

COMMONWEALTH DEPARTMENT OF HEALTH



Australian Radiation Laboratory

Natural Radioactivity in Bottled Mineral Water
available in Australia

by

M.B. Cooper, B.J. Ralph and M.J. Wilks

AUSTRALIAN RADIATION LABORATORY

NATURAL RADIOACTIVITY IN BOTTLED
MINERAL WATER AVAILABLE IN AUSTRALIA

by

M. B. Cooper, B. J. Ralph and M. J. Wilks

ARL/TR036
ISSN 0157-1400
AUGUST 1981

LOWER PLENTY ROAD,
YALLAMBIE, VIC. 3085
TELEPHONE: 433 2211

ABSTRACT

The levels of naturally-occurring radioactive elements in bottled mineral water, commercially available in Australia, have been assessed. The survey covered some 28 Australian and imported brands of natural mineral water, and concentrated upon those radionuclides which have a high toxicity in drinking water, namely radium-226 (^{226}Ra), radium-228 (^{228}Ra) and lead-210 (^{210}Pb).

Detectable levels of ^{226}Ra were found to range from 0.02Bq/l (0.5pCi/l) to 0.32Bq/l (8.6pCi/l) in locally-bottled water that is currently available to the public and from 0.02Bq/l (0.5pCi/l) to 0.44Bq/l (11.8pCi/l) in imported brands. ^{210}Pb levels were found to be generally very low (<0.08Bq/l). From the analysis of bottled mineral water and unprocessed water from Australian mineral springs it was concluded that the ^{228}Ra content of bottled water will have a similar distribution to that of ^{226}Ra . Concentrations of ^{228}Ra in excess of 0.7Bq/l were measured in a number of samples.

The radiological health implications of the consumption of bottled mineral water from natural sources are discussed with reference to existing drinking water standards and also in terms of radiation exposure and the increased risk to health. It was concluded that, although some brands of water contain radioactivity in excess of the drinking-water limits recommended by Australian and overseas authorities, the annual radiation dose to an individual, even in an extreme case, will be below the dose-equivalent limits recommended by the International Commission on Radiological Protection for life-long exposure. The increased risk of radiation-induced fatal disease due to the consumption of bottled mineral water is estimated to be less than 10^{-5} and is therefore negligible.

INTRODUCTION

The natural occurrence of radioactive elements of the uranium (^{238}U) and thorium (^{232}Th) series in ground waters and spring waters is well known from studies of drinking water supplies¹⁻⁴ and mineral water⁵⁻⁸.

Uranium and thorium are trace constituents in various minerals commonly associated with granitic and metamorphic rocks and sediments. Consequently, leaching by ground water will result in the release and transport of soluble radioactive elements. The presence of natural radioactivity in spring water will be a function of the geological formation and hydrogeology of the region, the geochemistry of uranium and thorium and the nature and concentration of other chemical constituents in the water.

Of all the radionuclides of the two series, when present in ground water from which mineral water or drinking water supplies are derived, ^{226}Ra , ^{228}Ra and ^{210}Pb are now identified as responsible for most of the radiation dose received by populations consuming the water⁹. Most studies of ground water and mineral springs have concentrated on ^{226}Ra content although recent publications^{4,8} have emphasised the additional importance of ^{228}Ra ; ^{210}Pb remains to be studied adequately.

In recent years, bottled mineral water has become increasingly popular in Australia, with an annual consumption estimated at some 40 million litres. Some of this mineral water is manufactured but most of it originates in natural mineral springs and bores, both at Australian and overseas locations. The present study was undertaken to investigate the concentration of ^{226}Ra , ^{228}Ra and ^{210}Pb in bottled mineral water, available commercially in Australia and derived from natural sources (both local and foreign). The investigation has included unprocessed water drawn from Victoria and Queensland mineral springs which are the sources for commercial bottling.

EXPERIMENTAL

Sampling Procedure

Samples of up to 30 bottles of mineral water were obtained directly from either the bottler or distributor of the particular brand. The sample for analysis was prepared by combining the contents of several bottles of that brand. Otherwise the bottled mineral water was not subjected to any treatment or preparation prior to analysis. A total of 15 Australian brands and 13

foreign brands were sampled and details are given in Tables 1 and 2. For many brands there was no identification by batch number to use as a reference for the data obtained.

Thirteen samples of unprocessed mineral water, of at least 15 litres, were also received from the Australian sources. These samples were taken directly from the mineral spring or bore or from the first stage holding tank prior to bottling. The bulk water samples were either acidified prior to receipt at the Laboratory or, immediately upon receipt, they were filtered through a 0.45µm membrane filter and acidified. Sample details appear in Table 3.

Analysis of bottled mineral water for ^{226}Ra

All samples of bottled mineral water were analysed for ^{226}Ra by a technique based on the liquid scintillation counting of ^{222}Rn and its short-lived daughters in toluene. The full procedure is presented elsewhere¹⁰. An aliquot of 1.0 to 1.5 litres was taken from each sample for ^{226}Ra analysis.

