Journal of Radioanalytical and Nuclear Chemistry, Vol. 249, No. 1 (2001) 173–176

Natural radioactivity in Brazilian bottled mineral waters and consequent doses

J. de Oliveira, B. Paci Mazzilli,* P. da Costa, P. Akiko Tanigava

Departamento de Radioproteção Ambiental, Instituto de Pesquisas Energéticas e Nucleares, Caixa Postal 11049, São Paulo, Brazil

(Received December 13, 2000)

The natural activity concentration levels of ^{226}Ra, ^{228}Ra and ^{210}Pb were analyzed in 17 brands of bottled mineral waters commercially available in the Southeast region of Brazil. Concentrations up to 647 mBq·l^{-1} and 741 mBq·l^{-1} were observed for ^{226}Ra and ^{228}Ra, whereas ^{210}Pb concentrations reached 85 mBq·l^{-1}. Average committed effective doses of $1.3\cdot10^{-2}$ mSv·y^{-1} for ^{226}Ra, $3.4\cdot10^{-2}$ mSv·y^{-1} for ^{228}Ra and $9.4\cdot10^{-3}$ mSv·y^{-1} for ^{210}Pb were estimated for the ingestion of these waters. A collective dose of 90 manSv was evaluated, considering the annual production of the bottled mineral waters analyzed in this study.

Introduction

Humans are exposed to ionizing radiation from a number of sources, which includes cosmic rays and natural radionuclides in air, food and drinking water. The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR),[1] has estimated that exposure to natural sources contributes more than 70% of the population radiation dose and the global average human exposure from natural sources is 2.4 mSv·y^{-1}.

The occurrence of natural radionuclides from ^{238}U and ^{232}Th series in drinking water has been the subject of extensive studies. Most of these studies were concerned with the drinking water standards for gross-alpha activity, gross-beta activity and Ra, established by Environmental Protection Agency (USEPA)[2] and World Health Organization (WHO).[3] These studies have been performed mostly for assessment of the dose and the resulting risk from drinking water.

Radium-226 and its daughter products are responsible for a major fraction of the internal dose received by humans from naturally-occurring radionuclides. It has long been known also that many mineral springs contain relatively high concentrations of radium and radon. Published values of ^{226}Ra in mineral waters ranged to more than 3.7 Bq·l^{-1} (100 pCi·l^{-1}), several times greater than values normally reported for public water supplies.[4] Many spring waters studied around the world contain ^{226}Ra in amounts that exceed the USEPA maximum contaminant level of 185 mBq·l^{-1} (5 pCi·l^{-1}).[5]

The radium content of public water supplies was reviewed comprehensively by COTHERN and REBERS.[6] HESS et al.[7] described the geological and geochemical factors that influence the concentration of radium isotopes in drinking water. Although there is more ^{232}Th than ^{238}U in nature on an activity basis, there are geochemical factors that cause local concentrations of uranium, which often results in greater amounts of ^{226}Ra relative to ^{228}Ra in natural waters.[8] Some published data about ^{210}Pb activity concentrations in potable and mineral waters with high ^{226}Ra levels has shown that ^{210}Pb in water is generally low relative to ^{226}Ra.[9,10] This seems to indicate a loss of ^{210}Pb owing to chemical precipitation, biological activity or other factors.[10]

Our research group has carried out a large survey concerning natural radioactivity levels in drinking water supplies of São Paulo State and mineral springs waters from São Paulo and Minas Gerais States.[11–16] In order to evaluate potential health hazards, doses due to the ingestion of these waters were estimated to assess the contribution of these radionuclides to public exposure from natural radioactivity.

This paper presents activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb determined in 17 brands of bottled mineral waters produced in the São Paulo and Minas Gerais States, representative of the Southeast region of Brazil. A conservative approach is used to assess total effective dose and collective dose received by the consumers of these waters. These data are compared with those obtained for the ingestion of drinking water supplies from São Paulo State and for mineral springs from Águas da Prata County, located in a high natural background area in the boundary between São Paulo and Minas Gerais States.

