HYDROCHEMICAL BEHAVIOUR OF LONG-LIVED NATURAL RADIONUCLIDES IN SPANISH GROUNDWATERS

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ABSTRACT

This research was focused on the analyses the hydrochemical behaviour of long-lived natural radionuclides (^{210}Po, ^{210}Pb, ^{234,238}U, ^{230,232}Th, ^{226,228}Ra) in groundwaters located in Spanish aquifers with different geological characteristics and evaluate the dose by ingestion of these waters. The study was performed by the gross alpha-beta, alpha spectrometry and physicochemical analysis of a set of bottled drinking waters. Radionuclide activities in the investigated aquifers were highly variable. High concentration of ^{210}Pb is associated with granitic bedrock and reducing conditions. On the other hand, the highest ^{238,234}U concentrations were found in carbonate aquifers. Activities of ^{226}Ra are largely controlled by ion exchange reactions due to the presence of relatively high concentration of chloride. Several waters exceeded the parametric value for gross alpha mainly due to ^{234}U, ^{226}Ra and/or ^{210}Pb concentrations. Moreover, the content of ^{226}Ra and ^{210}Pb in the water contributed mainly to the indicative dose.

KEYWORDS: *Groundwater, Natural Radioactivity, long-lived radionuclides, Alpha spectrometry, Indicative Dose, Spain.*

1. INTRODUCTION

Most European countries as well as in the rest of the world, the consumption of commercial mineral water from groundwater has increased significantly in the last two decades. Up to date, more than 2000 natural mineral waters have been recognised in the EU, where about 52 billion litres were consumed in 2017, corresponding to 26.2 % of the world's consumption (EFBW, 2019).

The mineral composition and properties of each natural mineral water are derived from the geological conditions present in the area where the water is extracted. The presence of natural radionuclides in the host rock and their interaction with water allow part of the natural radionuclides to be transferred into the water (Chau et al., 2011; Rozmaric et al., 2012). This fact can pose a risk to human health due to the ingestion of water, which is one of the pathways of incorporation of radioactive substances into the human body (Jia et al., 2009; Manu et al., 2014). Studying the concentration of natural radionuclides in drinking bottled water can be used to determine the behaviour of these radionuclides under different hydrogeological conditions (pH, ionic strength, redox potential, etc.).

The effective dose received through this pathway (consumption of bottled groundwater) is mainly due to ^{40}K, and both ^{238}U- and ^{232}Th-series radionuclides present in drinking water. Polonium-210 is one of the most radiotoxic natural radioactive isotopes known due to its relatively long half-life (138 days). Polonium and lead can be distributed throughout the soft tissue of the body and accumulate in the liver, kidneys and bones. The accumulation of ^{210}Pb in the skeleton provides another source of ^{210}Po over time (Carvalho et al., 2017). In addition, Ra is also one of the most toxic radioelements due to its tendency to be accumulated in the bones, since its chemical and biological behaviour is similar to that of alkaline earth metals (Ca, Sr, Ba) (Altikulac et al., 2015; Stackelberg

50   et al., 2018). Uranium seems to follow the same tendency (IAEA, 2014), as it is retained

51   in the body primarily in the skeleton (vertebrae, ribs and femur). In addition to these,

52   thorium is deposited mainly on bone surfaces, where it is retained for long time periods

53   (Bhatti et al., 2012).

54   In accordance with the Council Directive 2013/51/EURATOM, the contribution to the

55   exposure of the general public as a whole from practices which involve a risk from

56   ionising radiation must be kept as low as reasonably achievable. The strategies to indicate

57   radioactivity levels in drinking water may include screening for certain radionuclides, or

58   gross alpha-beta activity screening. Gross alpha and beta activities are very useful

59   parameters for the preliminary screening of waters. From the radiological point of view,

60   the most significant natural radionuclides in waters are ^{226}Ra, an alpha emitter ($t_{1/2} = 1600$

61   y), and ^{228}Ra, a beta emitter ($t_{1/2} = 5.75$ y) (IAEA, 2014). Other radionuclides, such as

62   ^{210}Pb, a beta emitter ($t_{1/2} = 22.3$ y), and ^{210}Po, an alpha emitter ($t_{1/2} = 138.4$ days), can also

63   limit the quality of drinking water (Ansoborlo et al., 2012).

64   The EU recommended screening levels for gross alpha activity of 0.1 Bq L^{-1} and for gross

65   beta activity of 1.0 Bq L^{-1} in order to keep that the Indicative Dose (ID) lower than 0.1

66   mSv (EURATOM, 2013). However, the concentrations of certain radionuclides, such as

67   ^{226,228}Ra, ^{210}Pb and ^{210}Po, among others, must be measured through accurate dose

68   assessments. Recently, Spanish regulations incorporated this directive about

69   requirements for the protection of the health of the general public with regard to

70   radioactive substances in water intended for human consumption (RD 314/2016).

71   Studies for measuring the natural radioactivity and estimating the effective dose of bottled

72   mineral drinking waters have been carried out worldwide (Kozlowska et al., 2007;

73   Karamanis et al., 2007; Wallner et al, 2008; Vasile et al., 2016). However, those

74 performed in Spain (Baeza et al., 1995; Ortega et al., 1996; Herranz et al., 1997; Dueñas

75 et al., 1997; Manjón et al., 1997; Martín Sanchez et al., 1999; Palomo et al., 2007), were

76 all published before the new regulations and the majority were focused on measuring

77 gross alpha and beta activity.

78 Moreover, the existence of high activity concentration of natural radionuclides in bottled

79 mineral drinking waters depends on the characteristics of the aquifer and the rock

80 substrate. The literature consulted (Chau et al., 2011; UNSCEAR, 2016) shows that the

81 concentration of uranium in igneous rocks is higher than in sedimentary rocks, and felsic

82 igneous rocks contain significantly more uranium than mafic rocks. Under oxidizing

83 conditions, insoluble U(IV) species dissolve, giving rise to highly soluble uranyl ion,

84 UO_2^{2+}. At pH range between 6 and 8, typical values for groundwater, uranyl ions tend to

85 form soluble complexes with inorganic ligands (i.e., phosphates and carbonates)

86 (Markich, 2002; Sherif and Sturchio, 2018). However, in solutions with low ionic

87 strength, the concentration of U can be limited by cation exchange and adsorption

88 processes.

89 The concentration of Ra isotopes in groundwater is typically correlated with the

90 concentration of uranium and thorium isotopes and their decay products in the bedrock.

91 Ra in dissolution can be produced by alpha recoil of its parent nuclide (^{230}Th), contained

92 in the solid materials surface of the aquifer since its parent is very insoluble, or can also

93 reach the solution phase by its direct dissolution from the bedrock (Vinson et al., 2013).

94 Meanwhile, the presence of radium isotopes in groundwaters depends mainly on the both

95 ^{230}Th and ^{226}Ra activity concentrations in the host rock and physicochemical properties

96 of the aquifer groundwater. The presence of both Fe and Mn hydroxides high

97 concentrations in the aquifer water tends to reduce the Ra solubility, but, on the other

98 hand, high ionic strength tends to increase the desorption of Ra-isotopes from the bedrock

99   into the groundwaters (Sturchio et al., 2001; Szabo et al., 2012, Sherif et al., 2019;

100   Stackelberg et al., 2018). Radium is also controlled by coprecipitation/dissolution

101   processes. For example, the very low solubility of the barite ($BaSO_4$), limits the Ra

102   concentration in the water due to the co-precipitation of Ra bound to barite (Grundl and

103   Cape, 2006; Grandia et al., 2008, Sherif and Sturchio 2018).

104   In view of these facts, knowledge of the distribution of long-lived natural radionuclides

105   in groundwater as a function of the geochemical and hydrological Spanish regional

106   conditions, can help to assess the exposure and to inform to population about the risk of

107   having waters with high activity concentration of a certain natural radionuclides. So, the

108   aim of this paper was to evaluate the radiological quality of a significant set of drinking

109   bottled waters of different Spanish brands with different geological origin, as well as to

110   study the behaviour of natural radionuclides (^{210}Po, ^{210}Pb, ^{234,238}U, ^{230,232}Th, ^{226,228}Ra) of

111   the groundwater.

112   **2. MATERIALS AND METHODS**

113   **2.1. SAMPLES**

114   Fifteen different brands of bottled drinking water from different Spanish locations were

115   purchased in local supermarkets in the area of Huelva in July 2016. Several samples were

116   taken for each brand to evaluate possible differences in the water properties between

117   batches. All mineral waters were preserved in their original bottles and their natural state

118   until the beginning of this work in September 2018. The waters selected are included in

119   Table 1, as well as the code of each batch and their origin.

120   Figure 1 shows the main lithologies of Spain and the location of the springs where the

121   bottled drinking waters were taken. As can be observed, the analysed waters belong to

122   different geologic origin, including igneous (granites), metamorphic (schists), carbonated

5

123   (limestones and dolomites) and sedimentary (conglomerate and gravels). More details of

124   the geology of the aquifers can be seen in Figure S1 of Supplementary Information.

125

126   ***Table 1.*** *Summarised information of the different brands of bottled water analysed.*

127

128   ***Figure 1.*** *General lithological map of Spain and the location of the bottled water sources*

129   *analysed.*

130

131   **2.2. PHYSICOCHEMICAL PARAMETERS**

132   The pH and electrical conductivity (EC) of the bottled water samples were measured

133   using a previously calibrated CRISON multi parameter electrode, model MM40+. The

134   trace elements were analysed using an ICP-MS, model Perkin Elmer Sciex ELAN 9000,

135   from Activation Laboratories Ltd. (Actlab, Canada). Concentrations of anions (F^-, Cl^-,

136   NO^2, NO^{3-} and SO_4^{2-}) were analysed at the University of Huelva through high-

137   performance liquid chromatography (HPLC) using a Metrohm 883 basic ion

138   chromatograph equipped with Metrosep columns. In all measurement techniques several

139   reference materials were used in order to assure the quality of the results.

