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Evaluation of ^{210}Po and ^{210}Pb in Some Mineral Spring Waters in Brazil

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ABSTRACT

Analysis of most natural waters shows that ^{210}Po, the last radioactive member of the uranium natural decay-series, is present at very low activities, usually lower than its insoluble precursor, ^{210}Pb. Recent papers, however, show that ^{210}Po can exist at very high concentrations in groundwaters of some shallow aquifers. Concentrations of ^{210}Po and ^{210}Pb have been analyzed in the mineral spring waters of a high background region of Brazil: Águas da Prata. The water samples were collected over a period of one year in springs used by the local population and tourists to the region.

Concentrations ranging from $< 3{\cdot}5$ mBq l^{-1} to $7{\cdot}80 \times 10^2$ mBq l^{-1} and from $3{\cdot}0$ mBq l^{-1} to $3{\cdot}98 \times 10^2$ mBq l^{-1} were observed for ^{210}Pb and ^{210}Po, respectively. Doses were estimated in order to evaluate the relative importance of the ingestion of such radionuclides. Based upon measured concentrations, effective doses up to $1{\cdot}8 \times 10^{-1}$ mSv y^{-1} were observed for ^{210}Pb and ^{210}Po. Doses up to $5{\cdot}9$ mSv y^{-1} for the ingestion of ^{210}Pb and up to $1{\cdot}9$ mSv y^{-1} for the ingestion of ^{210}Po were obtained for the critical organs.

INTRODUCTION

The nuclide ^{210}Po (half-life of 138·4 days) is the last radioactive member of the ^{238}U series. It is produced by the decay of ^{210}Pb (half-life of 22·3 years) via ^{210}Bi (half-life of 5·02 days). It is an alpha emitter and has a very high specific radioactivity. Analysis of most natural waters shows that ^{210}Po is present at very low activities, usually lower than its insoluble precursor, ^{210}Pb. Recent papers, however, show that ^{210}Po can occasionally exist at very high concentrations in groundwaters of some shallow aquifers (Cowart *et al*., 1987; Salonen, 1988; Harada *et al*., 1989; Narita *et al*., 1989). For example, Harada *et al.* (1989) found a shallow well in central Florida

which showed consistent unsupported activities of greater than 18,500 $mBq\,l^{-1}$ (500 $pCi\,l^{-1}$).

In Brazil, prior to this work, no data were found concerning the occurrence of ^{210}Po in mineral and drinking waters. In this investigation we have