The Brazilian production of bottled mineral water is about $1.8\cdot10^{9}$ l per year.[17] The Southeast region of Brazil (which comprises São Paulo and Minas Gerais States) is responsible for more than 65% of the Brazilian production.

Experimental

For this investigation, samples of bottled mineral water typical of those consumed by the population of São Paulo and Minas Gerais States were bought at the market over a period of 1 year and were analysed for

* E-mail: mazzilli@net.ipen.br

0236–5731/2001/USD 17.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

^{226}Ra, ^{228}Ra and ^{210}Pb using a sequential radiochemical method.[19] The water samples pH were adjusted by addition of 10 ml of 65% HNO_3, to prevent losses by sorption of the studied radionuclides onto the vessel walls. In order to perform these analyzes; a volume of 5 l of bottled mineral water was concentrated to 1 l by evaporation. These water samples were analysed in duplicate for each radionuclide.

The radiochemical procedure adopted for ^{226}Ra and ^{228}Ra determination is described in more detail in OLIVEIRA.[18] For these analyses, carriers of Ba^{2+} (20 mg) and Pb^{2+} (20 mg) were added to the sample as yield tracers, in the presence of 1M citric acid solution. The radiochemical separation was accomplished by addition of 3M H_2SO_4, with heating. Precipitate of barium, lead and radium sulphate was dissolved with nitrile triacetic acid/NaOH, for separation of the decay product ^{210}Pb by complexation at pH 12.5–13.0. The radium isotopes remain co-precipitated as a barium sulphate and the pH is adjusted to 4.5–5.0 with glacial acetic acid. The solution is then separated from the $Ba(Ra)SO_4$ precipitate by centrifugation and is used for the gross-beta determination of ^{210}Pb as $PbCrO_4$.

In order to purify the $Ba(Ra)SO_4$ precipitate obtained, it is dissolved with ethylene diamine tetracetic acid/NH_4OH and re-precipitated by adjusting the pH of this solution to 4.5–5.0 with glacial acetic acid. The $Ba(Ra)SO_4$ precipitate is then filtered and the chemical yield determined gravimetrically. Considering that 20 mg of Ba^{2+} carrier was added to the water samples at the beginning of the radiochemical procedure, a final total recovery of $Ba(Ra)SO_4$ precipitate would be 34.8 mg. The chemical recovery of $Ba(Ra)SO_4$ precipitate for these samples was (90±5)%.

The precipitation of ^{210}Pb is carried out by adding to the solution separated above 1 ml of 1M Na_2S, with heating. The PbS precipitate is then dissolved with 65% HNO_3 and 10 ml of deionized water. The solution containing Pb^{2+} is filtered and the pH adjusted by the addition of a 40% ammonium acetate solution. The precipitate of $PbCrO_4$ is obtained by addition of 2 ml of 30% Na_2CrO_4 solution with heating. The $PbCrO_4$ precipitate is filtered and the chemical yield determined gravimetrically. A final recovery of $PbCrO_4$ precipitate should be 31.4 mg based on the 20 mg of Pb^{2+} carrier added to the water samples at the beginning of the radiochemical procedure. The chemical recovery of $PbCrO_4$ precipitate for these samples was (80±10)%.[11]

The measurement of ^{226}Ra activity concentrations were carried out by counting the gross-alpha activity of a $Ba(Ra)SO_4$ precipitate using a low-background gas-flow proportional counter, after sufficient time had elapsed for decay of ^{223}Ra and ^{224}Ra (21 days). The self-absorption factor for the four alpha-particles emitted in secular equilibrium with ^{226}Ra (^{226}Ra – 4.8 MeV; ^{222}Rn – 5.5 MeV; ^{218}Po – 6.0 MeV; ^{214}Po – 7.7 MeV) was determined by adding a ^{226}Ra standard solution, with activity concentrations ranging between 8.7 and 20.3 Bq to a deionized water sample. The value of the self-absorption factor obtained was 0.3001± 0.0065. The ^{228}Ra activity concentration was determined by gross-beta counting of the same precipitate, measuring the activity of its daughter product ^{228}Ac, since it emits beta-particles of higher energy (1.2 and 2.1 MeV) in contrast to the lower energy of ^{228}Ra beta-particles (40 keV). Lower limits of detection (LLD) for this method are 2.2 $mBq \cdot l^{-1}$ for ^{226}Ra, for 100 minutes counting time, and 3.7 $mBq \cdot l^{-1}$ for ^{228}Ra, for 400 minutes counting time, at the 95% confidence level.[18]