140   A piper diagram was performed with EASY QUIM software (GHS, 2019). The Piper

141   diagram is used as visualisation tool for find out the hydro-chemical of groundwater

142   samples. The Piper diagram consists of two composition ternary diagrams, along with a

143   rhombus plot in the middle. The composition ternary on the left is mapped based on

144   normalised mass fractions of three cationic components (Ca^{2+}, Mg^{2+}, $Na^+ + K^+$), whilst

145   the aspect ternary on the right is based on three anionic components (Cl^-, SO_4^{2-}, CO_3^{2-} +

146   HCO_3^-) (Piper, 1953).

2.3. GROSS ALPHA-BETA ACTIVITY

Both the gross alpha and gross beta activities were measured to identify the most active samples, using a multi-detector low background α/β counting system (Berthold LB770). The sample detectors were window gas-flow counters with approximately 5.0 cm in diameter. The counting gas was a mixture of 90% argon and 10% methane. All samples were placed in a 5 cm diameter stainless steel planchet for counting. The operating voltage on the detector was selected to be 1700 V.

The system was calibrated for simultaneous α and β measurements by preparing standard samples with known concentrations of both ^{241}Am (27.5 ± 0.2 Bq g^{-1}) and ^{90}Sr/^{90}Y (160.8 $\pm$ 0.4 Bq g^{-1}) solutions. The counting efficiencies were 5–15% for α and 30–39% for β depending on mass thickness (mg/cm^2). The background of the detectors presented values of around 0.02 and 0.2 cpm for α and β windows, respectively.

To determine gross alpha and beta activities, aliquots of each sample were taken, ranging between 0.2 and 3 L, depending on their dry residue, to achieve a mass thickness of about 6-8 mg/cm^2. Then, the samples were evaporated at a controlled temperature up to few millilitres on a hot plate and then transferred to a striated stainless steel planchet. This was evaporated to dryness under an infrared lamp. The samples were kept in a desiccator for a few days, (between 2 and 7 days, in order to avoid the appearance of ^{222}Rn and its descendants) and then they were weighed and counted. Alpha/beta counting was determined by averaging the results obtained from two cycles of 600 min.

The determination of the gross alpha/beta activities was conducted following the ISO norms (UNE EN ISO 10704, 2016; UNE 73340-2, 2003). The validation of the method was carried out using several samples from intercomparison exercises organised by the Spanish Nuclear Safety Commission (Consejo de Seguridad Nuclear, CSN) (Table 2).

171   Since no certified water samples were available, the samples consisted of calcareous soil

172   (CSN-2016), an atmospheric filter (CSN-2017) and milk powder (CSN-2018).

173   ***Table 2.*** *Gross alpha and beta activity concentrations obtained in the intercomparison*

174   *exercises organised by the Spanish Nuclear Safety Commission (CSN).*

175   **2.4. RADIONUCLIDE CONCENTRATIONS BY ALPHA-PARTICLE**

176   **SPECTROMETRY**

177   The radiochemical procedure to isolate both U- and Th-isotopes was based on the

178   tributylphosphate (TBP) back-extraction methodology (Holm and Fukai, 1977). In this

179   method, the sample is dissolved in 8M HNO_3, and then the actinides are extracted into

180   tributilphosphate (TBP), whereas the aqueous nitric fraction contains the rest of the non-

181   actinide radioelements (Po, Ra, etc.). Th is back-extracted by using 1.5 M HCl + Xilen,

182   and then U is back-extracted from the organic phase with distilled water. On the other

183   hand, Po and Ra remain in the 8M HNO_3 phase, and Po is self-deposited onto silver disks

184   in 2M HCl by the method proposed by Flynn (1968). The Po remaining in dissolution

185   contains the Ra-isotopes, which are isolated by cation exchange chromatography, using

186   resins such as AG50X12 (Pérez-Moreno, 2019). The thin radioactive source for U and Th

187   was obtained by electrodeposition following the methodology described by Talvitie

188   (1972) and Hallstadius (1984), whereas the one for Ra was obtained by $BaSO_4$

189   microprecipitation (Blanco et al., 2002). Then, the activity concentrations of the different

190   isotopes were measured using passivated implanted planar silicon (PIPS) detectors, (EG

191   & G Ortec). For these determinations, the samples were spiked with accurately known

192   activities of ^{232}U (138.9 $\pm$ 0.6 mBq mL^{-1}), ^{229}Th (177.6 $\pm$ 1.1 mBq mL^{-1}) and ^{209}Po (105.6

193   $\pm$ 0.7 mBq mL^{-1}).

194 The quality control of the measurements was carried out by using: a) one blank and one

195 replicate every five samples, b) several samples from the intercomparison exercise

196 organised by the Spanish Nuclear Safety Commission (CSN) and c) certified reference

197 materials: phosphogypsum (CSN-2008) and soils (IAEA-326 and IAEA-327) (Table 3).

198 *Table 3. Results obtained in the intercomparison exercise and certified reference*

199 *materials.*

200 The activity concentration of ^{210}Pb in all water samples was considered to be in secular

201 equilibrium with ^{210}Po between the sampling time and the measuring time (2 years). Thus,

202 the activity concentration of ^{210}Pb was determined by measuring that of ^{210}Po.

203 **2.5. STATISTICAL ANALYSIS**

204 A principal component analysis (PCA) using XLSTAT was conducted to analyse the

205 groundwater data. This statistical analysis was carried out to find out if the samples are

206 related to each other. PCA is a method for reduce a large number of variables, finding

207 new variables (principal components), which are ordered so that the first few retain most

208 of the variation present in all of the original variables, making the data easier to

209 understand (Jolliffe, 2002).The PCA is used to study the relationship between variables

210 and identify how groups of variables change with respect to each other The Spearman

211 correlation matrix has been used since the majority of the variables do not follow a normal

212 distribution (Davis, 2002).

213

214 **2.6. INDICATIVE DOSE**

215 According to Directive EURATOM (2013), when the following formula is satisfied

216 (Concentration Index (CI)) (Eq. 1), it may be assumed that the ID is below the parametric

217 value of 0.1 mSv and no further investigation shall be required:

9

$$CI = \sum_{i=1}^{n} \frac{Ci\ (obs)}{Ci\ (der)} \leq 1 \qquad\qquad \text{Eq. 1}$$

218

219   Where:

220   Ci (obs) = observed concentration of radionuclide i

221   Ci (der) = derived concentration of radionuclide i

222   n = number of radionuclides detected.

223   The CI was calculated for all the water samples analysed. In those cases, in which the

224   parametric value was exceeded, the ID was determined according to the measured

225   radionuclide concentrations and the dose coefficients established in Annex 3 of RD

226   783/2001 (ICRP, 2007), using the following equation, based on 730 L of annual ingestion

227   for adults:

$$\text{ID} = \sum_j h(g)_j J_j \qquad\qquad \text{Eq. 2}$$

228

229   Where:

230    $h(g)_j$ = effective dose committed per unit of incorporation by radionuclide j (Sv Bq^{-1})

231   ingested by an individual belonging to the age group g;

232   J_j = the corresponding incorporation by ingestion of radionuclide j (Bq).

233   **3. RESULTS AND DISCUSSION**

234   **3.1. PHYSICOCHEMICAL PARAMETERS**

235   The physicochemical parameters and element concentrations for all water samples are

236   shown in Figures 2-4, and Table S1 of Supplementary Information, in which the waters

10

237   were classified according the lithology. The pH ranged from 6.5 to 7.5, showing the

238   neutral character of the studied waters. The waters from carbonate aquifers shows an

239   average slightly higher (7.2 ± 0.1) (uncertainty expressed as the standard deviation of the

240   mean) than waters from granite aquifers (6.7 ± 0.2). The electrical conductivity (EC) of

241   the samples ranged from 19 to 289 $\mu S\ cm^{-1}$, with an average of $84 \pm 20\ \mu S\ cm^{-1}$ for waters

242   from granite bedrock and $231 \pm 24\ \mu S\ cm^{-1}$ for carbonate bedrock. The dry residue (DR)

243   varied from 35 to 724 mg L^{-1} (average = 179 ± 43 mg L^{-1} in granite aquifers and $507 \pm$

244   62 mg L^{-1} in carbonate aquifers). Waters from carbonate bedrock present highest values

245   of these parameters in relation to waters from granite aquifers. Concretely, CAZ, VEL

246   and SIS waters presented the highest pH (pH = 7.2 -7.4), EC (274-289 $\mu S\ cm^{-1}$) and DR

247   (591-724 mg L^{-1}), whereas AQA and SIF showed the lowest values for these three

248   parameters (pH = 5.8-6.6; EC = 19-25 $\mu S\ cm^{-1}$; DR= 35-54 mg L^{-1}). This can be observed

249   in Figure 2, where higher pH shows higher EC and DR and vice versa.

250   *Figure 2. pH, EC and DR values of the bottled waters analysed.*

251   The relationship between pH, EC and DR mainly depend on the presence of ions in the

252   solution. The concentrations of the major elements and ions are shown as box and whisker

253   plots (Figure 3). The top and bottom of the box are the first quartile (Q1) and the third

254   quartile (Q3), respectively, and the distance between them is the Interquartile Range

255   (IQR). Data beyond the 1.5·IQR may be considered as outliers (extreme values),

256   extending the whiskers to the highest and lowest values. The existence of high maximum

257   values for concentrations of these elements in some waters causes mean values to be much

258   higher than the median. According to the median values, the elements and ions can be

259   ordered from highest to lowest concentrations as follows: $HCO_3^- > Ca > SO_4^{2-} > Cl > Mg$

260   $> NO_3^- > Na > Si > K > F$. The Shapiro-Wilk normality test results (Table S2-

261   Supplementary Information) indicated that, with the exception of NO_3^- and HCO_3^-, these

262   ions do not follow a normal distribution.

263   In most cases, the high concentration of bicarbonate and calcium ions are relevant with

264   respect to the other ions. The bicarbonate concentration ranged from 13 mg L^{-1} to 409 mg

265   L^{-1}, while calcium concentration varies from 1.0 ± 0.2 mg L^{-1} to 88 ± 4 mg L^{-1}. The highest

266   concentration of these ions is found in waters from carbonated aquifers (HCO_3^-: 284 ± 39

267   mg L^{-1}; Ca: 69 ± 8 mg L^{-1}) (NAT, SOL, CAZ, AQB, VEL, SIS). In addition, the

268   concentration of magnesium is especially high in these waters (15 - 46 mg L^{-1}). The high

269   mean concentration of HCO_3^- (195 ± 33 mg L^{-1}), Ca (41 ± 9 mg L^{-1}) and Mg (27 ± 5 mg

270   L^{-1}) is clearly related to the dissolution of the carbonated (limestone and dolomite) host

271   rocks of aquifers. These relations can be clearly observed in the correlation matrix of

272   principal component analysis (PCA) and Figures S1 and S2 of Supplementary

273   Information. This fact is associated with the dominant presence of HCO_3^- in the pH range

274   of water intended for human consumption (pH = 6-8).