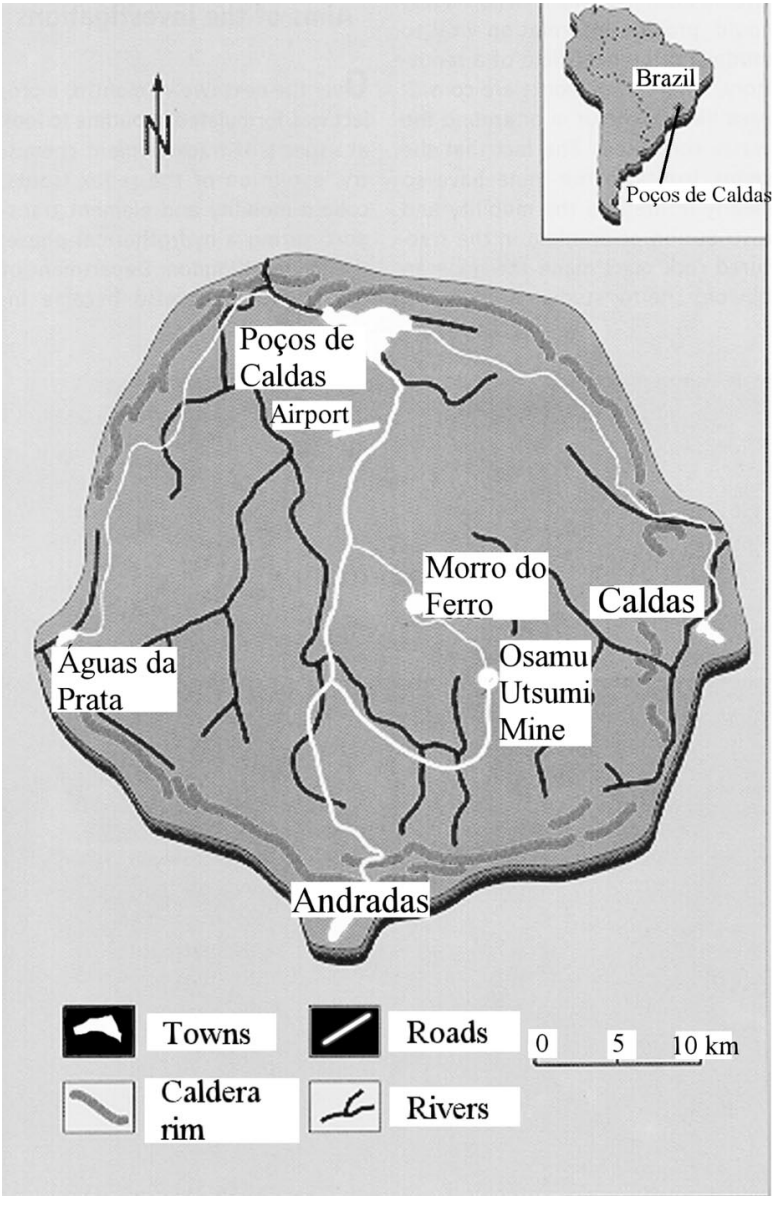

Fig. 1. The Poços de Caldas Plateau (Nagra Bulletin, 1993).

carried out a survey of the ^{210}Po activity concentration in the mineral spring waters of a high background region of Brazil. This region is a zone of volcanic alkaline intrusives, located in Poços de Caldas Plateau (Fig. 1). In this plateau many health resorts are found, based on sources of thermal and mineral waters. The Águas da Prata are among the most visited of these springs, not only by tourists and patients but also by the local population of the region. Several radionuclides of the uranium natural decay series have already been analyzed, by the second author, in these springs, namely: ^{238}U and ^{234}U (Camargo and Mazzilli, 1996), and ^{226}Ra, ^{210}Pb and ^{222}Rn (Oliveira *et al*., 1994; Jacomino *et al*., 1996). In order to study the isotopic equilibrium between ^{210}Po and ^{210}Pb, the activity concentration of ^{210}Pb was also determined in the water samples collected.

EXPERIMENTAL

Samples for ^{210}Po and ^{210}Pb analysis were collected from the spring sites used by tourists and the local population of Águas da Prata. The spring waters chosen for the present study were: Padre, Paiol, Balneário, Vitória, Prata Antiga, Prata Nova, Platina, Prata Radioativa, Vilela and São Bento. The location of these springs are shown in Fig. 2. The samples were acidified by addition of nitric acid, to a pH lower than 2, at the time of collection. Temperature and pH readings were made in the field and 20·0 mg of stable lead and 310 mBq of ^{208}Po were added as a yield tracer.

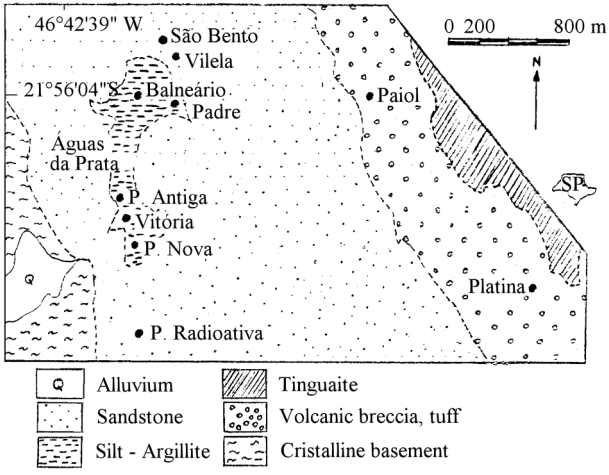

Fig. 2. Geologic map and location of the springs studied.

The procedure adopted for the analysis of ^{210}Po and ^{210}Pb is modified from that of Bunzl and Kracke (1979). Basically, 51 water samples in duplicate were concentrated to approximately 300 ml by evaporation, avoiding temperatures exceeding 80°C in order to prevent losses of polonium by volatilization. The final solution was then neutralized with 20M sodium hydroxide. The polonium was then coprecipitated with lead by addition of sodium sulfide. After 4–6 h of settling, the precipitate was filtered and oxidized to sulfate by addition of concentrated HNO_3. The precipitate was dried by heating on a sand bath and partially dissolved by addition of concentrated HNO_3 and water. The remaining precipitate of $PbSO_4$ is separated from the solution where most of the polonium is found.

