Hydrochemistry and $^{222}$Rn Concentrations in Spring Waters in the Arid Zone El Granero, Chihuahua, Mexico

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Abstract: Water in arid and semi-arid environments is characterized by the presentation of complex interactions, where dissolved chemical species in high concentrations have negative effects on the water quality. Radon is present in areas with a high uranium and radium content, and it is the main contributor of the annual effective dose received by humans. The objective of this study was to evaluate concentrations of $^{222}$Rn and the water quality of spring waters. Water was classified as calcium sulfated and sodium sulfated. Most of the water samples with high radon concentrations presented higher concentrations of sulfates, fluorides, and total dissolved solids. $^{222}$Rn concentrations may be attributed to possible enhancement of $^{226}$Ra due to temperature and salinity of water, as well as evaporation rate. In 100% of the sampled spring waters the $^{222}$Rn levels exceeded the maximum acceptable limit which is proposed by international institutions. Aridity increases radiological risk related to $^{222}$Rn dose because spring waters are the main supply source for local populations. The implementation of environmental education, strategies, and technologies to remove the contaminants from the water are essential in order to reduce the health risk for local inhabitants.

Keywords: dissolved chemical species; $^{222}$Rn; springs; arid zones; Chihuahua

1. Introduction

Surface and groundwater naturally contain dissolved chemical species, mainly as a result of leaching from rocks that are in contact with the water. However, the sum of the concentrations of $\text{Ca}^{+2}$, $\text{Mg}^{+2}$, $\text{K}^{+1}$, $\text{Na}^{+1}$, $\text{HCO}_3^-$, $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{F}^-$, $\text{NO}_3^-$, and $\text{H}_4\text{SiO}_4$ dissolved in the water can negatively affect the water quality for both use and human consumption.

$^{222}$Rn is a radioisotope that belongs to the uranium family. It is formed by the radioactive disintegration of $^{226}$Ra and is an alpha emitter [1]. Radon is an inert gas, which displaces relatively freely through pores in the soil or fragmented rocks. When these pores are saturated with water, as happens in soils and rocks situated below the water table, radon is dissolved into the water in which it is transported. Therefore, radon present in groundwater can reach the surface water from where it can emanate to the atmosphere. The solubility of radon in water depends mainly on its concentration, as well as water volume, temperature, and pressure; thus, the content of radon decreases with an increase in temperature [2,3] and increases to high pressure [4]. Exposure to radon and its disintegration products has been associated with an increase in the risk of lung and stomach cancer through inhalation.
or ingestion, respectively [5]. The exposure to radon by inhalation is likely 4 times higher than by ingestion. Therefore, the risk of lung cancer due to inhalation is far much higher than the risk of stomach cancer by water consumption. Furthermore, radon is considered to represent approximately 50% of the annual effective dose received by human beings, with an origin in natural sources [6]. Because of this, it is considered of vital importance to evaluate the levels of $^{222}\text{Rn}$ in the environment.

Previous results have shown that the concentrations of uranium, radium, and radon in surface and ground water, evaluated in several locations in the state of Chihuahua, are mainly elevated in the cities of Aldama and Chihuahua [7–11]. In addition, the water in the thermal springs of San Diego de Alcalá, close to the influx of the river Chuvíscar with the river Conchos, has been observed to have a high activity concentration of dissolved $^{226}\text{Ra}$, with levels of 5.6 Bq/L [7]. Due to this, studies on the content of dissolved chemical species in natural water bodies are always important. The objective of the present study was to evaluate concentrations of $^{222}\text{Rn}$ and the water quality of spring waters that are the principal water source of the local villages in the region of El Granero. These results can be used to select and test appropriate treatments for these waters, before they can be consumed or used by human beings.

