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Dose assessment to members of the pulic in Tunisia from intakes of some naturally occurring radionuclides in bottled mineral water

S. Labidi* and S. Gharbi

Université Tunis EL Manar , Institut Supérieur des Technologies Médicales de Tunis
Laboratoire de recherche de Biophysique et de Technologies Médicales 9, Avenue du Dr. Z. Essafi, Tunis 1006
University of Tunis El Manar , Higher Institute of Medical Technologies of Tunis, Tunisia
Laboratory Research in Biophysics and Medical Technologies, Tunisia

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Corresponding authors:
Dr. S. Labidi,
Fax: *+216 71 260 426*
E-mail: *labidisalam@yahoo.fr*

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ABSTRACT

Background: Total α- and β- as well as radium isotopes (^{226}Ra, ^{228}Ra) and uranium isotopes (^{234}U, ^{238}U) activity concentrations were determined in six most popular Tunisian bottled mineral waters samples. Materials and Methods: Total alpha/beta activity was measured by background gas-flow proportional counting system, and the activity concentrations of uranium were studied by radiochemical separation procedures followed by alpha spectrometry and that of radium isotopes by gamma-ray spectrometry. ***Materials and Methods***: The total-a activity ranged from 48 to 94 mBq L−1 and the total-b activity between 45 and 430 mBq L−1. The activity concentrations of ^{238}U, 234U, ^{226}Ra and ^{228}Ra in water samples varied in range 3.3 - 22.5 mBq.L−1, 4.0 - 34.2 mBq L−1, 2.0 - 67.0 mBq L−1 and 2.0 - 30.2 mBq L−1, respectively. These values are comparable with those reported for many other countries in the world for different types of water. The 234U/238U activity ratio were found to be higher than 1 in all cases. ***Results:*** Based on the activity concentration results obtained in this study, the estimated annual ingestion dose rates for three different age groups (< 1 year, 7-12 years, and > 17 years) due to the ingestion of radium and uranium isotopes through drinking water are lower than the limit of intake prescribed by WHO. The annual doses exceed the recommended value of 0.1 mSv y-1 in one case for age group < 1 year. ***Conclusion:*** According Based on the activity concentration results obtained in this study, the estimated annual ingestion dose rates for three different age groups (< 1 year, 7-12 years, and > 17 years) due to the ingestion of radium and uranium isotopes through drinking water are lower than the limit of intake prescribed by WHO. The annual doses exceed the recommended value of 0.1 mSv y -1 in one case for age group < 1 year.

Keywords: *Natural radioactivity, total alpha/beta activity, radium; uranium, mineral water, radiation dose.*

INTRODUCTION

Tunisia is rich in natural waters. Due to the importance of water for human life and the increased consumption of mineral waters, their quality must be carefully and systematically controlled. Natural waters generally contain naturally occurring radionuclides predominantly resulting from the uranium–radium decay series which are omnipresent in the Earth's crust. Their concentrations vary over a wide range, which depends on the nature of the aquifer and the chemical characteristics of the water [1]. The occurrence of radionuclide's in mineral water causes health hazards owing to human internal exposure from the decay of radio-nuclides absorbed into the body through ingestion.

The World Health Organisation (WHO 1993) [2] guidelines for drinking water suggest performing an indirect evaluation of committed doses by measuring alpha and beta total radioactivity and checking compliance to derived limit values; the proposed limit values are 0,1 Bq/l for total alpha and 1 Bq/l for total beta radioactivity. Nevertheless, it is desirable to identify single radionuclides contribution to alpha and beta activities in order to perform more accurate measurements of committed dose.

The natural radioactivity of bottled mineral waters has been a subject of numerous studies. However, most of these studies dealt only with a part of this radioactivity [3, 4,5]. In Tunisia, natural radioactivity in mineral waters was studied by Gharbi *et al.* [6]. As this concerns only uranium isotopes, such study needs the quantification of radium isotopes which was not the aim of the work. The determination of Ra-isotopes in environmental samples is very important from a radiological point of view. Due to their radiotoxicity, especially that of ^{226}Ra and ^{228}Ra, the contamination hazard is potentially dangerous to human beings even at low concentration levels. The principal health risks associated with the use of mineral waters containing elevated concentrations of dissolved radium are carcinomas of the head and sarcoma of bone[7]. An excess of 2% above the background cancer incidence rate due to ingestion of mineral spring waters was estimated [7].

The objective of the present study is to determine the level of total a and total b activities as well as the concentration of uranium and radium isotopes in the widely consumed mineral waters taken from six Tunisian cities and to estimate the effective doses for different age categories of the public.