Chemical Procedure

The water sample was first boiled to remove dissolved carbon dioxide and, in some cases, slightly acidified (<pH 4) to prevent premature precipitation of carbonates. Two millilitres of lead solution (100 mg Pb/ml) were added to the sample and radium was co-precipitated with lead sulphate by the addition of potassium sulphate (10.0g) and sulphuric acid (12ml). The mixture was heated to coagulate the precipitate and centrifuged to remove the supernate. The precipitate was then dissolved in 10ml of alkaline (pH 10) ammonium - EDTA (0.2M) with the gentle application of heat. At this stage the solution was quantitatively transferred to a liquid scintillation vial and 1ml of a barium solution (10 mg Ba/ml) was added. Radium was co-precipitated upon barium sulphate by lowering the pH of the solution to 4.6 with 6M acetic acid. Following isolation of the barium (radium) sulphate by centrifuging, 5ml of alkaline EDTA (0.2M) was added to dissolve the precipitate. The aqueous solution was diluted with the addition of 2ml of distilled water. A toluene-based liquid scintillation mixture (15ml) was added to the aqueous solution in the vial. The constituents of the mixture were naphthalene (200g/l toluene) and 2-(4-Biphenyl)-6-phenyl-benzoxazole (4g/l toluene). Nitrogen was bubbled through the aqueous and toluene phases in the vial to remove both dissolved oxygen and ^{222}Rn . The vials were then sealed and prior to counting were set aside to allow for ^{222}Rn ingrowth from ^{226}Ra .

Measurement of Radioactivity

At room temperature most of the ^{222}Rn will be dissolved in the toluene phase of the scintillation mixture (^{222}Rn distribution co-efficient for water : toluene is approximately 1 : 18)¹¹. Therefore the ^{226}Ra can be determined by liquid scintillation counting of the α and β - emissions of ^{222}Rn and its short-lived daughters after allowing for the degree of equilibrium attained.

For purposes of comparison, measurements were performed with two counting systems. In the first system, the scintillation detector consisted of an end-window photomultiplier tube of 50mm diameter mounted vertically in a light-tight lead castle of 75mm wall thickness. The sample was placed on the face of the photomultiplier tube and enclosed with a plastic cover having a white reflecting internal surface to improve light collection efficiency. The sample - detector configuration has been shown¹⁰ to be optimum in terms of counting efficiency and α -resolution for analysis of ^{226}Ra . The output pulses from the photomultiplier were amplified (Ortec 113 and 471) and counted (Tennelec TC 555P) after passing through a discriminator (Canberra 1432). The pulse height spectrum of the amplified pulses could be observed as desired on the Laboratory's Nuclear Data model ND6600 data acquisition system.

Samples were held for periods up to 14 days (92% of equilibrium) to allow for ingrowth of ^{222}Rn before counting. However, interim measurements, made after shorter periods of ingrowth (e.g. 5 days, 60% of equilibrium) gave satisfactory agreement with the results from the final counting. The counting period was fixed at 3000 sec.

In addition to the measurements described above, all samples were counted in a second system, comprising a commercial liquid scintillation counter (Searle Analytic 92) equipped with an automatic sample changer.

Both counting systems were calibrated using a set of calibration solutions having ^{226}Ra activities in the range 0.2Bq (5 pCi) to 3.0Bq (80 pCi). The calibration solutions were prepared by dilution of a standardized solution of ^{226}Ra obtained from the Radiochemical Centre, Amersham and restandardized in this Laboratory; their chemical composition was identical to that of the samples.

Analysis of Bottled Mineral Water for ^{210}Pb

For all samples of bottled mineral water the concentration of ^{210}Pb was determined by a method involving chemical separation of ^{210}Pb followed by

measurement of the β -activity of its short-lived daughter, ^{210}Bi . An aliquot of 500 to 700ml was taken from each bottled water sample.

Chemical Procedure

Following addition of 1ml of a lead/bismuth carrier solution (100 μg of each/ml) the lead and bismuth were extracted with three or more successive 20ml portions of 1% diethylammonium diethyldithiocarbamate in chloroform. After combination of the extracts and washings, the chloroform was evaporated and the remaining organic material destroyed with nitric acid and hydrogen peroxide, producing a colourless acidic solution. At this stage 1ml of lead solution (40mg Pb/ml) was added and, after adjustment of the pH of the solution to 4.0, lead chromate was formed by the addition of sodium chromate solution (20%). The lead chromate was mounted on a 23mm diameter filter in a metal planchet.

Measurement of Radioactivity

The β -activity determination of $^{210}\text{Pb}/^{210}\text{Bi}$ was made in a low-background β -counter, details of which have been given elsewhere¹². The β -counters were calibrated using $^{210}\text{Pb}/^{210}\text{Bi}$ sources prepared as lead chromate precipitates of mass identical to that used for the samples. The $^{210}\text{Pb}/^{210}\text{Bi}$ solution used for the preparation of calibration sources was obtained by accurate dilution of a standardized solution from the Radiochemical Centre, Amersham. The diluted solution was standardized within this Laboratory.

