ROLE OF LITHOLOGY IN THE PRESENCE OF NATURAL RADIOACTIVITY IN DRINKING WATER SAMPLES FROM TARRAGONA PROVINCE

Joana Martínez Ratia, Alejandra Peñalver Hernando, Carme Aguilar*, Francesc Borrull Ballarín

Departament de Química Analítica i Química Orgànica

Universitat Rovira i Virgili
Unitat de Radioquímica Ambiental i Sanitaria (URAIS)
Consorci d'Aigües de Tarragona (CAT)
Carretera Nacional 340, Km. 1094
43895 L'Ampolla, Tarragona, Spain

*Corresponding author: carme.aguilar@urv.cat

Abstract

One hundred and ninety-six drinking water samples from the different regions of Tarragona province (Catalonia, Spain) were analysed to determine the gross alpha and beta activity. Individual alpha emitting isotope activities were also determined to evaluate a possible relationship between their radiological content and the lithological and hydrogeological formations present in the studied area. The results obtained showed that approximately 23 % of the analysed samples, mainly from five of the evaluated regions, had a gross alpha index exceeding the parametric value of 0.1 Bq/L for waters intended for human consumption according to the current legislation. This could be related to the presence of natural radionuclides in these water samples. The differences between the radiological content in these samples could be related to the different lithological conditions of the areas included in this study. High activity levels of ^{234}U, ^{238}U, ^{224}Ra, ^{226}Ra and ^{228}Ra were detected in specific samples, mainly from granitic and carbonate areas. This research also focuses on evaluating the radiological risk associated with water ingestion. In this regard, consuming 95.5 % of the drinking water samples analysed would not imply a health risk to the population as the annual effective doses calculated were below 0.1 mSv/year. There was only one sample that exceeded this level with a value of 0.33 mSv/year. ^{226}Ra activity concentration was the radionuclide that mainly contributed to this dose.

Keywords: uranium isotopes; radium isotopes; gross alpha index; drinking water; lithology; annual effective dose

Introduction

Water intended for human consumption can be obtained from different sources. For example, in 2018 approximately 90.2 % of the Spanish water collected for drinking water had an underground origin while the rest corresponded to surface and rain water (Palau Miguel et al. 2020). Specifically, in Catalonia, the drinking water supply is a council competence. A total of 66 % of the supplying companies provide drinking water to consumers from their own sources, such as rivers, water reservoirs, mines or wells; 13 % buy drinking water from other wholesale water network organizations; while the rest, which comes to 21 %, provide drinking water from their own sources and also buy it from wholesale water network organizations (Agència Catalana de l'Aigua 2019). In particular, and as an example, the drinking water supplied in Tarragona province has three main origins. First, it comes from the Ebre River. In this case, some councils use this surface water as one of their own sources and treat it in drinking water treatment plants (DWTPs) before its consumption. Other councils that do not have their own sources buy drinking water from a wholesale water network organization which treats Ebre River surface water in a DWTP located in l'Ampolla. This installation takes water from the Ebre River and treats it. In 2019 it supplied a volume of 73.8 Hm^3 of drinking water to 63 municipalities and 26 industries located in Tarragona province. Some councils supply drinking water that is a mixture of potable water obtained from the mentioned DWTP and water from their own resources. Finally, other councils provide drinking water to the population from their own resources only, mainly groundwater such as mines or wells.

Surface water and groundwater may contain radioactive elements which can have a natural or anthropogenic origin. The presence of natural radionuclides in these waters could be due to the lithological properties of the rocks. Moreover, the activity level of radionuclides in water could be driven by different physical and chemical factors, such as the degree of interaction of the bedrock and the flowing water, the typology of rocks that compose the bedrock, the temperature, the Eh and the pH, among others (Dinh Chau et al. 2011; Fonollosa et al. 2016; Guerrero et al. 2016; Pérez-Moreno et al. 2020). For example, felsic rocks like granite contain high activity concentrations of U and Th, whereas the values are generally lower in sedimentary areas in which silico-clastic and carbonate deposits predominate (Sherif and Sturchio 2018; Guagliardi et al. 2020). Therefore, the activity concentration of naturally occurring radionuclides in water can differ widely depending on several parameters. There are several studies in the literature in which these differences in the natural radionuclide activity concentrations in water are related to the lithological or geochemical composition of the bedrocks in contact with the water (Yuce et al. 2009; Alonso et al. 2015; Kamenova-Totzeva et al. 2018; Moreno et al. 2018; Pérez-Moreno et al. 2020). For example, Yuce et al. (2009) reported a strong relationship between the radioactivity enrichment, in terms of U and Th, of the studied waters from aquifers in areas consisting of volcanic, granite, phonolite and pegmatite rocks in a region of Turkey. Kleinschmidt et al. (2011) who assessed the risk of exposure to naturally occurring radioactivity associated with Australian groundwater observed high activity concentrations of radium in samples from basic volcanic aquifers. Due to the presence of uranium and ^{226}Ra in granitic terrains, among other factors, previous studies in literature have observed that radon activity tends to be higher in groundwater that is in contact with these kinds of metamorphic rocks (Singaraja et al. 2016; Przylibski et al. 2020).

In general, surface and groundwater supplied to consumers is treated in DWTPs. The degree of removal of possible radionuclides present in these waters is mainly dependant on the water treatments performed in these water facilities (Nieto et al. 2013; Fonollosa et al. 2015a; Peñalver et al. 2020). Fonollosa *et al.* (2015a) pointed out in their review article that the most effective removal capacity procedures are those based on commercial ion exchange filters and membrane technologies.

The Spanish Royal Decree 314/2016 (2016), which incorporates the requirements of the Council Directive 2013/51/EURATOM (European Commission 2013), sets the requirements about the radioactive substances that can be present in drinking water and which are applicable for protecting the health of the population. Gross alpha and gross beta are the screening parameters used to evaluate the presence of radioactive substances in this type of water. It is considered that the indicative dose (the committed effective dose for one year of intake resulting from all the radionuclides that are present in the drinking water was detected) is lower than 0.1 mSv/year if both screening parameters are lower than or equal to 0.1 Bq/L and 1 Bq/L, respectively. However, if these parametric values are surpassed it is necessary to perform an additional analysis considering, firstly, natural radionuclides such as ^{210}Pb, ^{210}Po, $^{226, 228}$Ra and $^{234, 238}$U.

In view of this and to contribute to broadening the data on the natural radionuclides present in drinking water, the present study aims to determine gross alpha, gross beta and individual natural radionuclide activities in waters for human consumption from different regions of the Tarragona province to establish possible relationships with the lithological formations of each location. Finally, the possible radiological risks of consuming drinking water are determined by calculating the total annual effective dose to which the population (infants, children and adults) may be exposed.

Materials and methods

Study Area

Tarragona province is in eastern Spain, in the south of Catalonia. As Fig. 1 shows, it is divided into different regions, covers an area of 6308.2 km^2 and has a population of over 804664 inhabitants (2019) (Institut d'Estadística de Catalunya 2020). From a lithological point of view, this region belongs to one of the largest Spanish geological areas where lime soil predominates (Soto et al. 1995). Specifically, Tarragona province is composed by a large variety of rocks differentiated by their geological origin and characterized by the presence of sedimentary rocks like conglomerate, sandstone, slate, limestone, evaporites and gravel, sand and silt (Fig. 1). Moreover, there is also igneous rocks (granitoids) in certain areas, such as the Baix Camp, Conca de Barberà and Priorat regions, as can be observed in the Fig. 1 (Institut Cartogràfic i Geològic de Catalunya 2020). In the hydrogeological context, Tarragona province is formed by different formations mainly differentiated according to their lithological characteristics and a chronological criterion. These formations can be classified into three main categories: a) gravels, quaternary sand and silts, b) limestones and massive dolomites, and c) mixed formations in Neogene depressions (Institut Cartogràfic i Geològic de Catalunya 2017).