The dose reference level due to the ingestion of radionuclides through driking water suggested by WHO Guidelines [2] is 0.1 mSv y^{-1}. However, for bottled mineral waters, there are no reference levels of the recommended effective dose in Tunisia. Nevertheless, in this work, dose calculation was performed using values usually suggested by different international organizations for drinking water. The data generated in this study may serve as the base-line levels of natural radioactivity in mineral water and help in the development of future guidelines for radiological protection in Tunisia.

MATERIALS AND METHODS

Sampling

At each sampling site, twenty litres of water were collected directly from each source in polyethylene bottles with screw caps. Each sample was pretreated on site with nitric acid until reaching a pH level below 2, to prevent losses by sorption of the studied radionuclides onto the walls of the containers.

The principale dissolved constituents in these mineral waters are sodium, calcium, magnesium, sulphate, chloride and bicarbonate, and they occur in the form of electrically charged ions.

In all samples, total alpha and beta radioactivity and the natural radioelements of utmost interest were measured. The locations from where the samples are collected for the present study are shown in figure 1.

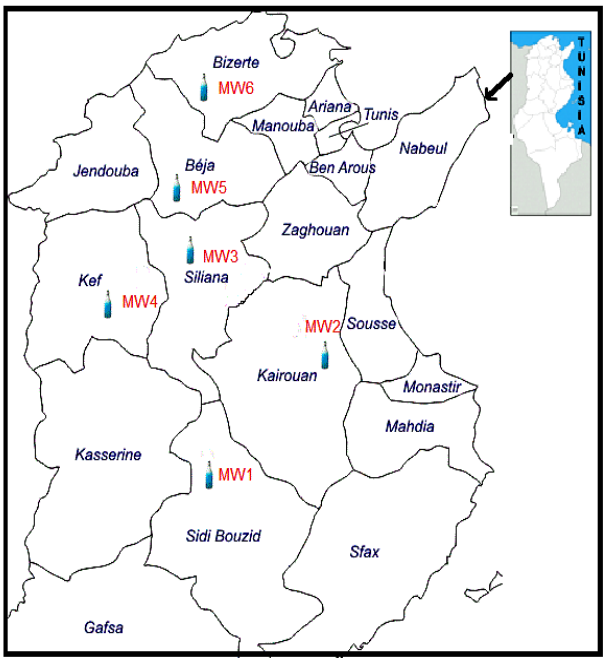

Figure 1. Map showing locations from which mineral water samples are collected for the study.

Total-alpha and total-beta measurements

An aliquot of 100 mL of each sample was evaporated at 80°C (in order to avoid boiling) down to a few milliliters and then transferred to a striated stainless steel planchet of 50 mm in diameter and evaporated to dryness. Special care was taken to ensure that, the total dissolved solids do not exceed a surface density of 5 mg/cm^2 for total alpha determination and 10 mg/cm^2 for total beta determination[8]. The instrumentation to count the total-α and total-β activities was a α/β counter of the low background multiple detector (Canberra-Tennelec). These detectors are gasflow window-type counters, approximately 5 cm in diameter. The counting gas was a mixture of 90% argon and 10% methane. Lead shielding was used to attenuate external radiation. The operating high voltage of the detector was set at 1500 V. ^{241}Am and ^{90}Sr were used to calibrate the system for α and β energies, respectively. The counting time was 36000 s for gross α and gross β activities. Typical minimum detectable activities (MDA) for acounting time of 500 min were estimated to be 3 mBq/l for α and 6 mBq/l for β.

Radium isotopes determination

The radiochemical procedure adopted in the present study for ^{226}Ra and ^{228}Ra determination is described in detail by Reyss *et al.* [9]. A known quantity of barium, in the chemical form of BaCO3 was then added to each water sample. After stirring, Ra isotopes were coprecipitated with BaSO4, formed by the addition of H_2SO4 (in drops), in the medium without significant changing of pH. After decantation, the precipitate containing radium was separated from the sample by centrifugation. The insoluble BaSO4 was rinsed with deionised water, and dried at room temperature. The obtained powder was sealed into a plastic ferrule with a size compatible with the dimensions of the well-type germanium detector used in the study. The ^{222}Rn daughter of ^{226}Ra is strongly retained in the barium sulfate precipitate, together with its short-lived progeny that emit gamma rays. The ^{228}Ac daughter of ^{228}Ra that emits gamma rays co-precipitates together with its parent. The gamma-ray spectrum for each sample was acquired after 3 weeks which is adequate to ensure radioactive equilibrium between Ra isotopes and their daughters. The activity of ^{228}Ra was determined from its daughter, the ^{228}Ac isotope (338.4 keV and 911.2 keV energies). The activity concentration of other radium isotope, ^{226}Ra, was determined from the gamma lines of its daughters ^{214}Pb (295.2 keV and 351.9 keV) and ^{214}Bi (609.3 keV and 1120.3 keV). The activity concentrations of the water samples were measured using high purity germanium detector (HPGe) of efficiency 20% and resolution (FWHM) 1.8keV at 1332 keV g-energy of ^{60}Co which was connected to a multi-channel analyser (MCA). In this work, the energy calibrations of the gamma ray spectra were done using standard radioactive sources of ^{137}Cs, ^{60}Co and ^{152}Eu. The minimum detection activity was determined with a confidence level of 95%. Spectral data from the detector was accumulated on an MCA and analyzed using Genie-2000 software from Canberra.