The lead chromate precipitates were counted immediately following preparation. It was assumed that ^{210}Pb and ^{210}Bi were in equilibrium in the mineral water and that the chemical procedures removed both ^{210}Pb and ^{210}Bi with equal efficiency. This assumption was confirmed by re-counting the precipitates several weeks after preparation.

Analysis of bulk mineral water for ^{210}Pb , ^{226}Ra , ^{228}Ra and ^{228}Th

For all samples of bulk mineral water the mineral contents were extracted by co-precipitation and analysed for ^{210}Pb , ^{226}Ra , ^{228}Ra , ^{228}Th by high resolution γ -ray spectrometry. ^{210}Pb was determined directly whereas ^{226}Ra , ^{228}Th and ^{228}Ra were assayed through their γ -emitting daughters. An aliquot of 10.0l of bulk mineral water was taken from each sample for analysis.

Chemical procedure

An aliquot of 10.0l was evaporated to approximately 1l and a co-precipitation technique applied to extract uranium, thorium and their daughters. Phosphoric acid (10.0ml) and 2.0ml of a ferrous sulphate solution (50mg Fe/ml) were added

to the sample and the pH adjusted to approximately 9 with ammonia solution. Under these conditions calcium phosphate and ferrous hydroxide will precipitate, together with other natural mineral salts, and carry radionuclides of the uranium and thorium series from solution with greater than 98% efficiency. After heating the mixture, the precipitate was separated by filtration, dried and sealed in a PVC container of standardized geometry and set aside for ingrowth of ^{226}Ra daughters prior to analysis.

γ -ray Spectrometry

Two high resolution γ -ray spectrometers were employed. Each system consisted of a lithium-drifted germanium detector (Ortec model VIP10) the output of which was amplified (Ortec 120-4, 472) and digitally converted (Nuclear Data ND570) for processing with the Laboratory's Nuclear Data model 6600 data acquisition system. Calibration of the spectrometers was performed using sources prepared from standardized thorium nitrate and pitchblende (New Brunswick Laboratory) contained in silica matrices. The geometry of the calibration sources was identical to that of sample sources.

Analysis of bottled mineral water for ^{228}Ra

Samples of bottled mineral water were analysed for ^{228}Ra by high resolution γ -spectrometry, ^{228}Ra being determined through its γ -emitting daughter ^{228}Ac ($T_{1/2} \sim 6\text{h}$). As described in the previous section, ^{228}Ra had been determined in bulk water samples from Australian mineral springs. This was considered adequate to describe ^{228}Ra levels in locally-bottled mineral water but to confirm this assumption three Australian brands, Taurina Spa (Helidon), Taurina Spa (Daylesford) and Safeway were analysed in addition to all thirteen imported brands of mineral water.

The chemical procedure and method for the measurement of radioactivity were the same as outlined in the previous section on the analysis of bulk mineral water samples except that only 1.0l of each sample was taken.

Quality Control

In order to assess the reliability and efficiency of the chemical procedures used for the analysis of ^{226}Ra and ^{210}Pb in bottled mineral water, each batch presented for analysis comprised six samples of mineral water plus one blank and one control having a known activity of ^{226}Ra or ^{210}Pb . The blanks and controls were prepared from distilled water to which the major constituents of natural

mineral water had been added, namely calcium, magnesium, sodium, bicarbonate, chloride and sulphate.

The results obtained from the quality controls were assessed to determine possible cross-contamination, the level of activity of ^{226}Ra and ^{210}Pb in the reagents used, the chemical yield of the procedures and batch to batch variations in yield. The reproducibility of analyses of the mineral waters was also determined by performing these in duplicate, and in some cases, in triplicate.

Limits of Detection

Following Currie¹³, the detection limit (L_D counts) for a specific radioactive measurement process can be expressed as,

$$L_D = 2.71 + 4.65 \sqrt{B},$$

where B is the background counts over the counting interval. This formula can be applied to determine approximate detection limits of the various measurement techniques used in this study. The calculated limits are listed in Table 4.

RESULTS AND DISCUSSION

^{226}Ra and ^{210}Pb Contents of Bottled Mineral Water

The results of the analyses of locally-bottled mineral water for ^{226}Ra are presented in Table 1. The ^{226}Ra and ^{210}Pb contents of imported brands of mineral water are given in Table 2. The data presented in Tables 1 and 2 are averages of duplicate analyses of each brand. Analytical uncertainties correspond to the 67% confidence interval. For all samples there was good agreement between the analytical results for ^{226}Ra in Tables 1 and 2 and activities measured with the commercial liquid scintillation counter.

All brands of mineral water bottled from Australian sources contained detectable levels of ^{226}Ra except those obtained from bores or springs in the Kyneton (Victoria) district. The concentration of ^{226}Ra varied from 0.02Bq/l (~0.5pCi/l) to 1.5Bq/l (~43pCi/l). The Taurina Spa brand bottled from the Iredale Spring, Helidon (Queensland) had the highest ^{226}Ra content, however this particular spring is no longer being used for commercial bottling. There is good agreement in ^{226}Ra concentrations between brands of mineral water bottled from the same source, namely Bisleri, Safeway and Deep Spring. For none of the locally-bottled brands was the ^{210}Pb concentration above detectable levels.