Sample Collection

One hundred and ninety-six drinking water samples devoted to human consumption were collected at different points from different regions of the Tarragona province, in particular in the Alt Camp, Baix Camp, Baix Ebre, Baix Penedès, Conca de Barberà, Priorat, Ribera d'Ebre, Tarragonès and Terra Alta regions (Fig. 1) during the campaign carried out from November 2017 to February 2020. As explained in the Introduction, the drinking water supplied to the population of Tarragona province can have different origins: a) from the potabilization of the Ebre River water, which takes place in the DWTP of l'Ampolla, b) from own sources, mainly groundwater, and c) from a mixture of the potable water obtained from the Ebre River water and own sources. The different analysed samples comprised waters from these three different origins.

All the water samples were gathered and preserved in 10-litre polyethylene bottles. In the case of ^{222}Rn determination, water samples were taken in glass bottles with a tetrafluoroethylene cap following a specific procedure for avoiding the presence of air bubbles in the container and preventing radon leakages. Samples were cooled to 4-6ºC when they were transported to the laboratory.

Radiochemical methods and measurement techniques

The electrical conductivity (EC) and the pH of the selected samples were measured using a portable conductometer Cond70+ (XS Instruments, Italy) and a pH electrode (CRISON, Spain), respectively.

The internal procedures used to determine the gross alpha and gross beta activity concentrations were based on the procedures described in UNE-EN ISO 10704:2019 (2019). These consist in reducing a given sample volume, previously acidified to pH 2 with HNO_3 65%, through evaporation. Then the sample is transferred to a stainless steel planchet and dried with an infrared lamp. The volume taken depends on the solid residue of the final sample. In this case, it was stablished in 20 mL for gross alpha and 200 mL for gross beta activity determination. These values ensure that a mass density of the residue of 5 mg/cm^2 and 25 mg/cm^2 is obtained, respectively. The planchets with the evaporated samples were stored in a desiccator and, after two days, they were measured in the ZnS (Ag) counter for gross alpha activity (photo multiplier tube and base preamplifier, model 2000 Canberra, USA) and in a gas flow proportional counter (Model LB 770 Berthold Technologies, Germany) for gross beta activity. The minimum detectable activities (MDA) were 0.025 Bq/L and 0.04 Bq/L, respectively.

Gross beta activity without ^{40}K was calculated by subtracting the contribution of ^{40}K from the gross beta activity. For this purpose, we determined the concentration of total potassium by using a flame photometer (Jenway, PFP7 model, UK).

The ^{210}Po method used was based on a co-precipitation of polonium in hydroxide form with $FeCl_3 \cdot 6\, H_2O$ followed by an auto-deposition onto silver disks at 85ºC for 3 hours, as described in a previous study by Fonollosa *et al.* (2015b). The activity was measured with alpha spectrometry (EG&G ORTEC, 676 Model, USA), which includes an ion-implanted silicon detector (ORTEC, size: 450 mm^2; alpha resolution: 25 keV FWHM at 5.48 MeV of ^{241}Am) in a vacuum chamber (Edwards, Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier and a multichannel pulse height analyser. The MDA was 0.018 Bq/L.

^{224}Ra and ^{226}Ra were determined using the method described previously by Palomo *et al*. (2007), which is based on the co-precipitation of radium with barium by using $BaCl_2$ and H_2SO_4. After some clean-up steps and pH adjustment, the radium/barium precipitates were deposited onto a planchet and measured in the ZnS (Ag) counter. The MDA values were 0.001 Bq/L for ^{224}Ra and 0.002 Bq/L for ^{226}Ra. The ^{228}Ra isotope activity was determined through its daughter, ^{228}Ac, by gamma spectrometry. For this, 4 L of water sample were evaporated, and the dry residue obtained was then measured for approximately 600000 seconds in a high-resolution germanium detector (HPGe) (Model 2020 Canberra Industries from Meriden, USA) equipped with a standard multichannel analyser. The MDA for this radium radionuclide was 0.020 Bq/L.

The uranium isotopes, ^{234}U, ^{235}U and ^{238}U were determined following the method described by Mola *et al*. (2013), which consisted in a radiochemical process involving uranium isotope precipitation followed by its separation/purification via UTEVA resin (Triskem, France). Then, the uranium present in the solution was electrodeposited for 2 hours onto a stainless-steel disk under a current density of 1.5 A/cm^2. Finally, it was measured with alpha spectrometry. The MDA was 0.001 Bq/L for both uranium radionuclides.

Lastly, ^{222}Rn was analysed in the water samples that had a groundwater origin. We followed the method described by Fonollosa *et al*. (2016), which is based on ISO 13164-4:2015(E) (2015), and consists in taking 10 mL of sample in a Teflon-coated PE vial that is then filled up with Ultima Gold F scintillation cocktail to avoid the presence of air bubble. Samples were measured during 30 minutes by liquid scintillation counting. The MDA for radon was 1 Bq/L.

To guarantee the quality of the results obtained by the different analytical methods, our laboratory regularly participates in different proficiency tests involving water samples. For example, the test organized by the Spanish Nuclear Safety Commission focused on determining natural and artificial radionuclides (CSN) in marine and surface water, and the test organized by the Finnish Environment Institute focused on analysing radon in underground water (SYKE), both in 2019. All the results obtained indicated that the procedures applied were robust and satisfactory for the intended purpose.

Radiation Dose Estimation

The indicative dose (ID) was calculated for all the analysed water samples following the equation introduced in the Spanish Royal Decree 314/2016 (2016), which is based on the criteria of considering an annual water ingestion of 730 L per adult.

$$ID = \sum_{i=1}^{n} \frac{C_i(obs)}{C_i(der)} \leq 1$$

C_i (obs) is the observed concentration of a radionuclide (i) obtained from the analysed drinking water samples, C_i (der) is the derived concentration of a radionuclide (i) defined in RD314/2016 (2016) and n is the number of radionuclides detected. The ^{226}Ra, ^{228}Ra, ^{234}U and ^{238}U derived concentrations used in the present study are 0.5, 0.2, 2.8 and 3 Bq/L, respectively.

When the previous formula was fulfilled, it was assumed that the indicative dose was less than the parametric value, 0.1 mSv/year, and no further additional radiological studies were required. However, for those samples that exceeded 1 it was necessary to calculate the total annual committed effective dose (AED_W) in mSv/year. In this case, AED_W was calculated for infants (1 year), children (10 years) and adults according to the following equation:

$$AED_W = \sum_{i=1}^{n} A_{W_i} \times I_W \times IF_{W_i}$$

A_{Wi} is the measured activity of radionuclide i (Bq/L), I_W is the estimated water consumption for a human in one year, which is 150 L for infants, 350 L for children and 730 L for adults, defined in RD 314/2016 (2016), and IF_{Wi} is the ingestion effective dose coefficient factor for infants, children and adults of radionuclide i (Sv/Bq). The ingestion effective dose coefficient factors are $6.6\cdot10^{-7}$, $2.6\cdot10^{-7}$ and $6.5\cdot10^{-8}$ for ^{224}Ra, $9.6\cdot10^{-7}$, $8\cdot10^{-7}$ and $2.8\cdot10^{-7}$ for ^{226}Ra, $5.7\cdot10^{-6}$, $3.9\cdot10^{-6}$ and $6.9\cdot10^{-7}$ for ^{228}Ra, $1.3\cdot10^{-7}$, $7.4\cdot10^{-8}$ and $4.9\cdot10^{-8}$ for ^{234}U and $1.2\cdot10^{-7}$, $6.8\cdot10^{-8}$ and $4.5\cdot10^{-8}$ Sv/Bq for ^{238}U, for infants, children and adults, respectively, defined in RD 783/2001 (2001).