Uranium isotopes determination

The detailed radioanalytical procedure for determination of uranium isotopes in water samples was described elsewhere [10]. For determination of uranium radioisotopes a known amount of ^{232}U tracer was added to the water sample previously acidified with concentrated HNO_3. Iron carrier ($FeCl_3$) was added to the solution. The uranium was coprecipitated with $Fe(OH)_3$ by addition of NH_4OH to have a pH concentration of 8 to 9. After stirring, the precipitate containing uranium was separated from the sample by centrifugation, and then dissolved in 8N HNO_3. After that, 3 mL mixture of $HClO_4$ and HF was added to the solution and the solution which was then evaporated to dryness. The dry residue was dissolved in 8N HCl and the hydroxides were precipitated at pH 8 to 9 with ammonium hydroxide. After dissolution, the sample was filtered to be ready for the ion exchange procedure, which is required to separate uranium from impurities. U and Fe are fixed on the resin in 8N HCl, and the impurities were collected with the effluent. Fe is then eluted with 15 mL of 8N HNO_3. U is eluted with 30 mL of 0.1N HCl and then evaporated to dryness. After these anionic exchange steps, U is separated from residual iron. Its purification is performed by diisopropyl ether extraction, followed by evaporation of the aqueous fraction containing U.

In the last step, U is extracted separately with TTA (1-(2-thenoyl)-3, 3, 3-trifluoroacetone) in toluene in a nitric media at pH 3. The organic phase containing U is evaporated on aluminium foil and flamed to remove any traces of carbon. Low-level activity measurements were performed using a Canberra alpha-spectrometry counting system with passivated implanted planar silicon (PIPS) semiconductor detectors, with an active area of 450 mm^2 and 28% efficiency for 25-mm diameter discs used for alpha-particle spectrometry measurements. The calibration of the detector was made with a standard radionuclide source, containing ^{238}U, ^{234}U, ^{239}Pu and

^{241}Am. The samples were measured for a period of 2–3 days. Data acquisition and analysis were performed with the Genie 2000 spectroscopy system software. The minimum detectable activity (MDA) calculated according to Currie's method [11] was around 0.3 mBq/l for two days counting. Chemical yields, determined by ^{232}U internal tracer, ranged from 65 to 85%.

RESULTS

The activity concentrations of the radionuclides

Total alpha and beta, uranium and radium isotopes concentrations are presented in table 1. The counting errors associated with the determination of the radionuclide concentration (at one sigma level) are also given with each data. Statistical analysis of the data (correlation plots and t-tests) was performed using Microcal Origin® software.

In order to guarantee an exposure lower than 0.1mSv/y due to radioactivity levels for drinking water, the WHO (World Health Organization) has set a guidline value for total alpha and total beta activities as 0.1 Bq L^{-1} and 1 Bq L^{-1} respectivley. The guideline levels were calculated for a daily water consumption rate of 2 L d^{-1}. The total alpha and beta activities of the analyzed bottled mineral waters were within the recommended values. For all samples the total-b activities were higher than the corresponding total-a activities. The total-a activity ranged from 48 to 94 mBq L^{-1} and the total-b activity from 45 to 420 mBq L^{-1}. As shown in table 1, the highest total-a and b-activity were determined in the mineral water sample MW1.

The uranium activity concentrations in the mineral water samples are in the range of 3.30–22.50mBq L^{-1} and 3.99–34.2mBq L^{-1} for ^{238}U and ^{234}U, respectively. The U isotopes ($^{234/238}$U) are common in mineral and underground waters as well. If there are no chemical or physical disturbing effects, they should be in radioactive equilibrium which means that the activity ratio of ^{234}U/^{238}U is around 1.00. However, as it was reported in table 1, the disequilibrium between ^{234}U and ^{238}U activity concentration was observed in most of the mineral water samples; values up to 2.2 were observed.

Among the radium isotopes, only ^{226}Ra and ^{228}Ra are considered in this radiological analysis. The ^{223}Ra as well as ^{224}Ra were ignored, the first because it has a very low abundance of its precursor ^{235}U and the second because of its comparatively short half life. The results show that activity concentrations of radium in water samples are in the range 2.0-67.0 mBqL^{-1} and 2.0 -30.2 mBq L^{-1} for ^{226}Ra and ^{228}Ra, respectively.