Approximately two-thirds of the brands of imported mineral water had detectable levels of ^{226}Ra with ^{226}Ra concentrations ranging from 0.02Bq/l

($\sim 0.5\text{pCi/l}$) to 0.44Bq/l ($\sim 12\text{pCi/l}$). A similar concentration range for ^{226}Ra content was reported in a recent study of bottled mineral water from European sources⁸. Although ^{210}Pb was detected in six imported brands, the levels were low with Badoit having the maximum concentration with 0.08Bq/l ($\sim 2\text{pCi/l}$).

Results from quality control analyses confirmed the reliability and accuracy of the analytical methods for ^{226}Ra and ^{210}Pb . Radioactive controls containing 0.83Bq of ^{226}Ra had a measured average activity of $0.79 \pm 0.04\text{Bq}$ (12 measurements). Reagent blanks for ^{226}Ra analysis had a mean activity of $0.001 \pm 0.006\text{Bq}$ (13 measurements). For ^{210}Pb analysis spiked controls containing 2.7Bq gave a measured average activity of 2.4 ± 0.1 (9 measurements). Reagent blanks had a mean activity of $0.001 \pm 0.005\text{Bq}$ (9 measurements). The average recoveries were 95% and 88% for ^{226}Ra and ^{210}Pb respectively.

Analysis of Mineral Water by γ -Spectrometry

The results of γ -spectrometric analysis of unprocessed mineral water from various Australian mineral springs are presented in Table 3. Overall, it is evident that the predominant radioactive species present in the mineral water samples are ^{226}Ra and ^{228}Ra . All samples, except that from the Darling Downs Spring, contained measurable ^{226}Ra , the levels ranging from 0.02Bq/l to 1.63Bq/l . The agreement between the ^{226}Ra concentrations in bottled water (Table 1) and the unprocessed water is quite satisfactory considering that some decrease in radionuclide content will occur in holding tanks or at other stages during bottling.

The concentration of ^{228}Ra showed a similar distribution to that of ^{226}Ra ; however, the detectable range is greater (0.08 to 2.21Bq/l). Although the ^{228}Ra concentration generally exceeds that of ^{226}Ra the ratio of ^{228}Ra to ^{226}Ra concentrations is quite variable. This variability has also been noted in recent publications on radium levels in bottled mineral water, commercially-available in the USA⁸, and in ground water studies⁴. Michel and Moore⁴ comment that variable concentration ratios of the radium isotopes are to be expected in ground water. ^{226}Ra and ^{228}Ra originate from separate natural series and the geochemical and solubility behaviour of the parents (^{238}U and ^{232}Th respectively) and the radium isotopes are quite different.

Although ^{228}Th is present in several of the samples analysed, the activities are well below the corresponding ^{228}Ra values. The dis-equilibria between the two species indicates that ^{228}Th is present only as a result of ingrowth from ^{228}Ra in the ground water over a short period of time. The solubilization and migration of thorium isotopes from the source material is considered most unlikely⁴.

^{210}Pb was not detected in any of the samples of unprocessed mineral water. Presumably ^{226}Ra and ^{210}Pb being members of the same natural series will occur in the mineral sources in similar activities. Therefore a correlation between their activities in ground water might be expected. However, the absence of ^{210}Pb even in samples with ^{226}Ra concentrations in excess of 0.5Bq/l could be explained in terms of the different solubility behaviour in ground water containing high levels of carbonates and other mineral salts. It is unlikely that the differences could be due to dis-equilibria in the mineral sources caused by ^{222}Rn emanation².

^{228}Ra Content of Bottled Mineral Water

The activities of ^{228}Ra in bottled mineral water can be assessed from the results presented in Tables 3 and 5. In the analysis of all samples of imported mineral water by γ -spectrometry (see Table 5), only two samples, namely Vichy and Badoit, contained detectable levels of ^{228}Ra (>0.3Bq/l). Only three samples of locally-bottled water were analysed by γ -spectrometry. These revealed detectable levels of ^{228}Ra with the highest activity of 2.81Bq/l in Taurina Spa bottled from the Helidon spring; this spring is no longer used for commercial bottling. There is good agreement between the ^{228}Ra levels found in the three samples of locally-bottled water and the activities in the corresponding unprocessed spring water (Table 3). This leads to the conclusion that the detectable ^{228}Ra concentrations in locally-bottled mineral water, commercially available at present, will fall within the same range, namely 0.08Bq/l to 1.0Bq/l.