275   On the other hand, Na and Cl, which are typically related to the dissolution of evaporites

276   and salts, showed low correlation in the waters studied (Figure S3a- Supplementary

277   Information). Na and Cl showed a minimum value (average: 3.9 ± 0.9 mg/L and 7.7 ± 2.4

278   mg/L, respectively) in aquifers from carbonate bedrock and maximum (average: 24 ± 8

279   mg/L and 9.8 ± 1.8, respectively) from granite aquifers.

280   The SO_4^{2-} ion is usually associated in aquifers with the dissolution of sulphate evaporites

281   (mainly gypsum) interbedded with carbonated host rocks. The SO_4^{2-} concentration

282   showed a mean concentration of 3.7 ± 1.3 mg L^{-1} in waters from granite aquifers, and 28

283   ± 6 mg L^{-1} in waters from carbonate bedrock. In the studied waters, good correlations of

284   SO_4^{2-} ion with Ca were found (Figure S3b- Supplementary Information), indicating the

285   dissolution of calcium sulphates compounds in the studied waters.

286   In contrast, Si showed clearly higher concentrations in the waters from igneous and

287   metamorphic host rocks, with a maximum of 30 ± 2 mg L^{-1} (AGS). In addition, Si shows

288   certain correlations with Na and K (PCA matrix correlation), suggesting the dissolution

289   of silicates.

290   *Figure 3. Box and whisker plots of major elements and ions.*

291   Figure 4 shows the Piper diagrams. In the anionic diagram it can be seen that most of the

292   analysed waters were carbonated; only two were chlorinated, and one was mixed. On the

293   other hand, calcium was the most abundant cation, according to the cationic diagram,

294   whereas some waters contained high concentrations of sodium and potassium cations.

295   Thus, from the central diagram, 57.1 % of the waters were classified as calcium

296   bicarbonated (AQB, CAZ, REG, NAT, VEL, LAN, SIS and SOL), 21.4 % as sodium

297   bicarbonated (AGS, CAB and MON), 14.3 % as calcium chlorinated (AQA and VIR) and

298   7.1 % as sodium chlorinated (SIF).

299   *Figure 4. Piper diagram of the bottled water sources.*

300   Waters from SIF displayed a relatively high concentrations of Al, As and Mn (143 µg L-

301   1, 2.9 µg L-1 and 14.5 µg L-1, respectively). Even though SIF has the highest As

302   concentration among the investigated aquifers, the As level is still below maximum

303   contaminant level of As in drinking water (Table S1-Supplementary Information). The

304   presence of As is probably due to conditions that favour the desorption or dissolution of

305   Al and Mn oxides and/or oxyhydroxides, in which As is adsorbed (Bowell et al., 2014).

306   The occurrence of strongly reducing conditions at near-neutral pH leads to the desorption

307   of As from mineral oxides (Smedley and Kinniburgh, 2002). Presumably, similar

308   conditions caused Pb to be released into the aquifer where AQA was taken (Clausen et

309   al., 2011). In addition, it is worth highlighting the presence of Li and Cs in AGS, CAB

310   and MON, which are waters characterized by high concentrations of Na in solution (Fig.

311   4). In those cases, Li and Cs seem to have the same behaviour as sodium (PCA matrix

312   correlation), which is probably related to the dissolution of silicates in which they are

313   bonded (Deverel et al., 1990). The content of Ba in LAN, REG, VEL and MON, Sr in

314   NAT, and Ni in VEL is mainly determined by the dissolution of $BaCO_3$, $SrCO_3$ and

315    $NiCO_3$ from the host rock, respectively. Several studies have confirmed that the presence

316   of bicarbonate ions in groundwaters ensures the existence of Ba^{2+}, Sr^{2+} and Ni^{2+} in

317   solution, forming highly soluble salts (Man and Hooda,2010; Giménez-Forcada and

318   Vega-Alegre., 2015; Tudorache et al., (2018)).

319   On the other hand, the concentrations of Cd, Cr, Cu, Fe, Hg and Se were below the

320   detection limit (0.01; 0.5; 0.2; 10; 0.2; 0.2 µg L^{-1}, respectively).

321   In general, the salinity range indicates that the investigated waters are below the

322   parametric value established in RD 1798/2010 (de 30 de diciembre). Thus, all the bottled

323   waters analysed in this work are considered potable from the physicochemical point of

324   view.

325   **3.2. GROSS ALPHA-BETA ACTIVITY CONCENTRATION**

326   Gross alpha and gross beta activity concentrations in the water samples are shown in

327   Figure 5 and Table S3 of Supplementary Information. The gross alpha activity

328   concentration ranged from 10 ± 2 mBq L^{-1} (VIR) to 195 ± 13 mBq L^{-1} (VEL) with an

329   average of 69 ± 22 mBq L^{-1} and 80 ± 21 mBq L^{-1} for granite and carbonate aquifers

330   respectively, although in three water samples (AGS, BEZ and SIS) it was below the

14

331   detection limit (DL = 10 mBq L^{-1}). Three of the investigated aquifers (MON, SIF, and

332   VEL) exceeded the EU recommended level for gross alpha (0.1 Bq L^{-1}). The high level

333   of alpha activity is likely related to the lithologic composition and hydrogeological

334   parameters of the bedrock (Chau et al., 2011). In these cases, the geology is governed by

335   carbonated rocks (limestone and dolomite) located in the centre of Spain and igneous

336   rocks (granite) located in the west, north and centre (Baeza et al., 1995; Dueñas et. al,

337   1997).

338   On the other hand, the gross beta activity concentration of the water samples ranged from

339   41 ± 1 mBq L^{-1} (VIR) to 585 ± 10 mBq L^{-1} (VEL), with an average of 157 ± 43 mBq L^{-1}

340   in waters from granite bedrock and 191 ± 63 mBq L^{-1} in the carbonate bedrock. In contrast

341   with the gross alpha activity, the gross beta activity concentration of all investigated

342   samples is below the EU recommended value for drinking water of 1 Bq L^{-1}. It is worth

343   highlighting that those waters with higher gross beta activity also had higher K and Na

344   concentrations. The gross beta activity is very related to K concentration since the ^{40}K/K

345   isotopic ratio in nature is constant, i.e. 320 Bq/kg of 40K = 1% of natural K. This fact,

346   joined to the concentration of the radionuclide ^{40}K is generally 1-2 orders of magnitude

347   higher than the remaining natural beta-emitters, justify the good fitting found between

348   gross beta and ^{40}K concentration, Gross beta = (0.78 ± 0.10) [40K] + (-10 ± 33) (R2 =

349   0.90). Na is really related to K since both elements belong to the silicate compound

350   present in the bedrock, giving this fact an indirect correlation with the gross beta, formed

351   mainly by the contribution of ^{40}K.

352   *Figure 5. Gross α and β activity concentrations of the analysed water samples (DL= 10*

353   *mBq L^{-1}).*

354 These results are consistent with those of previous works (Andreo and Carrasco, 1999;

355 Martín Sanchez et al., 1999; Palomo et al., 2007), where the gross alpha and beta activities

356 of some mineral waters were analysed (AGS, AQA, BEZ, CAB, LAN, MON, SOL and

357 VEL), and which confirm that higher alpha activity concentrations generally correspond

358 to areas where granitic formations are predominant. This is due to the fact that granitic

359 rock is characterized by a high concentration of radionuclides of the ^{238}U series (Korkmaz

360 Gorur et al., 2011; Sherif and Sturchio, 2018).

361

362 **3.3. RADIONUCLIDE ACTIVITY CONCENTRATIONS**

363 The concentrations of natural radionuclides (^{210}Pb, ^{234,238}U, ^{230,232}Th, ^{226,228}Ra) in the

364 bottled waters were measured by alpha-particle spectrometry and are shown in Table 4

365 and Figure 6.

366 ***Table 4.*** *Activity concentrations (mBq L^{-1}) of ^{210}Pb, $^{238-234}$U, $^{228-226}$Ra, activity ratios of*

367 *^{234}U/^{238}U, ^{226}Ra/^{234}U, ^{210}Pb/^{226}Ra and ^{226}Ra/^{228}Ra (DL = 1 mBq L^{-1}) and Concentration*

368 *Index (CI). *Derived Concentrations (DC) for radioactivity in water intended for human*

369 *consumption (RD 314/2016).*

370 The activity concentrations of ^{210}Pb ranged from 1.4 ± 0.5 (BEZ) to 78 ± 3 mBq L^{-1} (SIF),

371 with an average value of 20 ± 7 mBq L^{-1} (uncertainty expressed as the standard deviation

372 of the mean) in waters from granite bedrock and 5.6 ± 0.7 mBq L^{-1} in carbonate aquifers.

373 The activity concentration of 52 % of the bottled waters analysed was below 10 mBq L^{-1}

374 and that of 33 % was below the detection limit (1 mBq L^{-1}). The lowest activities of ^{210}Pb

375 were measured in waters, where sedimentary rocks exist, whereas the highest activities

376 were measured in aquifers of granitic bedrock, especially the ones located in Extremadura

377 (AQA and SIF). This zone consists mainly of acidic plutonic rock (basically granite),

378 formations of low-grade metamorphism, and tertiary and quaternary sedimentary

379 materials, notably alluvia, limestone, clay and materials from the erosion of shale and

380 granite with a range of ^{238}U activity concentration of 60-80 Bq kg^{-1} (Baeza et al., 1995;

381 CSN, 2000; Galán López and Martín Sánchez., 2008). Therefore, high values of ^{210}Pb in

382 these waters are attributed to the high rates of supply due to higher total U concentrations

383 in solids, and possibly high desorption rates of ^{210}Pb (Porcelli, 2014). In this sense, AQA

384 and SIF present high Mn concentration, indicating possibly reducing conditions in which

385 ^{210}Pb is released.