An attempt was made to correlate the activity concentrations of ^{226}Ra with ^{228}Ra, considering the data obtained in each mineral water separately. No significant correlation was found between the two radium isotopes. Although ^{226}Ra is the intermediate product of the ^{238}U decay chain, the correlation analysis shows that there is no statistically significant correlation between the two radionuclides in the analysed water samples.

Table 1. Total alpha/beta-activities and activity concentration values (in mBq L^{-1}) of natural radionuclides and isotopic ratio in the investigated bottled mineral waters.

Water Sample	Total alpha Activity	Total beta Activity	^{226}Ra	^{228}Ra	^{238}U	^{234}U	^{234}U/^{238}U
MW1	94.0 ± 12.0[a]	420.0 ± 71.0	67.0 ± 18.0	30.2 ± 4.5	3.3 ± 0.7	4.0 ± 0.6	1.2
MW2	67.0 ± 4.8	130.0 ± 15.5	11.5 ± 3.2	11.0 ± 2.5	8.5 ± 1.2	18.6 ± 2.9	2.2
MW3	87.0 ± 11.2	45.0 ± 9.4	19.8 ± 2.0	8.1 ± 1.5	22.5 ± 1.6	34.2 ± 2.9	1.5
MW4	56.0 ± 3.6	160.0 ± 25.1	9.0 ± 1.1	12.7 ± 1.9	9.7 ± 0.7	14.9 ± 1.1	1.5
MW5	48.0 ± 7.5	200.0 ± 42.6	12.0 ± 1.1	8.8 ± 1.8	4.7 ± 0.9	7.1 ± 0.6	1.5
MW6	62.0 ± 2.7	110.0 ± 13.0	12.1 ± 3.0	2.0 ± 1.1	6.4 ± 0.8	12.5 ± 2.3	1.9

[a] Indicates the counting error associated with determination of activity concentration

As shown in figures 1 and 2, positive correlations are observed between the ^{226}Ra and total-a activity with a correlation coefficient of 0.728 and between the ^{228}Ra and total-b activity with a correlation coefficient of 0.808 in the mineral water samples.

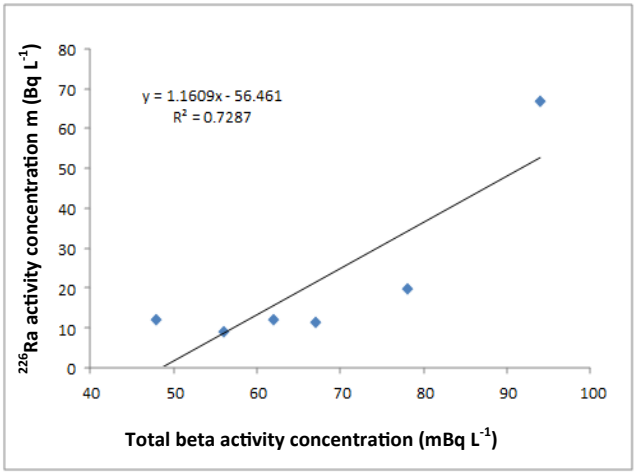

Figure 1. Correlation between total alpha and ^{226}Ra activity concentration.

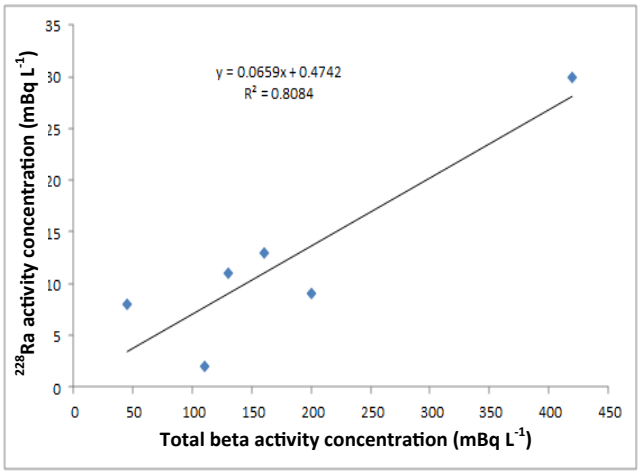

Figure 2. Correlation between total beta and ^{228}Ra activity concentration.