Health Implications of Natural Radioactivity in Bottled Mineral Water

Comparison with Australian Drinking Water Standards

Recommendations for the radiological quality of drinking water within Australia are contained in guidelines prepared by the National Health and Medical Research Council and the Australian Water Resources Council¹⁴. The recommended limits are based on drinking water standards issued in 1971 by the World Health Organisation¹⁵. Thus, they do not take account of more recent assessments of radiological protection¹⁶ embodied in a review of drinking water standards by a Working Group of the World Health Organisation in 1978¹⁷. The guidelines for Australian drinking water quality¹⁴, as they relate to ^{210}Pb , ^{226}Ra and ^{228}Ra are summarised in Table 6. ^{226}Ra is specifically included in the recommended limits. However, ^{210}Pb and ^{228}Ra are not specified. The recommendations are for application to drinking water supplies for continuous use by whole populations. It is stated that the health investigation levels are set well below those at which a health risk would actually occur.

Although no reference to mineral water from natural sources is made in the guidelines the levels of ^{226}Ra reported in the present study may be compared with the recommended limits for drinking water. From the data in Table 1 and Table 2 it can be seen that in every brand available for sale, with one exception, the ^{226}Ra activity lies below the maximum level of 0.488q/l (10pCi/l). This comparison implies, of course, that the source of drinking water for an individual is exclusively bottled mineral water. No specific comparison can be made for ^{210}Pb and ^{228}Ra .

Comparison with International Drinking Water Standards

In a recent review of drinking water standards for radioactivity, the World Health Organisation¹⁷ included bottled water from natural sources in its definition of drinking water. Mineral water for medicinal or curative purposes was specifically excluded. The recommendation of the WHO Working Group was that the annual dose equivalent attributable to drinking water be limited when practicable to no more than 0.05mSv. Using this basic criterion 'non-action' levels of 0.18q/l (.3pCi/l) and 0.88q/l (.20pCi/l) were proposed for gross alpha and gross beta activity, respectively. Below these levels water could be considered potable without complex radiological examination. The non-action levels are based upon the assumption that the most toxic radionuclides ^{226}Ra and/or ^{90}Sr are present in the water.

In comparison with the WHO recommended limit of 0.18q/l for gross alpha activity, 6 brands of locally-bottled mineral water and 5 imported brands were found to have ^{226}Ra levels exceeding this limit. However, the activities due to ^{228}Ra and ^{210}Pb , which are β -emitters with α -emitting daughters, must also be included in a comparison with the limits for gross activity¹⁷. Therefore, referring to the data in Tables 2, 3 and 5 for ^{228}Ra and ^{210}Pb content, the conclusion is reached that more than 50 per cent of the brands of bottled mineral water examined would have gross alpha activities in excess of 0.18q/l (.3pCi/l). Consequently, it is necessary to perform a more detailed assessment of the possible radiation dose and risk to health with the knowledge of the likely concentration ranges for ^{226}Ra , ^{228}Ra and ^{210}Pb .

Radiation Doses Due to Consumption of Bottled Mineral Water

The critical group to consider for assessment of radiation exposure following ingestion of ^{210}Pb , ^{226}Ra and ^{228}Ra in mineral water comprises those members of the public for whom bottled mineral water is the sole source of drinking water. The methodology developed by the International Commission on Radiological Protection for estimating radiation doses to organs and tissues following

ingestion of radionuclides¹⁶ may be applied to such a critical group without loss of generality. If the critical group, in a hypothetical situation, consumes 2 litres of bottled mineral water per day, all of which contains the maximum levels of ^{210}Pb , ^{226}Ra and ^{228}Ra as determined in this study (excluding Taurina Spa (Helidon)), namely 0.1Bq/l, 0.5Bq/l and 0.8Bq/l respectively, each member of the group is estimated to receive an annual dose equivalent of approximately 0.8mSv taken over all organs and tissues. Details of the calculation are given in Table 7.

The estimated annual dose equivalent of 0.8mSv is considerably less than the ICRP recommended limit* of 5mSv/y for critical groups when exposure is short-term only (i.e. a few years) and below the 1mSv/y suggested for life-long exposure for individuals in the critical group¹⁶.

Increased risk of Fatal Disease Following Consumption of Radioactivity

The total risk of incurring radiation-induced fatal disease has been estimated by several authorities as approximately 10^{-2} Sv^{-1} ^{16, 19}. For the critical group receiving 0.8mSv per annum from radioactivity in drinking water, there would be an increased risk of fatal disease from this source of 8×10^{-6} per year. For the consumption of a single bottle of mineral water, containing natural radioactivity as described, the increased risk of fatal illness would be in the order of 4×10^{-9} for all time (see Appendix I). Risks to health of an individual, of these magnitudes, are extremely small compared with other risks of every-day life.

