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Estimation of radiation doses due to groundwater intake at a volcanic island: Tenerife (Canary Islands, Spain)

María López-Pérez [a], Candelaria Martín-Luis [b,*], Antonio Catalán [a,c], Pedro A. Salazar-Carballo [a,c]

[a] Laboratorio de Física Médica y Radioactividad Ambiental, SEGAI, Universidad de La Laguna, Spain
[b] Departamento de Biología Animal, Edafología y Geología, Universidad de La Laguna, Spain
[c] Departamento de Medicina Física y Farmacología, Universidad de La Laguna, Spain

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ABSTRACT

The main source of drinking water in the volcanic island of Tenerife (Canary Islands, Spain) is groundwater (ca. 80%), which is extracted through an extremely dense network of galleries and wells (with a total cumulative length of about 1600 km). This is a singular feature compared to mainland territories, where surface water is the main source of drinking water. In addition, in volcanic contexts, radionuclide concentration activity can increase because of enhanced water-rock reactions due to thermal anomalies and carbon dioxide-enriched groundwater. Natural radioactivity in groundwater from this island was measured on 74 samples from galleries, wells and water channels. Gross alpha, gross beta and gross beta without potassium activity concentrations were in the range of <0.001–1.22 Bq/L, 0.127–3.46 Bq/L and <0.010–1.44 Bq/L, respectively. A complete radiological characterization was determined in 42 groundwater samples in which gross alpha and/or gross beta without potassium activity concentrations exceeded the WHO and Spanish recommendations. Average radionuclide activity concentrations decreased in the order: ^{234}U, ^{238}U, ^{210}Pb, ^{235}U, ^{230}Th, ^{210}Po, ^{232}Th, ^{226}Ra. The contribution of groundwater to the total annual effective dose from all measured radionuclides for each age group was 56 ± 8 μSv/year (1–2 years), 44 ± 6 μSv/year (2–7 years), 35 ± 4 μSv/year (7–12 years), 32 ± 3 μSv/year (12–17 years) and 31 ± 4 μSv/year (>17 years). These values are below the 100 μSv/year reference level of the effective dose recommended by WHO.

1. Introduction

Humans are constantly exposed to radiation from external as well as from internal sources, this last through inhalation and ingestion by food and water consumption (UNSCEAR, 2000). The main contribution to dose is largely due to the presence of naturally occurring radionuclides of both uranium and thorium decay chains, and from ^{40}K, which are omnipresent in the Earth's crust and are leached by surface waters and especially by groundwater. Groundwater usually shows higher contents of natural radionuclides compared to surface water (Baeza, Del Rio, Jimenez, Miro, & Paniagua, 1995; Rožmarić, Rogić, Benedik, & Štrok, 2012). These radionuclides can get into groundwater due to water-rock interactions, where several physical and geochemical processes might affect their concentration, leading to large variability in the same region. Some radionuclides can dissolve in water, depending on the mineralogical and geochemical composition of the soils and rocks, redox and pH conditions and the residence time of groundwater in the aquifer formations (Banks, Røyset, Strand, & Skarphagen, 1995; Vesterbacka, 2007). Subsequently, these radionuclides dissolved in groundwater can enter the food chain through irrigation waters and the water supply systems, originating human internal exposure (Turhan, Özçtak, Taşkn, & Varinlioğ;lu, 2013).

The measurement of radioactivity in drinking water allows the determination of population exposure by the habitual consumption of water. Potential health hazards from natural radionuclides in consuming water have been considered worldwide (Bonotto, Bueno, Tessari, & Silva, 2009) and several international and national standards for limiting radiation exposure establish maximum permissible radionuclides concentration in drinking water (see for instance (CAC, 2001; EPA, 1997; WHO, 2011)).

Natural radioactivity monitoring in drinking water is important due to the cumulative radiation effects on human health and because of the

* Corresponding author.
E-mail address: mcmartin@ull.edu.es (C. Martín-Luis).

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relatively high radiotoxicity of some natural radionuclides, such as ^{210}Po and ^{228}Ra (Harrison, Leggett, Lloyd, Phipps, & Scott, 2007; Leggett & Eckerman, 2001; Mays, Rowland, & Stehney, 1985), which contributions to the dose are more pronounced. Therefore, for accurate dose assessment, it is necessary that specific radionuclides in drinking water are identified, and their activity concentrations measured since the dose coefficients are always related to the specific radionuclides.

In Europe, the natural radioactivity of drinking waters is legislated by the European Council Directives 98/83/EC (EU, 1998) and 2013/51/EURATOM (EU, 2013). These regulations have been adopted by national policies of all member countries, including Spain (Garranzo-Asensio et al., 2016; RD140, 2003). To ease the monitoring tasks of law-enforcement bodies, general screening values are indicated. In Spain, the screening values considered are 0.1 Bq/L for gross alpha activity, 1 Bq/L for gross beta without potassium activity (that is the gross beta activity minus ^{40}K concentration, radon (+progeny) and tritium content), and 0.10 mSv/year for the total annual effective dose (Garranzo-Asensio et al., 2016). Even though the latest WHO guidelines for drinking water quality (WHO, 2011) changed the proposed limiting value for gross alpha activity to 0.5 Bq/L, this modification has not been yet adopted by the Spanish legislation.

The present study was carried out on the Tenerife Island, in the Canarian archipelago. The Canary Islands are a volcanically active archipelago formed by eight main islands and located northwest of the African coast, between 27° 37' - 29° 25′ N latitude and 13° 20' - 18° 10′ W longitude. Due to its volcanic origin, and especially due to the wide compositional range of the eruptive rocks existing at this island (from mafic to felsic volcanic rocks), uranium, thorium and their progeny and potassium as well, can be found in different concentrations. From a radiological point of view, ultra-basic and basic rocks such as basanites, basalts and tephrites, contain low ^{238}U, ^{226}Ra, ^{232}Th, and ^{40}K concentrations. However felsic and intermediate rocks such as trachybasalts, tephriphonolites, trachyandesites, trachytes and phonolites, contain higher concentrations of radioactive elements (Arnedo et al., 2017; López-Pérez et al., 2021).

At the Canary Islands water is scarce, being groundwater the main natural water resource, especially at the western islands (Tenerife, La Palma, La Gomera and El Hierro). Eastern islands (Lanzarote and Fuerteventura) are in the worst situation, depending almost 100% on industrial production of water through desalinization plants. At Tenerife, the largest (2034 km^2) in the Canary Islands, groundwater constitutes about 80% of the total water supply, which is obtained through a dense network of galleries and wells. Differently from other mainland Spanish territories, where water is obtained from surface reservoirs (mainly rivers and lakes), drinking water in Tenerife Island is obtained in a very peculiar way. Due to the scarcity of surface water, galleries (horizontal blind tunnels, several kilometers long and around 2 m diameter) and wells constitute the main water supply. Only at Tenerife island, more than 1000 galleries and more than 400 wells, with a total cumulative length of more than 1600 km, have been drilled for groundwater exploitation (D319, 1996) (Fig. 1).

