Naturally-Occurring Radionuclides In Drinking Water From Surface And Groundwater Reservoirs

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Abstract. Radioactivity in water for human consumption is under closer scrutiny than ever before and many countries adopted guideline values based on total alpha and total beta activity measurements. Although most waters from surface circulation meet these guidelines, it is frequently found that groundwater exceed guideline values. Results of water analyses by alpha spectrometry clarified that the main radionuclides present are from the uranium decay series, such as uranium isotopes, radium (^{226}Ra), radon (^{222}Rn), and also ^{210}Pb and ^{210}Po. Occasionally, groundwater displayed ^{226}Ra concentrations higher than 1 Bq L^{-1} and ^{222}Rn concentrations above 1000 Bq L^{-1}. Nevertheless, lack of conformity of these waters with guidelines adopted, generally, is not due to anthropogenic inputs.

Keywords: Drinking water, radioactivity, indicative dose, uranium, radium, radon.
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INTRODUCTION

Increasing attention is paid to the radiological quality of water for human consumption, as reflected in the water guidelines adopted by many countries. This is the case for the European Union Directive 98/83/CE that set up the limits of 0.1 Bq L^{-1}, 1.0 Bq L^{-1} and 100 Bq L^{-1} respectively for total alpha activity, total beta activity and tritium in water for human consumption. Also an indicative dose limit was set at 0.1 mSv y^{-1}, and recommended as a maximum permitted dose resulting from the consumption of water. These limits have been enforced by EU Member States and triggered radioactivity monitoring in drinking water elsewhere also. [1, 2, 3]

Analysis of water samples from a large number of supply networks in Portugal gave us a general view on the occurrence of water with activity concentrations below and above standards set up by the EU Directive. This paper reports analytical results of surface waters and groundwater and discusses the reasons for varying radionuclide concentrations in water.

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MATERIALS AND METHODS

Water samples for analysis of total alpha, total beta and specific radionuclides by radiochemistry and alpha spectrometry, were collected in polyethylene bottles of 5 L capacity and acidified to pH<2. Water samples for tritium analyses were collected in polyethylene bottles, leaving no head space, and were not acidified. Water samples for radon measurement were collected with a graduated syringe directly into a scintillation vial, injected under the surface of the scintillation cocktail and tightly capped.

In general, water for human consumption collected from the tap was analyzed without filtration, *i. e.,* was analyzed as consumed. As prior to distribution this water is treated, most of particulate matter is removed. Water samples collected from surface reservoirs and aquifers were analyzed for radioactivity following filtration through 0.45 μm pore size membrane filter to remove suspended particles.

Total alpha and total beta activities were determined according to well established methods, based on the measurement of dry residue.[4,5] Determination of dissolved radon (^{222}Rn) is performed by liquid scintillation counting as described elsewhere.[6] Determination of tritium (^{3}H), performed after isotopic enrichment by electrolysis, follows the official method NP4362.[7] Determination of specific radionuclides such as uranium isotopes, thorium (^{232}Th, ^{230}Th), radium (^{226}Ra), polonium (^{210}Po) and lead (^{210}Pb) was made by alpha spectrometry following radiochemical separation of radionuclides.[8, 9] Analytical quality control was periodically made through analyses of certified reference materials and participation in international intercomparison exercises organized by the IAEA and EU.

RESULTS AND DISCUSSION

Water delivered for human consumption

Water samples collected from the tap in cities and towns across the country showed total alpha and total beta activities generally below the recommended limits. Only a few samples have shown total alpha above the limit of 0.1 Bq L^{-1}, and none has shown activity concentrations above the total beta activity limit of 1.0 Bq L^{-1} (Figure 1). Similar water samples from small towns and villages in the granite regions of the centre-North of Portugal, where uranium mineralization is known to occur, showed a higher frequency of values above limits for total alpha activity in the water (Figure 1). Many of these water supplies are in areas where there is no industrial activity and, therefore, lack of conformity of radioactivity in water with guidelines seemed unlikely to be originated by anthropogenic inputs.