Radiation dose estimation

In order to evaluate the relative importance of the radionuclides analyzed in mineral water to the population radiation exposure, annual effective dose (Deff) due to the ingestion of the bottled mineral waters was estimated. The annual doses were estimated using the activity concentrations of radium and uranium isotopes, dose coefficients and annual water consumption as follows:

D_{eff} (Sv y^{-1}) = A. (Bq L^{-1}) × V (L y^{-1}) × CF (Sv Bq^{-1})

Where; D_{eff} is the annual effective dose (Sv.y^{-1}) due to ingestion of radionuclides from the consumption of bottled water, A is the activity concentration of radionuclides in the ingested mineral water (^{226}Ra, ^{228}Ra, ^{238}U and ^{234}U) (mBq L^{-1}), V is the annual water consumption (L y^{-1}) and CF is the ingested dose conversion factor for public (Sv Bq^{-1}).

Annual doses due to radium and uranium isotopes were calculated for babies in lactation age (< 1 year), for children of the age group (7-12 years) and for adults (> 17 years).

For our calculations, we used the following dose conversion factors for ^{226}Ra, ^{228}Ra, ^{238}U and ^{234}U published by the International Commission on Radiological Protection (ICRP, 1996)[12], they are (4.7 × 10^{-6}, 3.0 × 10^{-5}, 3.4 × 10^{-7} and 3.7 × 10^{-7} Sv Bq^{-1}) for ïnfacts, (8.0 × 10^{-7}, 3.9 × 10^{-6}, 6.8 × 10^{-8} and 7.4 × 10^{-8} Sv Bq^{-1}) for children of 7-12y years and (2.8 ×10^{-7}, 6.9 × 10^{-7}, 4.5 × 10^{-8} and 4.9 × 10^{-8} Sv Bq^{-1}) for adults, respectively. A water consumption of 250, 350 and 730 L y^{-1} was considered respectively for ïnfacts, children and adults [13] for the annual dose calculations.

The calculated annual effective doses for different age groups ïnfacts, children and adults are presented in table 2. It should be noted that the cumulative annual doses from ^{226}Ra, ^{228}Ra, ^{238}U and ^{234}U ranged from 0.031 – 0.306mSv y^{-1} for ïnfacts, 0.013 – 0.060mSv y^{-1} for children and 0.004 – 0.029 mSv y^{-1} for adults.

The percentages of the annual dose delivred by radium and uranium isotopes to the different age groups were estimated and the results are prestend in table 3. It is evident that ^{226}Ra and especially ^{228}Ra are the radionuclides relevant to annual dose calculation. For adults, the annual effective dose from the Ra isotopes is between 80.8 and 99.1% of the sum dose. For children this range is between 92.2 and 99.7%, and for ïnfacts it is between 94.3 and 99.8%.

As seen from figures 3, 4 and 5, the contribution of both uranium isotopes (^{234}U and ^{238}U) is very low for all mineral water samples and age groups due to the relatively low

radiotoxicity compared to radium isotopes. Considering the high radiotoxicity of ^{226}Ra and ^{228}Ra, their presence in water and the associated health risks require a particular attention.

From figure 6, it was observed that the annual effective doses received by ïnfacts were much higher than that received by children and adults, which makes them the most critical population group.

Table 2. Annual effective ingestion doses (μSv y−1) for different age groups due to the intake of naturally occurring radionuclides through bottled mineral waters.

Sample	ïnfacts (< 1 year)					Children (7-12 years)					Adults (> 17 years)				
	^{226}Ra	^{228}Ra	^{238}U	^{234}U	Total dose	^{226}Ra	^{228}Ra	^{238}U	^{234}U	Total dose	^{226}Ra	^{228}Ra	^{238}U	^{234}U	Total dose
MW1	78.7 ±21.2	226.5 33.8±	0.3 0.1±	0.8 0.1±	305.9 ±39.8	18.8 ±5.0	41.2 6.1±	0.1 0.01±	0.1 0.01±	60.2 ±7.9	13.7 3.7±	15.2 2.3±	0.1 0.02±	0.1 0.02±	29.1 ±4.3
MW2	13.5 3.8±	82.5 18.8±	0.7 ±0.1	1.7 0.3±	98.4 ±19.1	3.2 0.9±	15.0 3.4±	0.2 0.02±	0.5 0.07±	18.9 ±3.5	2.3 0.6±	5.5 1.3±	0.3 0.03±	0.6 0.1±	8.8 ±2.5
MW3	23.3 2.4±	60.8 11.3±	1.9 ±0.1	3.1 0.3±	89.1 ±11.5	5.5 0.6±	11.0 2.0±	0.5 0.03±	0.9 0.1±	18.0 ±2.1	4.0 0.4±	4.1 0.7±	0.7 0.05±	1.2 0.1±	10.0 ±1.4
MW4	10.6 1.3±	95.3 14.3±	0.8 ±0.1	1.4 0.1±	108.0 ±14.3	2.5 0.3±	17.3 2.6±	0.2 0.01±	0.4 0.1±	20.5 ±2.6	1.8 0.2±	6.4 0.9±	0.3 0.02±	0.5 0.03±	9.0 ±2.5
MW5	14.1 1.3±	66.0 13.5±	0.4 ±0.1	0.7 0.1±	81.1 ±13.6	3.4 0.3±	12.0 2.5±	0.1 0.02±	0.2 0.1±	15.6 ±2.5	2.4 0.2±	4.4 0.9±	0.2 0.03±	0.2 0.02±	7.3 0.9±
MW6	14.2 3.8±	15.0 6.23±	0.5 ±0.1	1.2 0.2±	30.9 7.3±	3.4 0.8±	2.7 1.5±	0.2 0.01±	0.3 0.1±	6.6 ±1.7	2.5 0.6±	1.0 0.5±	0.2 0.02±	0.4 0.08±	4.1 0.8±