2. Materials and Methods

2.1. Study Area

The reservoir Luis L. León (Granero dam) is located in the municipality of Aldama, a region characterized mostly by a desert aspect, and presents a rocky mountain range of the northern central plateau. Physiographically, it is located in the ancient lake area of the Sierra Madre Oriental [12], around 28°59′7″ N and 105°16′48″ W, with an altitude of 1080 m. The Granero region is composed of elongated mountain ranges that follow a general N-NW orientation and that stand in isolation from the desert plains of this region. The outcropping rocks in the region are sedimentary (mainly of marine origin), intrusive igneous, and volcanic, dating from the Upper Jurassic to the present [13].

On the other hand, the semiconfined aquifer is placed in alluvial deposit and sequences of rocks of low permeability [14]. The exposed lithologic sequences are composed of carbonate and sandy-clay rocks (Paleozoic rocks), calcareous-clayey sequence from Upper Jurassic, evaporitic and carbonated rocks (Cretaceous sequence), and continental rocks (composed by silica) from Paleogene-Neogene. This aquifer is divided in four hydrogeological units, according to their physical properties. The springs under study are placed in the hydrogeological unit denominated UH3 [14]. It is constituted by lower Cretaceous limestones that have secondary porosity due to dissolution; towards mountain ranges foothills, the contact of water with low permeability rocks originates springs. The most important spring is located in Chorreras Village. Figure 1 shows the locations of the springs that were sampled. Likewise, the geological conditions of El Granero reservoir zone are presented in Figure 2.
Figure 1. Satellite image of the study area, reservoir El Granero. The sampling points indicate the locations of the springs (P1, P2, P3, P4, P5, and P6).
2.2. Sampling

Sampling was carried out in November 2014. Surrounding the El Granero dam, there are six sources of spring water which were selected to sampling. The water from the springs feed the reservoir El Granero and are the main water supply for the local inhabitants. The physical-chemical properties temperature (T), total dissolved solids (TDS), oxidation-reduction potential (ORP), and pH of the spring waters were determined in situ. These parameters were measured using a multiparametric portable equipment (Oakton, Waterproof Multi-parameter Tests), previously calibrated using confidence solutions to pH, ORP, and conductivity (OAKTON). To determine radon in the water, samples were collected in 20 mL scintillation vials [15]; a duplicate was collected for every sample. The sampling locations were marked with a global positioning system (GPS). In addition, a second water sample was collected in 1 L polyethylene recipients with the capacity to determine fluorides, hardness, sulfates, nitrates, calcium, magnesium, and sodium. These samples were preserved on ice at a temperature of approximately 4 °C.

2.3. Determination of Dissolved Ions

Dissolved chemical species were determined using different normative methods standardized in the Department of Water Quality of the Research Center of Advanced Materials (CIMAV). Every sample was analyzed by triplicate. Anions were determined using the following methods: (a) for sulfates the method proposed by HACH was used, using a HACH spectrophotometer, model DR 2010 (<1% of measurement uncertainty); and (b) fluorides were analyzed using the ion-selective electrode method based on the operation procedure of the equipment Orion 1260. Cations such as Ca, Mg, Na, K, and Si were determined following Mexican regulations [16] using an atomic absorption spectrophotometer (Model Avanta, Sigma, GBC Scientific Equipment, Hampshire, IL, USA). Because the hardness of the water is mainly influenced by the ions Ca^{2+} and Mg^{2+}, expressed in mg/L of CaCO_3 or meq/L, it was calculated using Equation (1):
Hardness (mg/L CaCO$_3$) = (meq Ca/L + meq Mg/L) $\times$ 50 \hspace{1cm} (1)

where 1 meq/L CaCO$_3$ is equivalent to 50 mg/L CaCO$_3$.

2.4. Determination of $^{222}$Rn

Preparation of the samples to determine the concentration of $^{222}$Rn in surface water was performed using the external standard method (relative analysis) of liquid scintillation. To extract radon, 20 mL of the sample was taken and mixed with the liquid scintillant Betaplate HiSafe by shaking for 1 min. The organic phase was placed in a glass vial with a capacity of 20 mL. Once radon was extracted, the sample was stored for approximately 3 h to prevent chemical “shut down”. The measurement of the samples was performed using the liquid scintillation detector TRIATHLER HIDEX OY, with a measurement time of 50 min. For the relative analysis, 0.25 mL of a standard of $^{226}$Ra (SRM-4965 certified material by US NIST) was added to the vial and filled with Betaplate HiSafe liquid scintillator until completing 20 mL. The measurement efficiency was 60%.

