



Seasonal Variations of ^{226}Ra and ^{222}Rn in Mineral Spring Waters of Aguas da Prata, Brazil

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In this paper the activity concentrations of ^{226}Ra and ^{222}Rn were assayed in the mineral spring waters of Aguas da Prata in order to evaluate the seasonal variations of such radionuclides. The results obtained were related to the chemical composition of the water as well as to the lithology of the aquifer and temperature. Higher activity concentrations up to $1.8 \times 10^3 \text{ mBq L}^{-1}$ for ^{226}Ra and $1.2 \times 10^2 \text{ Bq L}^{-1}$ for ^{222}Rn have been observed in waters with low levels of soluble salts. Waters which present high levels of carbonate and sulphate salts showed maximum values of $2.5 \times 10^2 \text{ mBq L}^{-1}$ for ^{226}Ra and $2.7 \times 10^1 \text{ Bq L}^{-1}$ for ^{222}Rn . This behaviour is mainly due to the physico-chemical properties of these radionuclides in water as well as to the lithologic structure of the aquifers. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

In the last few decades, the behaviour of uranium and thorium decay series nuclides in groundwater has contributed to an understanding of the mechanisms of geochemical reactions and transport processes in rock-water systems. However, many uncertainties persist regarding the behaviour in rock-water systems, mainly due to the relative importance of nuclear alpha-particle recoil and chemical processes, such as ion exchange, sorption and precipitation. Two major factors to be considered to better understand such interactions are: the role of aquifer solids in controlling the radionuclides' behaviour in water and their total solution composition in the water.

Concentration levels of ^{226}Ra and ^{222}Rn have been analysed in most of the mineral spring waters available in the Aguas da Prata region, which is located in the Poços de Caldas plateau, one of the biggest weathered alkaline intrusions in the world and one of the most highly radioactive natural regions of Brazil (Fig. 1). In this plateau can be found many health resorts based on springs of thermal and mineral waters. The Aguas da Prata spring waters show large variations in composition. Bicarbonate, carbonate and sulphate salts have

been observed in these mineral waters. The Aguas da Prata spring waters chosen for the present study are: Vilela, Platina, Padre, Paiol, Balneário Teotônio Vilela, Prata Antiga, Prata Nova, Prata Radioativa and Vitória.

The ^{226}Ra was assayed by gross-alpha counting of a $\text{Ba}(\text{Ra})\text{SO}_4$ precipitate. The measurement was carried out in a low-background gas-flow proportional counter. The ^{222}Rn concentrations were measured by liquid scintillation method.

Water samples were randomly collected at nine spring sites over a period of one year, in order to evaluate the seasonal variation of these two radionuclides. According to previous studies concerning the local temperature, rainfall, evaporation and relative humidity, the climate of the region can be considered to be tropical or sub-tropical, with a well-defined dry season from April to October and a wet season from October to March. The average temperature in Aguas da Prata is 20.5°C and the annual rainfall is above 1500 mm y^{-1} (Szikszay, 1981).

Paiol, Platina and Vitória springs are considered as hypothermals, since their temperature is slightly higher than the annual average of the region. The remainder can be classified as cold waters. Regarding the aquifer lithology, the Aguas da Prata springs can be classified into two main groups: the first, which includes the springs Vilela and Prata

