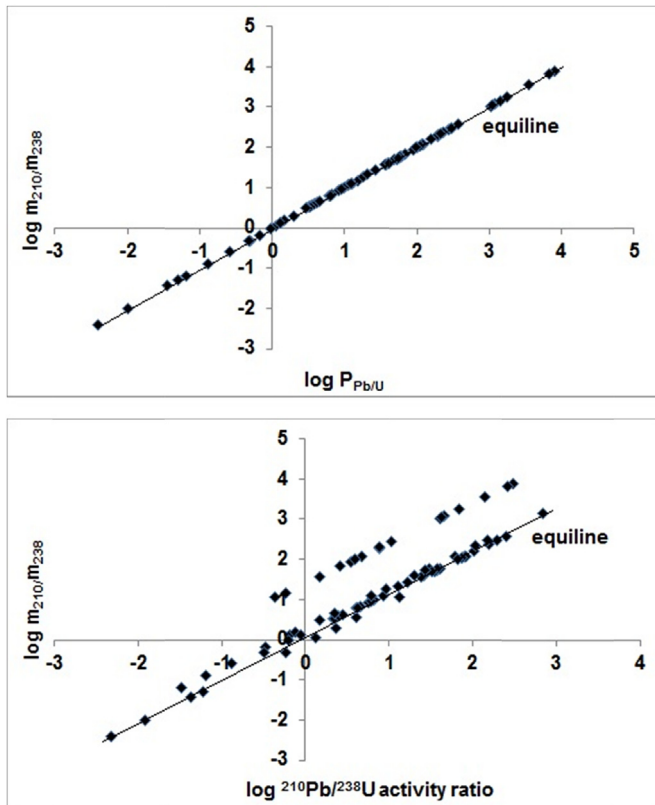


Fig. 4. Plots in logarithmic scale of the (top) ratios m_{210}/m_{238} vs. $P_{pb/U}$ and (bottom) ratios m_{210}/m_{238} vs. $^{210}\text{Pb}/^{238}\text{U}$ activity ratios in the spas groundwaters from south-eastern Brazil.

0.01–5.17 kg/m³. For ^{238}U , the m_{238} range is higher (0.0001–5.66 kg/m³) as reported by Bonotto (2017) (Table 3).

Bonotto and Andrews (1993, 2000) and Bonotto et al. (2001) suggested a different dimensionless ratio (Preference Ratio, P) in order to evaluate the uranium migration to waters interacting with carbonates and granites. It can also be used here to compare the relative mobilities of ^{210}Pb and its ancestor ^{238}U , adopting the following equation: $P_{pb/U} = (^{210}\text{Pb}/^{238}\text{U})_{\text{water}} / (^{210}\text{Pb}/^{238}\text{U})_{\text{rock}}$. This formula expresses the ratio of ^{210}Pb and ^{238}U in the waters divided by the ratio of ^{210}Pb and ^{238}U in the rock matrices. Table 3 shows the $P_{pb/U}$ values estimated from the data, which are in the range of 0.004–7994.

The Preference Ratio $P_{pb/U}$ for each spa groundwater is the same of the ratio m_{210}/m_{238} as calculated from the values reported in Table 3. They are mathematically legitimated from their definitions as also confirmed by the excellent expected linear relationship between them (Fig. 4, top). However, such direct correlation does not occur when the m_{210}/m_{238} ratios (or $P_{pb/U}$) are plotted against the $^{210}\text{Pb}/^{238}\text{U}$ activity ratio of the spas groundwaters. Fig. 4 (bottom) indicates that one additional straight line may be plotted above the equiline, showing several m_{210}/m_{238} ratios (or $P_{pb/U}$) much higher than the $^{210}\text{Pb}/^{238}\text{U}$ activity ratio of the spas groundwaters. Such second line parallel to the equiline fits 17 sampling points at the spas of Águas de Lindóia (SP), Serra Negra (SP), and Lindóia (SP). The mean U concentration in rocks of that region is 13.8 µg/g (Bonotto, 2017), exceeding the values in other lithologies. Thus, these enhanced U-levels in the rock matrices justify the increased values of the m_{210}/m_{238} ratios (and $P_{pb/U}$) above the equiline (Fig. 4, bottom).

It is important to emphasize again that the $^{210}\text{Pb}/^{238}\text{U}$ activity

ratios refer only to the liquid phase data, whereas the m_{210}/m_{238} ratios and $P_{pb/U}$ reflect data of both phases, liquid and solid. One consequence of the findings in this paper is that the $^{210}\text{Pb}/^{238}\text{U}$ activity ratio suggests in some cases preferential ^{238}U transport relative to ^{210}Pb into the liquid phase, whereas the m_{210}/m_{238} ratio (and $P_{pb/U}$) indicates the opposite. Therefore, because the “mobility” indices based on data providing from the rock matrices add extra information on the radionuclides release into the liquid phase during the water/rock interactions, they should be preferred for discussing processes affecting their migration in the aquifer systems.