The $^{222}$Rn activity concentration (Bq/L) was determined using the following equation:

$$C_{\text{Rn}} = \frac{\text{CPS}_\alpha}{(a \times \varepsilon \times V)} \hspace{1cm} (2)$$

where CPS$_\alpha$ is a net count index in counts per second, registered for the region of detection alpha, $\varepsilon$ is the detection efficiency, $a$ is the number of alpha disintegrations of $^{222}$Rn and its descendants $^{218}$Po and $^{214}$Po, and $V$ is the water volume added to the vial in liters. In addition, corrections were applied in function of the decay time of radon from the time of sample collection to the time of measurement. The relative error of the $^{222}$Rn activity concentration was less than 5%.

The annual effective doses by ingestion from spring water samples was calculated using the equation described in [5]:

$$E_{w1} (\text{nSv/y}) = C_{\text{Rn}} \times C_w \times EDc \hspace{1cm} (3)$$

where $E_{w1}$ is the effective dose for $^{222}$Rn ingestion, $C_{\text{Rn}}$ is the radon concentration in water (Bq/L), $C_w$ is the weighted estimated of water consumption (60 L/y), and EDc is the Effective Dose Coefficient for ingestion (3.5 nSv/Bq).

2.5. Statistical Analysis

A multiple linear regression model was performed to determine the change of every ion with respect to TDS, by using the PROC GLM, SAS® (SAS Institute: Cary, NC, USA); under Equation (4). Previously, an analysis to select the ions that contribute significantly in the model was performed, using the regression stepwise method.

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \ldots \ldots + \beta_nX_n + \varepsilon \hspace{1cm} (4)$$

where $Y$ is the TDS concentration, $\beta$ is the ion coefficient, $X$ is the ion concentrations, and $\varepsilon$ is the randomness error.

2.6. Generation of the Spatial Distribution for the Inverse of the Distance (IDW)

The distribution map for the $^{222}$Rn concentrations in water was obtained by Spatial Analysis and Geoprocessing-Interpolation. This raster map was generated using Inverse Distance Weighted (IDW) interpolation in ArcGIS 9.0 (ESRI, Redlands, CA, USA).

3. Results

Water quality is determined by its physical and chemical parameters, as well as the contents of trace elements. Moreover, with the evaluation of these characteristics, the water quality can be determined in terms of its different uses: consumption, irrigation, and supporting aquatic life. Table 1
shows the results of parameters measured in situ such as pH, temperature (T), oxidation-reduction potential (ORP), and total dissolved solids (TDS), as well as the geographic coordinates of each sampling point.

Table 1. Results of the physical-chemical parameters measured in situ, and geographic coordinates of each sampling point.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>T (°C)</th>
<th>ORP (mV)</th>
<th>TDS (mg/L)</th>
<th>North (N)</th>
<th>West (O)</th>
<th>Altitude (MSL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>6.9</td>
<td>28.2</td>
<td>158</td>
<td>410</td>
<td>28°51′2.11″</td>
<td>105°16′11.49″</td>
<td>1168</td>
</tr>
<tr>
<td>P2</td>
<td>6.6</td>
<td>30.7</td>
<td>149</td>
<td>440</td>
<td>28°51′1.23″</td>
<td>105°16′13.85″</td>
<td>1168</td>
</tr>
<tr>
<td>P3</td>
<td>6.5</td>
<td>31.4</td>
<td>153</td>
<td>420</td>
<td>28°50′58.52″</td>
<td>105°16′20.16″</td>
<td>1160</td>
</tr>
<tr>
<td>P4</td>
<td>6.6</td>
<td>27.2</td>
<td>132</td>
<td>270</td>
<td>28°54′22.10″</td>
<td>105°20′9.86″</td>
<td>1029</td>
</tr>
<tr>
<td>P5</td>
<td>6.8</td>
<td>28.5</td>
<td>138</td>
<td>930</td>
<td>28°55′0.45″</td>
<td>105°20′4.66″</td>
<td>1043</td>
</tr>
<tr>
<td>P6</td>
<td>6.4</td>
<td>27.2</td>
<td>158</td>
<td>1180</td>
<td>28°54′7.25″</td>
<td>105°16′18.36″</td>
<td>1084</td>
</tr>
</tbody>
</table>