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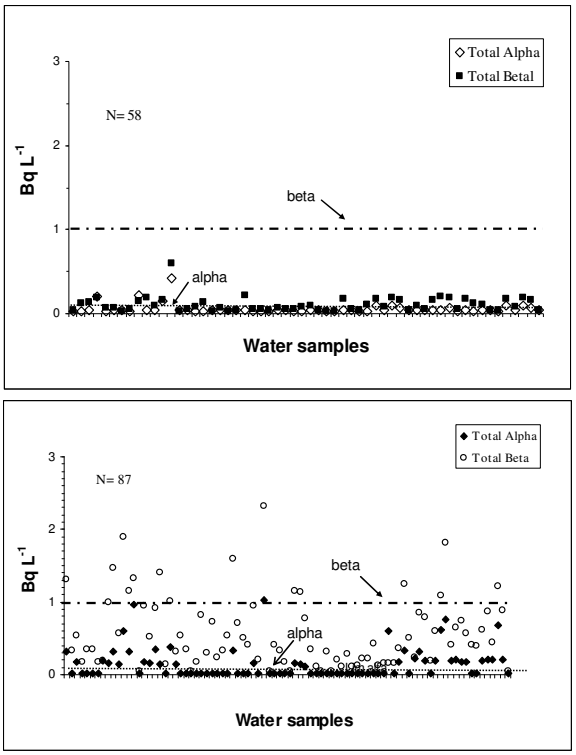

FIGURE 1. Total alpha and total beta activities in tap water. Top: cities mainly supplied from surface reservoirs. Bottom: small towns often with their own local water supply from groundwater.

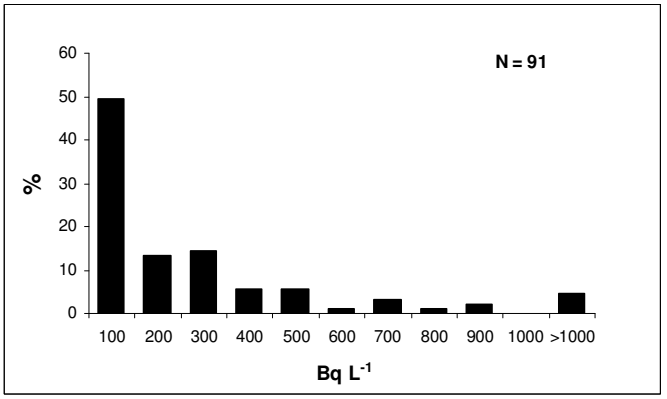

FIGURE 2. Frequency of radon concentrations in public water supplies across the country.

To check for the potential origin of radionuclides, waters from two specific locations on the Tagus valley, in the centre of the country, namely Vila Velha de Rodão near the Spanish border, and Sacavém, near Lisbon, during 2003 were monitored monthly for total alpha, total beta and tritium. Rodão is a small town supplied with water from a local source in quartzite of the south edge of the Serra da Estrela mountain

range. Sacavém is supplied with water from the distribution network for the Lisbon area. This water is collected at several places, mainly at the artificial lake of Castelo do Bode on the Zêzere River tributary to the Tagus, and in the Tagus River at Valada do Ribatejo. Water from these sources is treated and, at least, partly mixed in the distribution network before arrival to the consumer's tap in Lisbon area.

All year round, total alpha and total beta activity concentrations of these waters displayed no seasonal fluctuations and the annual average concentrations were different between towns. In Sacavém, total alpha was usually (n=12) lower than 0.04 Bq L^{-1} (Minimum Detectable Activity, MDA) and in Rodão was 0.08±0.02 Bq L^{-1} (n=11). During the same period, total beta activity was 0.07±0.03 Bq L^{-1} (n=12) and 0.12±0.03 Bq L^{-1} (n=11) in the same towns, respectively. Therefore, water distributed to Sacavém that originated in surface reservoirs in rivers, displayed average total alpha and total beta activities lower than water at Rodão, which originated in a local spring source.

Tritium analysis in both waters has shown that water at Sacavém has average concentrations slightly higher (2.6±0.3 Bq L^{-1}) than Rodão (1.6±0.8 Bq L^{-1}) indicating a contribution of radionuclides from artificial sources, exactly the opposite found for total alpha and total beta. Actually, this tritium originates in the Almaraz nuclear power plant, on the Tagus valley across the border.

Radon concentration in tap water across the country was variable. For example, in Lisbon, samples collected at various points of the city systematically displayed concentrations lower than 0.2 Bq L^{-1} (MDA). However, radon concentrations in water from towns in centre-North of the country, including the granite massif, generally were much higher and, on occasion, above 1000 Bq L^{-1} (Figure 2).

It was observed that waters containing radioactivity concentrations in non conformity with total alpha or total beta limits did not contain tritium in excess. This suggested that excess activities were unlikely to be due to artificial radionuclides. Furthermore, water with alpha and beta activity concentrations in excess was also high in dissolved radon and this seemed to be related to the geology of the terrain. These observations triggered a number of analyses for identification and quantification of specific radionuclides in water.