3.3. Radiation dose due to ^{210}Pb and ^{210}Po

WHO (2011) established guidance levels for several radionuclides in drinking water, assuming that 730 L is the annual ingested volume of water. WHO (2011) proposed a guidance level of 0.1 Bq/L for the activity concentration in drinking water due to both radionuclides, ^{210}Pb and ^{210}Po , in order to not exceed the reference level of the Committed Effective Dose (CED) equal to 0.1 mSv from 1 year's consumption. A comparison of the guideline value of 0.1 Bq/L with the results reported in S1 indicates that ^{210}Po exceeded it in four sampling points located at Minas Gerais State: two from Caxambu city (samples VIO and BZA) and two from PCAM-Poços de Caldas alkaline massif (samples SIN and AMO). This massif is a well-known suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) that possesses an accumulation of natural radionuclides and rare-earth elements (REEs) (Schorscher and Shea, 1992).

Radiation dose calculations are helpful to integrate the ^{210}Pb and ^{210}Po activity concentration data. The adoption of some dose conversion factor (DCF) (IAEA, 1996; WHO, 2011) is required to estimate the CED due to the radionuclides in waters. WHO (2011) reported 6.9×10^{-7} Sv/Bq and 1.2×10^{-6} Sv/Bq as DCF for ^{210}Pb and ^{210}Po , respectively. Considering these values and taking into account an annual consumption of 2 L of water per day, as well the ^{210}Pb and ^{210}Po activity concentration in each water source, then, it is possible estimate a total CED range of 0.0015–0.35 mSv/yr (Table 4).

The dose guideline reference level of 0.1 mSv/yr established by WHO (2011) was reached or surpassed in the same waters exhibiting the highest ^{210}Po levels: VIO, BZA, SIN and AMO. Nieri Neto and Mazzilli (1998) reported a CED value of 0.18 mSv/yr in waters of Águas da Prata (SP) city at the PCAM, where are also located the waters SIN and AMO. The CED data due to dissolved ^{210}Pb and ^{210}Po in the spas groundwaters indicates a major (68%, 51 samples) ^{210}Po contribution to the total dose balance.

Therefore, according to the WHO (2011) guidelines, four spas groundwaters are unsuitable for ingestion due to the ^{210}Po levels. Despite this, they have been utilized or directly consumed in taps installed at public sites of Poços de Caldas, Pocinhos do Rio Verde and Caxambu cities that are touristic centers exhibiting infrastructure with hotels and other facilities for users. Thus, people traditionally visit those centers to ingest water commonly considered “good for health”. Additionally, by the same reason, the local population prefers drinking them rather than those of the public water-supply systems. Consequently, the traditional practices, dietary habits and economic aspects difficult the adequate management of such spas groundwaters.

4. Conclusion

The ^{210}Po and ^{210}Pb activity concentrations in spas groundwaters from São Paulo (SP) and Minas Gerais (MG) states, Brazil, were lognormally distributed, with median, modal, and mean values

Table 4
Radiation dose due to ^{210}Pb and ^{210}Po and respective total Committed Effective Dose (CED) in spas groundwaters from southeastern Brazil. Assuming a drinking water consumption rate = 2 L/day (WHO, 2011).