It should be noted that Tenerife holds a stable population of approximately 920,000 inhabitants and receives, on average, ca. 6 million tourists per year (https://www.webtenerife.com/investigacion/situacion-turistica/indicadores-turisticos/). For this reason, water consumption with different contents of radioactive elements could cause an elevated collective dose.

In addition, residual volcanic manifestations in the form of CO_2 diffuse emissions and thermal anomalies are frequent at the central zone of this island, where the main aquifer (the Cañadas aquifer) is located (Amonte et al., 2021). In this area, dissolved CO_2 and higher temperatures may produce a significant increase of the radionuclide content in groundwater due to their effect in accelerating water-rock interactions (Rihs & Condomines, 2002), especially when groundwater is hosted in felsic and intermediate rocks.

In this work, gross alpha, gross beta, gross beta without potassium, ^{238}U, ^{234}U, ^{235}U, ^{232}Th, ^{230}Th, ^{210}Po, ^{226}Ra, ^{224}Ra, ^{228}Ra and ^{210}Pb activity concentrations in groundwater of Tenerife Island were determined

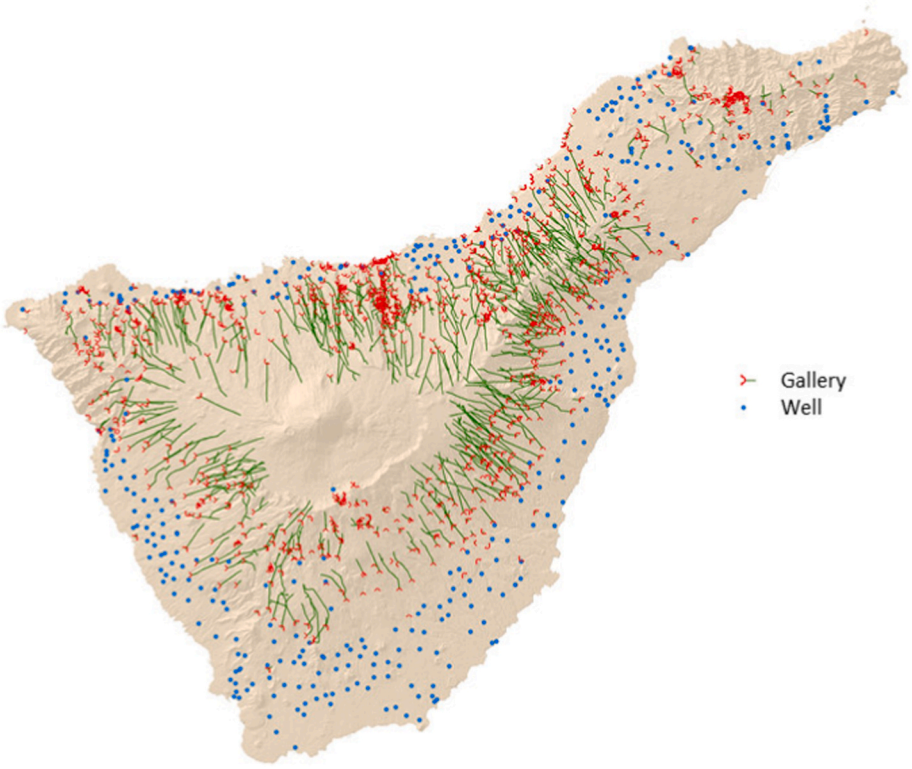

Fig. 1. Location map of galleries (green lines with the red symbol of gallery entrance) and wells (blue dots) at Tenerife Island (modified from https://www.aguastenerife.org/).

to evaluate the radiological hazard associated with their intake. A complete radiological characterization was determined in water samples in which gross alpha and/or gross beta without potassium activity concentrations exceeded the WHO and Spanish recommendations. Finally, the total annual effective doses of different age groups were calculated and compared against the effective dose recommended by WHO.

2. Materials and methods

2.1. Samples collection and preservation

55 water samples were collected at the pithead of 30 galleries and 25 wells, also 19 samples were taken at several water channels of the volcanic Tenerife Island. Fig. 2 shows the location map of sampling sites.

At the time of collection, water temperature, pH and conductivity were determined *in situ*. Each sample was collected in a 5 L plastic container. One aliquot (0.1 L) of water from each site was separated, without changing their pH, for potassium determination. The rest of the samples were acidulated to pH 2 with nitric acid and stored until required (UNE-EN, 2019). To avoid radon and radio-iodine losses during transportation, low-gas-permeability bottles were used. These bottles were filled to the top and sealed to avoid gas diffusion from the water to the air.

2.2. Gross alpha and gross beta activity concentration

Gross alpha and gross beta activity concentrations were determined by evaporation of the water samples at pH 2 in 50 mm diameter stainless steel planchets. The deposited residue was formed as a thin layer of uniform surface density to limit self-absorption phenomena and ensure similarity with the calibration source geometry. The surface density of the deposit was lower than 5 mg/cm^2 on the planchet (ISO 9696, 2017; ISO 9697, 2018; M. Llauradó et al., 2006; M Llauradó et al., 2004). The planchets were measured with a multiple sample gas-flow proportional counter (Berthold LB770) 2 days after preparation (to minimize the contribution of radon daughters). The calibration of each detector was performed by using planchets with an activity of ^{241}Am of 27.2 ± 0.8 Bq (alpha activity) and another planchet of ^{90}Sr/^{90}Y with an activity of 100 ± 2 Bq (beta activity), purchased from Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) Madrid, Spain. Calibration sources with the same standard activity were prepared with the same sample preparation procedure to allow the determination of absorption factors. Self-absorption corrections were applied to the results for the mass density obtained for each sample. The average detection limit of the low background proportional counter was 0.070 Bq/L and 0.060 Bq/L for alpha and beta activity respectively. The efficiency was 25% for alpha and 35% for beta. Due to the low concentration of alpha and beta emitters in the water samples, a counting time of 36,000 s was used for each measurement. Background measurements were carried out each week using similar counting times as for normal