The solution containing polonium was transferred to a plating cell where the polonium was spontaneously deposited onto a copper disc. The alpha spectrum of polonium was obtained by using a surface barrier detector. The counting efficiency was 30% and the lower limit of detection achieved for this methodology was 0·34 $mBq\,l^{-1}$. For spiked samples of deionized water, this procedure produced yields of 60–90%; for natural waters the yields were considerably less, ranging from 20 to 78%.

The precipitate of $PbSO_4$ was then dissolved by addition of ammonium acetate, under heating, the pH adjusted to 4–5, and 1·0 ml of a Na_2CrO_4 solution was added. The $^{210}PbCrO_4$ precipitate formed was collected on a filter paper. After its separation ^{210}Pb was determined, when equilibrium has been reached, through ^{210}Bi (immediate decay product of ^{210}Pb with a beta particle of 1·17 MeV) by measuring the gross beta activity of the precipitate, using a low background gas flow proportional counter. In order to avoid the interference of the emission of the weak beta peak of ^{210}Pb (18 keV) in the measurement, the precipitate was covered with a filter paper. Typical lower limit of detection for this method was 3·5 $mBq\,l^{-1}$. The procedure provided yields of 30–100% for natural waters and from 76–95% for spiked samples of deionized water.

The methodology was checked experimentally by measuring a standard ^{210}Pb solution from EPA. The reproducibility was characterized by coefficient of variation values of 7% and 3%, with an accuracy of 23% and 29% for ^{210}Pb and ^{210}Po, respectively (Nieri Neto, 1996).

RESULTS AND DISCUSSION

The radionuclide concentration data are presented in Table 1 for ^{210}Po and ^{210}Pb. The concentration varied from $< 3{\cdot}5\ mBq\,l^{-1}$ to $7{\cdot}80 \times 10^2\ mBq\,l^{-1}$ and from $3{\cdot}0\ mBq\,l^{-1}$ to $3{\cdot}98 \times 10^2\ mBq\,l^{-1}$, for ^{210}Pb and ^{210}Po, respectively. In addition to ^{210}Po and ^{210}Pb measurements, the pH and

TABLE 1
Temperature, pH, Radionuclide Concentration Data for ^{210}Po and ^{210}Pb, and $^{210}Po/^{210}Pb$ Activity Ratios Range for Each Spring