Other Considerations

In an examination of the data in Table 3 it is noted that suspended solids (mainly hydrated iron oxides) contributed a large proportion to the total radium content in some samples of unprocessed mineral water. It is possible that the long-term build-up of radium isotopes in solids in holding-tanks, filters, etc. within bottling plants and the subsequent disposal of such residues presents a potential problem. Most natural mineral waters contain iron in a soluble form (Fe^{2+}) and radium will co-precipitate with hydrated iron oxides during prolonged exposure of the water to oxygen in the atmosphere. This is well-demonstrated by the data in Table 4 for Iredale Spring water. Aeration of the water, as a result of spraying at 1400l/hr brought about a considerable decrease in the soluble radium content. The degree to which radium will be removed from solution will depend upon a number of factors:

* Although the recommendations of the ICRP are not to be applied to exposure from natural sources of radioactivity, the WHO in their review of drinking water standards¹⁷ draw on the ICRP limits¹⁶ in assessing radiation doses due to natural radionuclides in drinking water.

- a. soluble iron content
- b. exposure to the atmosphere during handling and treatment
- c. residence time in holding tanks
- d. extent of filtration.

The potential problem may be greater, of course, if aeration of the mineral water is included as part of the bottling procedure.

One further point arises from this present study. Australian and overseas standards^{14,17} for drinking water propose that gross alpha and beta activity be determined in the initial examination of radiological quality. It is extremely doubtful that gross activity measurements could be performed on mineral water samples by the use of standard techniques. The high content of dissolved mineral salts will produce a large mass of residue which would be unsuitable for counting. In addition, gross alpha activity will not provide a measurement of the total ^{228}Ra and ^{226}Ra content due to the disequilibria between ^{228}Ra and its α -emitting daughters, ^{228}Th and ^{224}Ra , in mineral water.

Conclusions

Naturally-occurring radium isotopes, ^{226}Ra and ^{228}Ra have been detected in a large number of samples of bottled mineral water (Australian and imported) and local spa water. The levels of natural radioactivity, in some cases, exceed the limits recommended by Australian and overseas authorities for drinking water. However, the radiation dose received by members of the public consuming natural mineral water (with the levels of activity that were measured in this study) represents an increased risk to health of little significance on the basis of internationally-accepted criteria for radiation protection.

Because ^{228}Ra has a high radiotoxicity and may make a significant contribution to the total radium content in mineral water, it is suggested that analysis for this radionuclide be specifically included in any examination of the radiological quality of mineral or spa water.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the invaluable assistance of officers of the Victorian Health Commission. Ms T Colin, Mr J Hodge and Mr D Sharpe, in providing the samples of bottled and unprocessed mineral water for analysis. The co-operation of the various commercial bottlers and distributors during this study was also appreciated.

We also wish to thank several officers of this Laboratory for their contribution to this work, namely Mr P Burns for providing standardized radioactive solutions, Mr R Statham for data processing and Mrs C Telfer for typing the manuscript. We are also grateful to Mr J Moroney and Mr T Swindon of ARL for helpful discussions.

REFERENCES

1. Lucas, H.F. and Ilcewicz, F.H. (1958). J. Am. Water Works Assoc., 50, 1523-32.
2. Holtzman, R.B. in "The Natural Radiation Environment II", Proceedings of the Second International Symposium, Houston, Texas, August 7-11 1972, Adams, J.A.S., Lowder, W.M. and Gesell, T.F. (Eds), p.227-237.
3. Asikainen, M. and Kahlos, H. (1979). Geochim. Cosmochim. Acta, 43, 1681-6.
4. Michel, J. and Moore, M.S. (1980). Health Physics., 38, 663-71.
5. Remy, M.L. and Pellerin, P. (1968). Bull. Inst. Nat. Sante Rech. Med., 23; 23-61.
6. Heinberger, P.L., de Oliveira, I.R., Salles Andrade, H.A., Zundel, G. and Cullen, T.L. (1974). Radiation Data Rep., 15, 483-488.
7. Mastinu, G.G. and Santaroni, G.P. in "The Natural Radiation Environment III", Proceedings of the International Symposium, Houston, Texas, April 23-28, 1978. Gesell, T.F. and Lowder, W.M. (Eds), p.810-825.
8. McCurdy, D.E. and Mellor, R.A. (1981). Health Phys. 40, 250-253.
9. Holtzman, R.B. in "The Natural Radiation Environment III", Proceedings of the International Symposium, Houston, Texas, April 23-28, 1978. Gesell, T.F. and Lowder, W.M. (Eds), p.755-782.
10. Cooper, M.B. and Wilks, M. Australian Radiation Laboratory Tech. Report, in preparation.
11. Parks, N.J. and Tsuboi, K.K. (1978). Intern. J. Appl. Rad. and Isotopes, 29, 77-80.
12. Bonnyman, J. (1967). Commonwealth X-ray and Radium Lab., Tech. Report CXRL/3.
13. Currie, L.A. (1968). Anal. Chem., 40, 586-593.
14. National Health and Medical Research Council and Australian Water Resources Council, (1980). "Desirable Quality for Drinking Water in Australia", Report R80/359, Australian Govt. Publ. Service, Canberra.
15. World Health Organisation, (1971). International Standards for Drinking Water, 3rd edn.
16. Sowby, F.D., ed., (1977). Recommendations of the International Commission on Radiological Protection, ICRP Publication 26, Oxford, Pergamon Press.
17. World Health Organisation, (1979). "Radiological Examination of Drinking Water", Report on a Working Group, EURO Report No. 17, Copenhagen, WHO.
18. Sowby, F.D. ed., Recommendations of the International Commission on Radiological Protection, ICRP Publication 30, Annals of the ICRP, Oxford, Pergamon Press, 1979.