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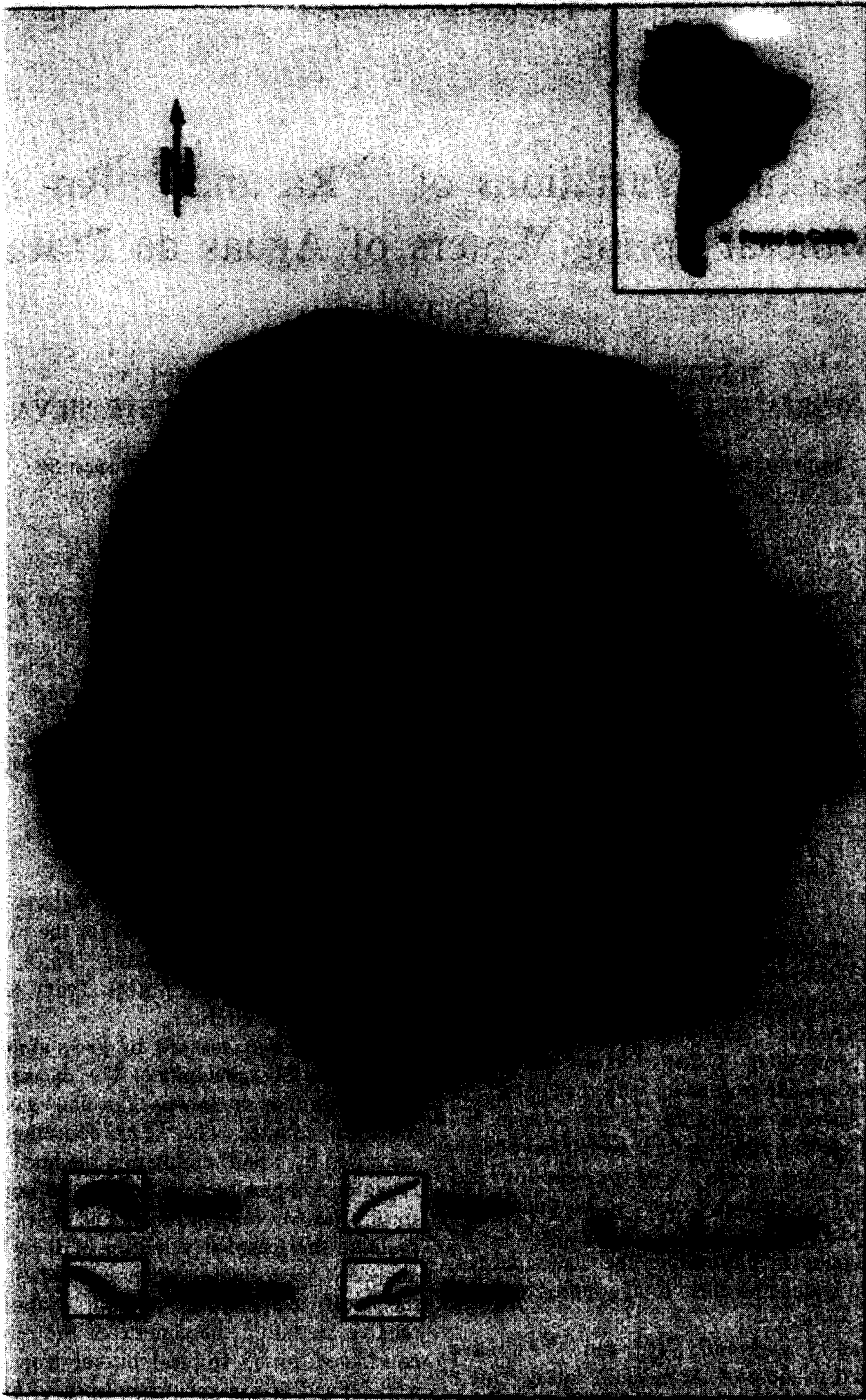


Fig. 1. The Poços de Caldas Plateau (Nagra Bulletin, 1993).

Radioativa, is fed by aquifers composed of sandstone rocks; the second, in which are included the remnant sources, is fed by water passing through alkaline rocks of volcanic origin (Szikszay and Sampa, 1982). The waters of the second group, which rise through alkaline rocks of volcanic origin aquifers, have deep sources, are highly mineralized, and present pH values around 7.0. These waters present high concentrations of bicarbonate and sul-

phate salts in their composition. On the other hand, waters rising from sandstone rock aquifers are poorly mineralized, have no deep sources, and present low conductivity and pH, around 5.0.