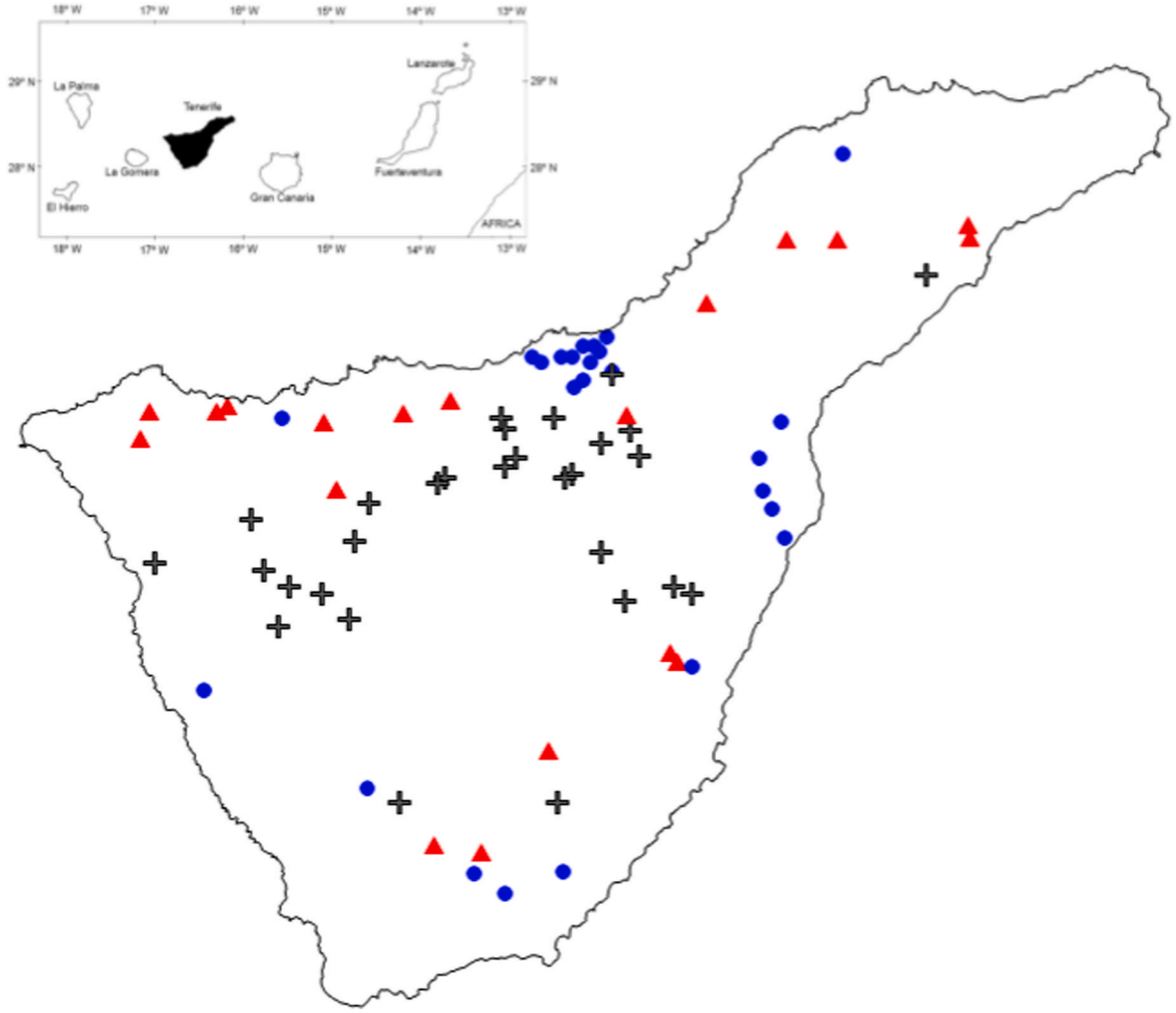

Fig. 2. Study area and sample sites: water channels (triangles), galleries (plus) and wells (circles).

sample measurements. A background subtraction procedure was applied to each of gross alpha and gross beta measurements.

Additional measurements of gross alpha concentration were performed using ZnS (Ag) scintillation detectors (photomultiplier tube and base preamplifier, model 2015A Canberra, USA), with a voltage of 800 V. A planchet containing ^{241}Am with an activity concentration of 27.2 ± 0.8 Bq provided CIEMAT was used to determine the alpha detection efficiency. The blank of each detector was determined by counting an empty planchet for 86,400 s. The efficiency was 38% and Minimum Detectable Activity (MDA) was 0.001 Bq/L.

2.3. ^{40}K determination

The concentrations of potassium (and hence the activities of ^{40}K) in the water samples were determined by Flame Atomic Absorption Mass Spectrometry (2380 PerkinElmer). Small quantities of cesium chloride were added to all samples to avoid interferences during measurement.

The procedure for gross beta activity without potassium contribution is based on the Spanish norm (UNE 73340–2, 2003). Radon progeny corrections were unnecessary since gross beta activity had already been calculated without this contribution.

2.4. Uranium and thorium isotopes determination

The uranium and thorium isotopes were determined by co-precipitation method with $Fe(OH)_3$ (Bolivar, Garcia-Tenorio, & Vaca, 2000; Martínez-Aguirre, 1991). A quantity of ^{232}U and ^{229}Th tracers were added at the beginning of the chemical preparation to the acidified water. The chemical separation of U and Th and isotopes from the original water matrix was performed with ionic exchange resins (Dowex AG1 - X8). Finally, the depositions of the concentrated samples were electrodeposited onto stainless steel plates according to (Hallstadius, 1984). The mean chemical yield resulted in ca. 70% for both radionuclides.

Uranium (^{234}U, ^{235}U, ^{238}U) and thorium isotopes (^{230}Th, ^{232}Th) activity concentrations were determined by alpha spectrometry (Canberra Industries Inc., USA) with Passivated Implanted Planar Silicon (PIPS) semiconductor detectors. Genie 2 k Software was used for acquiring and analyzing the experimental spectra. Both samples and their respective backgrounds were counted for around 4 days. MDA was calculated according to Currie's publication (Currie, 1968) and was 0.001 Bq/L for uranium and thorium isotopes.

2.5. ^{210}Po determination

The activity concentration of ^{210}Po was determined by spontaneous deposition onto stainless steel plates using ^{209}Po as radiotracer (ca. 55 mBq) (Vallés-Murciano, 1994). The polonium was deposited for 3 h at 90 °C under stirring conditions and then washed with distilled water, ethanol and dried at 105 °C overnight.

^{210}Po activity concentration was measured by alpha spectrometry using PIPS (Canberra Industries Inc., USA) detectors with a sensitive area of 300 mm^2 and 20% efficiency. The spectra were analyzed using Genie2k software. The samples and background were counted around 345,600 s. The MDA was between 0.001 and 0.003 Bq/L for ^{210}Po. The mean yield of the measurement was 80%.

2.6. ^{210}Pb determination

^{210}Pb was isolated from the water sample by precipitation of $PbSO_4$ (Vallés-Murciano, 1994). The dry lead fraction residue was dissolved in water acidulated with concentrated H_2SO_4. The precipitate was transferred to a counting planchet, and its daughter radionuclide ^{210}Bi was measured at equilibrium on a low background gas flow proportional counter (Berthold LB770, Germany). The equilibrium conditions were obtained 25 days after the radiochemical separation. The samples were measured during 36,000 s, allowing detection limits lower than 0.015 Bq/L.

The lead chemical yield was calculated by the gravimetric method, obtaining values between 50% and 80%.

2.7. ^{226}Ra and ^{224}Ra determination

The radium isotopes (^{226}Ra and ^{224}Ra) were co-precipitated with barium into $Ba(Ra)SO_4$ form (Suárez González del Rey, González González, & De Pablo SanMartin, 1987; Vallés-Murciano, 1994). Both ^{224}Ra and ^{226}Ra activity concentrations were measured using a multiple sample gas-flow proportional counter (Berthold LB770).

^{226}Ra and ^{224}Ra activity concentrations were measured 2 and 21 days respectively after radium separation. The average MDAs were 0.005 Bq/L for ^{226}Ra and 0.009 Bq/L for ^{224}Ra, for 36,000 s counting time.