Results and discussion

As stated in the Introduction, Tarragona province has complex and variable lithological characteristics throughout its surface area. This could influence the composition of the water consumed in this province, which has different origins, in terms of natural radioactivity. Therefore, it is of high interest to focus on this area, which has never previously been studied, to evaluate the radiological content of different drinking water samples and correlate this with the lithology of the area.

In this section, determining gross alpha and gross beta activity values of drinking water from the Alt Camp, Baix Camp, Baix Ebre, Baix Penedès, Conca de Barberà, Priorat, Ribera d'Ebre, Tarragonès and Terra Alta regions is used as a preliminary screening strategy to evaluate the possible presence of natural radioactivity in the samples. Then, those samples exceeding the gross alpha parametrical value were studied further to establish a relationship between the results obtained and the lithological origin of the analysed samples and to evaluate the possible risk for the population associated with consuming these waters.

Gross alpha and gross beta activity concentrations

Before determining the gross alpha and gross beta activity concentrations in the water samples, the EC was determined to establish approximately the optimal sample volume to be taken for the radioactivity determinations (Llauradó et al. 2004; Corbacho et al. 2014). The EC as well as the pH were very variable among the different samples probably due to the diversity of lithological formations present in the evaluated area, as some authors have pointed out (Guerrero et al. 2016; Pérez-Moreno et al. 2020). pH values ranged from 7.02 to 9.01, with an average of 7.95, revealing the neutral to alkaline character of the analysed water samples. All these values were within the parametric values for pH in drinking water (6.5 and 9.5) recommended in the Spanish Royal Decree 140/2003 (2003), which establishes the sanitary criteria for the quality of water for human consumption. The EC values ranged between 411 and 2064 µS/cm, with a mean value of 941 µS/cm, and are lower than the parametrical value 2500 µS/cm at 20º C (RD 140/2003 2003).

Gross alpha activity concentration values for all the analysed water samples ranged from 0.03 ± 0.03 Bq/L to 2.88 ± 0.32 Bq/L. Fig. 2 shows the percentage of samples for each region with a gross alpha value lower than 0.1 Bq/L, which is the parametrical value of current legislation (RD 314/2016 2016). It can be concluded that 77 % of the drinking water samples analysed have gross alpha activities below that values. It can be observed that the areas which show a higher percentage of samples with gross alpha activity values exceeding 0.1 Bq/L are in specific areas of the Tarragona province, in the Baix Camp, Baix Penedès, Conca de Barberà, Priorat and Tarragonès regions, representing 23% of the total.

From among these five regions, Baix Penedès and Tarragonès are the regions that have mean gross alpha activity concentration values below 0.1 Bq/L. Only some individual samples of these two regions exceeded this parametrical value. For example, the mean gross alpha activity concentration of water samples from the same sampling point in Baix Penedès was 0.09 ± 0.03 Bq/L, even though some samples exceed this value. For this sampling point, the highest gross alpha activity concentration found was 0.11 ± 0.03 Bq/L. These relatively high values are probably related to the groundwater origin. In this area, there is a carbonate dominant lithology (Agència Catalana de l'Aigua 2005a). According to Pérez-Moreno et al (2020), this kind of lithologic composition is related to high level alpha activities in water. In the case of the Tarragonès region, some of the analysed water samples have their origin in the Ebre River, which basin covers several geological terrains and has a complex hydrological regime as the river flow is variable and irregular and also depends on seasonality (Balasch et al. 2019). It is important to highlight that the samples from this sampling point were collected in different seasons, and we could observe that the gross alpha activity values were in the range from 0.03 ± 0.03 Bq/L to 0.18 ± 0.04 Bq/L. These values show an important variation, which it was already observed in a previous study performed in our laboratory (Nieto et al. 2015). Moreover, our broad experience in this area, since we have analysed weekly Ebre River water samples, allow us to conclude that there is a pattern in the fluctuation of the gross alpha activity as well as in the natural uranium concentration related with the seasonal variability of the Ebre River as it can be observed in Fig. 3. Between late winter and early spring, the mean Ebre River flow increases from 100 m^3/s to 500-700 m^3/s due mainly to the contribution of its tributaries, for example the Cinca and the Segre, which hydrogeological regime is characterized by the Pyrenees snowmelt. This lower salinity water apport could be a dilution factor and the gross alpha activity, as well as the uranium concentration, diminished in comparison with other seasons. In this sense, from early winter to late spring the gross alpha activity values were higher, in some cases even exceeding the parametrical value of 0.1 Bq/L.

The seasonal variation of gross alpha activity and natural uranium concentration has been also observed in other variables as chlorides, sulphates (which are mainly present due to the discharges of the Ebre River tributaries) and conductivity. The positive correlation of the mentioned variables is strong as it could observed through a Spearman statistical analysis of data from 2009 to 2020 (Table 1) which indicate that there is also a fluctuation pattern of the mentioned variables related with the Ebre River hydrodynamic cycle.

For the other three mentioned regions, Baix Camp, Conca de Barberà and Priorat, the mean gross alpha activity concentration values exceeded 0.1 Bq/L, as it can be observed in Fig. 2. This behaviour could be related to the presence of natural radionuclides in the areas where these water samples were collected because, for example, granitic rocks tend to be composed of uranium and radium, which are the main alpha emitter contributors to the gross alpha activity (Palomo et al. 2007).

Regarding gross beta activity concentration, 100% of the samples showed results below the parametric value of 1 Bq/L (RD 314/2016 2016). For this parameter, values ranged from 0.04 ± 0.04 Bq/L to 0.90 ± 0.09 Bq/L. Moreover, the gross beta without ^{40}K activity was generally below 0.04 Bq/L, demonstrating that ^{40}K is the main contributor to beta counts. However, there were some specific samples, in particular from granitic areas in the Baix Camp and Priorat regions, with high values of gross alpha, gross beta and gross beta without ^{40}K activities, exceeding 0.04 Bq/L. For example, a sample with gross alpha and beta activity values of 1.63 ± 0.21 Bq/L and 0.76 ± 0.09 Bq/L, respectively, showed a gross beta without ^{40}K activity value of 0.63 ± 0.09 Bq/L. These results suggest the probable contribution of ^{210}Tl, ^{210}Pb, ^{210}Bi, ^{234m}Pa and ^{234}Th. These beta emitting isotopes could be present in water samples from granitic areas due to disintegration and their high content of ^{238}U since they are in the disintegration chain of this uranium isotope.

Individual radionuclide activities and their distribution in particular regions

An additional study was performed to determine the main individual radionuclides contribute to a higher degree to the gross alpha activity for those samples exceeding 0.1 Bq/L. We focused on drinking water samples from the Baix Camp, Conca de Barberà and Priorat regions. Fig. 4 illustrates the locations of these samples. The main purpose of this study was to associate the radiological content of these analysed water samples with the lithological composition of the area where they were taken.

The results in terms of activity concentration of the gross alpha index, ^{222}Rn and ^{238}U and ^{232}Th decay series radionuclides measured for all these samples, as well as their origin, are shown in Table 2.

From the table it can be observed that the drinking water samples taken from different collection points of the same town in the Baix Camp region (BC-1.1 – BC-1.6) have gross alpha activities in the range between 0.10 ± 0.04 Bq/L and 0.19 ± 0.05 Bq/L and showed the presence of isotopes from the ^{238}U series. The water for human consumption in this town is a mixture of potable water from the Ebre River (obtained from the DWTP of l'Ampolla) and water from own sources, such as groundwater or surface water from the Siurana-Riudecanyes reservoir system (Ajuntament de Reus et al. 2020). The obtained results could then be related to the origin of the water. On one hand, the alpha activity may vary due to the fluctuations in the water river flow due to seasonal changes as explained previously. On the other hand, the presence of ^{222}Rn in BC-1.4 and BC-1.5 samples also indicated a groundwater contribution to the levels of radionuclides, which are the main contributors to gross alpha activity.