Ten days after separation, ^{210}Pb activity concentration was determined via ^{210}Bi by measuring the gross-beta activity of the $PbCrO_4$ precipitate, using the same low-background gas-flow proportional counter described above. The lower limit of detection for this method is 4.9 $mBq \cdot l^{-1}$ for ^{210}Pb, for 400 minutes counting time, at the 95% confidence level.[11]

All methodologies used were checked experimentally by participating in Quality Assurance Programs, organized by Instituto de Radioproteção e Dosimetria (Brazilian Nuclear Energy Commission).

Results and discussion

The ^{226}Ra, ^{228}Ra and ^{210}Pb activity concentrations determined in 35 samples of bottled mineral waters commercially available in the São Paulo and Minas Gerais States, randomly purchased in 1998 and 1999, are presented in Table 1. Arithmetic mean activities ranged from <2.2 to 647 $mBq \cdot l^{-1}$ and from 12 to 741 $mBq \cdot l^{-1}$ for ^{226}Ra and ^{228}Ra. For ^{210}Pb, the arithmetic mean activity concentrations varied from <4.9 to 85 $mBq \cdot l^{-1}$. These results showed that the maximum contaminant level of 185 $mBq \cdot l^{-1}$ recommended by USEPA[2] for ^{226}Ra in drinking water was exceeded in only three samples (São Lourenço, Minas Gerais). Considering the recommended radioactivity standards for drinking water established by Brazilian authority Ministério da Saúde,[19] the gross-alpha activity limit of 0.1 $Bq \cdot l^{-1}$ was exceeded by the radium isotopes alone in four of the 35 samples studied in this work. These higher ^{226}Ra levels were evaluated by comparison with 1/50 of the corresponding annual limit of intake (ALI) established for ^{226}Ra ingestion by workers in the Brazilian Reference Guide CNEN-NE 3.01,[20] that is 1,400 $Bq \cdot y^{-1}$.

Table 1. ^{226}Ra, ^{228}Ra and ^{210}Pb arithmetic mean concentrations (in mBq·l^{-1} ± standard deviation) in 35 samples of bottled mineral waters commercially available in São Paulo and Minas Gerais States

Sample (*n*)*	^{226}Ra	^{228}Ra	^{210}Pb
Lambari MG(1)	136 ± 17	87 ± 25	–
Magna MG(1)	24 ± 21	27 ± 10	–
Minalba SP(6)	8.6 ± 1.0	16 ± 2	18 ± 5
Minalba c/gas SP(2)	9.5 ± 0.6	22 ± 1	13 ± 2
São Lourenço MG(3)	647 ± 84	741 ± 48	28 ± 4
Prata SP(3)	47 ± 6	15 ± 2	16 ± 1
Prata c/gas SP(1)	42 ± 4	14 ± 3	85 ± 1
Levíssima SP(3)	21 ± 1	42 ± 3	11 ± 3
Ibirá SP(2)	10 ± 1	18 ± 0	7.2 ± 2.0
Embú SP(3)	15 ± 1	15 ± 2	6.2 ± 1.2
Araxá MG(1)	57 ± 19	53 ± 3	–
Crystal SP(2)	15 ± 1	29 ± 2	5.7 ± 1.9
Indaiá SP(2)	11 ± 1	17 ± 2	24 ± 3
Lindoya SP(1)	3.3 ± 0.1	23 ± 2	22 ± 1
Lindoya Genuína SP(2)	13 ± 1	24 ± 5	13 ± 1
Nestlé SP(1)	<LLD	12 ± 1	<LLD
Santa Barbara SP(1)	<LLD	18 ± 1	<LLD
Average:	63	69	18

* Number of samples analyzed.
LLD(lower limit of detection): ^{226}Ra = 2.2 mBq·l^{-1}; ^{228}Ra = 3.7 mBq·l^{-1}; ^{210}Pb = 4.9 mBq·l^{-1}.
MG = Minas Gerais State.
SP = São Paulo State.