To validate the methods, we participate in various inter-laboratory comparisons to measure gross alpha, gross beta, gross beta activity without potassium and radionuclides activity concentration in water samples organized by the International Atomic Energy Agency (IAEA) and the Spanish Nuclear Safety Council (CSN) (Jobbagy, Dupuis, Emteborg, & Hult, 2021). The z-score test was below 2 for all the tested radioactivity parameters, which indicates that the deployed methods provided satisfactory results.

2.8. Estimation of annual effective doses

The contribution of every radionuclide activity concentration to the annual effective dose from water ingestion was estimated according to equation (1) (UNSCEAR, 2000).

$$D_c = A_c \, x \, C_c \, x \, A_{int} \quad (1)$$

where D_c is annual effective ingestion dose (μSv/year); A_c is the geometric mean activity concentration of the radionuclide in groundwater (Bq/L); C_c is the ingestion effective dose conversion factor for radionuclides (μSv/Bq), which varies with the age range of the individuals; and A_{int} is the annual intake of drinking water for different age groups (L/year). The total annual effective ingestion dose *TD* (μSv/year) was calculated by summing the contributions from all radionuclides present in the water samples according to equation (2):

$$TD = \sum D_{c_i} = \sum \left(A_c \, x \, C_c \, x \, A_{int}\right)_i \quad (2)$$

The age-related dose coefficients for ingestion used in the estimations were taken from the EC Directive 96/29/Euratom (EC, 1996). The annual average water intake values for every age group were 274 L for the age class 1–2 years, 365 L for the age classes 2–7, 7–12, 12–17 years and 730 L for the age class >17 years (WHO, 2011).

2.9. Quality control and statistical analysis

All the radiochemical methods of analysis have been validated at two levels of activity concentration (1–10 MDA and 10–100 MDA) with spiked (ISO 17025, 2017; Örnemark, 2014). A validated method ensures the accuracy, precision as well as reproducibility of results. The accuracy of the different methods is less than 10% and precision is smaller than 12% and fits for purposes.

The gross alpha, gross beta and gross beta without potassium measurements are continuously and periodically subjected to double quality control. Such control ensures the quality of the data reported in the present work. Our laboratory (Medical Physics and Environmental Radioactivity Laboratory of La Laguna University (FIMERALL) is accredited according to UNE-EN ISO/IEC 17025:2017 for these measurements in water, which implies rigorous quality control of the entire measurement process, including periodic international inter-laboratory comparisons (proficiency test). In addition, we participate, every year,

in various inter-laboratory comparisons to measure gross alpha, gross beta, gross beta activity without potassium and radionuclides activity concentration in water samples organized by the International Atomic Energy Agency (IAEA) and the Spanish Nuclear Safety Council (CSN) (Jobbagy et al., 2021; Jobbágy, Merešová, & Wätjen, 2014; Sobiech--Matura, Máté, & Altzitzoglou, 2017). The last z-score test, obtained in 2021, was below 1 for all the tested radioactivity parameters, which indicates that the deployed methods provided satisfactory results.

The expanded uncertainties for the radiometric measurements were calculated considering a confidence level of approximately 95% (k = 2) (ISO 98-3, 2008). The expanded uncertainty was approximately 4% for gross alpha activity and 2% for gross beta activity. These uncertainties are the sum of the errors caused by the volume sample, preparation of standard alpha and beta sources and the emission rates occurring on the alpha and beta standards as a result of the applied method used for source preparation. For ^{238}U, ^{234}U, ^{235}U, ^{232}Th, ^{230}Th, ^{210}Po, ^{226}Ra, ^{224}Ra, ^{228}Ra and ^{210}Pb radionuclides the expanded uncertainties were below 10% in all measurements.

3. Results and discussion

3.1. The activity concentrations of gross alpha, gross beta and gross beta without potassium activity

A total of 74 groundwater samples (Fig. 2) were collected and analyzed from water galleries, wells and channels distributed randomly around Tenerife Island (for details see above).

Gross alpha, gross beta and gross beta without potassium activity concentrations presented non-normal distribution as observed in Fig. 3 (box and whisker plot) and Fig. 4 (frequency distribution).

Quantile-quantile plot (Fig. 4) confirmed the right-skewed distribution of the analyzed parameters with a significant number of samples with higher values with respect to the normal distribution. Therefore, sampling sites exhibit noticeable variations in gross alpha, gross beta and gross beta without potassium activities (Fig. 3), which might be due to lithologic variations in the aquifer formations. This is commonly observed in other regions where the spatial variability of the water radiochemistry is attributable to factors such as mineralogical and geochemical variations in the bedrock, the residence time of groundwater in the aquifer and different water-rock interactions (Vesterbacka, 2007; Yuce et al., 2009). According to national legislation (Garranzo-Asensio et al., 2016), different legal limits are recommended for both parameters due to the exposure risk for alpha emitters is higher than that of beta emitters in drinking water.

The 74 water samples presented a geometric mean value for gross alpha activity of 0.111 ± 0.004 Bq/L and a range of gross alpha activity values from 0.004 to 1.22 Bq/L, only two samples reached a value lower than the level of detection. The use of the geometric mean instead the arithmetic mean, as centralization parameter, can be justified due to the log-normal distribution obtained previously. Due to non-normal distribution the use of the arithmetic mean may produce under/over-estimation of the studied parameter. 57% of the samples exceeded the screening level (0.1 Bq/L, see Fig. 3) for gross alpha activity established in the Spanish legislation (14 galleries, 13 wells and 15 water channels), (Garranzo-Asensio et al., 2016). Ten (1 water channel and 9 galleries) of the samples had activities above 0.5 Bq/L (see Fig. 3), the limit value given by the WHO guidelines recommended for drinking-water quality (WHO, 2011).

Geometric mean gross beta and gross beta without potassium activities presented values of 0.699 ± 0.002 and 0.129 ± 0.002 Bq/L respectively. Gross beta activity varied between 0.127 and 3.46 Bq/L and gross beta without potassium activity varied between <0.010 and 1.44 Bq/L, (35 water samples had gross beta without potassium values lower than the MDA). Most of the studied groundwater samples presented gross beta without potassium activity below the screening level of 1 Bq/L (see Fig. 3), with only two water samples from two galleries exceeding this value (Garranzo-Asensio et al., 2016; WHO, 2011).

The spatial distribution of gross alpha, gross beta and gross beta without potassium activity concentrations as well as of potassium concentration in the analyzed water samples is shown in Fig. 5.

In general, higher levels of gross alpha and gross beta activities as well as of potassium concentration are observed in groundwater of the northern part of the island. These waters flow from the Las Cañadas aquifer, located in the central region, an area where the dissolution of volcanic gases, mainly CO_2, originates highly mineralized waters, mainly of alkaline-bicarbonate rich type (Marrero-Díaz, 2010). Part of these waters is transported through water channels to the northeastern municipalities.