In contrast, BC-2 and BC-3 samples (collected in other locations also in the Baix Camp region) have a groundwater origin. In these cases, the values found for the different tested parameters can be linked primarily to the local lithology in these areas.

Sample BC-2 was from groundwater from low permeable areas with local aquifers predominating metamorphic and granitic material (Agència Catalana de l'Aigua 2005b, c). These formations, specifically the granitic one, tend to increase the natural radioactivity in the water when it is in contact with them. As it has been reported in different studies, high concentrations of uranium and thorium have been found in the range of 5 ppm and 17 ppm, respectively (Moreno et al. 2018; Guagliardi et al. 2020; Pérez-Moreno et al. 2020). Therefore, water in contact with these kinds of formations can contain high activity concentrations of ^{238}U and ^{232}Th disintegration chain radionuclides. The findings for sample BC-2 shown in Table 2 are in agreement with the studies in the literature.

For sample BC-3 it should be pointed out that its origin is from groundwater from Triassic sedimentary rocks: conglomerate, sandstone, limestone, gypsum and variegated mudstone areas located close to granitic areas (Fig. 4) (Agència Catalana de l'Aigua 2005c). The geographical area where this sample comes from is also close to the Priorat metamorphic rock area. It is important to highlight that among all the results shown in Table 2, this sample shows the highest ^{234}U/^{238}U ratio, with a value of 3.5. According to Pérez-Moreno (2020), who determined natural radionuclide in Spanish groundwaters, the disequilibrium of the ^{234}U/^{238}U isotopic ratio with values higher than 1 shows the enrichment of ^{234}U in water samples (Fonollosa et al. 2016; Guerrero et al. 2016; Khattab 2016; Linhoff et al. 2020; Pérez-Moreno et al. 2020). Therefore, BC-3 water is a ^{234}U enriched sample and, as stated in the literature, this is probably related to it having a carbonate aquifer origin (Pérez-Moreno et al. 2020).

Sample BC-3 also showed the highest ^{226}Ra activity concentration value and ^{226}Ra/^{234}U ratio, which was 8.4. These high values could be related to the reducing conditions of the water origin, which favour ^{226}Ra solubility (Faraj et al. 2020), the presence of a large fault nearby (Fonollosa et al. 2016) as well as various important factors, including alfa recoil, adsorption/desorption processes onto aquifer surfaces and the dissolution or precipitation of minerals containing radium, among others (International Atomic Energy Agency 2014; Sherif and Sturchio 2018). A high activity value of ^{224}Ra was also determined for this sample, probably due to the displacement of atoms from solid to liquid phase or lattice destruction by alpha recoil (Nguyen Dinh et al. 2017).

Samples P-1 and P-2 collected from the Priorat region show different behaviour from each other. This could be related to the variation in the terrain's lithology. The P-1 drinking water sample has its origin in a granitic area like sample BC-2, whereas sample P-2 is from a terrain like sample BC-3, composed by Triassic sedimentary rocks, very close to metamorphic rocks. Table 2 shows that sample P-2 has the highest ^{234}U and ^{238}U activity concentrations. Moreover, the two samples contained ^{232}Th decay series isotopes, such as ^{224}Ra and ^{228}Ra. Sample P-1 had a higher ^{224}Ra activity concentration than ^{226}Ra (from the ^{238}U series). As Sherif and Sturchio (2018) stated, this is related to the activity concentration of the parent nuclides present in the rocks, the equilibrium state between parent and daughter and the rock-water interaction time, among other factors.

In Table 2 it is also possible to observe that some water samples from the Baix Camp, Conca de Barberà and Priorat regions show the presence of ^{222}Rn due to their groundwater origin, mainly aquifers and wells located close to faults, which can enhance the ^{226}Ra and ^{222}Rn activity concentration (Ródenas et al. 2008).

These findings are in accordance with a previous study performed in our laboratory in which ^{222}Rn activities were determined in water samples from granitic Baix Camp areas near a fault (Fonollosa et al. 2016).

Finally, it should be pointed out that drinking water samples from the Conca de Barberà region (CB-1 to CB-4) were mainly from groundwater and the lithology of the area of origin is mainly comprised of conglomerate, sandstone, slate, limestone and evaporites (Fig. 4) (Agència Catalana de l'Aigua 2005d). In particular, the area has limestone formations and lacustrine detrital deposits and the water samples analysed show mainly isotopes from the ^{238}U chain probably due to their contact with limestones. These results are in agreement with Amrane and Oufni (2017) who relate the presence of ^{238}U in water samples to their contact with uraniferous rocks formed by limestone deposits.

Due to the high number of samples and determined variables, the Spearman correlation coefficients were calculated and presented in Table 3 to identify possible relevant correlations between gross alpha and gross beta index, pH, EC, dry residue and the activity of natural radionuclides. The Spearman statistical analysis, which was conducted because many variables do not follow a normal distribution, was performed using XLSTAT considering that missed measures have been replaced by the mean value of the variable. From the correlation matrix it is possible to observe some relationships that has been explained throughout this research study.

Gross alpha activity presents a positive correlation with ^{234}U (0.96), ^{238}U (0.57) and ^{226}Ra (0.62) because these radionuclides are the main contributors to these parameters as it has been observed in studies carried out by other authors (Pérez-Moreno et al. 2020). For example, in the case of BC-3 the high gross alpha activity, 2.88 ± 0.32 Bq/L, is mainly governed by the high content of ^{226}Ra found, 1339 ± 45 mBq/L, probably due the contact of this water with sedimentary rocks that are near granitic ones. In addition, ^{224}Ra shows a positive correlation with ^{226}Ra (0.56) and ^{228}Ra (0.77) since they are three isotopes from radium and have similar chemical and solubility properties. Moreover, ^{226}Ra correlates with ^{222}Rn (0.70) because this latter is the immediate progeny of ^{226}Ra.

Annual effective doses from drinking water consumption

After determining the different possible contributors to the radiological content of the analysed samples, we calculated the ID and the AEDw due to water ingestion for adults. The calculations were based on the activity concentration, the derived concentration and the ingestion effective dose coefficient factors for each determined radionuclide. Based on the results obtained it can be concluded that 95.5 % of the drinking water samples analysed showed an ID lower than 1. Therefore, it can be concluded that these samples do not exceed the legislation level of 0.1 mSv/year.

The AEDw was estimated for infants, children and adults for those samples with a gross alpha exceeding 0.1 Bq/L. As it can be observed in Table 4, only one sample, BC-3, exceeded the individual dose criterion of 0.1 mSv/year (RD 314/2016 2016; World Health Organization 2018) for all three groups. The AEDw calculation differed between infants, children and adults because each group has a different ingestion effective dose coefficient factor per radionuclide and a different water consumption rate.

Fig. 5 represents the contribution to the AEDw of each analysed radionuclide in the case of infants, children and adults due to the supposed ingestion of the BC-3 water sample. As can be observed, ^{226}Ra is the main individual contributor to the AEDw for adults, children and infants (82 %, 73.7 % and 65.5 %, respectively) due to its high radiotoxicity, its long half-life (1600 years) and its high effective dose coefficient factor (International Atomic Energy Agency 1963). However, the other radium isotopes determined, ^{224}Ra and ^{228}Ra, also contributed to the total annual effective dose in the order, infants, children and adults, respectively, due to the differences in the ingestion effective dose coefficient factors.