* MSL, meters above sea level. T, temperature; ORP, oxidation-reduction potential; TDS, total dissolved solids.

In the samples taken from the spring waters of El Granero, the pH values varied from slightly acidic to neutral. In addition, in the spring water the T was found to vary between 27.2 and 31.4 °C, whereas the results from ORP presented a slight variation from 132 to 158 mV, which indicates that the water featured suboxic conditions [17]. Furthermore, the values of TDS presented a high variability, with a concentration range from 270 up to 1180 mg/L.

The results of the dissolved ion analysis are shown in Table 2. The dominant cations were Ca, Na, and Si. Based on the measured concentrations of Ca and Mg, the values of hardness ranged from 104 to 293 mg CaCO$_3$/L. The anions with the highest concentrations were the sulfates, ranging from 44 to 800 mg/L. Finally, the results for $^{222}$Rn concentrations and the calculated annual effective dose (calculated using Equation (3)) by ingestion are showed in Table 3. The $^{222}$Rn concentration in the spring waters in the zone of El Granero showed concentrations ranging from 52 to 229.3 Bq/L. Likewise, the annual effective dose caused by radon ingestion ranged from 10.9 to 79.8 µSv/y.

Table 2. Concentration of the main anions and cations (mg/L) and their standard deviation (SD). Likewise, the maximum allowed limits for some ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO$_4^{2-}$</th>
<th>F$^-$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Si</th>
<th>Hardness *</th>
</tr>
</thead>
<tbody>
<tr>
<td>NORM</td>
<td>400</td>
<td>1.5</td>
<td>50</td>
<td>200</td>
<td>-</td>
<td>-</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>WHO</td>
<td>45 (0.592)</td>
<td>1.05</td>
<td>75</td>
<td>23 (0.004)</td>
<td>47.4 (0.019)</td>
<td>6.3 (0.039)</td>
<td>17.3 (0.133)</td>
<td>104 (0.016)</td>
</tr>
<tr>
<td>P1</td>
<td>71 (0.295)</td>
<td>1.11</td>
<td>42.1 (0.001)</td>
<td>2.4 (0.010)</td>
<td>48.6 (0.006)</td>
<td>5.9 (0.036)</td>
<td>18.2 (0.362)</td>
<td>113 (0.042)</td>
</tr>
<tr>
<td>P2</td>
<td>80 (0.050)</td>
<td>1.12</td>
<td>38.6 (0.001)</td>
<td>2.5 (0.006)</td>
<td>47.7 (0.004)</td>
<td>6.4 (0.012)</td>
<td>16.6 (0.202)</td>
<td>107 (0.028)</td>
</tr>
<tr>
<td>P3</td>
<td>44 (0.092)</td>
<td>1.12</td>
<td>19.8 (0.002)</td>
<td>2.4 (0.016)</td>
<td>48.6 (0.006)</td>
<td>5.5 (0.056)</td>
<td>15.3 (0.054)</td>
<td>59 (0.061)</td>
</tr>
<tr>
<td>P4</td>
<td>420 (0.367)</td>
<td>2.38</td>
<td>48.5 (0.017)</td>
<td>14.0 (0.001)</td>
<td>79.3 (0.009)</td>
<td>2.3 (0.015)</td>
<td>35.2 (0.097)</td>
<td>179 (0.042)</td>
</tr>
<tr>
<td>P5</td>
<td>800 (0.182)</td>
<td>1.84</td>
<td>96.7 (0.012)</td>
<td>12.5 (0.001)</td>
<td>72.6 (0.016)</td>
<td>6.7 (0.081)</td>
<td>27.7 (0.014)</td>
<td>293 (0.029)</td>
</tr>
</tbody>
</table>