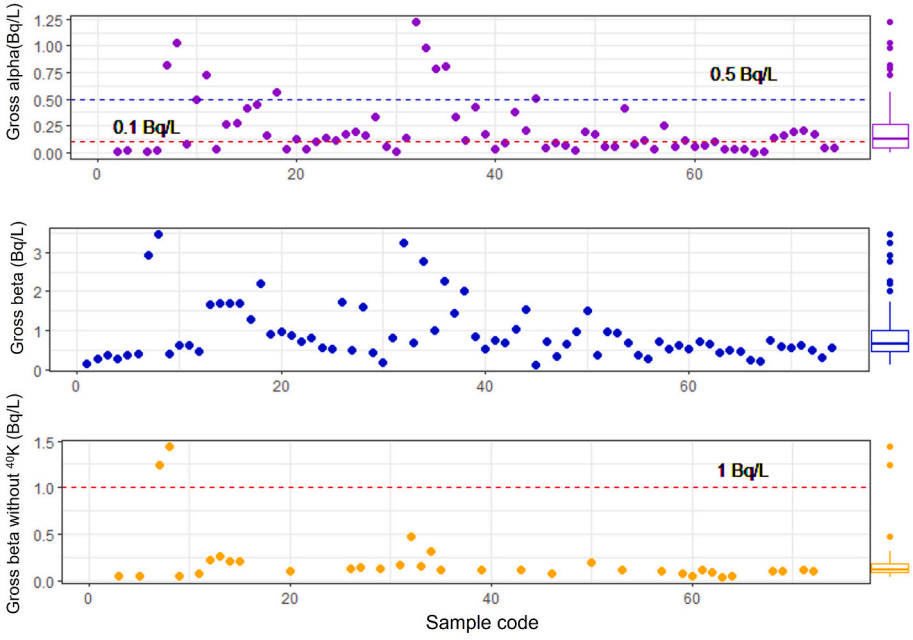

Fig. 3. Gross alpha, gross beta, gross beta without potassium activity concentrations and their respective box-plot diagrams obtained for the analyzed water samples. Dashed lines display the different limits recommended by WHO and Spanish law (WHO, 2011; RD314, 2016).

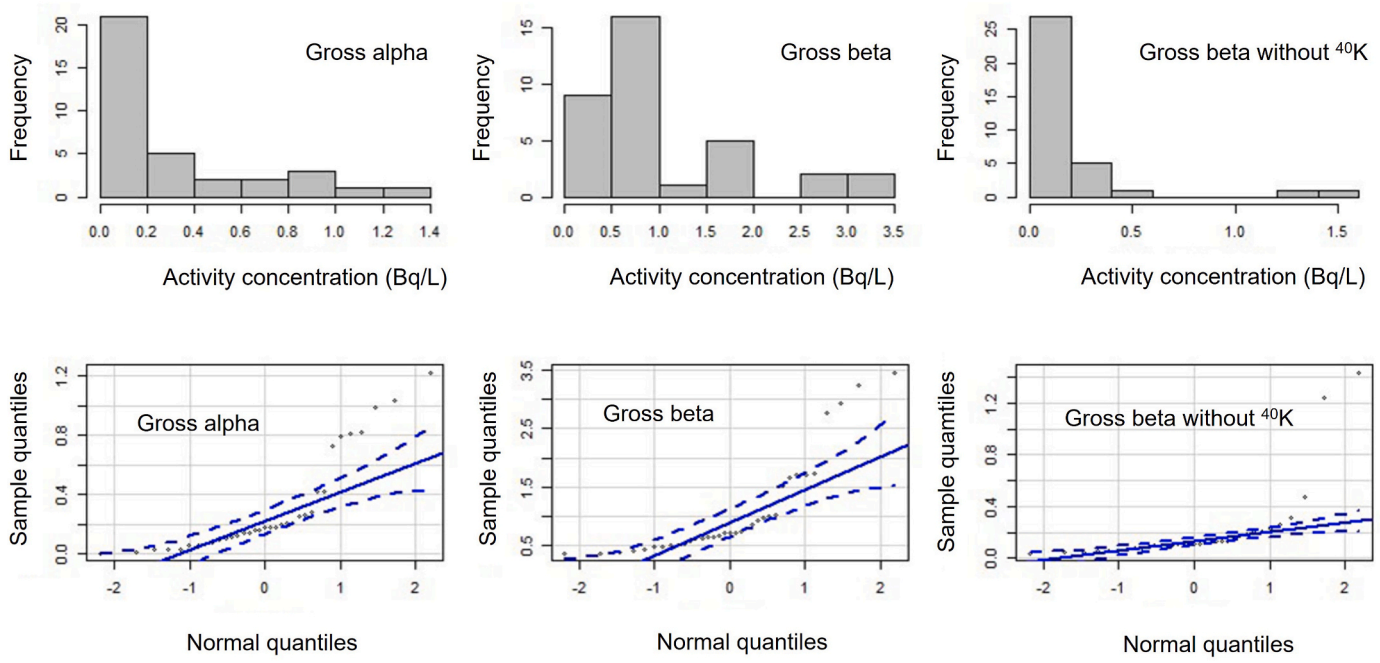

Fig. 4. Frequency distributions and quantile-quantile plots for gross alpha, gross beta and gross beta without potassium activity concentrations obtained for the water samples analyzed in the present work.

The extraordinary good spatial correlation between gross beta activity (Fig. 5b) and potassium concentration (Fig. 5d) maps indicates that most of the gross beta activity in groundwater of Tenerife is due to the ^{40}K content. This is further corroborated by gross beta without potassium activity distribution map Fig. 5c), where most of the sampling points exhibit very low values or even values below the MDA, with only two water samples of two galleries having values higher than 1 Bq/L. At these two points, further radiochemical analysis of beta emitters would be needed for better characterization.

Table 1 presents a comparative study of gross alpha and gross beta activity concentrations obtained in the present work with other mainland Spanish and European territories as well as with other countries around the world. The average and range values obtained for gross alpha and gross beta activity concentrations in the analyzed water samples are in good concordance with the world average mean values (WHO, 2011). Our values are lower than the previous data reported for Saudi Arabia (Almasoud, Ababneh, Alanazi, Khandaker, & Sayyed, 2020) and are similar to those of Nigeria (Bello, Nasiru, Garba, & Adeyemo, 2020) and Turkey (Turhan, Özçtak, Taşkn, & Varinlioğlu, 2013). On the other hand, our results are relatively higher than other studies reported in India (Sarvajayakesavalu et al., 2018), Jordan (Al-Amir, Al-Hamarneh, Al-Abed, & Awadallah, 2012), Brazil (Bonotto et al., 2009), Spain (Pujol & Sánchez-Cabeza, 2000), Italy (Borio et al., 2007) and Serbia (Janković, Todorović, Todorović, & Nikolov, 2012). The differences found against other world regions, with different geological and geochemical properties, can be explained by the different water-rock interactions that occur in our volcanic territory. In this regard, higher activity concentrations at Tenerife can be attributable to the residual volcanic activity existing at the central region of the island, an area where the dissolution of volcanic CO_2 enhances the water-rock interactions in the saturated zone, leading to highly mineralized waters and the increase of radionuclides leaching, especially beta emitters (^{40}K). Considering these results, water management authorities may adopt special corrective actions, such as desalination and/or the mixture of different water sources to reduce the effective dose received by the population, if necessary.