Spring	*Temp.°C*	*pH*	^{210}Po *N*	^{210}Po *Range* ($mBq\,l^{-1}$)	^{210}Po *Geometric mean* ($mBq\,l^{-1}$)	^{210}Pb *N*	^{210}Pb *Range* ($mBq\,l^{-1}$)	^{210}Pb *Geometric mean* ($mBq\,l^{-1}$)	$^{210}Po/^{210}Pb$ *activity ratio*
Padre	20–22	6·9–7·5	4	3·0–6·0	3·8	5	$< 3{\cdot}5$–$1{\cdot}4 \times 10^1$	5·9	0·26–1·6
Paiol	21–22	7·0–7·4	4	$8{\cdot}8$–$1{\cdot}1 \times 10^1$	$9{\cdot}5 \times 10^1$	4	$< 3{\cdot}5$–$1{\cdot}0 \times 10^1$	7·7	0·91–1·8
Balneário	22–24	6·7–7·8	3	$9{\cdot}4$–$1{\cdot}4 \times 10^1$	$1{\cdot}1 \times 10^1$	3	$1{\cdot}4 \times 10^1$–$2{\cdot}4 \times 10^1$	$1{\cdot}8 \times 10^1$	0·40–0·86
Vitória	22–24	7·8–8·2	3	$1{\cdot}0 \times 10^1$–$1{\cdot}5 \times 10^1$	$1{\cdot}2 \times 10^1$	5	$1{\cdot}0 \times 10^1$–$2{\cdot}9 \times 10^1$	$2{\cdot}0 \times 10^1$	0·52–1·1
Prata Antiga	19–22	7·6–8·0	5	$1{\cdot}1 \times 10^1$ –$2{\cdot}3 \times 10^1$	$1{\cdot}7 \times 10^1$	5	$9{\cdot}0$–$3{\cdot}1 \times 10^1$	$2{\cdot}1 \times 10^1$	0·52–2·6
Prata Nova	22–26	6·9–7·1	5	$2{\cdot}1 \times 10^1$ –$3{\cdot}6 \times 10^1$	$3{\cdot}0 \times 10^1$	5	$4{\cdot}2 \times 10^1$–$5{\cdot}2 \times 10^1$	$4{\cdot}5 \times 10^1$	0·44–0·8
Platina	23–25	8·2–8·5	4	$2{\cdot}3 \times 10^1$–$5{\cdot}3 \times 10^1$	$3{\cdot}9 \times 10^1$	5	$2{\cdot}3 \times 10^1$–$7{\cdot}3 \times 10^1$	$4{\cdot}2 \times 10^1$	0·73–0·9
Prata Radioativa[a]	20–24	6·9–7·2	5	$2{\cdot}6 \times 10^1$–$9{\cdot}2 \times 10^1$	$4{\cdot}0 \times 10^1$	5	$3{\cdot}4 \times 10^1$–$5{\cdot}9 \times 10^1$	$4{\cdot}3 \times 10^1$	0·73–1·6
Vilela[a]	21–22	4·7–5·4	5	$1{\cdot}20 \times 10^2$–$2{\cdot}34 \times 10^2$	$1{\cdot}78 \times 10^2$	5	$2{\cdot}10 \times 10^2$–$4{\cdot}86 \times 10^2$	$3{\cdot}26 \times 10^2$	0·47–0·66
São Bento[a]	20–21	4·7–5·0	5	$2{\cdot}78 \times 10^2$–$3{\cdot}98 \times 10^2$	$3{\cdot}35 \times 10^2$	5	$4{\cdot}97 \times 10^2$–$7{\cdot}80 \times 10^2$	$5{\cdot}87 \times 10^2$	0·51–0·72

[a] Highly mineralized springs.
N = number of measured samples.

temperature were analyzed for each sample in the field. The results are also presented in Table 1.

Regarding the aquifer lithology, the springs studied can be classified into two main groups: the first one, which includes the springs Vilela, São Bento and Prata Radioativa, is fed by aquifers composed of sandstone rocks. These waters, with low total dissolved solids, presented the highest activity concentrations, up to $7{\cdot}80 \times 10^2$ mBq l^{-1} and $3{\cdot}98 \times 10^2$ mBq l^{-1}, for ^{210}Pb and ^{210}Po, respectively. In this specific case, such activity concentrations can be explained by the fact that these springs are associated with sandstones with 0·1–0·2% of U_3O_8 in their composition (Longo, 1967). Also, Vilela and São Bento springs have the lowest pH of all the springs studied. The second one, in which are included the remnant sources, is fed by water passing through alkaline rocks of volcanic origin. The waters of this group have a deep origin, and are highly mineralized with pH values around 7·0 These waters contained lower activity concentrations (Table 1).

The temperatures for these samples varied over rather small ranges and no correlation with ^{210}Po and ^{210}Pb was found. The other parameter studied, the pH, seems to correlate with the polonium and lead concentration, at least it can explain the low activity concentration noted in the Prata Radioativa spring compared to the other springs of the same group. The pH observed for this spring (6·9–7·2) may be favouring the coprecipitation of lead and polonium.

Calculation of polonium and lead isotopic activity ratios was carried out, giving values ranging from 0·26 to 2·6 (Table 1). Only in 5 of 42 samples analyzed was this ratio above unity. Although the analysis of most natural waters shows that ^{210}Po is present at very low activities, usually lower than its insoluble precursor (^{210}Po/^{210}Pb activity ratios ranging from 0·2 to 1), Harada *et al.* (1989) have found that ^{210}Po exists at very high concentrations in some ground waters in west central Florida. All of the high-polonium groundwaters discovered in Florida were characterized by low total dissolved solids, were slightly acidic (pH around 5) and contained some sulfide.