19. United Nations Scientific Committee on the Effects of Atomic Radiation (1977). "Sources and Effects of Radiation". 1977 Report to the General Assembly, New York, United Nations.

TABLE 1

Concentration of ^{226}Ra in Bottled Natural Mineral Water from Australian Sources

Brand Name	Spring and Location	^{226}Ra Concentration in Bq/l (pCi/l)*
Acqua Minerali Salutina	Kyneton, Victoria	0.02 \pm 0.01 (0.5)
Bisleri	Deep Creek, Eganstown, Victoria	0.23 \pm 0.02 (6.9)
Boon Spa	Sailors Falls, Daylesford, Victoria	0.03 \pm 0.01 (0.8)
Calandra	West Kyneton Mineral Spring, Kyneton, Victoria	ND
Deep Spring	Deep Creek, Eganstown, Victoria	0.29 \pm 0.02 (7.7)
Hepburn Spa	Hepburn Spring, Sutton Springs	0.12 \pm 0.01 (3.3)
Kyneton Mineral Spring	West Kyneton Mineral Springs, Kyneton, Victoria	ND
Natural Mineral Water	Sailors Falls, Daylesford, Victoria	0.03 \pm 0.01 (0.8)
Safeway	Deep Creek, Eganstown, Victoria	0.32 \pm 0.02 (8.6)
Sostanza	Helidon District, Toowoomba, Queensland	0.02 \pm 0.01 (0.5)
Taurina Spa (Daylesford)	Glenlyon Recreation Reserve, Daylesford, Victoria	0.28 \pm 0.02 (7.5) $^{\Delta}$
Taurina Spa (Daylesford)**	Glenlyon Recreation Reserve, Daylesford, Victoria	0.04 \pm 0.01 (1.0)
Taurina Spa (Helidon)	Iredale Spring, Helidon, Queensland	1.58 \pm 0.04 (42.7) $^{\Delta}$
Taurina Spa (Darling Downs)	Darling Downs Spring, Toowoomba, Queensland	ND
Woolworths	Helidon District, Queensland	0.02 \pm 0.01 (0.5)

Δ analyses carried out on bottled water which was not available for sale.

* ND - below limit of detection.

** bottling process now includes treatment of water to remove radium.

TABLE 2

Concentration of ^{226}Ra and ^{210}Pb in Bottled, Natural Mineral Water from Overseas Sources

Brand Name	Country of Origin	Radioactive concentration in Bq/l (pCi/l)*	
		^{226}Ra	^{210}Pb
Acqua Della Madonna	Italy	0.04±0.01 (1.0)	0.02±0.01 (0.5)
Appolinaris	West Germany	0.14±0.01 (3.8)	0.05±0.01 (1.4)
Badoit	France	0.13±0.01 (3.6)	0.08±0.01 (2.2)
Crodo	Italy	ND	ND
Evian	France	ND	ND
Ferrarelle	Italy	ND	ND
Gerolsteiner Sprudel	West Germany	ND	ND
S Pelegrino	Italy	0.20±0.02 (5.4)	ND
Perrier	France	ND	0.04±0.01 (1.1)
Rodenska	Yugoslavia	0.15±0.02 (4.0)	0.02±0.01 (0.5)
Sangemini	Italy	0.03±0.01 (0.8)	ND
Vichy	France	0.44±0.03 (11.9)	0.02±0.01 (0.5)
Vittel	France	0.02±0.01 (0.5)	ND

* ND - below limit of detection.

TABLE 3

Analysis of Water from Local Mineral Springs using γ -Spectrometry

Spring Source	Sampling Location	Radionuclide Concentration (Bq/l)			
		^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th
Iredale Spring, Helidon	From spring	1.63 \pm 0.05	ND	2.21 \pm 0.08	0.08 \pm 0.01
Iredale Spring, Helidon	Spring water sprayed at 1400 l/hour	0.02 \pm 0.01	ND	ND	ND
Darling Downs Spring, Toowoomba	From bore	ND	ND	ND	ND
Glen Lyon Recreation Reserve, Daylesford	As received by Tanker at Bottling Company	A. 0.54 \pm 0.05	ND	0.75 \pm 0.03	0.04 \pm 0.01
		B. 0.34 \pm 0.04	ND	0.42 \pm 0.02	0.02 \pm 0.01
Deep Creek, Eganstown, Victoria	From holding tanks - at Bottler 1	0.34 \pm 0.06	ND	0.38 \pm 0.03	0.03 \pm 0.01
	at Bottler 2	0.24 \pm 0.05	ND	0.13 \pm 0.02	ND
Hepburn Spring	From spring	A. 0.21 \pm 0.05	ND	0.20 \pm 0.02	ND
		B. 0.29 \pm 0.03	ND	0.39 \pm 0.02	0.02 \pm 0.01
Sutton Spring, Hepburn	From spring	0.10 \pm 0.05	ND	0.08 \pm 0.03	ND
Sailors Falls, Daylesford	From spring	0.90 \pm 0.10	ND	1.03 \pm 0.05	0.12 \pm 0.01
West Kyneton Mineral Springs	From spring	0.30 \pm 0.01	ND	ND	ND
Glen Luce Mineral Springs, Castlemaine	From spring	0.57 \pm 0.06	ND	1.06 \pm 0.05	0.16 \pm 0.02
Helidon District, Queensland	From bore	0.21 \pm 0.01	ND	0.12 \pm 0.02	ND