Sample code	^{210}Pb (mSv/yr)	^{210}Po (mSv/yr)	CED (mSv/yr)	Sample Code	^{210}Pb (mSv/yr)	^{210}Po (mSv/yr)	CED (mSv/yr)
ALS	0.0085	0.0002	0.0086	LA6	0.0014	0.0039	0.0053
GIO	0.0406	0.0001	0.0407	SL7	0.0034	0.0008	0.0042
JUV	0.0046	0.0005	0.0052	SL5	0.0006	0.0017	0.0022
PLA	0.0048	0.0005	0.0053	SL6	0.0005	0.0029	0.0034
POL	0.0011	0.0005	0.0016	SL3	0.0020	0.0042	0.0061
VIT	0.0106	0.0002	0.0108	SL4	0.0062	0.0002	0.0064
BOI	0.00008	0.0153	0.0154	SL1	0.0039	0.0010	0.0049
PTA	0.0014	0.0001	0.0015	SL10	0.0012	0.0044	0.0056
VIL	0.0146	0.0025	0.0171	SL9	0.0059	0.0003	0.0062
PDE	0.0007	0.0037	0.0044	ROR	0.0236	0.0003	0.0239
SIL	0.0002	0.0033	0.0035	REW	0.0019	0.0020	0.0039
FIL	0.0035	0.0003	0.0038	CAF	0.0017	0.0021	0.0037
BEL	0.0021	0.0034	0.0055	FEP	0.0002	0.0154	0.0156
SRE	0.0003	0.0028	0.0031	MAR	0.0002	0.0100	0.0102
COM	0.0002	0.0014	0.0016	SLI	0.0033	0.0016	0.0049
LIN	0.0384	0.0018	0.0402	GFL	0.0081	0.0076	0.0158
CUR	0.0040	0.0005	0.0045	VEN	0.0277	0.0002	0.0279
SJO	0.0014	0.0017	0.0031	MAY	0.0817	0.0070	0.0887
SCA	0.0034	0.0028	0.0062	EGU	0.0030	0.0276	0.0306
ITA	0.0008	0.0174	0.0181	VIO	0.1047	0.0048	0.1095
SLU	0.0538	0.0002	0.0540	DPE	0.0245	0.0266	0.0510
SAT	0.0473	0.0109	0.0582	BZA	0.3517	0.0010	0.3527
BRU	0.0266	0.00004	0.0267	DXE	0.0040	0.0101	0.0142
LAN	0.0121	0.0004	0.0125	LEO	0.0236	0.0023	0.0259
SAA	0.0001	0.0161	0.0162	ISA	0.0189	0.0084	0.0273
SBE	0.0081	0.0061	0.0142	QUI	0.0060	0.0017	0.0077
BIO	0.0008	0.0015	0.0023	NOV	0.0117	0.0051	0.0168
JOR	0.0215	0.0005	0.0220	MAC	0.0173	0.0003	0.0176
ADB	0.0247	0.00009	0.0248	SIN	0.0892	0.0076	0.0968
CGO	0.0093	0.00007	0.0093	FRA	0.0105	0.00008	0.0106
SRC	0.0042	0.0018	0.0059	PEB	0.0041	0.0008	0.0049
SEI	0.0043	0.0016	0.0060	RIV	0.0242	0.0091	0.0333
BMU	0.0047	0.0001	0.0049	SMA	0.0212	0.0027	0.0239
LA1	0.0309	0.0003	0.0311	SJO	0.0052	0.0034	0.0086
LA2	0.0035	0.0025	0.0060	AMO	0.1534	0.0035	0.1570
LA3	0.0199	0.0100	0.0299	DBJ	0.0068	0.0130	0.0198
LA4	0.0168	0.0018	0.0187	AJU	0.0068	0.0061	0.0129
LA5	0.0002	0.0047	0.0049				

corresponding to 2.9, 14.9, and 6.6 mBq/L for ^{210}Po and 2.6, 8.3, and 4.7 mBq/L for ^{210}Pb , respectively. Co-variations among the ratios $^{210}\text{Pb}/^{226}\text{Ra}$, $^{210}\text{Po}/^{226}\text{Ra}$, $^{210}\text{Pb}/^{238}\text{U}$ and $^{210}\text{Po}/^{238}\text{U}$ in them indicated great deviation from the radioactive equilibrium condition as also verified for the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios. The ratios $^{210}\text{Pb}/^{226}\text{Ra}$ always pointed out accentuated ^{210}Pb depletion in the waters relatively to its ancestor ^{226}Ra , whereas the ratios $^{210}\text{Pb}/^{238}\text{U}$ and $^{210}\text{Po}/^{238}\text{U}$ were above unity in many cases. The acquired database allowed verify that two different indices for investigating the mobility of the radionuclides provided equivalent results, adding information of the rock matrices on the radionuclides release into the liquid phase during the water/rock interactions. The mobility indices comparing the solubility of ^{210}Pb and ^{238}U were more helpful than the $^{210}\text{Pb}/^{238}\text{U}$ activity ratios for evaluating processes affecting their migration in the aquifer systems studied in this paper. Radiation dose calculations permitted integrate the activity concentration data obtained for both radionuclides, ^{210}Pb and ^{210}Po , allowing estimate a total Committed Effective Dose (CED) range of 0.0015–0.35 mSv/yr. Four spas groundwaters exhibiting high ^{210}Po levels possessed CED values equivalent or above of the WHO guideline reference level of 0.1 mSv from 1 year's consumption of drinking water. Two of them are located at the PCAM that is a well-known suite of alkaline volcanic and plutonic rocks enriched in natural radionuclides and rare-earth elements (REEs).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvrad.2017.03.006>.

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