Surface waters

Total activity of surface waters indicated that concentrations of dissolved radionuclides were generally low. Radon was generally present in very low concentrations also*, i.e,* <0.2 Bq L^{-1}, and tend to decrease with water treatment. Specific radionuclides have also low concentrations (Table 1). For example, in Tagus water total uranium concentration was 15 mBq L^{-1} and in the artificial lake of Castelo do Bode was 0.62 mBq L^{-1}. Concentrations of dissolved radium (^{226}Ra) were generally proportional to dissolved uranium concentrations, while ^{210}Pb and ^{210}Po concentrations were generally much lower than Uranium and Radium concentrations and show no correlation with them. The isotopic ratio $^{234}U/^{238}U$ was always close to unity.

Groundwater

In groundwater, total alpha and also total beta activities were higher than in surface waters and frequently closer or even above concentration limits. In mineral groundwater, very often high concentrations of ^{226}Ra and ^{222}Rn are measured. In these waters ^{226}Ra and ^{222}Rn concentrations may exceed 1 Bq L^{-1} and 1000 Bq L^{-1}, respectively.

Concentrations of tritium in these waters were low and frequently below 0.8 Bq L^{-1} (MDA). Most of the tritium in the environment originates in releases from nuclear

power plants and dissolves in surface water bodies rapidly. However, some aquifers may display ^{3}H concentrations identical to surface waters due to contamination following the peak of atmospheric radioactivity in the early sixties during nuclear weapons testing.[10] Groundwater from deep aquifers with very slow turnover time may be tritium free.

Although the range of concentrations of uranium series radionuclides may vary widely, as a result of complex chemical interactions between water and the aquifer host rock, in groundwater uranium and radium concentrations are higher than in surface waters (Table 1). Concentrations of dissolved uranium correlate positively with concentrations of dissolved salts and with concentrations of dissolved ^{226}Ra ($p<0.01$).

TABLE1.Radionuclide concentrations (mBq L^{-1}± 1 SD) in drinking water from various origins.

	Location	^{238}U	^{235}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po
A	MANGUALDE	20.2±0.6	1.0±0.1	18.4±0.6	0.25±0.02	12.8±5.3	47.8±1.7	3.6±0.1
A	Belmonte	6.1±0.3	0.28±0.04	6.0±0.3	0.57±0.07	3.7±0.4	-	5.8±0.2
A	Aguiar da Beira	25.0±0.7	1.1±0.1	26.2±0.7	1.7±0.1	12.2±0.6	-	22.3±1.3
A	Guarda	1.6±0.2	0.08±0.04	2.0±0.2	-	3.2±0.2	-	3.3±0.2
B	Tagus River (Valada)	6.1±0.3	-	8.9±0.5	-	0.88±0.02	0.80±0.33	0.59±0.05
B	Zêzere River (C. de Bode)	0.31±0.02	-	0.31±0.02	0.24±0.11	0.27±0.01	2.1±0.1	0.10±0.09
C	Viseu, Campo	22.4±0.9	1.0±0.1	28.7±1.1	0.49±0.07	6.6±0.5	47.5±1.3	12.7±0.6
C	Sátão	29.4±1.2	1.5±0.2	33.6±1.3	0.34±0.05	9.4±0.5	-	7.4±0.2
C	Portalegre	2.0±0.1	0.11±0.02	5.1±0.2	0.09±0.02	50.1±2.4	21.6±0.7	20.8±0.7
B	Coimbra	3.8±0.1	0.17±0.03	4.0±0.2	0.09±0.02	2.8±0.3	37.4±1.2	36.0±1.2

A- Tap water sampled in various cities. B- Surface water sampled from reservoirs; C- Groundwater sampled at the source.

CONCLUSIONS

Total alpha and total beta activities in water distributed for human consumption and sampled at the consumer's tap in large cities, generally did not exceed guideline values for those parameters. Water distribution networks in main urban areas generally use water from lakes and reservoirs. Radon concentrations in these surface waters are also low and tritium, originated in atmospheric releases from nuclear power plants, is present in concentrations that do not exceed guideline values. Therefore, regular consumption of these waters does not expose the members of the public to radiation doses above the recommended safety limit of 0.1 mSv y^{-1}.

Total alpha and total beta activities in groundwater may exceed guideline concentrations. The activity is due to higher concentrations of naturally occurring radionuclides from the uranium series, such as ^{226}Ra, ^{222}Rn and ^{210}Pb. However, in many cases, the radiation dose computed using the actual data on water specific

radionuclide composition allows verifying that the dose equivalent does not exceed the recommended safety limit. Moreover, lack of conformity of these waters with recommended radioactivity limits is not due to anthropogenic input of radionuclides.

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