386 The activity concentrations of ^{238}U ranged from 1.8 ± 0.2 (AQA) to 33 ± 2 mBq L^{-1}

387 (REG), with an average of 7.5 ± 3.3 mBq L^{-1} (granite aquifers) and 9.9 ± 1.8 mBq L^{-1}

388 (carbonate aquifers), whereas those of ^{234}U ranged between 1.8 ± 0.3 (BEZ) and 55 ± 4

389 mBq L^{-1} (SOL), with an average of 11 ± 5 mBq L^{-1} (granite aquifers) and 22 ± 6 mBq L^{-}

390 ^{1} (carbonate aquifers). Furthermore, the concentration of three waters (CAB, VIR and

391 AGS) was below the detection limit (1 mBq L^{-1}). It is worth highlighting the values of

392 ^{238}U and ^{234}U in REG water, with a concentration of 33 ± 2 mBq L^{-1} and 53 ± 3 mBq L^{-}

393 ^{1}, respectively; and in SOL water, whose concentrations for ^{238}U and ^{234}U were 20 ± 2

394 mBq L^{-1} and 55 ± 4 mBq L^{-1}. The activity concentration of ^{238}U was in agreement with

395 the uranium concentration measured by ICP-MS (R = 0.95), with an intercept value of -

396 0.38 ± 1.1 and a slope of 15 ± 1. These data are in line with the conversion factor of

397 radioelement concentration given by IAEA (2003).

398 Some samples displayed a clear disequilibrium between ^{238}U and ^{234}U. The ^{234}U/^{238}U

399 activity ratio ranged from 0.95 ± 0.22 to 3.1 ± 1.3 (Table 4); in most cases it was greater

400 than unity. The disequilibrium between these two isotopes in water is due to the

401 preferential leaching of ^{234}U, favored by alpha recoil effects (Chau et al., 2011,

17

402   UNSCEAR, 2016). The highest activity concentrations of ^{234}U were found in waters from

403   springs formed in carbonated rock, where the greatest disequilibrium between ^{238}U and

404   ^{234}U was found (SOL, CAZ, AQB, VEL and SIS). The high activity concentration of U

405   isotopes in waters from carbonated aquifers may be attributed to the formation of soluble

406   carbonate complexes such as $UO_2(CO_3)_2{}^{2-}$ and $UO_2(CO_3)_3{}^{4-}$ under oxidising conditions

407   and neutral pH (Shabana and Kinsara, 2014; Guerrero et al., 2016; Wu et al., 2018; Erőss

408   et al., 2018).

409   In some waters, the secular equilibrium between ^{238}U and ^{234}U is reached, specifically

410   NAT, LAN, BEZ, SIF and MON. This may occur as a result of two factors: 1) the long

411   residence time of the water in the aquifer, greater than the half-life of U^{234}, and 2) low

412   concentration of U^{238} in the aquifer solids, thus both isotopes could reach the equilibrium

413   in the dissolved phase.

414

415   The activity concentrations of Th-isotopes (^{228}Th, ^{230}Th and ^{232}Th) were below the

416   detection limit (1 mBq L^{-1}) in all waters. This is due to the fact that Th has only one stable

417   oxidation state (IV) under all redox conditions in natural waters. Therefore it has a very

418   low mobility under most environmental conditions, mainly due to the high stability of the

419   insoluble oxide ThO_2 (Santschi et al., 2006; Bhatti et al., 2012).

420   The activity concentrations of ^{226}Ra ranged from 1.1 ± 0.1 mBq L^{-1} (VIR) to 194 ± 9 mBq

421   L^{-1} (MON) (average of granite aquifers: 35 ± 17 mBq L^{-1}; average of carbonate aquifers:

422   20 ± 9 mBq L^{-1}). The activity concentration of 56 % of the analysed waters was lower than

423   10 mBq L^{-1} and that of only 7.4 % of the samples was below the detection limit (1 mBq

424   L^{-1}). The occurrence of Ra in groundwater depends on the concentration of the parent in

425   the rock matrix, but also on variations in Ra supply to water by alpha recoil,

426   adsorption/desorption, ion exchange and dissolution/precipitation processes (Sherif et al.,

427   2018). The relation of Ra concentrations with dominant solutes present in the waters can

428   reflect the hydrochemical factors that control their presence (Sherif and Sturchio, 2018).

429   The highest activity concentration was found in waters with granitic rock interaction,

430   specifically in the northeast of Spain (AQA, SIF and MON). This fact is expected since

431   the highest concentrations of ^{238}U (progenitor of ^{226}Ra) are found in these kinds of rocks,

432   concretely about 60-80 Bq kg^{-1} of ^{238}U in Extremadura and 80-350 Bq kg^{-1} of ^{238}U in

433   Galicia (Stackelberg et al., 2018; CSN, 2000; Taboada et al., 2006). However, VEL,

434   which interacted with carbonate rock, also presented a high activity concentration of

435   ^{226}Ra, possibly due to the preferential leaching of ^{234}U. But also, the cation exchange

436   process could be affecting the presence of radium since there is a high correlation of ^{226}Ra

437   with Cl^{-} concentration (Figure S2 – Supplementary Information).

438   The activity concentration of ^{228}Ra varied between 1.2 ± 0.5 mBq L^{-1} (CAB) and 52 ± 4

439   mBq L^{-1} (MON) (Table 4), with an average of 17 ± 5 mBq L^{-1} in waters from granite

440   bedrock and 6.7 ± 1.6 mBq L^{-1} in the carbonate bedrock one. The activity concentration

441   of 70 % of the waters was below 10 mBq L^{-1}, 26 % was between 10-50 mBq L^{-1}, and 4%

442   was above 50 mBq L^{-1}. As in the case of ^{226}Ra, the highest concentrations of ^{228}Ra were

443   found in waters from granite bedrock (AQA, REG and MON) and exceptionally in a

444   carbonate aquifers (VEL), probably because of the existence of high ion strength that

445   tends to increase the desorption of Ra isotopes (Vinson et al., 2013). These waters from

446   carbonate aquifers presented the lowest ^{228}Ra/^{226}Ra activity ratio (<< 1) (Table 4). This

447   fact is related to the preferential leaching of ^{226}Ra from the host rock with respect to ^{228}Ra

448   in waters with high carbonate concentrations, but also depend on the both ^{228}Ra and ^{226}Ra

449   half-lives (5.7 y, and 1600 y, respectively). (Chau et al., 2011; Sherif et al., 2018).

450   However in most granite aquifers, the ^{226}Ra/^{228}Ra isotopic ratio was close to one. This

451   fact is related to the ratio of the activity concentrations of its parent ^{232}Th/^{238}U in the

452   bedrock, and it is typically close to the unity for granitic or siliceous materials.

453   Most of the waters with granitic host rock presented a high disequilibrium between ^{226}Ra

454   and ^{234}U (AQA, MON and SIF) (Table 4), which indicates the preferential leaching of

455   radium over uranium. However, NAT presented an activity concentration of ^{226}Ra in

456   secular equilibrium with the decay series parents (^{238}U and ^{234}U), since they have equal

457   activities (^{234}U/^{238}U ~ 1; ^{238}U/^{226}Ra ~ 1), which means that the aquifer is sufficiently old

458   (>10^5 years) to reach the secular equilibrium between all the radionuclides of the ^{238}U

459   series.

460   Furthermore, some waters from aquifers located in Extremadura (e.g., AQA and SIF)

461   with high concentrations of ^{226}Ra also showed high concentrations of ^{210}Pb, although

462   these did not seem to be in equilibrium (Table 4). The conditions of these aquifers suggest

463   that the redox conditions are slightly predominant by comparison with the ion strength

464   in which ^{210}Pb and ^{226}Ra are released into the water respectively.

465   The existence of high maximum values for concentrations of ^{210}Pb, ^{226}Ra and ^{228}Ra causes

466   mean values to be far above the median (Figure 6), which indicates that the distribution

467   is very asymmetric. According to the Shapiro-Wilk normality test results (Table S2,

468   Supplementary Information) none of these natural radionuclides follow a normal

469   distribution.

470   *Figure 6. Box and whisker plots of natural radionuclide activity concentrations.*

471   Waters with high concentrations of ^{226}Ra, ^{234}U and/or ^{210}Po (MON, SIF, and VEL)

472   indicated gross alpha in excess of the recommended level. In addition, the gross alpha

473   calculated (G$\alpha_{calculated}$) from the activity concentration of alpha emitter radionuclides

474   contained in the waters presented a strong correlation with the gross alpha measured

475   ($G\alpha_{calculated} = (1.6 \pm 19) + (0.92 \pm 0.21) \cdot G\alpha_{measured}$; $R^2 = 0.65$).

476   The natural radionuclides activity concentrations found in the bottled waters analysed

477   were similar to those ones measured in previous studies in the Spanish region (Ortega et.

478   al., 1996; Manjon et al., 1997) and other studied aquifers (Khandaker et al., 2017; Jankovic

479   et al., 2012; UNSCEAR, 2008; Jia and Torri 2007; Kralik et al., 2003; Somlai et al.,

480   2002), not being in any case above the EU maximum level (^{238}U activity 3.0 Bq L^{-1}, ^{234}U

481   activity 2.8 Bq L^{-1}, ^{226}Ra activity 0.5 Bq L^{-1}, ^{228}Ra activity 0.2 Bq L^{-1}, ^{210}Pb activity 0.2

482   Bq L^{-1}, 210Po 0.1 Bq L^{-1}) given by a dose of 0.1 mSv (EURATOM, 2013).

483   **3.4. STATISTICAL ANALYSIS**

484   A principal component analysis (PCA) was carried out to summarize the relationships

485   between the measurement variables (Jolliffe, 2002), in order to detect relevant

486   correlations between the behaviour of the chemical components and natural radionuclides

487   in the water and the hydrochemistry of the host rock (Table 5). The concentrations below

488   the detection limit (DL) were replaced with DL/2 for the statistical analysis, since the

489   percentage of non-detects was below 15% (U.S. EPA, 2006). From the correlation matrix,

490   it is possible to observe relevant hydrochemical relationships between the dissolution of

491   the host rock and the behaviour of the elements and radionuclides in the studied water, as

492   has been commented throughout this work.