Table 2. Average committed effective doses (in mSv·y^{-1}) from the consumption of bottled mineral waters commercially available in São Paulo and Minas Gerais States

	^{226}Ra	^{228}Ra	^{210}Pb
He	$1.3\cdot10^{-2}$	$3.4\cdot10^{-2}$	$9.4\cdot10^{-3}$

He – Average committed effective dose, mSv·y^{-1}.

In all these cases, if an annual consumption rate of 730 l·y^{-1} of water is considered, the maximum amount of ^{226}Ra ingested by drinking the bottled mineral waters studied are below the 1/50 ALI limit. Besides that, both ^{228}Ra and ^{210}Pb concentrations observed in the bottled mineral waters studied in this work did not exceed the reference value of 1 Bq·l^{-1}, established as a limit for gross-beta activity in drinking waters by the Brazilian authority Ministério da Saúde.[19] Thus, according to these data, these bottled mineral waters are acceptable for human consumption.

Based upon the arithmetic mean concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb obtained from all the 35 samples of bottled mineral waters studied in this work, the committed effective doses were evaluated. Effective doses were estimated by considering a daily consumption rate of 2 l and the arithmetic mean activity concentration obtained for each brand.[3] The annual doses per activity of ingested ^{226}Ra, ^{228}Ra and ^{210}Pb used in these calculations (in Sv·Bq^{-1}) were taken from ICRP Report 67,[21] assuming an adult metabolism and a 50 years lifetime period of exposure after the intake of the studied radionuclides.

The average committed effective doses due the consumption of the bottled mineral waters analyzed in São Paulo and Minas Gerais States are shown in Table 2. The highest values of the committed effective doses per year obtained in this work were $1.3\cdot10^{-1}$ mSv·y^{-1} for ^{226}Ra, $3.6\cdot10^{-1}$ mSv·y^{-1} for ^{228}Ra and $4.3\cdot10^{-2}$ mSv·y^{-1} for ^{210}Pb. The average committed effective doses per year were $1.3\cdot10^{-2}$ mSv·y^{-1}, $3.4\cdot10^{-2}$ mSv·y^{-1} and $9.4\cdot10^{-3}$ mSv·y^{-1} for ^{226}Ra, ^{228}Ra and ^{210}Pb, respectively. The corresponding total committed effective dose obtained was $5.6\cdot10^{-2}$ mSv·y^{-1}. This value represents less than 2.3% of the average effective dose attributable annually from natural background radiation.

Collective dose due to the consumption of these waters was evaluated, according to:

$$\frac{5.6\cdot10^{-2}\ \mathrm{mSv}\cdot\mathrm{y}^{-1}\cdot1.8\cdot10^{9}\ \mathrm{l}\cdot\mathrm{y}^{-1}\cdot0.65}{2\mathrm{l}\cdot\mathrm{d}^{-1}\cdot365\,\mathrm{d}\cdot\mathrm{y}^{-1}} = 90\ \mathrm{manSv}$$

For this calculation it was considered that the Brazilian production of bottled mineral water is about $1.8\cdot10^{9}$ l per year[17] and that the Southeast region of Brazil (which comprises São Paulo and Minas Gerais States) is responsible for more than 65% of the Brazilian production.

BETTENCOURT et al.[22] determined the natural radioactivity levels of Portuguese mineral and table waters. According to BETTENCOURT et al.[22] the highest expected effective dose value found in Portugal due to ^{226}Ra and ^{210}Pb intake was 0.2 mSv·y^{-1}. This value is similar to the data obtained in this work for the ingestion of the same radionuclides.