Conclusions

The natural radionuclides activity was determined for one hundred and ninety-six drinking water samples intended for human consumption covering the different regions of Tarragona province. A total of 23 % of the analysed samples exceeded the gross alpha parametrical value, 0.1 Bq/L, and these also presented differences in their individual radionuclide content, mainly related to the composition of the lithological area. Samples from the Baix Camp, Conca de Barberà and Priorat regions had the highest activity concentration values of ^{234}U, ^{238}U, ^{224}Ra, ^{226}Ra and ^{228}Ra. This could be related to the granitic and carbonate aquifer compositions of the areas where the water comes from, among other lithological formations. Finally, ^{222}Rn activity concentrations were measured in different samples. They ranged from < 2 Bq/L to 24.3 ± 2.8 Bq/L due to their groundwater origin from granitic areas and the presence of a nearby fault. Lastly, the total annual effective dose in water samples with gross alpha activity exceeding 0.1 Bq/L was calculated for infants, children and adults. In general, the obtained results show that the annual effective dose parametric value (0.1 mSv/year) is not surpassed. This means that, from a radiological perspective, the drinking water can be safely consumed. However, one of the analysed samples did not fulfil the legal requirements and further research must be performed to adopt and apply corrective and preventive measures to avoid a possible human health risk.

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Availability of data and materials Not applicable

Competing interests

The authors declare that they have no competing interests

Funding Not applicable

Authors' contributions

JMR and APH contributed to the study conception and design. Material preparation, data collection and analysis were performed by JMR. The first draft of the manuscript was written by JMR and APH, CA and FBB commented on previous versions of the manuscript. JMR, APH, CA and FBB read and approved the final manuscript.

Acknowledgements

The authors would like to thank the *Consorci d'Aigües de Tarragona (CAT)* for their invaluable cooperation.

Bibliography

Agència Catalana de l'Aigua (2019) Estudi de volums d'aigua subministrats i captats a Catalunya. Any 2018. http://aca.gencat.cat/web/.content/10_ACA/J_Publicacions/06-estudis-consums-i-volums/06_eess_cens2018_ca.pdf. Accessed 31 Mar 2020

Agència Catalana de l'Aigua (2005a) Masses d'aigua subterrània de Catalunya. Bloc de Gaià - Sant Martí Sarroca - Bonastre 27. https://aca-web.gencat.cat/aca/documents/ca/fitxes_masses_aigua_subterrania/mas_20_def.pdf. Accessed 22 Apr 2020

Agència Catalana de l'Aigua (2005b) Masses d'aigua subterrània de Catalunya. Priorat 50. https://aca-web.gencat.cat/aca/documents/ca/fitxes_masses_aigua_subterrania/mas_50_def.pdf. Accessed 22 Apr 2020

Agència Catalana de l'Aigua (2005c) Masses d'aigua subterrània de Catalunya. Llaberia-Prades Meridional 28. https://aca-web.gencat.cat/aca/documents/ca/fitxes_masses_aigua_subterrania/mas_28_def.pdf. Accessed 22 Apr 2020

Agència Catalana de l'Aigua (2005d) Masses d'aigua subterrània de Catalunya. Prades - Alt Francolí 27. https://aca-web.gencat.cat/aca/documents/ca/fitxes_masses_aigua_subterrania/mas_27_def.pdf. Accessed 22 Apr 2020

Ajuntament de Reus, Aigües de Reus, Agència Catalana de l'Aigua (2020) Rutes de l'aigua a Reus. https://www.reus.cat/sites/reus/files/Fitxers/arees/medi_ambient/documents/rutesAigua.pdf. Accessed 10 May 2020

Alonso H, Cruz-Fuentes T, Rubiano JG, et al (2015) Radon in groundwater of the Northeastern Gran Canaria aquifer. Water 7:2575–2590. doi: 10.3390/w7062575

Amrane M, Oufni L (2017) Determination for levels of uranium and thorium in water along Oum Er-Rabia river using alpha track detectors. J Radiat Res Appl Sci 10:246–251. doi: 10.1016/j.jrras.2017.05.002

Balasch JC, Pino D, Ruiz-Bellet JL, et al (2019) The extreme floods in the Ebro River basin since 1600 CE. Sci Total Environ 646:645–660. doi: 10.1016/j.scitotenv.2018.07.325

Corbacho JA, Guillén J, Miralles Y, Baeza A (2014) Procedimiento para la determinación de los índices de actividad alfa total en aguas potables mediante la metodología de desecación y medida en detectores de ZNS(ag) o en contador proporcional. Colección Informes Técnicos 11.2014. Serie Vigilancia Radiológ

Dinh Chau N, Dulinski M, Jodlowski P, et al (2011) Natural radioactivity in groundwater - a review. Isotopes Environ Health Stud 47:415–437. doi: 10.1080/10256016.2011.628123

European Commission (2013) Council Directive 2013/51/EURATOM of 22 October 2013 laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption

Faraj T, Ragab A, El Alfy M (2020) Geochemical and hydrogeological factors influencing high levels of radium contamination in groundwater in arid regions. Environ Res 184:109303. doi: 10.1016/j.envres.2020.109303

Fonollosa E, Nieto A, Peñalver A, et al (2015a) Presence of radionuclides in sludge from conventional drinking water treatment plants. A review. J Environ Radioact 141:24–31. doi: 10.1016/j.jenvrad.2014.11.017

Fonollosa E, Peñalver A, Aguilar C, Borrull F (2015b) Polonium-210 levels in different environmental samples. Environ Sci Pollut Res 22:20032–20040. doi: 10.1007/s11356-015-5158-3

Fonollosa E, Peñalver A, Borrull F, Aguilar C (2016) Radon in spring waters in the south of Catalonia. J Environ Radioact 151:275–281. doi: 10.1016/j.jenvrad.2015.10.019

Guagliardi I, Zuzolo D, Albanese S, et al (2020) Uranium, thorium and potassium insights on Campania region (Italy) soils: Sources patterns based on compositional data analysis and fractal model. J Geochemical Explor 212:106508. doi: 10.1016/j.gexplo.2020.106508

Guerrero JL, Vallejos Á, Cerón JC, et al (2016) U-isotopes and 226Ra as tracers of hydrogeochemical processes in carbonated karst aquifers from arid areas. J Environ Radioact 158–159:9–20. doi: 10.1016/j.jenvrad.2016.03.015

Institut Cartogràfic i Geològic de Catalunya (2020) InstaMaps. https://www.instamaps.cat. Accessed 2 Apr 2020

Institut Cartogràfic i Geològic de Catalunya (2017) Technical report of the Hydrogeological Area Map of Catalonia 1:250.000 (catalan)

Institut d'Estadística de Catalunya (2020) Densidad de población. Comarcas y Aran, ámbitos y provincias. 2019. https://www.idescat.cat/pub/?id=aec&n=249&lang=es. Accessed 27 Apr 2020

International Atomic Energy Agency (2014) The environmental behaviour of radium: revised edition. In: Tech. Reports Ser. no. 476. https://www-pub.iaea.org/MTCD/Publications/PDF/trs476web-45482131.pdf. Accessed 2 May 2020

International Atomic Energy Agency (1963) A basic toxicity classification of radionuclides. In: Tech.