ND - below limit of detection

A - water filtered (0.45 μm) then acidified

B - suspended solids

TABLE 4

Limits of Detection for the Radioactive Measurement Techniques

Method	Background count rate (cps)	Counting Time (secs)	L_D (counts)	Detection Limit (Bq)
Liquid Scintillation for ^{226}Ra				
a. manual system	0.28	3000	135	0.01
b. commercial counter	1.50	3000	315	0.03
β -counting for ^{210}Pb	0.012	12000	60	0.02
γ -spectrometry				
a. ^{210}Pb	0.0008	50000	22	0.4
b. ^{226}Ra (^{214}Pb -295 keV)	0.0012	50000	39	0.2
c. ^{228}Ra (^{228}Ac -338 keV)	0.0009	50000	34	0.3
d. ^{228}Th (^{212}Pb - 238 keV)	0.0025	50000	55	0.1

TABLE 5

Analysis of Bottled Mineral Water Samples by γ -Spectrometry

Brand	Radionuclide Concentration (Bq/l) ^a		
	²²⁶ Ra	²²⁸ Ra	²²⁸ Th
<u>Imported</u> ^b			
Badoit	0.22 \pm 0.15	0.85 \pm 0.14	ND
Rodenska	0.18 \pm 0.07	ND	ND
Vichy	0.45 \pm 0.10	0.28 \pm 0.12	0.13 \pm 0.04
<u>Local</u>			
Safeway	0.38 \pm 0.25	0.34 \pm 0.09	ND
Taurina Spa (Daylesford) ^c	0.38 \pm 0.09	0.39 \pm 0.10	ND
Taurina Spa (Helidon) ^c	1.87 \pm 0.24	2.81 \pm 0.13	0.13 \pm 0.03

a ND - radionuclide concentration below detectable levels.

b activities of γ -emitters in all other samples of imported mineral water were not detectable by this method.

c analyses performed on bottled water which was not available for sale.

TABLE 6

Recommended Levels for Radionuclides in Drinking Water in Australia
(Reference No.14)

Characteristic	Desirable Current Criteria	Long Term Objectives	Health Investigation Levels (Bq/l)
	Maximum Levels (Bq/l)		If levels exceeded:
(i) Specified Radionuclides			
Strontium-90	1.0	1.0	1.0
Radium-226	0.4	0.4	0.4
(ii) Unspecified Radionuclides			
Gross Alpha Activity	0.1	0.1	0.1
Gross Beta Activity	1.0	1.0	1.0

TABLE 7

Annual Effective Dose-Equivalents for the Ingestion of ^{226}Ra , ^{228}Ra and ^{210}Pb in Bottled Natural Mineral Water

Radionuclide	Maximum Concentration in Water (Bq/l), from present study	Annual Intake at 2l/day Bq	Annual Limit of Intake (Bq) for 0.05Sv*	Annual Effective Dose Equivalent (mSv)
^{226}Ra	0.5	365	7×10^4	.26
^{228}Ra	0.8	584	9×10^4	.32
^{210}Pb	0.1	72	2×10^4	.18

* Reference No. 18

APPENDIX I

Absolute Risk of Inducing Fatal Cancer from the Consumption of One Litre of Bottled Mineral Water with ^{226}Ra content of 0.58q and ^{228}Ra content of 0.88q

Organ or Tissue at Risk	Committed Dose Equivalent per Bq of activity (Sv/Bq) ^a		Committed Dose-Equivalent (Sv)		Average Risk Factor ^b (Sv ⁻¹ x 10 ²)	Absolute Risk of Fatal Cancer
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra		
Gonads	9.2×10^{-8}	1.6×10^{-7}	4.6×10^{-8}	1.3×10^{-7}	0.40	7×10^{-10}
Breast	-	1.6×10^{-7}	-	1.3×10^{-7}	0.25	3×10^{-10}
Red-Bone Marrow	6.0×10^{-7}	6.5×10^{-7}	3.0×10^{-7}	5.2×10^{-7}	0.20	2×10^{-9}
Lungs	-	1.6×10^{-7}	-	1.3×10^{-7}	0.20	2×10^{-9}
Bone Surface	6.8×10^{-6}	5.8×10^{-6}	3.4×10^{-6}	4.6×10^{-6}	0.05	4×10^{-9}

a. Reference No. 18.

b. Reference No. 16.