The ^{226}Ra average activity concentration measured in Brazilian bottled mineral waters presented in this paper is similar to those determined by BOMBEN et al.[23] in bottled mineral waters from Argentina. BOMBEN et al.[23] also found that the concentration of natural radionuclides measured in bottled mineral waters from Argentina were below the derived values for drinking water established in that country, 180 $mBq \cdot l^{-1}$ for ^{226}Ra and 100 $\mu g \cdot l^{-1}$ for natural uranium.

Another study was recently performed by MARTIN SANCHEZ et al.,[24] who determined the radioactivity concentrations in 43 samples of bottled mineral waters consumed in France, Portugal and Spain. The corresponding ^{226}Ra concentration activities varied from <60 to 1,860 mBq/l. The highest concentration value determined by MARTIN SANCHEZ et al.[24] was one order of magnitude greater than the maximum ^{226}Ra concentration value observed in São Lourenço brand in this work.

The average activity concentrations of ^{226}Ra and ^{228}Ra obtained in all the 35 samples of bottled mineral water analyzed here were also similar to those data obtained by OLIVEIRA et al.[25] in a previous study covering 452 sources of drinking water supplies from São Paulo State. Concentrations up to 235 $mBq \cdot l^{-1}$ and 131 $mBq \cdot l^{-1}$ were observed for ^{226}Ra and ^{228}Ra in drinking water supplies of São Paulo State.[25] The corresponding committed effective doses found were $6 \cdot 10^{-3}$ $mSv \cdot y^{-1}$ and $2 \cdot 10^{-2}$ $mSv \cdot y^{-1}$ for the ingestion of ^{226}Ra and ^{228}Ra, respectively.[25]

The results obtained in this study were also compared with those determined in mineral springs from Águas da Prata County, by the same authors.[14] Arithmetic mean activity concentrations varying from <2.2 to $2.2 \cdot 10^{3}$ $mBq \cdot l^{-1}$, from <3.7 to 23.1 $mBq \cdot l^{-1}$ and from <3.5 to $1.4 \cdot 10^{3}$ $mBq \cdot l^{-1}$ were observed in Aguas da Prata mineral springs for ^{226}Ra, ^{228}Ra and ^{210}Pb, respectively.[14] Committed effective doses due to ingestion of Águas da Prata mineral spring waters achieved values up $4.7 \cdot 10^{-1}$ $mSv \cdot y^{-1}$ for ^{226}Ra, $1.0 \cdot 10^{-2}$ $mSv \cdot y^{-1}$ for ^{228}Ra and 1.1 $mSv \cdot y^{-1}$ for ^{210}Pb. These values are two orders of magnitude higher than those evaluated in the present work.

Conclusions

Assuming the ingestion of ^{226}Ra, ^{228}Ra and ^{210}Pb at the levels measured in 17 brands of bottled mineral waters studied in São Paulo and Minas Gerais States, representative of 65% of the annual production of Brazilian bottled mineral water industry, the expected average committed effective doses per year were $1.3 \cdot 10^{-2}$ $mSv \cdot y^{-1}$, $3.4 \cdot 10^{-2}$ $mSv \cdot y^{-1}$ and $9.4 \cdot 10^{-3}$ $mSv \cdot y^{-1}$, respectively. The corresponding total committed effective dose was $5.6 \cdot 10^{-2}$ $mSv \cdot y^{-1}$ and the collective dose was estimated at 90 manSv.

*

This work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo - FAPESP, under fellowship contract numbers 98/15219-6 and 98/15217-3. Funding for this study was also provided by Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq, grant n° 300835/95-7.