Table 3. $^{222}$Rn concentrations (its uncertainty) and the annual effective dose by ingestion based on Equation (3). Likewise, the maximum allowed limits for radon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{222}$Rn (Bq/L)</th>
<th>Annual Effective Dose (µSv/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td>UNSCEAR</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>EU</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>P1</td>
<td>67 (2.7)</td>
<td>14.07</td>
</tr>
<tr>
<td>P2</td>
<td>83 (4.1)</td>
<td>17.43</td>
</tr>
<tr>
<td>P3</td>
<td>52 (2.3)</td>
<td>10.92</td>
</tr>
<tr>
<td>P4</td>
<td>380 (11.4)</td>
<td>79.80</td>
</tr>
<tr>
<td>P5</td>
<td>161 (6.4)</td>
<td>33.81</td>
</tr>
<tr>
<td>P6</td>
<td>229 (6.9)</td>
<td>48.09</td>
</tr>
</tbody>
</table>

4. Discussion

In general, the highest cation concentrations were of Ca, Na, and Si, and the lowest concentrations of Mg and K, whereas in anions the sulfates were dominant in the analyzed water. This behavior has previously been observed in spring waters with similar T and pH conditions to those in the present study [23,24]. The results show that TDS in sampling points P5 and P6 were higher compared to the other sampling points. The TDS were composed of inorganic salts such as bicarbonates, chlorides, and sulfates of Ca, Mg, K, and Na, as well as of small amounts of organic material [19]. In 2006, water from this aquifer was analyzed. The authors obtained TDS concentrations in the range of 380 to 3286 mg/L [14], according to those values found in this research. The highest values for anions and cations were found in those sampling points, confirming the results for the concentrations of TDS measured in situ. Moreover, some correlations were found between TDS and the determined anions and cations. From the screening made by regression stepwise methodology, Si, Mg, Na, and F were the most significant ions ($p$ value < 0.05) to contribute to TDS. Therefore, the ion coefficients were found by using Equation (4) and are shown in Table 4.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Coefficients</th>
<th>Coefficients Values</th>
<th>$p$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>$\beta_0$</td>
<td>-5227.78</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Si</td>
<td>$\beta_1$</td>
<td>-42.53</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>$\beta_2$</td>
<td>177.77</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>$\beta_3$</td>
<td>98.37</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>F$^-$</td>
<td>$\beta_4$</td>
<td>105.01</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

In water, the presence of magnesium and calcium salts depends fundamentally on the geological formations. The landscape of El Granero is mainly formed by limestone, mudstone, and gypsum [25,26]. Likewise, the aquifer recharge comes from the direct infiltration of precipitation and surface streams [14]. Under these conditions, when groundwater comes into contact with Ca and Mg minerals, they are solubilized and provide concentrations of those non-alkaline elements to this water. Thus, with the Ca and Mg concentrations found in these springs, this water can be classified as moderately hard to hard (>100 mg/L CaCO$_3$). Likewise, Figure 3 shows some significant correlations between dissolved ions ($p$ value < 0.05). From Table 4, TDS showed that Mg contributes to its concentrations; therefore, because hardness is determined by the concentration of dissolved ions Ca and Mg, a linear correlation between TDS and hardness ($r = 0.97$) was observed (see Figure 3a). Despite Ca ion not being a main contributor of TDS, it was also linearly correlated with TDS ($r = 0.90$) (Figure 3b). In water, the pH, T, and Eh determine the solubility of chemical species. Thus, at a neutral pH carbonates and bicarbonates are usually the dissolved species; when the pH increases hydroxides are the main anions present in water [27], whereas at a low pH chemical species such as chlorides, fluorides, and acids will be predominant. The dissolution of elements present in minerals such as Mg, Ca, Al, Na, and K into the environment depends mainly on the presence of water with a certain acidity [28]. The pH measured in these water samples was slightly acid (<7). Hence, the concentration of these elements in the water can be attributed to this parameter and to the geological conditions of the study area.