Finally, 42 water samples out of 74 exceeded the limit value for gross alpha (0.1 Bq/L) or gross beta without potassium activity concentrations (1 Bq/L) imposed by the Spanish legislation and therefore additional analysis of radionuclides was required. At these samples, ^{238}U, ^{234}U, ^{235}U, ^{232}Th, ^{230}Th, ^{210}Po, ^{226}Ra, ^{224}Ra, ^{228}Ra and ^{210}Pb activity concentrations were determined to evaluate the radiological hazard associated with their intake (see below).

3.2. Radionuclides concentration

Table 2 and Fig. 6 summarize the results for the radionuclide activity concentrations obtained in this study (only concentrations measured above the MDA are displayed). Fig. 6 shows that the higher radionuclide activity concentrations and data dispersion (interquartile rank) correspond to uranium isotopes, mainly ^{234}U and ^{238}U.The average radionuclide activity concentration in the groundwater samples decreased in this order: $^{234}U > {}^{238}U > {}^{210}Pb > {}^{235}U > {}^{230}Th > {}^{210}Po > {}^{232}Th > {}^{226}Ra$.

The uranium activity concentrations in the groundwater samples were in the range of 0.029–0.865 Bq/L for ^{234}U, < 0.001–0.031 Bq/L for ^{235}U and 0.019–0.812 Bq/L for ^{238}U (see Table 2). ^{235}U was measured above the MDA (0.001 Bq/L) in 17 of the 42 analyzed water samples. The measured ^{234}U and ^{238}U activity concentrations were found to be below the WHO recommended (WHO, 2011) limits of 1 Bq/L and 10 Bq/L, respectively, for drinking water. Uranium-series disequilibria were found, with a ^{234}U/^{238}U ratio ranging from 0.9 to 3.0, with the average value of 1.5 ± 0.6. These values imply that no equilibrium exists between ^{234}U and ^{238}U, which is always in favor of ^{234}U. The lack of uranium isotopic equilibrium in waters is a well-known phenomenon, being ^{234}U recoil, crystal damage and leaching the main mechanisms responsible for the ^{234}U/^{238}U disequilibrium in groundwater (Borio et al., 2007).

Usually, the highest thorium contribution in water is found in the suspended mineral particle fraction due to its low solubility. Our study reveals that 88% of the ^{230}Th activity concentration values were above the MDA, with activity values ranging from 0.003 to 0.076 Bq/L. Interestingly, ^{232}Th only was detected above the MDA (0.001 Bq/L) in 4 groundwater samples, within a range from 0.004 to 0.016 Bq/L. Finally, the ^{230}Th and ^{232}Th activity levels were below the limit value (<1 Bq/L) given by WHO (WHO, 2011).

^{226}Ra activity concentrations above the MDA value were detected in

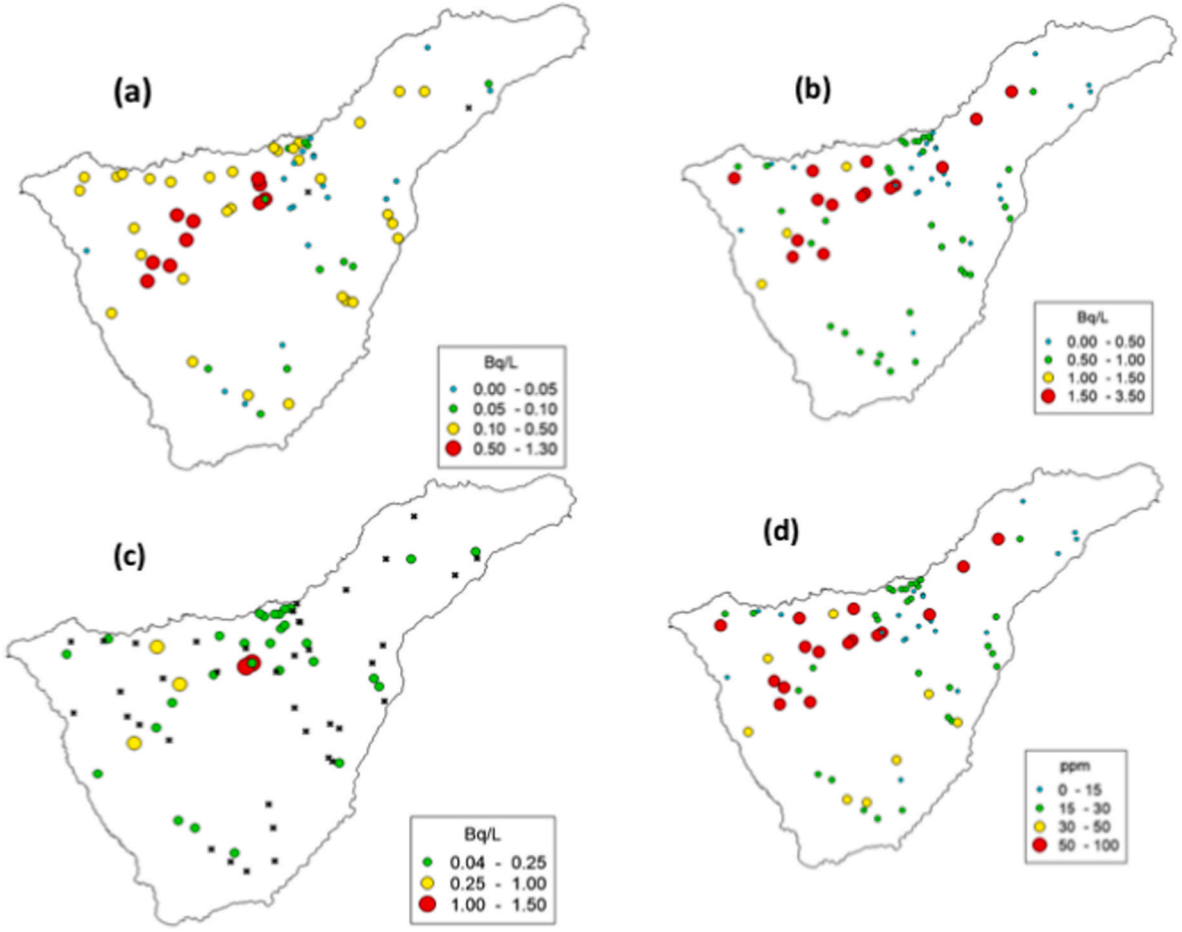

Fig. 5. Distribution of (a) gross alpha, (b) gross beta and (c) gross beta without potassium activity concentrations (Bq/L) and (d) potassium concentration (ppm) in groundwater of Tenerife Island. Black crosses represent values below the MDA. Color codes in a) are related to the screening levels for gross alpha activity established in Spain (0.1 Bq/L; (RD 314:2016) and WHO guidelines (0.5 Bq/L; (WHO, 2011). Red color in c) represents water samples exceeding the screening level of 1 Bq/L for gross beta without potassium activity (RD 314:2016, WHO, 2011).

Table 1
Gross alpha and gross beta activity concentrations in water (Bq/L) comparison with literature data.