Based upon measured concentrations, doses were evaluated for ^{210}Po and ^{210}Pb. The individual dose was evaluated by considering a daily consumption of 1·21 (ICRP 23), dose factors from ICRP 67 and the geometric mean concentration for each spring. The annual dose equivalents per unit activity of ingested ^{210}Po and ^{210}Pb, used in the calculations, in Sv Bq^{-1} were: $1{\cdot}3 \times 10^{-5}$ and $1{\cdot}2 \times 10^{-6}$ for the kidney and committed effective dose, and $2{\cdot}3 \times 10^{-5}$ and $7{\cdot}0 \times 10^{-7}$ for the bone surface and committed effective dose, respectively. The results obtained are presented in Table 2, for ^{210}Po and ^{210}Pb. Effective doses up to $1{\cdot}8 \times 10^{-1}$ mSv y^{-1} were observed for ^{210}Pb and ^{210}Po. Doses up to 5·9 mSv y^{-1} for the ingestion of

TABLE 2
Expected Doses Resulting From the Consumption of the Spring Waters Studied

Spring	^{210}Po H_{kidney} $(mSv\,y^{-1})$	^{210}Po H_E $(mSv\,y^{-1})$	^{210}Pb $H_{bone\ surface}$ $(mSv\,y^{-1})$	^{210}Pb H_E $(mSv\,y^{-1})$
Padre	$2{\cdot}2\times10^{-2}$	$2{\cdot}0\times10^{-3}$	$5{\cdot}9\times10^{-2}$	$1{\cdot}8\times10^{-3}$
Paiol	$5{\cdot}4\times10^{-2}$	$5{\cdot}0\times10^{-3}$	$7{\cdot}8\times10^{-2}$	$2{\cdot}4\times10^{-3}$
Balneário	$6{\cdot}3\times10^{-2}$	$5{\cdot}8\times10^{-3}$	$1{\cdot}8\times10^{-1}$	$5{\cdot}5\times10^{-3}$
Vitória	$6{\cdot}8\times10^{-2}$	$6{\cdot}3\times10^{-3}$	$2{\cdot}0\times10^{-1}$	$6{\cdot}1\times10^{-3}$
Prata Antiga	$9{\cdot}7\times10^{-2}$	$8{\cdot}9\times10^{-3}$	$2{\cdot}1\times10^{-1}$	$6{\cdot}4\times10^{-3}$
Prata Nova	$1{\cdot}7\times10^{-1}$	$1{\cdot}6\times10^{-2}$	$4{\cdot}5\times10^{-1}$	$1{\cdot}4\times10^{-2}$
Platina	$2{\cdot}2\times10^{-1}$	$2{\cdot}0\times10^{-2}$	$4{\cdot}3\times10^{-1}$	$1{\cdot}3\times10^{-2}$
Prata Radioativa	$2{\cdot}3\times10^{-1}$	$2{\cdot}1\times10^{-2}$	$4{\cdot}3\times10^{-1}$	$1{\cdot}3\times10^{-2}$
Vilela	1·0	$9{\cdot}4\times10^{-2}$	3·3	$1{\cdot}0\times10^{-1}$
São Bento	1·9	$1{\cdot}8\times10^{-1}$	5·9	$1{\cdot}8\times10^{-1}$

H_{kidney} = committed dose to the kidney.
H_{bone} = committed dose to the bone surface.
H_E = committed effective dose.

^{210}Pb and up to 1·9 mSv y^{-1} for the ingestion of ^{210}Po were obtained for the critical organs. The expected doses estimated for the ingestion of ^{210}Po and ^{210}Pb are of the same order of magnitude as those obtained, by the second author, in a previous work for the ingestion of ^{226}Ra and ^{210}Pb in the same spring waters (Oliveira *et al*., 1994). The doses obtained for the ^{238}U and ^{234}U (Camargo *et al*., 1996), on the other hand, were two orders of magnitude lower than the doses evaluated in the present paper for ^{210}Pb and ^{210}Po.

Finally, the results of the dose calculation show that ^{210}Pb and ^{210}Po are possibly significant radionuclides as far as the consumption of such waters is considered. Vilela spring is the most critical, not only because of the higher expected doses but also because it is the one most used by visitors and inhabitants of Águas da Prata.

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