Table 3. Percentage of dose delivred by radium and uranium isotopes to different age groups.

Sample	ïnfacts (< 1 year)		Children (7-12 years)		Adults (> 17 years)	
	%dose from Ra isotopes	%dose from U isotopes	%dose from Ra isotopes	%dose from U isotopes	%dose from Ra isotopes	%dose from U isotopes
MW1	99.8	0.22	99.7	0.3	99.1	0.9
MW2	97.5	2.47	96.4	3.6	89.4	10.6
MW3	94.3	5.68	92.2	7.8	80.8	19.2
MW4	98.0	2.03	97.0	3.0	90.7	9.3
MW5	98.7	1.28	98.2	1.9	94.5	5.5
MW6	94.5	5.47	92.6	7.2	84.5	15.5

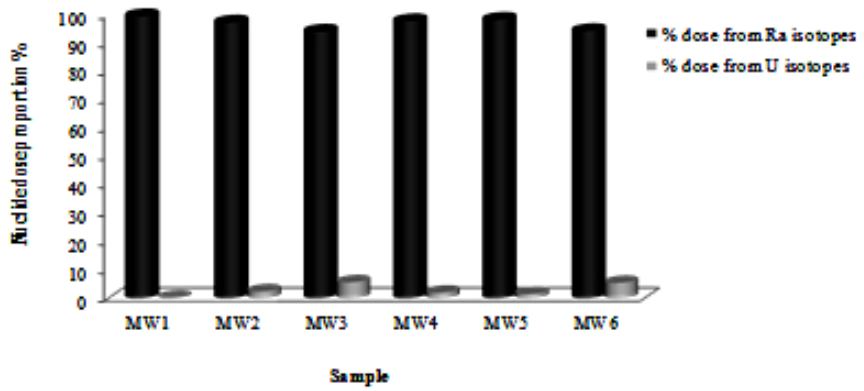

Figure 3. Percentage contribution of Ra and U isotopes to the total annual effective dose for infants (<1 year) due to the intake of bottled mineral waters.

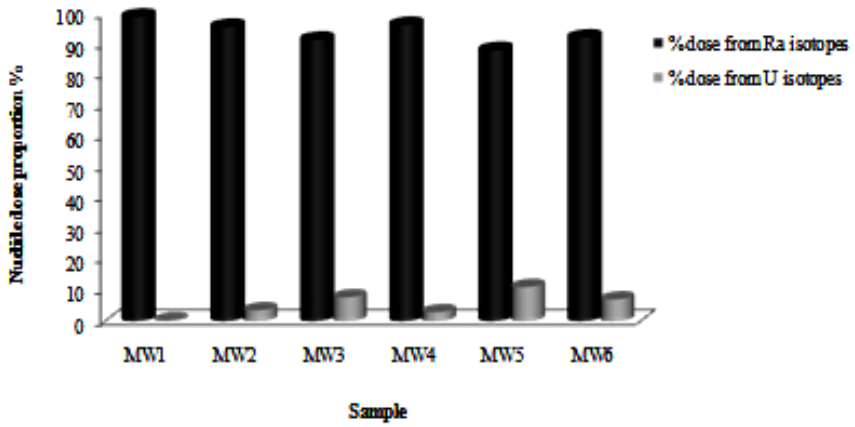

Figure 4. Percentage contribution of Ra and U isotopes to the total annual effective dose for children (7-12 years) due to the intake of bottled mineral waters.