Arid and semi-arid regions are characterized by processes that take place over long time periods, due to low precipitation and high evaporation rates. Thereby, the temperature (T) of water and the dry environmental conditions play an important role in the dissolution of chemical species. In the study area, the environmental T reaches values over 44 °C, with reported evaporation rates of 200 mm/month [13], and with an annual average of 2635 mm measured in the last 40 years. Consequently, sulfated and carbonate salts present in spring water can be precipitated. In water, the CaCO$_3$ solubility (solubility product constant $K_{sp} = 8.7 \times 10^{-9}$) is lower than MgCO$_3$ solubility ($K_{sp} = 4.0 \times 10^{-5}$) at 25 °C [29,30]. Additionally, CaCO$_3$ solubility decreases with the increase of T. Thus, environmental dryness and spring water T (>28 °C) induce mainly the precipitation of CaCO$_3$.
salts. In addition, a distinction in the total hardness can be proposed: temporal hardness due to the presence of carbonates and permanent hardness caused by sulfates, chlorides, and fluorides. This is corroborated by the strong correlation showed between hardness and sulfate content \( r = 0.98 \) in these water samples (see Figure 3c). Other correlations were found of \( \text{SO}_4^{2-} \) with Ca \( r = 0.93 \), Mg \( r = 0.88 \), and Na \( r = 0.85 \) (Figure 3d–f, respectively), indicating the presence of sulfated salts. In the study area, these sulfates (Ca, Mg, and Na) can be the result of leaching from rocks that contain CaSO_4 (gypsum) and from sediments in the rivers of the region that contain gypsum [26]. From a geological point of view, the typical rocks in the municipality of Aldama, specifically in the zone of El Granero, are limestones (of sedimentary marine origin), rhyolites (extrusive igneous rocks), and deposits of gypsum [26,31]. Likewise, the soil in this region is mainly leptosol and calcisol, which have a high content of CaCO_3 as a result of the arid climate and the limestone rocks in the study area.

Soils and different types of water naturally contain fluorine. Commonly, F\(^-\) is found as apatite in sedimentary rocks and as fluorite in sediments [32]. Depending on the geographic zone, fluorine shows concentrations ranging from 1.0 to more than 35 mg/L in groundwater [33], from 0.8 to 1.3 mg/L in sea water, and varying from 1 to 25 mg/L in rivers [34]. The spring water analyzed in the present study shows concentration of fluorides in agreement with these concentration ranges for both groundwater and surface water (Table 2). In addition, fluorine is a highly electronegative element that presents a strong tendency to be attracted by positively charged ions such as Ca, Si, Al, and B [35]. The concentrations of F\(^-\) that were determined in these spring waters showed a strong correlation with the contents of Si \( r = 0.99 \), Na \( r = 0.98 \), and Mg \( r = 0.97 \) (Figure 3g–i, respectively). Different authors have found a similar correlation of F\(^-\) with Si and Na in groundwater [36], which can be explained by the origin of this element in rock silicates. Therefore, fluorine present in silicates in the rocks/sediments of the study area is being leached and put into solution in the water of these springs.