493   ***Table 5.*** *Spearman correlation matrix (non-Gaussian variables). * Significant*

494   *correlations at significant level p < 0.05.*

495

496   The 4 principal factors explain 79% of the sampling variance, although only the first two

497   are of interest (F1: 38%; F2: 22%). This percentage is relatively low, probably due to the

498   heterogeneity of the aquifer systems. F1 explains 38% of the total variance and is

499   determined by pH, EC, DR and the concentration of Ca, Mg, HCO_3^- and SO_4^- (Figure

500   7A). The concentration of Ca, Mg and HCO_3^- presented a high correlation with EC

501   (Figure S1, Supplementary Information). Thus, F1 is strongly related to the bulk

502   dissolution factor of the host rock. In the observation plot (Figure 7B), two groups of

503   waters can be distinguished: one is characterised by water from highly carbonated

504   aquifers (NAT, SOL, CAZ, AQB, VEL, REG and SIS) and the other one is characterised

505   by granitic host rock (AQA, SIF, AGS, MON, CAB, LAN and VIR). On the other hand,

506   F2 explains 22% of the total variance and is determined mainly by Cl concentration, gross

507   alpha, ^{226}Ra and ^{228}Ra activity concentration, probably associated with the presence of

508   chloride salts in solution.

509   **Figure 7.** *PCA results plot of variables (a) and observations (b).*

510   With respect to the physicochemical parameters, ^{238}U presents a relatively positive

511   correlation with Sr (0.66) and As (0.60), whereas ^{234}U shows correlation with Sr (0.76),

512   Ca (0.65), SO_4^- (0.64), pH (0.62), HCO_3^- (0.58), DR (0.57) and EC (0.56). This is the

513   reason why ^{234}U/^{238}U has the same positive correlations (pH, EC, DR, Ca, Mg and HCO_3^-

514   ). These relationships are associated with the dissolution of the carbonated host rock.

515   Moreover, the gross alpha presents a positive correlation with ^{238}U (0.67), ^{226}Ra (0.67)

516   and ^{234}U (0.55), as was expected, since they are emitters of alpha particles. Likewise,

517   ^{226}Ra shows a positive correlation with ^{228}Ra (0.83), probably due to their similar

518   chemical behaviour, Cl (0.56), possibly due to the existence of soluble complexes, and

519   ^{238}U (0.54), which is its decay series parent.

520 On the contrary, ^{210}Pb has a negative correlation with ^{234}U/^{238}U (-0.80), Ca (-0.71), pH (-

521 0.61), HCO$_3^-$ (-0.60), EC (-0.57) and DR (-0.57), whereas it only presents a positive

522 correlation with Cs (0.71) and ^{226}Ra/^{234}U (0.70).

523 **3.5. INDICATIVE DOSE**

524 The Concentration Index (CI) of the analysed waters from Equation 1 is shown in Table

525 6. Most of the waters presented a very low CI; specifically, 80 % showed a CI in a range

526 of 0.02-0.35. On the other hand, AQA and MON had a CI > 0.5. SIF is the only water

527 that obtained a CI above 1, suggesting that it could exceed the parametric value of 0.1

528 mSv. The high values are mainly due to the activity concentration of ^{226}Ra, ^{228}Ra, ^{210}Pb

529 and ^{210}Po present in these waters, which in turn are related to the granitic host rock.

530 The CI parameter only indicates whether some waters could exceed the parametric value

531 (0.1 mSv/year); for more accurate information, the dose received by ingestion should be

532 calculated. Table 5 shows the estimated annual doses by internal exposure from drinking

533 SIF, AQA and MON waters (CI > 0.5). The results indicate that only SIF waters among

534 the investigated aquifers exceed the parametric value (0.1 mSv).

535 ***Table 6.*** *Estimated annual indicative doses (ID) (mSv) by ingestion of 730 L year^{-1} for*

536 *adults from some bottled mineral waters.*

537 **4. CONCLUSION**

538 In this work, fifteen different brands of bottled drinking water from different regions of

539 Spain were characterised physicochemically and radiologically. The aims were to

540 evaluate their quality according to the current Spanish legislation of water intended for

541 human consumption, as well as to analyse the behaviour of the natural radionuclides

542 according to the hydrogeology of the water springs.

543　The waters presented a neutral character (pH around 6-7) and a low mineralization (DR

544　< 500 mg L^{-1}), with carbonate and calcium being the major ions present in aquifers with

545　carbonated lithology, whereas Si, Na and Cl were the main elements found in granitic

546　aquifers. From the physicochemical point of view, the waters complied with the criteria

547　of Spanish regulations.

548　The bottled mineral waters presented a high variability in concentrations of natural

549　radionuclides, which depend on the geology and hydrochemical conditions of the aquifer.

550　Several waters exceeded the parametric value for gross alpha, mainly due to ^{234}U, ^{226}Ra

551　and/or ^{210}Pb concentrations. These natural radionuclides are easily leached from the host

552　rock into the water under certain conditions. ^{234}U is easily leachate in presence of high

553　concentration of carbonate in solutions. ^{226}Ra in water is mainly related to the existence

554　of high concentration of chloride ions and ^{210}Pb with the reduction conditions of aquifers.

555　The estimated annual indicative doses calculated by ingestion indicated that SIF exceed

556　0.1 mSv per year. The natural radionuclides that contribute to the indicative doses are

557　especially ^{226}Ra and ^{210}Pb. In view of these facts, further research is suggested to evaluate

558　the potential risk to human health.

565

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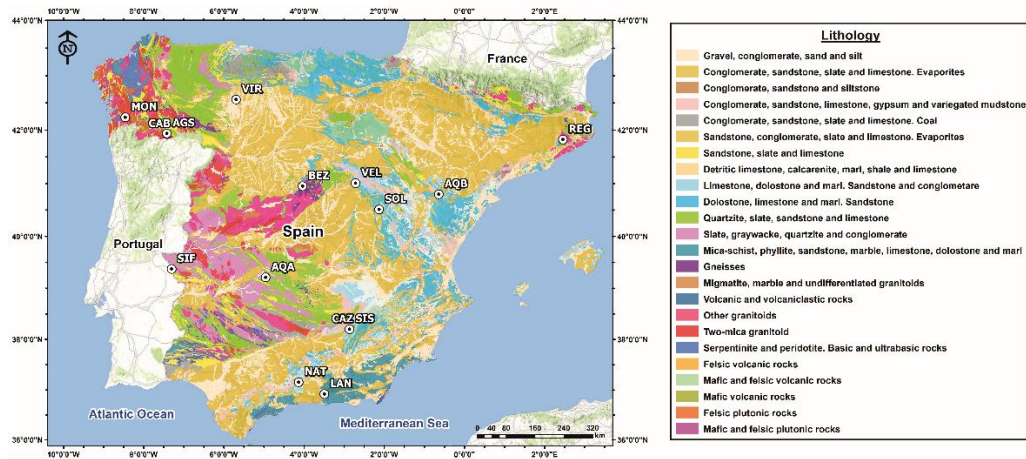
Figure 1. *General lithological map of Spain and the location of the bottled water sources analysed.*
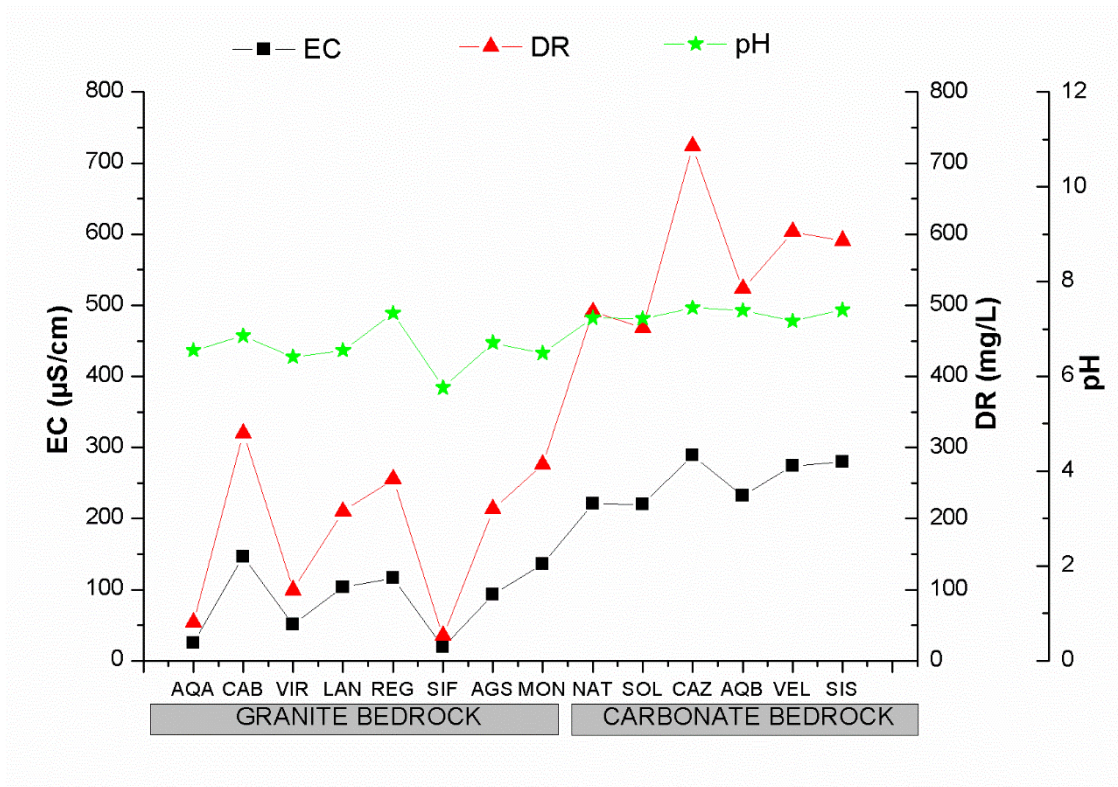
Figure 2. *pH, EC and DR values of the bottled waters analysed.*
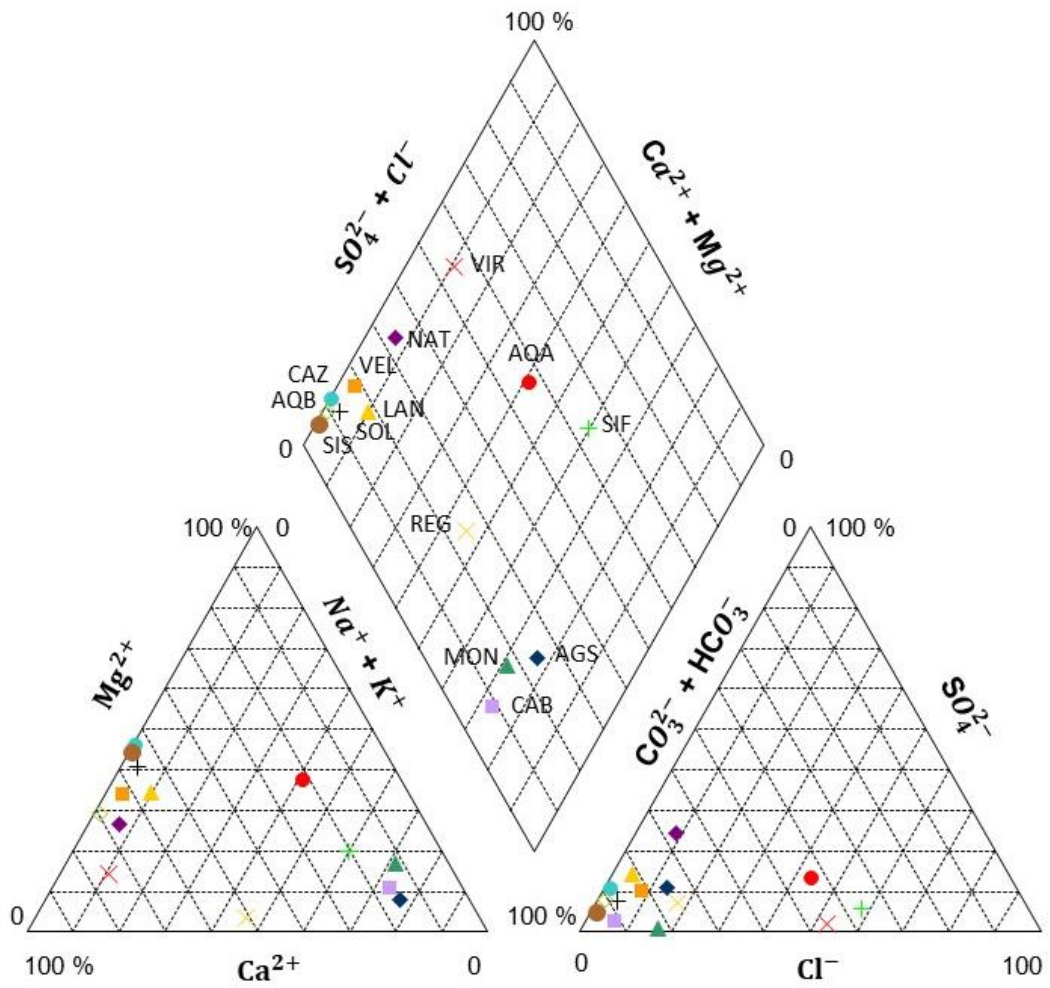
Figure 3. *Box and whisker plots of major elements and ions.*