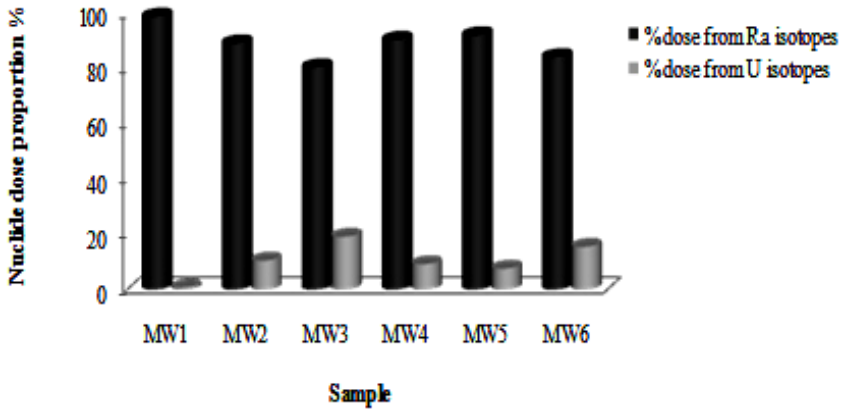

Figure 5. Percentage contribution of Ra and U isotopes to the total annual effective dose for adults (> 17 years) due to the intake of bottled mineral water.

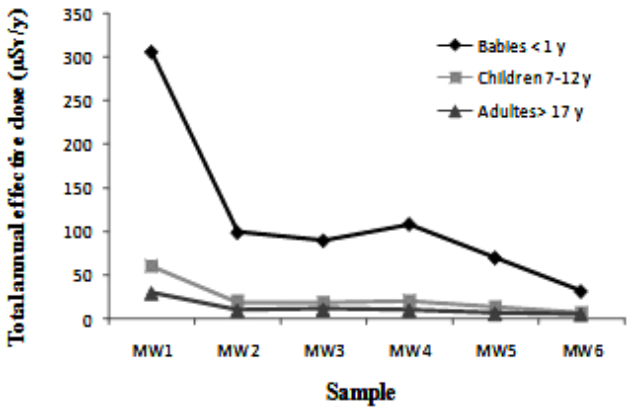

Figure 6. Annual effective dose in bottled mineral water caused by ^{226}Ra + ^{228}Ra + ^{238}U and ^{234}U for different age groups.

Annual dose values for adults and children were all clearly below the indicative dose of 0.1 mSv y^{-1}given by WHO. Annal dose calculations for ïnfacts, however, showed that this level was reached and even exceeded in the case of sample MW1, with a value of 0.306 mSv yr^{-1}. This value represents 13% of the total average annual human exposure from natural sources estimated at 2.4 mSv by the United Nations Scientific Committee on the Effects of Atomic Radiation [14].

However, it shoud be mentioned that for more accurate dose evaluation, the doses from other important a emitters, such as, ^{210}Po and ^{212}Po and b emitters, such as ^{210}Pb and ^{40}K, etc., should also be included.

DISCUSSION

The total alpha and beta-activities should be obviously equal to the sum of activities of alpha and beta-isotopes, respectively. In all cases disparities are observed. In all mineral water samples the measured total alpha activities were higher than the sum of activities of ^{226}Ra, ^{238}U and ^{234}U, and the measured total beta activities were higher than the activity of ^{228}Ra. Apart from the mentioned radionuclides in the analysed waters, this fact can be connected to the other radionuclides such as ^{210}Po, ^{212}Po and ^{40}K which were not determined in the paper, but could occur elsewhere.

The water of sample MW1 is relatively high in beta-activity, probably mainly caused by ^{40}K in the bedrock in this region.

These results observed in the present study were similar to those reported in various other countries, such as, 35-85 and 200-330 mBq L^{-1} in mineral water in northeastern Brazil [15] and 10-126 and 29-884 mBq L^{-1} in drinking waters from Albania [16]. Also, the screening levels for gross α and gross β (<38 mBq L^{-1}) to 92 mBq L^{-1} and (<41 mBq L^{-1}) to 328 mBq L^{-1}, respectively in drinking water samples used in North Guilan province of Iran, were below of these measured in this study[17].

The radium concentration of the investigated mineral waters varies over a wide range. One reason for this can be the geological differences of the aquifers and also the different chemical characteristic of water. However, these values of ^{226}Ra and ^{228}Ra concentrations are well below the recommended WHO guideline activity concentrations of drinking water [18]. According to the data of this study, the radium concentrations in mineral water samples in Tunisia are relatively low compared to some data in the literature. The values of ^{226}Ra and ^{228}Ra in the drinking water of some other countries varied from : 27 to 2431 mBq L^{-1} and 36 to 270 mBq L^{-1} respectively in Turkey[19] ; 52.2 to 235 mBq L^{-1} and 53.7 to 131 mBq L^{-1} in Brazil[20] ; 44 to 420 Bq L^{-1} and 7,4 to 440Bq L^{-1} in the Texas drinking water[21]. Another study conducted in different part of Marmara region in Turkey with 15 bottled mineral water samples reported the ^{226}Ra concentration in mineral waters was found to vary from 0.074 to 0.625 Bq L^{-1} with an average value of 0.267 Bq L^{-1}. The measurements were performed using RAD 7, a solid state alpha detector [22]. But, the levels of radium in the investigated water samples were slightly higher than those reported from Iran, in the drinking water of Zahedan city [23].