Radium and Radon in Groundwater

Radium occurs as a natural component of all groundwater in an extremely wide range of activi-

Table 1. Annual arithmetic mean of ^{226}Ra and ^{222}Rn activity concentrations in mineral spring waters

Spring	^{226}Ra (mBq L ⁻¹)	Concentration range(mBq L ⁻¹)	^{222}Rn (Bq L ⁻¹)	Concentration range(Bq L ⁻¹)
Vilela	$(1.8 \pm 0.3) \times 10^3$	1.4×10^3 – 2.2×10^3	$(1.2 \pm 0.1) \times 10^2$	1.0×10^2 – 1.3×10^2
Paíol	4.5 ± 3.7	< LLD– 1.1×10^1	5.8 ± 0.4	5.3 – 6.3
Padre	5.7 ± 3.3	< LLD– 1.1×10^1	1.3 ± 1.1	< LLD– 2.3
Platina	3.0 ± 1.1	< LLD– 4.4	3.8 ± 3.3	0.9 – 7.2
Prata Nova	$(5.2 \pm 0.8) \times 10^1$	4.2×10^1 – 6.4×10^1	$(2.7 \pm 0.3) \times 10^1$	2.2×10^1 – 3.0×10^1
Prata Antiga	$(1.7 \pm 0.2) \times 10^2$	1.3×10^2 – 1.8×10^2	3.8 ± 1.4	2.6 – 5.7
Prata Radioativa	$(4.4 \pm 0.7) \times 10^1$	3.3×10^1 – 4.9×10^1	$(1.2 \pm 0.3) \times 10^1$	7.7 – 1.6×10^1
Vitória	$(2.5 \pm 0.5) \times 10^2$	1.6×10^2 – 3.2×10^2	8.0 ± 5.9	4.3 – 1.9×10^1
Balneário Teotônio Vilela	$(6.2 \pm 2.3) \times 10^1$	2.3×10^1 – 8.8×10^1	5.8 ± 3.5	1.2 – 1.0×10^1

LLD = lower limit of detection

ties. This element rarely occurs alone, but as a rule is generated by the decay of the natural uranium and thorium. The concentration of radium in groundwater will depend on the means by which it enters in water, the amount of radium in the source, the mechanisms that remove radium from the water, and processes that move the radium away from its source.

Radium manifests chemical properties similar to the other alkaline earth elements of Group IIA to which it belongs. However, its low natural abundance of 10^{-12} g L⁻¹ in surface water rarely allows Ra salts to reach a solubility product concentration in natural water. Therefore, the important chemical reactions are those of adsorption to active surfaces of all kinds and co-precipitation with Ca and Ba salts in particular (Dick and Jonasson, 1986). In a few cases, co-precipitation with Mg, Fe and Mn can occur.

Since the average natural abundance of radium in rocks is around 10^{-12} g g⁻¹, radium concentrations are extremely low in matrix rocks, and it has been shown that radium daughters are more concentrated in microfractures and along grain boundaries (Osmond *et al.*, 1983). The first step in the separation of radium from its uranium-bearing rock is generally due to the fact that Ra^{2+} is a large cation (1.4) relative to U^{4+} (1.04). The loss of radium probably occurs by diffusion in the original host mineral and by diffusion through the water layer adsorbed on the grain surface, and hence into solution. Apparently, the radiation damage caused by the recoil of an atom when it undergoes alpha decay permits the increased mobility of daughters and increase in solid-state diffusion of Ra^{2+} (Brookins, 1984).

Groundwater, and even river water, are generally enriched with ^{222}Rn over its parent ^{226}Ra . The background concentration of radon varies considerably and depends not only on the amount of Ra present in the vicinity, but also on the emanation efficiency of the substrate. The observation of temporal variations of radium and radon activities in groundwater supplies suggested that the scale length of ^{222}Rn migration in groundwater transport may be greater than that of ^{226}Ra , despite the much longer half-life of ^{226}Ra . It appears that the trans-

port of radium by groundwater may be extremely limited owing to continual exchange with the aquifer solids (King *et al.*, 1982). The escape of radon from solids has been studied by numerous workers. It has been observed that this escape occurs mainly through direct recoil, indirect recoil, and diffusion.