Figure 4. *Piper diagram of the bottled water sources.*
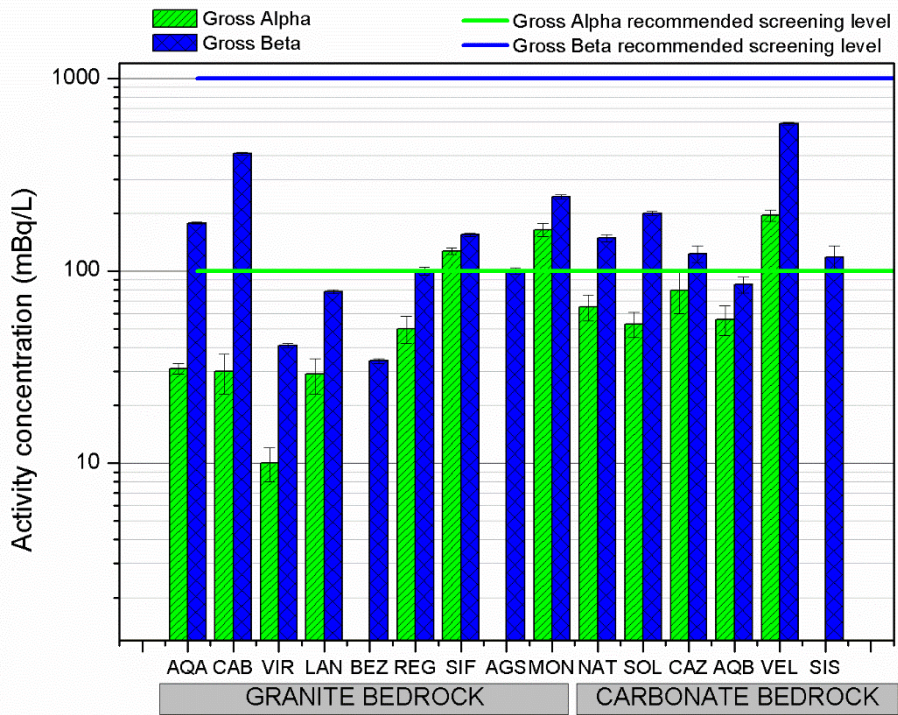
Figure 5. *Gross α and β activity concentrations of the analysed water samples (DL= 10 mBq L⁻¹).*

Figure 6. *Box and whisker plots of natural radionuclide activity concentrations.*

A

B

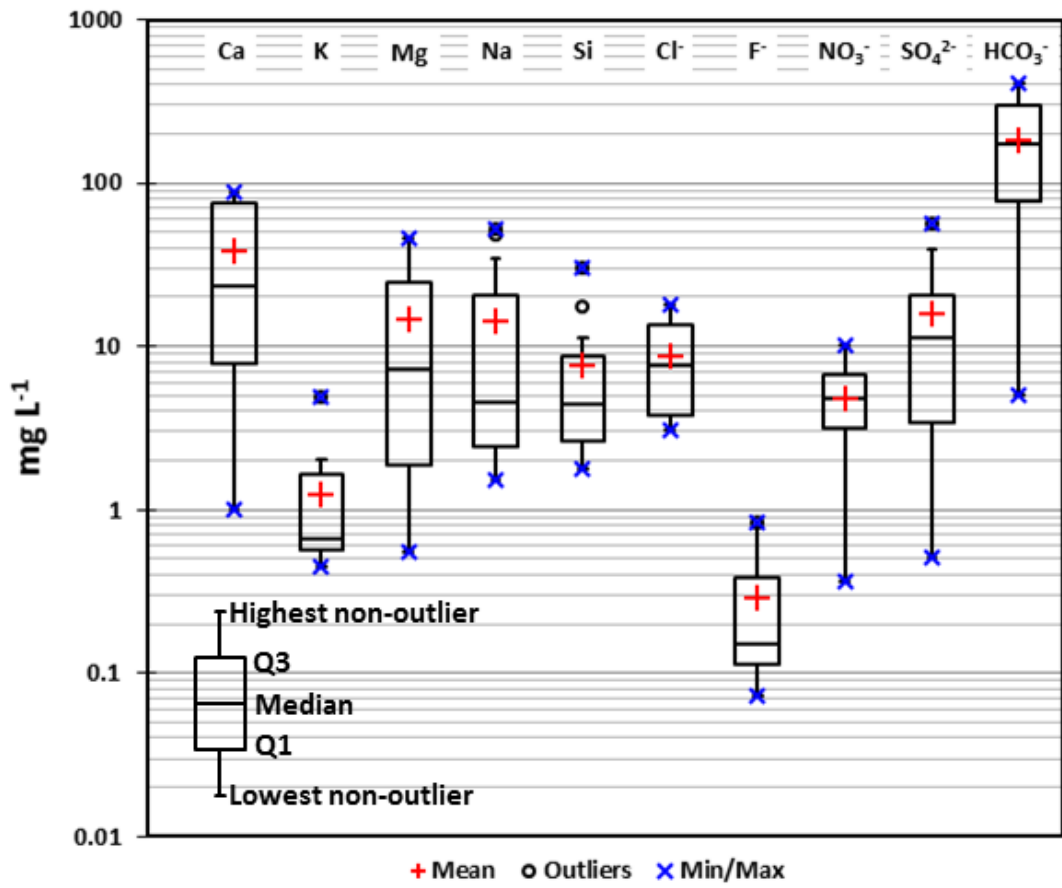**Figure 7.** *PCA results plot of variables (a) and observations (b).*