Country	Source type	Gross Alpha activity (mean)	Gross Alpha activity (range)	Gross beta activity (mean)	Gross beta activity (range)	Reference
Jordan	Tap water	0.096	<0.050–0.25	0.251	<0.188–0.327	Al-Amir et al. (2012)
Turkey	Groundwater	0.192	0.080–0.380	0.579	0.120–3.470	Turhan et al. (2013)
Saudi Arabia	Groundwater	3.51	0.96–8.97	3.48	1.26–6.63	Almasoud et al. (2020)
Nigeria	Groundwater	0.246	0.028–0.665	0.535	0.153–1.326	Bello et al. (2020)
Brazil	Groundwater	0.009	0.001–0.050	0.26	0.03–0.5	Bonotto et al., 2008
Italy	Drinking water	–	0.008–0.296	–	0.078–0.923	Borio et al. (2007)
Serbia	Tap water	–	0.005–0.008	–	0.056–0.151	Janković et al. (2012)
Spain	Surface	0.095	0.07–0.15	0.213	<0.13–0.30	Pujol et al., 2000
India	Groundwater	0.006	0.001–0.015	0.058	0.015–0.109	Sarvajayakesavalu et al. (2018)
World average	Drinking water	0.5	–	1.0	–	WHO (2011)
Tenerife	Groundwater	0.111	0.004–1.22	0.699	0.127–3.46	This work

7 groundwater samples, representing the 17% of the total analyzed samples, with a geometric mean value of 0.004 ± 0.003 Bq/L and a range of concentration from 0.001 to 0.016 Bq/L, well below the WHO recommended limit value of 1 Bq/L (WHO, 2011). ^{224}Ra activity concentration was always lower than the MDA in all groundwater samples.

15 groundwater samples (36%) presented ^{210}Pb activity concentration values above the MDA, with a geometric mean value of 0.029 ± 0.002 Bq/L and a range of concentration from 0.006 to 0.116 Bq/L. Only one water sample presented a ^{210}Pb concentration level higher than the limit of 0.1 Bq/L given by WHO (WHO, 2011).

The ^{210}Po activity concentrations were relatively low, ranging from 0.001 to 0.022 Bq/L. Although this range of concentration is similar to the obtained for ^{234}U and ^{238}U radionuclides, its extreme radiotoxicity may cause significant health risk to the population. Only two samples out of the 42 had ^{210}Po activity concentration lower than the MDA, being all the remainder ^{210}Po concentration values lower than the WHO

Table 2
Activity concentration (geometric mean, maximum and minimum) of natural radionuclides measured in groundwater samples from Tenerife Island (in Bq/L).

Radionuclide	%[a]	Geometric Mean[b]	Minimum	Maximum
^{234}U	100	0.135 ± 0.002	0.029	0.865
^{235}U	40	0.008 ± 0.002	0.003	0.031
^{238}U	100	0.093 ± 0.002	0.019	0.812
^{230}Th	88	0.007 ± 0.002	0.003	0.076
^{232}Th	10	0.006 ± 0.002	0.004	0.016
^{226}Ra	17	0.004 ± 0.003	0.001	0.016
^{210}Pb	36	0.029 ± 0.002	0.006	0.116
^{210}Po	95	0.007 ± 0.002	0.001	0.022

Geometric mean values are shown together with the geometric standard deviation.
Each activity concentration value was affected by expanded uncertainties of 10% respectively.
[a] % of water samples with concentrations above the MDA of the total 42 analyzed samples.
[b] Water samples with activity concentration below the MDA have not been considered.

drinking water standard limit of 0.1 Bq/L (WHO, 2011).

3.3. Annual effective dose

The geometric mean activity concentrations of ^{234}U, ^{238}U, ^{210}Pb, ^{235}U, ^{230}Th, ^{210}Po, ^{232}Th and ^{226}Ra in groundwater samples were used to estimate the annual effective doses (Table 3). In this regard, it is important to emphasize that groundwater is the main source of daily water consumption in Tenerife Island, being of vital importance to the knowledge of the total annual effective ingestion doses due to the groundwater. Contributions of each radionuclide to the total dose for 5 critical age groups of the population, that is, infants (1–2 years), younger children (2–7 years), older children (7–12 years), teenagers (12–17 years) and adults (>17 years), were calculated using Eq. (1) and Eq. (2) as described above (see section 2.8).

Table 3 and Fig. 7 show the contributions from each analyzed radionuclide to the total effective ingestion dose for different age groups. ^{210}Pb represents ca. 50% of the total annual doses for all age groups. ^{210}Po contribution was ca. 30 and 25% of the total contribution for infants (1–2 years) and younger children (2–7 years) respectively, decreasing in the other age ranges.

Interestingly, both ^{210}Po and ^{210}Pb radionuclides are at very low concentrations in the groundwater samples, as observed in Fig. 6. The reason for this high contribution to the total doses is due to their high radiotoxicity and hence, their high dose conversion factors. Therefore, their dose contributions are higher than those from uranium isotopes (^{234}U and ^{238}U), which presented higher activity concentrations, but posse very low radiotoxicity, compared to ^{210}Po and ^{210}Pb radionuclides. Finally, the contribution of ^{226}Ra, ^{230}Th and ^{232}Th only represented a small percent (ca. 5–10%) for all the age ranges studied.

The contribution of groundwater to the total annual effective dose from all the analyzed radionuclides was 56 ± 8 μSv/year (1–2 years), 44 ± 6 μSv/year (2–7 years), 35 ± 4 μSv/year (7–12 years), 32 ± 3 μSv/year (12–17 years) and 31 ± 4 μSv/year (>17 years) for each age group. Based on these data, the highest doses were obtained for infants from 1 to 2 years old, which makes them the most critical population group. However, these results indicate that the annual effective doses for our age groups are below the reference level of 0.1 mSv/year recommended by WHO (WHO, 2011).

4. Conclusions

In this work, a complete radiological characterization of the groundwater of Tenerife Island has been performed for the first time. Besides, up to our knowledge, our dose data are the first reported for groundwater consumption obtained in a volcanic context.

Table 3
Total effective ingestion doses (μSv/year) from individual radionuclides due to groundwater consumption for different age groups (data calculated using the geometric mean value of each radionuclide activity concentration for calculations).

Radionuclide	1–2 years	2–7 years	7–12 years	12–17 years	>17 years
^{234}U	4.8 ± 0.1	4.3 ± 0.1	3.6 ± 0.1	3.6 ± 0.1	4.8 ± 0.1
^{235}U	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.1
^{238}U	3.1 ± 0.1	2.7 ± 0.1	2.3 ± 0.1	2.3 ± 0.1	3.1 ± 0.1
^{230}Th	0.8 ± 0.2	0.8 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	1.1 ± 0.3
^{232}Th	0.7 ± 0.2	0.8 ± 0.3	0.6 ± 0.2	0.5 ± 0.2	1.0 ± 0.3
^{226}Ra	0.7 ± 0.5	0.5 ± 0.4	0.4 ± 0.3	0.3 ± 0.2	0.2 ± 0.1
^{210}Pb	29 ± 2	23 ± 2	20 ± 1	20 ± 1	15 ± 1
^{210}Po	17 ± 5	11 ± 3	7 ± 2	4 ± 1	6 ± 2

Geometric mean values are shown together with the geometric standard deviation.