Reports Ser. no. 15. https://inis.iaea.org/collection/NCLCollectionStore/_Public/24/072/24072024.pdf. Accessed 2 May 2020

ISO 13164-4:2015(E) (2015) Water quality - Radon-222 - Part 4: Test method using two-phase liquid scintillation counting

Kamenova-Totzeva RM, Totzev A V., Kotova RM (2018) Radium content in Bulgarian mineral waters. Nucl Technol Radiat Prot 33:133–138. doi: 10.2298/NTRP1801133K

Khattab M (2016) Determination of uranium concentrations and 234U/ 238U activity ratio in some granitic rock samples by alpha spectrometry: Application of a radiochemical procedure. Radiat Prot Environ 39:122–127. doi: 10.4103/0972-0464.194961

Kleinschmidt R, Black J, Akber R (2011) Mapping radioactivity in groundwater to identify elevated exposure in remote and rural communities. J Environ Radioact 102:235–243. doi: 10.1016/j.jenvrad.2010.11.013

Linhoff B, Charette M, Wadham J (2020) Rapid mineral surface weathering beneath the Greenland Ice Sheet shown by radium and uranium isotopes. Chem Geol 547:119663. doi: 10.1016/j.chemgeo.2020.119663

Llauradó M, Vallés I, Abelairas A, et al (2004) Procedimientos de determinación de los índices de actividad beta total y beta resto en aguas mediante contador proporcional. Colección Informes Técnicos 11.2004. Serie Vigilancia Radiológica Ambiental. Procedimiento 1.5

Mola M, Palomo M, Peñalver A, et al (2013) Comparative study of different analytical methods for the determination of 238U, 234U, 235U, 230Th and 232Th in NORM samples (Southern Catalonia). J Environ Radioact 115:207–213. doi: 10.1016/j.jenvrad.2012.05.029

Moreno V, Bach J, Zarroca M, et al (2018) Characterization of radon levels in soil and groundwater in the North Maladeta Fault area (Central Pyrenees) and their effects on indoor radon concentration in a thermal spa. J Environ Radioact 189:1–13. doi: 10.1016/j.jenvrad.2018.03.001

Nguyen Dinh C, Rajchel L, Duong Van H, Nowak J (2017) 224Ra and the 224Ra/228Ra activity ratio in selected mineral waters from the Polish Carpathians. Geol Q 61:771–778. doi: 10.7306/gq.1365

Nieto A, Palomo M, Ruana J, et al (2013) Evaluation of the use of reverse osmosis to eliminate natural radionuclides from water samples. Water Environ Res 85:2265–2270. doi: 10.2175/106143013X13807328848298

Nieto A, Ruana J, X P, et al (2015) Study of the radiological impact caused by the extraction of the residue of a dicalcium phosphate industrial plant. Radioprotection 50:135–140. doi: 10.1051/radiopro/2014038

Palau Miguel M, Guevara Alemany E, Cáceres Monllor DA, Moreno Seisdedos M (2020) Informe Técnico: Calidad del agua de consumo humano en España 2018. https://www.mscbs.gob.es/profesionales/saludPublica/saludAmbLaboral/aguas/aconsumo/Doc/ult_ver_2018_INFORME_AGUA_CONSUMO.pdf. Accessed 3 May 2020

Palomo M, Peñalver A, Borrull F, Aguilar C (2007) Measurement of radioactivity in bottled drinking water in Spain. Appl Radiat Isot 65:1165–1172. doi: 10.1016/j.apradiso.2007.04.022

Peñalver A, Baciu T, Borrull F, Aguilar C (2020) Possible Factors Influencing the Accumulation of Different Radionuclides in Sludge from a Drinking Water Treatment Plant Located in Southern Catalonia Between 2002 and 2018. Water Air Soil Pollut 231:. doi: 10.1007/s11270-020-04491-4

Pérez-Moreno SM, Guerrero JL, Mosqueda F, et al (2020) Hydrochemical behaviour of long-lived natural radionuclides in Spanish groundwaters. Catena 191:1–13. doi: 10.1016/j.catena.2020.104558

Przylibski TA, Domin E, Gorecka J, Kowalska A (2020) 222Rn concentration in groundwaters circulating in granitoid massifs of Poland. Water 12:. doi: 10.3390/w12030748

RD 140/2003 (2003) Real Decreto 140/2003, de 7 de febrero, por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano. Boletín Oficial del Estado, número 45. Madrid, 21 de febrero de 2003

RD 314/2016 (2016) Real Decreto 314/2016, de 29 de julio, por el que se modifican el Real Decreto 140/2003, de 7 de febrero, por el que se establecen los criterios sanitarios de la calidad del agua de consumo humano, el Real Decreto 1798/2010, de 30 de diciembre, por el que. Boletín Oficial del Estado, número 183. Madrid, 30 de julio de 2016

RD 783/2001 (2001) Real Decreto 783/2001, de 6 de julio, por el que se aprueba el Reglamento sobre protección sanitaria contra radiaciones ionizantes. Boletín Oficial del Estado, número 178. Madrid, 26 de julio de 2001

Ródenas C, Gómez J, Soto J, Maraver F (2008) Natural radioactivity of spring water used as spas in Spain. J Radioanal Nucl Chem 277:625–630. doi: 10.1007/s10967-007-7158-3

Sherif MI, Sturchio NC (2018) Radionuclide geochemistry of groundwater in the Eastern Desert, Egypt. Appl Geochemistry 93:69–80. doi: 10.1016/j.apgeochem.2018.04.004

Singaraja C, Chidambaram S, Jacob N, et al (2016) Radon levels in groundwater in the Tuticorin district of Tamil Nadu, South India. J Radioanal Nucl Chem 307:1165–1173. doi: 10.1007/s10967-015-4312-1

Soto J, Fernández L, Gómez J, Ródenas C (1995) Study of the occurrence of 222Rn and 226Ra in drinking water in Spain. Health Phys 69:961–965. doi: 10.1097/00004032-199512000-00012

UNE-EN ISO 10704:2019 (2019) Water quality - Gross alpha and gross beta activity - Test method using thin source deposit (Endorsed by Asociación Española de Normalización in May of 2019.)

World Health Organization (2018) Management of radioactivity in drinking-water. https://apps.who.int/iris/bitstream/handle/10665/272995/9789241513746-eng.pdf?ua=1. Accessed 28 May 2020

Yuce G, Ugurluoglu D, Dilaver AT, et al (2009) The effects of lithology on water pollution: Natural radioactivity and trace elements in water resources of Eskisehir Region (Turkey). Water Air Soil Pollut 202:69–89. doi: 10.1007/s11270-008-9959-6

FIGURE CAPTIONS

Fig. 1 Lithological map of Tarragona province (Catalonia, Spain) showing the regions where drinking water samples were collected in this study (Institut Cartogràfic i Geològic de Catalunya 2020)

Fig. 2 Percentage of analysed water samples with gross α < 0.1 Bq/L, mean gross alfa activity results and the number of analysed water samples (n) per region

Fig. 3 Gross alpha activity and natural uranium concentration pattern behavior related with seasonal variations

Fig. 4 Lithological map of Tarragona province and location of water samples with gross α > 0.1 Bq/L from the Baix Camp, Conca de Barberà and Priorat regions (Institut Cartogràfic i Geològic de Catalunya 2020)

Fig. 5 Contribution (in percentage) of each analysed radionuclide to the AEDw for infants, children and adults for sample BC-3

Table 1 Spearman correlation matrix of chlorides, sulphates, gross alpha, uranium and conductivity (significant correlations at significant level $p < 0.05$)

Variables	Chlorides	Sulphates	Gross Alpha	Uranium	Conductivity
Chlorides	**1.00**				
Sulphates	0.96	**1.00**			
Gross Alpha	0.69	0.75	**1.00**		
Uranium	0.79	0.86	0.78	**1.00**	
Conductivity	0.97	0.98	0.72	0.84	**1.00**

Table 2 Gross α, ^{222}Rn, ^{228}Ra, ^{224}Ra, ^{238}U, ^{234}U and ^{226}Ra activity concentration of water samples with gross α > 0.1 Bq/L