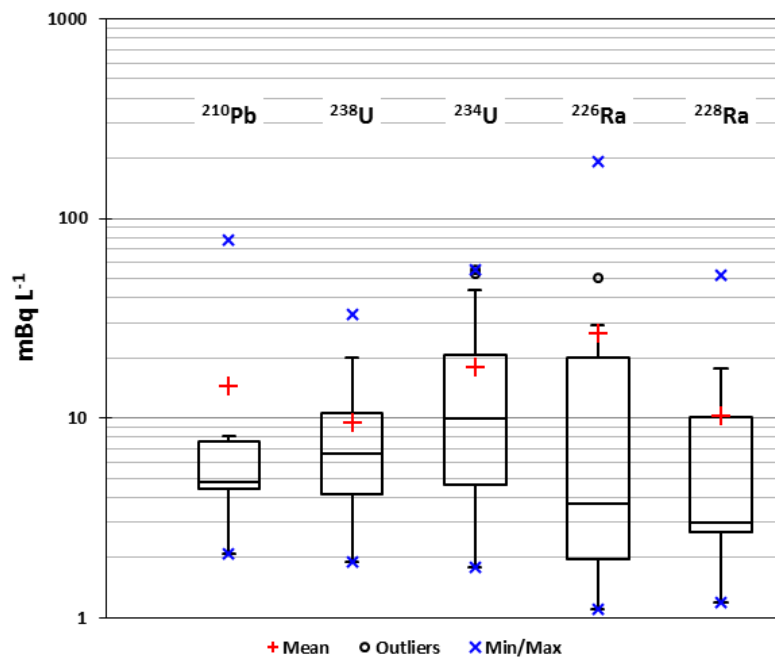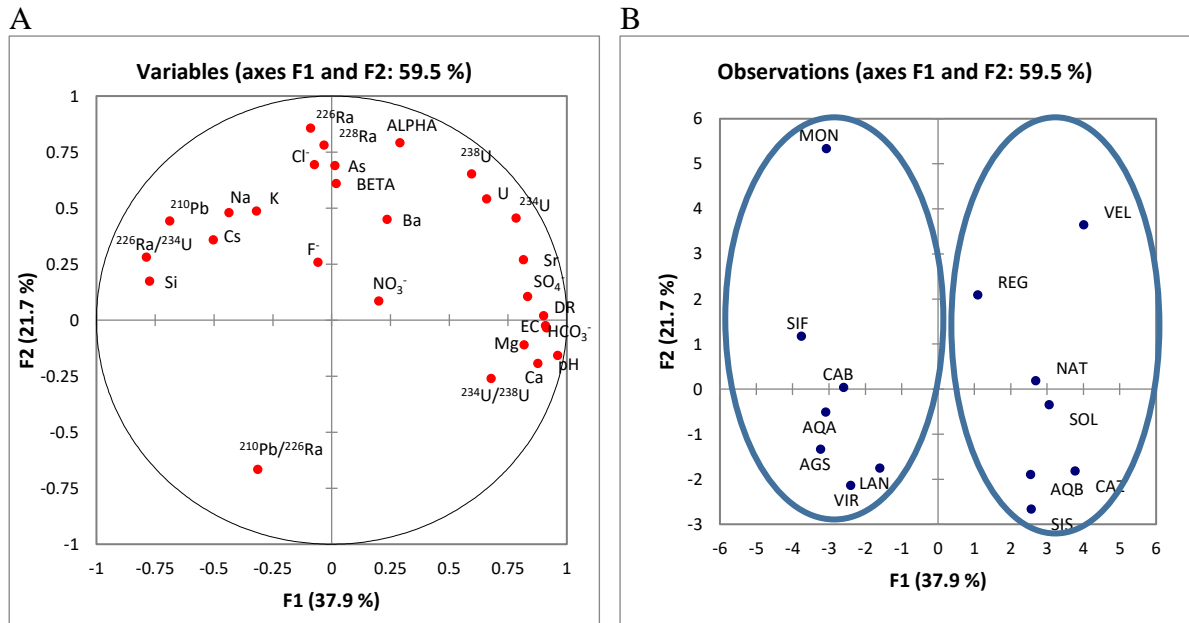| Code	Commercial Name	Batch	Province (Region)	Rock
1A-AQA	Aquarel	L616679412	Badajoz (Extremadura)	Igneous and metamorphic (granites and gneisses)
1B-AQA	Aquarel	L618379412		
1C-AQA	Aquarel	L616779412		
2A-NAT	Font Natura	8429359275006	Granada (Andalucía).	Carbonated (limestones)
2B-NAT	Font Natura	8480017269966		
2C-NAT	Font Natura	8429359275006		
3A-CAB	Cabreiroá	L:14-09-17 18:29	Orense (Galicia)	Igneous (granites)
3B-CAB	Cabreiroá	L:27-12-17 11:27		
4-VIR	Virgen del Camino	170GDMML 08:55	León (Castilla y León).	Sedimentary (Conglomerates and siliceous gravels)
5A-SOL	Solán de Cabras	L0261691256	Cuenca (Castilla La Mancha).	Carbonated (limestones)
5B-SOL	Solán de Cabras	L0261820852		
6-CAZ	Cazorla	L-27/01/18-1	Jaén (Andalucía).	Carbonated (limestones and dolomites)
7A-AQB	Aquabona	C2X1844	Teruel (Aragón).	Carbonated (limestones and dolomites)
7B-AQB	Aquabona	02M2048		
8A-LAN	Lanjarón	L-29-06-18 E21:45	Granada (Andalucía).	Metamorphic (schists)
8B-LAN	Lanjarón	L-04-07-18 E08:38		
8C-LAN	Lanjarón	L-02-06-18 E19:38		
9A-BEZ	Bezoya	LC1596	Segovia (Castilla y León).	Metamorphic (gneisses)
9B-BEZ	Bezoya	LE1746		
10A-VEL	Font Vella	L:10-06-18 JJ10:18	Guadalajara (Castilla La Mancha).	Carbonated (limestones and dolomites)
10B-VEL	Font Vella	L:22-06-18 J21:57		
10C-VEL	Font Vella	L:09-06-18 K20:52		
11-REG	Font de Regás	1411 L16167	Girona (Cataluña).	Granites and gneisses
12-SIF	Sierra Fría	27F0401	Cáceres (Extremadura)	Granites and gneisses
13-SIS	Sierra de Segura	L-17/06/18-6	Jaén (Andalucía).	Carbonated (limestones and dolomites)
14-AGS	Aguas de Sousas	07/07/2016 8:50	Ourense (Galicia).	Granites and gneisses
15-MON	Mondariz	020818-1121	Pontevedra (Galicia).	Granites and gneisses

Table 1. *Summarised information of the different brands of bottled water analysed.*

Samples	Certified activity values (Bq/kg)	Measured activity values (Bq/kg)	$Z_{score} = \dfrac{\lvert X_{measured} - X_{certified} \rvert}{\sqrt{\sigma^2_{measured} - \sigma^2_{certified}}}$
Gross alpha			
CSN-2016	282 ± 56	279 ± 32	0.05
CSN-2017	0.113 ± 0.004	0.184 ± 0.006	0.07
CSN-2018	36 ± 21	51 ± 12	0.65
Gross beta			
CSN-2016	570 ± 114	640 ± 18	0.61
CSN-2017	1.39 ± 0.03	1.66 ± 0.03	0.27
CSN-2018	625 ± 52	686 ± 14	1.15

Table 2. *Gross alpha and beta activity concentrations obtained in the intercomparison exercises organised by the Spanish Nuclear Safety Commission (CSN).*

Samples	Radionuclides	Certified activity values (Bq/kg)	Measured activity values (Bq/kg)	Zscore
CSN-2008	^{210}Po	568 ± 157	574 ± 28	0.04
	^{238}U	55 ± 10	55 ± 4	0.03
	^{234}U	56 ± 10	55 ± 4	0.07
	^{230}Th	332 ± 66	335 ± 11	0.05
	^{232}Th	6.1 ± 1.2	6.5 ± 0.8	0.28
	^{226}Ra	573 ± 115	607 ± 25	0.54
IAEA-326	^{210}Po	25.7 ± 9.0	31.3 ± 1.9	0.62
	^{238}U	29.4 ± 2.8	23.5 ± 1.6	1.53
	^{234}U	29.3 ± 2.8	24.5 ± 1.6	1.81
	^{230}Th	34.1 ± 4.6	33.3 ± 2.5	0.15
	^{232}Th	39.4 ± 3.6	39.8 ± 2.7	0.09
	^{226}Ra	32.6 ± 3.2	35.7 ± 3.0	1.00
	^{228}Ra	40.1 ± 0.6	38.8 ± 9.2	0.40
IAEA-327	^{210}Po	28.4 ± 9.8	33.7 ± 2.1	0.53
	^{238}U	32.8 ± 2.0	29.1 ± 2.5	1.8
	^{234}U	31.9 ± 3.0	27.1 ± 2.4	0.71
	^{230}Th	34.1 ± 3.4	31.7 ± 1.9	0.62
	^{232}Th	38.7 ± 3.0	40.6 ± 2.2	0.51
	^{226}Ra	34.1 ± 2.8	29.7 ± 2.5	1.69
	^{228}Ra	38.7 ± 1.8	38.1 ± 8.7	0.07

Table 3. *Results obtained in the intercomparison exercises and certified reference materials.*