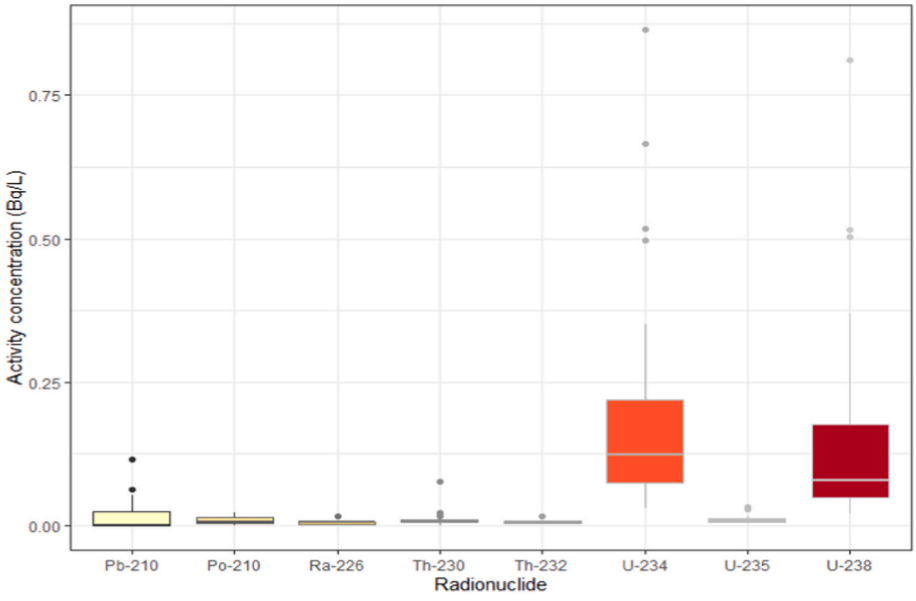

Fig. 6. Box-and-whisker plots of radionuclide activity concentration in groundwater samples.

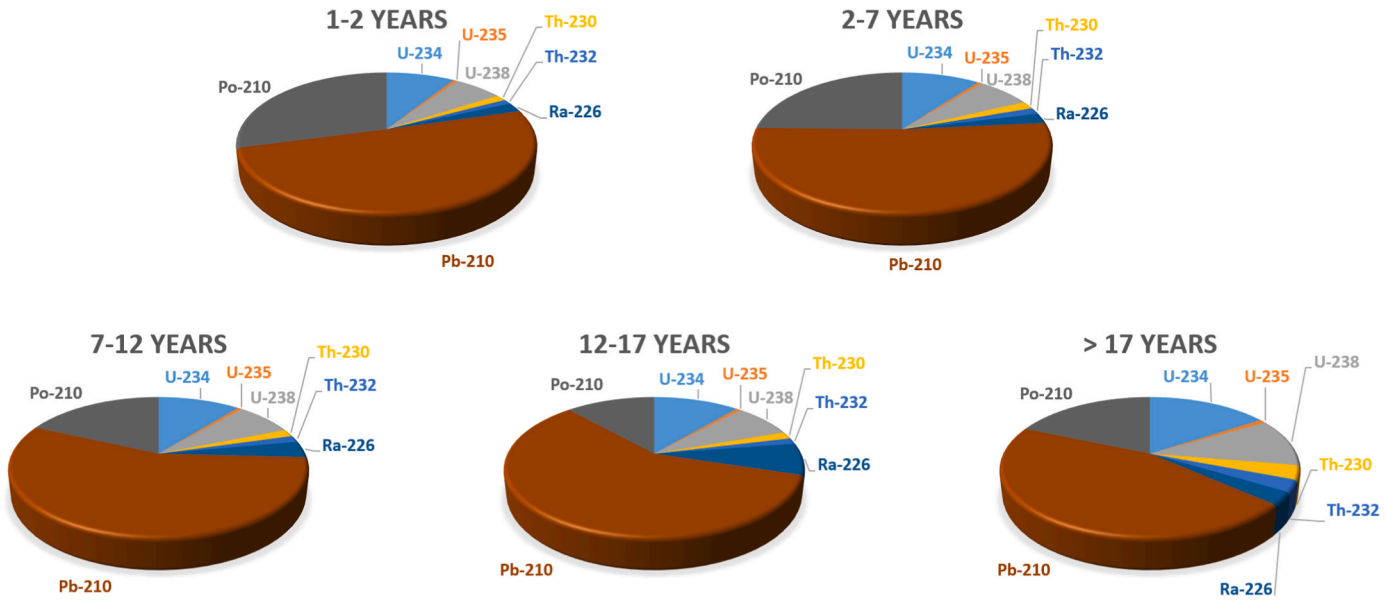

Fig. 7. Contribution of each measured radionuclide to the total annual effective doses for different age groups.

The present study determined the radioactivity concentrations in 74 groundwater samples collected from galleries, wells and water channels distributed in Tenerife Island. 57% of the samples exceeded the screening level of 0.1 Bq/L established in the Spanish legislation for gross alpha activity concentration (Garranzo-Asensio et al., 2016). The activity concentration recommended by the WHO guidelines for drinking water was exceeding 10 cases for gross alpha activity (0.5 Bq/L) and in 2 cases for the gross beta without potassium activity (1 Bq/L) (WHO, 2011).

A complete radiological characterization of 42 groundwater samples was performed. The results showed that the highest activity concentrations in groundwater are due to uranium isotopes. In general, the activity concentrations of the measured radionuclides were decreasing in this order: $^{234}U > ^{238}U > ^{210}Pb > ^{235}U > ^{230}Th > ^{210}Po > ^{232}Th > ^{226}Ra$. Only one sample presented ^{210}Pb activity concentration higher than 0.1 Bq/L, the reference level recommended by WHO (WHO, 2011).

Based on the geometric mean value of the activity concentration of each radionuclide, the total annual effective ingestion doses for five different age groups and the contribution of each radionuclide to the assessed doses were calculated. The highest doses were obtained for babies from 1 to 2 years old, however, all values for all population groups were well below the reference level of the effective dose due to water consumption (0.1 mSv/year) recommended by WHO (WHO, 2011). The highest effective dose from water ingestion for all age groups was caused by ^{210}Pb, constituting ca. 50% of the total effective dose. Therefore, natural radioactivity in the groundwater of Tenerife does not represent a substantial increment to the radiological risk of the population of this island due to natural sources. However, in surveillance and assessment programs, corrective measures are recommended in case of groundwater coming from the central volcanically active area is supplied, in order to reduce even more the dose received by the population and according to the ALARA (*as low as reasonably achievable*) recommendation.

CRediT authorship contribution statement

María López-Pérez: Investigation, Methodology, Formal analysis, Writing – original draft, Supervision. **Candelaria Martín-Luis:** Investigation, Methodology, Formal analysis, Writing – original draft. **Antonio Catalán:** Methodology, Investigation, Formal analysis, Writing – original draft. **Pedro A. Salazar-Carballo:** Investigation, Methodology, Formal analysis, Writing – original draft, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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