Tarragona *comarques*	**Origin source**	**Samples**	**Gross α [Bq/L]**	**^{222}Rn [Bq/L]**	**^{228}Ra [mBq/L]**	**^{224}Ra [mBq/L]**	**^{238}U [mBq/L]**	**^{234}U [mBq/L]**	**^{226}Ra [mBq/L]**	**^{234}U/^{238}U**	**^{226}Ra/^{234}U**
Baix Camp	Mixture[a]	BC-1.1	0.19 ± 0.05	-	<20	<24	125 ± 17	108 ± 15	<30	0.9	
	Mixture[a]	BC-1.2	0.12 ± 0.03	<1.0	<50	<5	53 ± 5	66 ± 6	<5	1.2	
	Mixture[a]	BC-1.3	0.10 ± 0.04	<1.0	<50	<5	67 ± 7	61 ± 7	<5	0.9	
	Mixture[a]	BC-1.4	0.19 ± 0.04	7.7 ± 1.1	<56	<2	78 ± 8	94 ± 9	8 ± 1	1.2	0.1
	Mixture[a]	BC-1.5	0.13 ± 0.04	2.3 ± 0.5	<46	<5	40 ± 4	66 ± 6	<5	1.7	
	Mixture[a]	BC-1.6	0.11 ± 0.04	<2.0	57 ± 11	<1	46 ± 7	58 ± 8	<1	1.3	
	Groundwater	BC-2	0.24 ± 0.04	6.6 ± 1.0	<20	<2	124 ± 9	155 ± 11	<2	1.3	
	Groundwater	BC-3	2.88 ± 0.32	11.3 ± 1.3	67 ± 33	411 ± 78	46 ± 5	159 ± 9	1339 ± 45	3.5	8.4
Conca de Barberà	Groundwater	CB-1	0.13 ± 0.03	-	<20	<1	73 ± 8	79 ± 8	<1	1.1	
	Groundwater and surface water	CB-2	0.22 ± 0.05	13.7 ± 1.7	<20	<2	120 ± 9	116 ± 9	16 ± 2	1.0	0.1
	Groundwater	CB-3.1	0.15 ± 0.06	-	<20	<1	97 ± 6	96 ± 6	12 ± 2	1.0	0.1
	Groundwater	CB-3.2	0.13 ± 0.04	-	<20	<1	56 ± 5	58 ± 5	8 ± 1	1.0	0.1
	Groundwater	CB-4	0.32 ± 0.05	-	<20	<1	154 ± 18	146 ± 17	5 ± 1	0.9	0.0
Priorat	Groundwater	P-1	0.24 ± 0.05	16.9 ± 2.0	55 ± 46	17 ± 2	69 ± 5	122 ± 9	9 ± 1	1.8	0.1
	Groundwater	P-2	0.92 ± 0.15	24.3 ± 2.8	43 ± 19	30 ± 3	383 ± 25	319 ± 21	93 ± 5	0.8	0.3

- not analysed

[a] Mixture of potable water composed of groundwater, surface and Ebre River water

Table 3 Spearman correlation matrix (significant correlations at significant level $p < 0.05$)

Variables	Gross alpha index	Gross beta index	^{222}Rn	^{228}Ra	^{224}Ra	^{238}U	^{234}U	^{226}Ra	pH	EC	Dry residue
Gross alpha index	**1.00**										
Gross beta index	0.08	**1.00**									
^{222}Rn	**0.74**	0.10	**1.00**								
^{228}Ra	0.24	0.34	0.22	**1.00**							
^{224}Ra	0.33	0.20	0.12	**0.77**	**1.00**						
^{238}U	**0.57**	0.06	0.43	-0.26	-0.11	**1.00**					
^{234}U	**0.96**	0.09	**0.64**	0.30	0.38	**0.61**	**1.00**				
^{226}Ra	**0.62**	-0.03	**0.68**	0.37	**0.56**	0.32	**0.57**	**1.00**			
pH	-0.11	-0.12	-0.09	-0.18	-0.06	0.00	-0.06	-0.03	**1.00**		
EC	0.10	-0.37	0.24	-0.13	-0.14	0.23	0.00	0.29	0.26	**1.00**	
Dry residue	0.04	0.15	0.36	-0.11	0.14	0.30	-0.05	**0.53**	-0.23	0.32	**1.00**

Table 4 ID and AED_w for infants, children and adults from water samples with gross α > 0.1 Bq/L

Comarques	**Samples**	**ID**	**AED_W infants [mSv/year]**	**AED_W children [mSv/year]**	**AED_W adults [mSv/year]**
Baix Camp	BC-1.1	0.08	0.004	0.006	0.008
	BC-1.2	0.04	0.002	0.003	0.004
	BC-1.3	0.04	0.002	0.003	0.004
	BC-1.4	0.08	0.004	0.007	0.008
	BC-1.5	0.04	0.002	0.003	0.004
	BC-1.6	0.32	0.002	0.003	0.004
	BC-2	0.10	0.005	0.007	0.010
	BC-3	3.34	0.295	0.509	0.334
Conca de Barberà	CB-1	0.05	0.003	0.004	0.005
	CB-2	0.11	0.006	0.010	0.011
	CB-3.1	0.09	0.005	0.008	0.009
	CB-3.2	0.06	0.003	0.005	0.006
	CB-4	0.11	0.006	0.009	0.011
Priorat	P-1	0.37	0.054	0.084	0.037
	P-2	0.67	0.066	0.105	0.066