	Samples	^{238}U (mBq/L)	^{234}U (mBq/L)	^{226}Ra (mBq/L)	^{210}Pb (mBq/L)	^{228}Ra (mBq/L)	^{234}U/^{238}U	^{226}Ra/^{234}U	^{210}Pb/^{226}Ra	^{228}Ra/^{226}Ra	CI
	DC*	2800	3000	500	100	200	-	-	-	-	-
GRANITE AQUIFERS	AQA-1	1.8 ± 0.2	2.8 ± 0.3	34 ± 3	31 ± 1	37 ± 7	1.6 ± 0.2	12 ± 2	0.91 ± 0.09	1.1 ± 0.2	0.72
	AQA-2	1.9 ± 0.2	3.3 ± 0.3	27 ± 3	36 ± 1	26 ± 6	1.7 ± 0.2	8 ± 1	1.3 ± 0.2	1.0 ± 0.2	0.73
	AQA-3	2.1 ± 0.2	2.9 ± 0.3	26 ± 3	43 ± 1	39 ± 7	1.4 ± 0.2	9 ± 1	1.7 ± 0.2	1.5 ± 0.3	0.89
	CAB-1	<LD	<LD	<LD	4.8 ± 0.7	<LD	-	-	-	-	0.06
	CAB-2	<LD	<LD	3.7 ± 0.3	6.0 ± 0.9	1.2 ± 0.5	-	-	1.6 ± 0.3	0.3 ± 0.1	0.07
	VIR	<LD	<LD	1.1 ± 0.1	< LD	1.3 ± 0.4	-	-	-	1.2 ± 0.4	0.01
	BEZ-1	1.9 ± 0.3	1.8 ± 0.3	2.4 ± 0.2	1.4 ± 0.5	3.4 ± 0.7	0.95 ± 0.22	1.3 ± 0.2	0.58 ± 0.21	1.4 ± 0.3	0.04
	BEZ-2	<LD	<LD	<LD	5.0 ± 0.9	2.5 ± 0.6	-	-	-	-	0.09
	REG	33 ± 2	53 ± 3	5.7 ± 0.3	2.8 ± 0.5	13 ± 1	1.6 ± 0.1	0.11 ± 0.01	0.49 ± 0.09	2.3 ± 0.2	0.15
	SIF	6.9 ± 0.5	6.1 ± 0.4	50 ± 2	78 ± 3	7.3 ± 0.8	0.88 ± 0.09	8.2 ± 0.6	1.6 ± 0.1	0.1 ± 0.1	1.31
	AGS	<LD	<LD	2.3 ± 0.2	4.6 ± 0.5	2.5 ± 0.5	-	-	2.0 ± 0.3	1.1 ± 0.2	0.09
	MON	5.1 ± 1.1	5.1 ± 1.0	194 ± 9	7.1 ± 0.8	52 ± 4	1.0 ± 0.3	38 ± 8	0.04 ± 0.01	0.3 ± 0.1	0.76
	MEAN	**7.5 ± 3.3**	**11 ± 5**	**35 ± 17**	**20 ± 7**	**17 ± 5**	**1.3 ± 0.1**	**11 ± 3.7**	**1.1 ± 0.2**	**1.0 ± 0.2**	**0.41 ± 0.13**
CARBONATE AQUIFERS	NAT-1	9.6 ± 0.9	11 ± 1	8.0 ± 0.5	4.8 ± 0.6	2.6 ± 0.8	1.1 ± 0.1	0.73 ± 0.08	0.60 ± 0.09	0.3 ± 0.1	0.11
	NAT-2	8.3 ± 0.8	8.9 ± 0.8	6.9 ± 0.4	<LD	2.6 ± 1.1	1.1 ± 0.1	0.78 ± 0.08	-	0.4 ± 0.2	0.03
	NAT-3	8.7 ± 0.7	11 ± 1	7.5 ± 0.4	<LD	3.2 ± 0.8	1.3 ± 0.2	0.68 ± 0.07	-	0.4 ± 0.1	0.04
	SOL-1	17 ± 1	50 ± 2	9.0 ± 0.7	< LD	5.7 ± 1.3	2.9 ± 0.2	0.18 ± 0.02	-	0.6 ± 0.2	0.07
	SOL-2	23 ± 2	60 ± 5	13 ± 1	< LD	5.6 ± 1.4	2.6 ± 0.3	0.22 ± 0.02	-	0.4 ± 0.1	0.08
	CAZ	6.3 ± 1.2	12 ± 2	2.2 ± 0.2	2.1 ± 0.7	2.9 ± 0.7	1.9 ± 0.5	0.18 ± 0.03	0.95 ± 0.33	1.3 ± 0.3	0.06
	AQB-1	6.2 ± 1.2	14 ± 2	1.2 ± 0.2	< LD	3.0 ± 0.6	2.3 ± 0.5	0.09 ± 0.02	-	2.5 ± 0.7	0.02
	AQB-2	8.0 ± 1.7	12 ± 2	1.7 ± 0.2	< LD	2.7 ± 0.6	1.5 ± 0.4	0.14 ± 0.03	-	1.6 ± 0.4	0.02
	LAN-1	3.5 ± 1.0	3.6 ± 0.9	1.6 ± 0.2	8.5 ± 0.6	3.4 ± 0.6	1.0 ± 0.4	0.44 ± 0.12	5.3 ± 0.8	2.1 ± 0.5	0.15
	LAN-2	2.8 ± 1.3	2.3 ± 0.9	2.0 ± 0.3	7.6 ± 0.6	5.2 ± 0.9	0.96 ± 0.57	0.74 ± 0.30	3.8 ± 0.6	2.6 ± 0.6	0.15
	LAN-3	4.0 ± 0.9	3.5 ± 0.8	1.6 ± 0.3	8.1 ± 0.6	8.6 ± 1.4	0.95 ± 0.31	0.42 ± 0.13	5.1 ± 1.0	5.4 ± 1.3	0.17
	VEL-1	19 ± 4	52 ± 9	90 ± 3	4.3 ± 0.5	17 ± 1	2.7 ± 0.7	1.7 ± 0.3	0.05 ± 0.01	0.2 ± 0.1	0.35
	VEL-2	14 ± 2	39 ± 5	76 ± 3	4.1 ± 0.5	15 ± 1	2.8 ± 0.5	1.9 ± 0.3	0.05 ± 0.01	0.2 ± 0.1	0.31
	VEL-3	13 ± 4	40 ± 12	85 ± 3	<LD	21 ± 2	3.1 ± 1.3	2.1 ± 0.6	-	0.3 ± 0.1	0.29
	SIS	4.4 ± 1.6	9.7 ± 2.6	1.3 ± 0.2	<LD	2.6 ± 0.6	2.2 ± 1.0	0.13 ± 0.04	-	2.0 ± 0.6	0.02
	MEAN	**9.9 ± 1.8**	**22 ± 6**	**20 ± 9**	**5.6 ± 0.7**	**6.7 ± 1.6**	**1.9 ± 0.2**	**0.7 ± 0.2**	**2.3 ± 0.6**	**1.4 ± 0.4**	**0.13 ± 0.03**

3

Table 4. *Activity concentrations (mBq L⁻¹) of ^{210}Pb, $^{238-234}$U, $^{228-226}$Ra, activity ratios of ^{234}U/^{238}U, ^{226}Ra/^{234}U, ^{210}Pb/^{226}Ra and ^{226}Ra/^{228}Ra (DL = 1 mBq L⁻¹) and Concentration Index (CI). *Derived Concentrations (DC) for radioactivity in water intended for human consumption (RD 314/2016).*

Variables	pH	EC	DR	As	Ba	Ca	Cs	K	Mg	Na	Si	Sr	U	Cl⁻	F⁻	NO₃⁻	SO₄⁻	HCO₃⁻	ALPHA	BETA	^{238}U	^{234}U	^{226}Ra	^{228}Ra	^{210}Pb	^{234}U/^{238}U	^{226}Ra/^{234}U	^{210}Pb/^{226}Ra
pH	**1.00**																											
EC	**0.84**	**1.00**																										
DR	**0.83**	**0.99**	**1.00**																									
As	-0.28	-0.15	-0.16	**1.00**																								
Ba	-0.04	0.15	0.13	0.50	**1.00**																							
Ca	**0.86**	**0.91**	**0.89**	-0.05	0.27	**1.00**																						
Cs	-0.28	-0.27	-0.25	0.09	-0.11	-0.49	**1.00**																					
K	-0.47	-0.14	-0.09	0.21	0.25	-0.36	0.51	**1.00**																				
Mg	**0.70**	**0.90**	**0.88**	-0.13	0.16	**0.82**	-0.34	-0.12	**1.00**																			
Na	-0.31	-0.24	-0.20	0.02	0.09	-0.47	**0.79**	**0.76**	-0.35	**1.00**																		
Si	**-0.56**	**-0.67**	**-0.64**	-0.09	-0.05	**-0.76**	**0.72**	0.52	**-0.70**	**0.76**	**1.00**																	
Sr	**0.75**	**0.73**	**0.73**	0.20	0.40	**0.78**	-0.08	-0.10	**0.55**	-0.04	-0.44	**1.00**																
U	0.49	0.41	0.42	0.53	0.33	0.49	-0.26	-0.07	0.29	-0.11	-0.39	**0.72**	**1.00**															
Cl⁻	-0.22	-0.06	0.01	0.18	0.38	-0.18	0.13	0.45	-0.20	**0.54**	0.20	0.16	0.24	**1.00**														
F⁻	0.21	0.17	0.20	-0.14	0.05	-0.02	**0.79**	0.40	-0.03	**0.78**	0.52	0.29	-0.04	0.21	**1.00**													
NO₃⁻	0.08	0.32	0.37	0.21	-0.28	0.22	0.14	0.22	0.25	-0.03	-0.29	0.13	0.05	-0.09	0.09	**1.00**												
SO₄⁻	**0.77**	**0.78**	**0.79**	0.15	0.17	**0.82**	-0.14	-0.17	**0.77**	-0.19	**-0.58**	**0.79**	0.58	-0.11	0.18	0.42	**1.00**											
HCO₃⁻	**0.84**	**1.00**	**0.99**	-0.17	0.16	**0.90**	-0.30	-0.13	**0.91**	-0.26	**-0.66**	**0.71**	0.42	-0.07	0.14	0.28	**0.77**	**1.00**										
ALPHA	0.00	0.25	0.29	**0.64**	0.29	0.15	0.07	0.23	0.16	0.01	-0.24	0.39	**0.56**	0.43	-0.05	0.38	0.28	0.24	**1.00**									
BETA	-0.07	0.19	0.24	0.10	-0.13	-0.15	0.26	0.48	0.17	0.41	0.06	-0.02	0.18	0.50	0.18	0.23	0.05	0.20	**0.56**	**1.00**								
^{238}U	0.40	0.37	0.39	**0.60**	0.36	0.43	-0.20	-0.02	0.24	-0.06	-0.36	**0.66**	**0.97**	0.34	-0.02	0.11	0.53	0.38	**0.67**	0.27	**1.00**							
^{234}U	**0.62**	**0.56**	**0.57**	0.43	0.39	**0.65**	-0.35	-0.16	0.42	-0.22	-0.48	**0.76**	**0.96**	0.17	-0.03	0.03	**0.64**	**0.58**	0.55	0.58	**0.94**	**1.00**						
^{226}Ra	-0.28	-0.16	-0.11	**0.58**	0.27	-0.29	0.16	0.33	-0.09	0.24	0.07	0.00	0.45	**0.56**	-0.05	0.02	-0.01	-0.15	**0.67**	**0.57**	0.54	0.34	**1.00**					
^{228}Ra	-0.20	-0.15	-0.14	**0.65**	0.48	-0.18	0.08	0.10	-0.10	0.08	0.08	0.05	0.45	0.35	-0.07	-0.27	-0.04	-0.13	**0.62**	0.38	0.52	0.44	**0.83**	**1.00**				
^{210}Pb	**-0.61**	**-0.57**	**-0.57**	0.42	-0.18	**-0.71**	**0.71**	0.30	-0.50	0.44	0.52	-0.47	-0.26	0.07	0.24	0.17	-0.34	**-0.60**	0.22	0.33	-0.15	-0.39	0.45	0.41	**1.00**			
^{234}U/^{238}U	**0.59**	**0.63**	**0.67**	-0.44	-0.04	**0.62**	-0.62	-0.09	**0.61**	-0.32	-0.46	0.33	0.29	-0.02	-0.20	0.05	0.42	**0.68**	-0.02	0.15	0.19	0.42	-0.21	-0.25	**-0.80**	**1.00**		
^{226}Ra/^{234}U	**-0.82**	**-0.61**	**-0.57**	0.04	-0.18	**-0.81**	0.43	0.42	-0.51	0.39	0.48	**-0.70**	**-0.57**	0.38	-0.02	0.08	**-0.65**	**-0.62**	0.14	0.41	-0.44	**-0.66**	0.41	0.21	**0.70**	-0.51	**1.00**	
^{210}Pb/^{226}Ra	-0.22	-0.33	-0.37	-0.18	-0.41	-0.22	-0.02	-0.04	-0.12	-0.22	0.15	-0.43	-0.40	**-0.77**	-0.24	0.10	-0.19	-0.31	**-0.59**	-0.49	-0.49	-0.46	-0.50	-0.52	0.03	-0.09	-0.08	**1.00**

Table 5. Spearman correlation matrix (non-Gaussian variables). * Significant correlations at significant level p < 0.05.

Samples	ID
SIF	0.12
AQA	0.07
MON	0.08

Table 6. *Estimated annual indicative doses (ID) (mSv) by ingestion of 730 L year^{-1} for adults from some bottled mineral waters.*