It was observed that in most cases, ^{226}Ra concentrations were generally higher than ^{228}Ra concentrations in the mineral water samples indicating that the area is enriched with ^{238}U relative to ^{232}Th. The distributions of ^{226}Ra and ^{228}Ra in water are a function of the Th and U contents in the aquifer, the geochemical properties of the aquifer solids, and the half-lives of each isotope. The thorium is a particularly insoluble element in natural water and is usually found to be associated with solids [24]. Hence, it has no disposition for transition with the water. On the contrary, the uranium element has normal distribution with the water affected by some factors such as temperature and salinity.

The values obtained show that a large amount of ^{226}Ra does not necessarily indicate a high ^{238}U content, since the radium may migrate and be deposited randomly from the surrounding rock areas [25]. This can be related to the fact that the bottled mineral waters are

derived from underground waters where redox conditions often prevail and uranium appear exclusively in the compounds which have low dissolution coefficient. Radium, on the contrary, always appears in second valence and behaves like calcium. It can be then easily leached from the solid matrix.

The concentration of uranium in waters can be affected by several different and independent factors such as the geological composition of reservoirs, rocks, chemical elements in the water and water temperature. Compared with similar studies in other parts of the world, the levels in drinking water were reported to vary from 0.41 mBq L^{-1} to 6.07 mBq L^{-1} and 0.41 mBq L^{-1} to 40.41 mBq L^{-1} for ^{238}U and ^{234}U, respectively in Sarajevo [26]. In 16 drinking water samples from Upper and Lower Silesia Regions in Poland, the concentrations of ^{234}U and ^{238}U ranged from 2.07 to 52.08 mBq L^{-1} and from 2.18 to 43.38 mBq L^{-1} respectively[27]. The results of the activity levels of ^{238}U, ^{234}U in two different groups of drinking bottled water (natural spring and natural mineral) produced in Croatia are in the range of (2.1–14.6) mBq L^{-1} and (4.7–36.5) mBq L^{-1} for ^{238}U and ^{234}U, respectively [28]. All of these reported values in the literature are in very good agreement with the results of our analysis. Yet, these values are considerably lower than those reported from Italy [29] and India [30] and well below the limit values given by European Commission [31] and World Health Organization [13].

Activity ratio in this study range from 1.2 to 2.2. The lack of uranium isotopic equilibrium in waters is a well-known phenomenon and has been ascribed to erosion mechanism of rocks and to the less stable position of ^{234}U in the lattice after recoil following alpha decay [32]. $^{234}U/^{238}U$ activity ratio value larger than 2 indicates a more intensive solid to liquid phase transition than normal and/or transition to liquid phase in slow moving waters, while the value lower than 1 indicates less intensive dissolution or contact with fast moving waters [26].

Investigation of the contribution of particular radionuclides to the assessed total annual effective ingestion doses for three different age groups, showed high variability and mostly reflected the variability of radionuclide activity concentrations in different water sample and variability of dose coefficients among different age groups.

^{226}Ra is a highly radiotoxic isotope with a high dose conversion factor. Its dose contribution is thus higher than from uranium isotopes despite its low activity concentration in all samples. It should be noted that mineral water is extensively used for powder milk preparation; as a consequence, bottled waters may greatly contribute to committed dose for the lowest classes of age.

Estimates of annual effective doses from natural radionuclides were reported in various countries. Different radionuclides were included in the annual dose estimates and a comparison of the results was therefore difficult. However, the results indicated that large variation exists in annual dose estimates. If we compare the results of this study with those reported in different countries, it is clear that they are generally low in term of bottled drinking water in Bangladesh[3] and in Algerian bottled mineral waters[33]. Studies in some sachet drinking water samples produced in Nigeria all gave much larger internal exposures than the UNSCEAR reported world average value of 0.12 mSv y^{-1} and the WHO and ICRP reference limits of 0.1 mSv y^{-1} and 1.0 mSv y^{-1} respectively [34].

CONCLUSION

This study showed that the total a and total b, uranium and radium isotopes concentrations in six of the most popular bottled mineral waters produced in Tunisia are well within the guideline values given by WHO. The natural radioactivity values are comparable with those reported in many other countries in the world for different types of water. The estimated annual ingestion dose rates for people in the age groups < 1 year, 7-12 years and older than 17 years due to the ingestion of radium and uranium isotopes through drinking water are lower than the limit of intake prescribed by

WHO. The annual doses exceed the recommended value of 0.1 mSv y^{-1} in one case for ïnfacts.

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