Figure revised

Figure 1

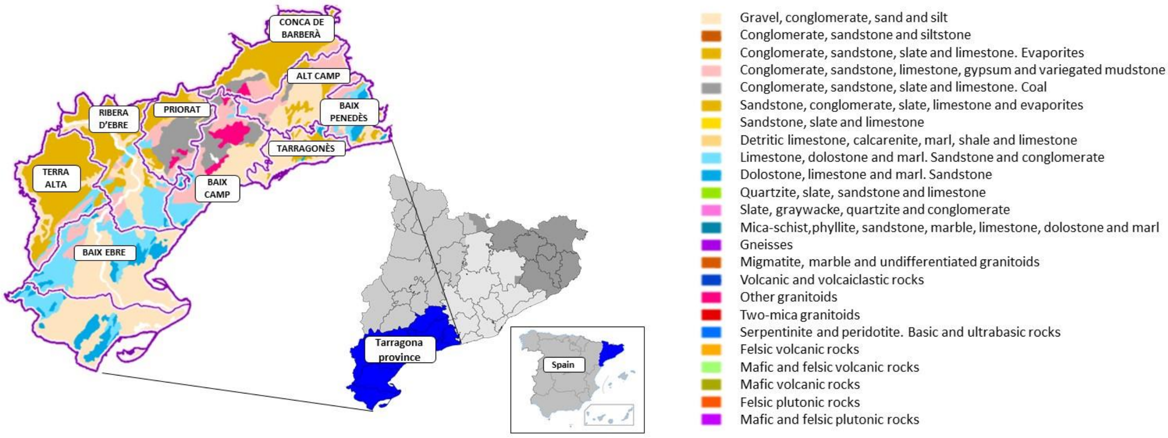
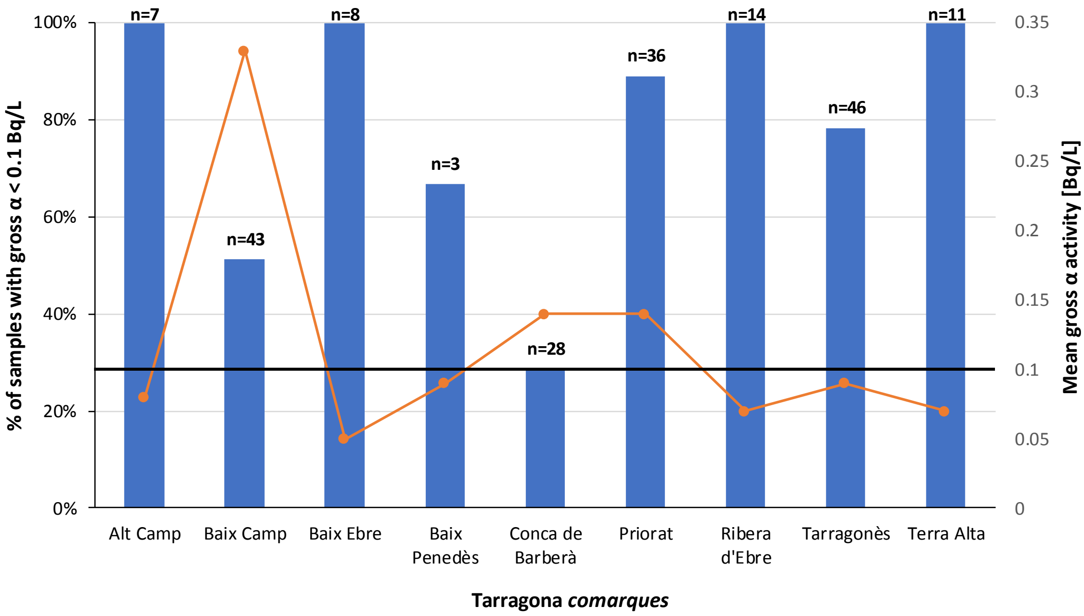
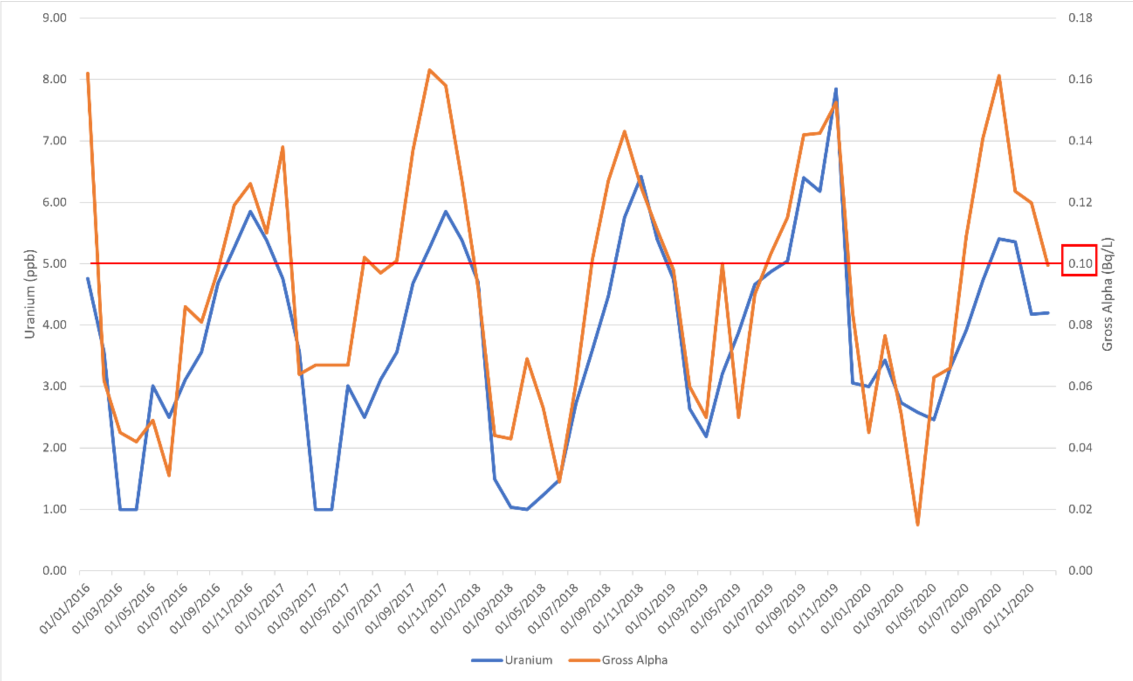


Figure 2



% of samples with gross α < 0.1 Bq/L
Mean gross α activity [Bq/L]
100%
80%
60%
40%
20%
0%
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
n=7
n=43
n=8
n=3
n=28
n=36
n=14
n=46
n=11
Alt Camp
Baix Camp
Baix Ebre
Baix Penedès
Conca de Barberà
Priorat
Ribera d'Ebre
Tarragonès
Terra Alta
Tarragona *comarques*

Figure 3



9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Uranium (ppb)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Gross Alpha (Bq/L)
01/01/2016
01/03/2016
01/05/2016
01/07/2016
01/09/2016
01/11/2016
01/01/2017
01/03/2017
01/05/2017
01/07/2017
01/09/2017
01/11/2017
01/01/2018
01/03/2018
01/05/2018
01/07/2018
01/09/2018
01/11/2018
01/01/2019
01/03/2019
01/05/2019
01/07/2019
01/09/2019
01/11/2019
01/01/2020
01/03/2020
01/05/2020
01/07/2020
01/09/2020
01/11/2020
Uranium
Gross Alpha

Figure 4

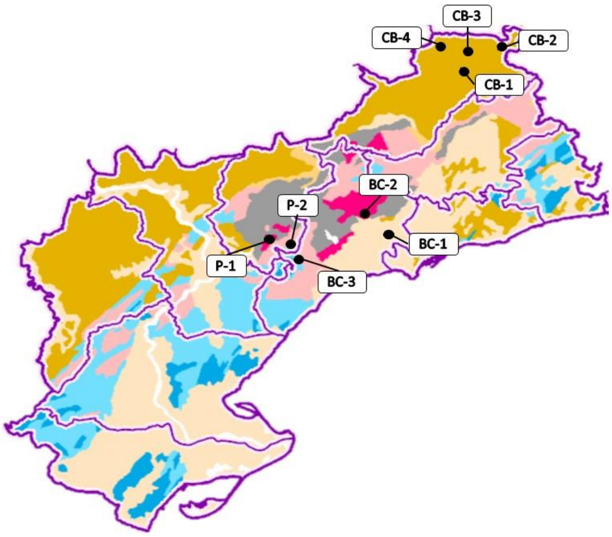
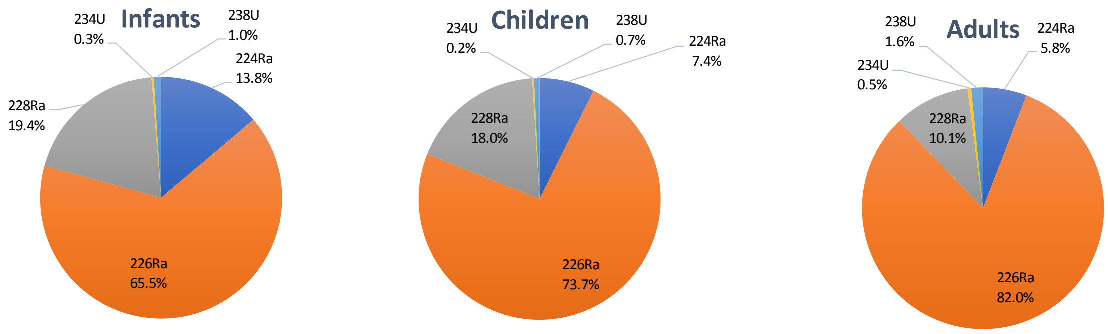


Figure 5


Infants
234U
0.3%
238U
1.0%
224Ra
13.8%
228Ra
19.4%
226Ra
65.5%
Children
234U
0.2%
238U
0.7%
224Ra
7.4%
228Ra
18.0%
226Ra
73.7%
Adults
238U
1.6%
224Ra
5.8%
234U
0.5%
228Ra
10.1%
226Ra
82.0%