References

1. UNSCEAR, Sources and Effects of Ionizing Radiation. Report to the General Assembly, United Nations, New York, 1993.
2. EPA, Final Draft for the Drinking Water Criteria Document on Radium, U.S.EPA, Washington, DC, 1991, TR-1241-85.
3. WHO, Guidelines for drinking water quality, Recommendations, Vol. 1, Geneva, 1993.
4. M. EISENBUD, Environmental Radioactivity from Natural, Industrial and Military Sources, Academic Press, Inc., California, 1987.
5. M. ASIKAINEN, H. KHALOS. Health Phys., 39 (1980) 77.
6. C. R. COTHERN, P. REBERS, Radon, Radium and Uranium in Drinking Water. Lewis Publishers, Inc., Michigan, 1990.
7. C. T. HESS, J. MICHEL, T. R. HORTON, H. M. PRICHARD, W. A. CONIGLIO, Health Phys., 48 (1985) 553.
8. International Atomic Energy Agency, The chemistry and radiochemistry of radium and the other elements of the uranium and thorium natural decay series, in: The Environmental Behaviour of Radium, Vol. 1, Chapter 1–2, Vienna, 1990.
9. R. B. HOLTZMAN, Lead-210 and polonium-210 in potable waters in Illinois, in: The Natural Radiation Environment I. J. A. S. ADAMS, and W. M. LOWDER (Eds), Chicago, Illinois, 1964, p. 227.
10. K. HARADA, W. C. BURNETT, P. A. LAROCK, Geochim. Cosmochim. Acta, 53 (1989) 143.
11. J. OLIVEIRA, S. R. D. MOREIRA, B. P. MAZZILLI, Radiat. Prot. Dosim., 55 (1994) No. 1, 57.
12. I. M. C. CAMARGO, B. P. MAZZILLI, J. Radioanal. Nucl. Chem., 212 (1996) 251.
13. V. M. F. JACOMINO, S. A. BELLINTANI, J. OLIVEIRA, B. P. MAZZILLI, D. FIELDS, M. H. O. SAMPA, B. SILVA, J. Environ. Radioact., 33 (1996) 319.
14. B. P. MAZZILLI, I. M. C. CAMARGO, J. OLIVEIRA, A. NIERI, M. H. O. SAMPA, B. SILVA, Radiat. Res., 150 (1998) No. 2, 250.
15. J. OLIVEIRA, B. P. MAZZILLI, M. H. O. SAMPA, B. SILVA, Appl. Radiation Isotopes, 49 (1998) 423.
16. J. OLIVEIRA, Determinação dos níveis de radioatividade natural em águas utilizadas para abastecimento público no Estado de São Paulo, Vols 1 and 2, Tese de Doutorado, Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, São Paulo, 1998.
17. ABINAM, Revista Água Mineral, 2 (1997) 8. Associação Brasileira da Indústria de Águas Minerais.
18. J. OLIVEIRA, Determinação de ^{226}Ra e ^{228}Ra em águas minerais da região de Águas da Prata, Dissertação de Mestrado, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 1993.
19. Ministério da Saúde, Normas e Padrão da Potabilidade de Água Destinada ao Consumo Humano, Portaria n° 36/GM, 1990.
20. CNEN, Diretrizes Básicas de Radioproteção, CNEN-NE 3.01, Rio de Janeiro, 1988.
21. ICRP, Age-dependent Doses to Members of the Public from Intake of Radionuclides, Part 2, Ingestion Dose Coefficients, Publication No. 67, Pergamon Press, Oxford, 1993.
22. A. O. BETTENCOURT, M. M. G. R. TEIXEIRA, M. C. FAISCA, I. A. VIEIRA, G. C. FERRADOR, Radiat. Prot. Dosim., 24 (1988) 139.
23. A. M. BOMBEN, H. E. EQUILLOR, A. A. OLIVEIRA, Radiat. Prot. Dosim., 67 (1996) 221.
24. A. MARTIN SANCHEZ, M. P. RUBIO MONTERO, V. GOMEZ ESCOBAR, M. JURADO VARGAS, Appl. Radiation Isotopes, 50 (1999) 1049.
25. J. OLIVEIRA, B. P. MAZZILLI, M. H. O. SAMPA, E. BAMBALAS, J. Environ. Radioact., to be published.