Material and Methods

The water samples were seasonally collected over a period of one year in the springs already described. For ^{226}Ra determination, the samples were collected in vessels of 10 L, in which a solution of 6 M nitric acid was previously added, in order to get a final pH lower than 1.5. This procedure was adopted to prevent losses by sorption of the radionuclides in the vessels. The samples were evaporated in order to reduce the volume from 5 to 1 L and each analysis was carried out in duplicate.

The ^{226}Ra activity concentration was determined by co-precipitation with barium sulphate at pH 4.5–5.0 in the presence of ethylenediamine tetraacetic acid, after separation from its daughters by complexing with NTA at pH 12.5–13.0. The ^{226}Ra was assayed by gross-alpha counting of the $\text{Ba}(\text{Ra})\text{SO}_4$ precipitate, after the decay of ^{224}Ra and ^{223}Ra ; that is, after 25 days. The measurement was carried out in a low-background gas-flow proportional counter. The lower limit of detection (LLD) for this method was 2.2 mBq L⁻¹ for ^{226}Ra , at a 95% confidence level (Oliveira, 1993).

The ^{222}Rn activity concentration was assayed by the liquid scintillation method. For this analysis, the samples were collected directly in the counting vessels, in which the scintillation solution Aquasol had previously been added. The lower limit of detection for this method was 1.8×10^{-1} Bq L⁻¹, at a 95% confidence level (Sampa, 1979).

Results and Conclusion

The radionuclide activity concentration data are presented in Table 1. Arithmetic means ranging from 3.0 to 1.8×10^3 mBq L⁻¹ were observed for ^{226}Ra , the lowest value being for the Platina spring, which presents in its composition carbonate, bicarbonate and sulphate salts, and the highest value

Table 2. Seasonal variation of ^{222}Rn activity concentrations (Bq L^{-1})

	Winter	Spring	Summer	Autumn
Vilela	$(1.3 \pm 0.1) \times 10^2$	$(1.2 \pm 0.1) \times 10^2$	$(1.2 \pm 0.1) \times 10^2$	$(1.0 \pm 0.1) \times 10^2$
Paiol	6.0 ± 0.5	6.3 ± 0.0	5.3 ± 0.3	5.8 ± 0.2
Padre	1.8 ± 0.1	< LLD	2.3 ± 0.2	2.1 ± 0.2
Platina	7.2 ± 0.1	5.9 ± 0.4	0.9 ± 0.1	1.1 ± 0.1
Prata Nova	$(2.8 \pm 0.1) \times 10^1$	$(3.0 \pm 0.1) \times 10^1$	$(2.2 \pm 0.1) \times 10^1$	$(2.7 \pm 0.1) \times 10^1$
Prata Antiga	2.6 ± 0.2	5.7 ± 0.2	4.2 ± 0.6	2.9 ± 0.1
Prata Radioativa	$(1.1 \pm 0.1) \times 10^1$	$(1.4 \pm 0.1) \times 10^1$	7.7 ± 0.1	$(1.6 \pm 0.1) \times 10^1$
Vitória	5.9 ± 0.3	5.7 ± 0.1	$(1.9 \pm 0.1) \times 10^1$	4.3 ± 0.4
Balneário Teotônio Vilela	$(1.1 \pm 0.1) \times 10^1$	1.2 ± 0.6	7.7 ± 0.6	5.6 ± 0.8

LLD = lower limit of detection.

Table 3. Seasonal variation of ^{226}Ra activity concentrations (mBq L^{-1})

	Winter	Spring	Summer	Autumn
Vilela	$(2.2 \pm 0.3) \times 10^3$	$(1.9 \pm 0.3) \times 10^3$	$(1.7 \pm 0.1) \times 10^3$	$(1.4 \pm 0.9) \times 10^3$
Paiol	1.1×10^1 *	< LLD	< LLD	5.2 ± 1.9
Padre	$(1.1 \pm 0.5) \times 10^1$	3.1 ± 0.2	< LLD	5.2 ± 1.9
Platina	4.4 ± 0.2	< LLD	< LLD	4.1*
Prata Nova	$(6.4 \pm 0.5) \times 10^1$	$(5.5 \pm 0.6) \times 10^1$	$(5.5 \pm 0.0) \times 10^1$	$(4.5 \pm 0.1) \times 10^1$
Prata Antiga	1.8×10^2 *	$(1.8 \pm 0.9) \times 10^2$	$(1.7 \pm 0.2) \times 10^2$	$(1.3 \pm 0.1) \times 10^2$
Prata Radioativa	$(4.8 \pm 0.4) \times 10^1$	$(4.4 \pm 0.4) \times 10^1$	$(3.3 \pm 0.5) \times 10^1$	$(4.9 \pm 1.4) \times 10^1$
Vitória	$(3.2 \pm 0.1) \times 10^2$	$(2.8 \pm 0.2) \times 10^2$	$(2.7 \pm 0.1) \times 10^2$	$(1.6 \pm 0.0) \times 10^2$
Balneário Teotônio Vilela	8.8×10^1 *	6.3×10^1 *	$(2.3 \pm 0.1) \times 10^1$	$(4.9 \pm 0.4) \times 10^1$

LLD = lower limit of detection.

*Only one measurement.

being for Vilela spring, which presents a lower level of soluble salts.

The arithmetic means for ^{222}Rn varied from 1.3 to $1.2 \times 10^2 \text{ Bq L}^{-1}$, the lowest value being observed for Padre spring, which presents in its composition bicarbonate salts, and the highest for Vilela spring, which presents low levels of soluble salts.

As far as the chemical composition of the water is considered, it can be concluded that the waters having low levels of soluble salts presented higher concentrations of ^{226}Ra and ^{222}Rn . In this specific case, such activity concentrations can be explained by the fact that these springs are associated with sandstones with 0.3% of U_3O_8 in their composition (Longo, 1967). Therefore, the prevailing mobilization process for radium and radon in the rock-water system is the nuclear alpha recoil, since these waters are poorly mineralized and the time of interaction between water and rock is relatively short.

Ra^{2+} is moderately soluble in natural water, although a high SO_4^{2-} content will favour its removal as mixed sulphate salts, such as $\text{Ba}(\text{Ra})\text{SO}_4$ or for high CO_3^{2-} water, removal as $(\text{M,Ra})\text{CO}_3$. High sulphate concentrations may provide for the formation of RaSO_4 , although Ra^{2+} concentrations rarely approach the solubility limit. Radium in solution is not strongly dependent on anionic species. It is known to form sulphate complexes, but not carbonate complexes (Benes *et al.*, 1982). It has been observed that both U and Ra are enriched in low and high pH waters than waters at intermediate pH levels. These behaviours have been observed in the present paper, where the water springs with pHs around 5.0 presented higher concentrations of ^{226}Ra and ^{222}Rn and can explain why ^{226}Ra and

^{222}Rn concentrations are lower in water springs which present sulphate and carbonate salts. Moreover, the ^{226}Ra prevailing solubilization process in such water-rock systems is the chemical reaction, since these waters are mineralized and present a relatively higher contact period between rock and water.

Some authors (e.g. Cadigan and Felmlee, 1977) have observed that increasing groundwater temperature decreases the radium concentration. This is possibly because the warmer water had higher sulphate concentrations. Similar behaviour is also found in the waters studied in the present paper, where the springs having high concentration of sulphate and bicarbonate salts, mainly Platina and Paiol, considered as hypothermals, present the lowest activity concentrations of ^{226}Ra .

Based upon the results obtained for the radionuclide concentrations over a period of one year (Tables 2 and 3), it can be concluded that the lowest activity concentrations were mostly found in the rainy season (summer), which provides 80% of the annual rainfall of the region (1500 mm y^{-1}). In some springs, however, these concentrations are observed to be lower later in the rainy season (autumn). A possible explanation is that these springs are fed from deep aquifers and the rainfall contribution to their flows is delayed.

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