On the other hand, \(^{222}\text{Rn}\) is a gas and is part of the disintegration chain of the \(^{238}\text{U}\); its presence in the environment is associated with the concentration of its progenitor \(^{226}\text{Ra}\). The interactions between water and rock directly affect the elemental concentrations in both systems. In rock systems, secular...
radioactive equilibrium is common, while surface and ground waters are characterized by significant disequilibria. This radioactive disequilibrium allows for the determination of the mobility and the distribution of the radioisotopes present in an aquifer. The concentrations of $^{222}\text{Rn}$ determined in the present study reach levels of 380 Bq/L, and are not below 50 Bq/L. Some authors have found that radon concentrations in rock aquifers are characterized by their variability. Thus, $^{222}\text{Rn}$ in groundwater varies from 1 to 50 Bq/L in aquifers with sedimentary rocks, from 100 to 50,000 Bq/L in aquifers with crystalline rocks, and from 10 to 30,000 Bq/L in wells of alluvial deposits [5, 37–39]. The study area is characterized by sedimentary rocks such as lutite-sandstone and sandstone-conglomerate. These types of rocks can contain high amounts of $^{238}\text{U}$ because of its retention in the clay, lime, and organic matter that they are composed of [40]. Additionally, in the geophysical information of the subsoil, the material that fills the valleys contains conglomerates and alluvial deposits, which in some places alternate laterally with rhyolites and acidic tuffs [14]. Rhyolites tend to have high contents of thorium and uranium in a range from 12 to 230 Bq/kg [41, 42].

When $^{222}\text{Rn}$ is freed from the $^{238}\text{U}$ decay chain, it is solubilized in the water of aquifers. In Figure 4 the distribution of the $^{222}\text{Rn}$ concentrations is shown using IDW.

![Figure 4](image_url)

**Figure 4.** Spatial distribution of $^{222}\text{Rn}$ in the spring waters of the region El Granero.

It is shown that sampling points 4 and 6 present the highest radon concentrations, which could be originating directly from rocky material. Conversely, the lowest radon concentrations were in sampling points 1, 2, and 3, springs that are located in the area with a higher amount of conglomerate (sedimentary rocks) (see Figure 2). However, radon concentrations in groundwater are around 50 Bq/L in saturated soils with a porosity of 20%, with $^{226}\text{Ra}$ concentrations of 40 Bq/kg (world average in the earth crust), and are under conditions of equilibrium [5]. In addition, in the sandstone rock with U concentration of 0.5–1 mg/Kg (<12 Bq/Kg, to $^{238}\text{U}$) and porosity of 20%, the $^{222}\text{Rn}$ activity that could be produced by the rocks is no more than 6000 dpm/L (tens of Bq/L) [43], which is 10% of the radon effectively ejected to the pore space fluid.
Nevertheless, the highest $^{222}$Rn concentrations in these springs can be attributed to an additional source. $^{226}$Ra is continuously produced from the $^{238}$U decay chain, directly from $^{230}$Th disintegration. This last radioisotope is present in mineral from sediments and rocks of aquifer. The $^{226}$Ra mobility is strongly influenced by both high $T$ and/or high salt contents, as well as the redox state (lower oxygen concentrations). In saline groundwater, $^{226}$Radium is more mobile due to ion exchange competition with other major cations present in water [39,44]. Water from the aquifer under study is classified predominantly as Calcium-sulfated and Sodium-sulfated [14]. Here, the correlation found of sulfates with Ca, Mg, and Na corroborate that classification. Thus, in this aquifer, $^{226}$Ra concentrations may be present in solution by two factors: (1) the relatively high temperature of spring waters flowing through rocks with both uranium and thorium contents; and (2) the high level of salinity.

Moreover, in arid and semi-arid regions, the low precipitation and high evaporation induce the precipitation of certain chemical species at the surface level. Hence, the main precipitated salts may be CaSO$_4$ and MgSO$_4$ or with their chemical congeners such as Ba, Sr, and Ra. This behavior is described by Kiro et al. [43]; the authors showed that $^{226}$Ra is removed from water by the co-precipitation process with barite. Therefore, dissolved radium present in groundwater upon reaching the surface is precipitated as oxisalt, which contributes to producing $^{222}$Rn concentrations. In addition, in a previous study that was performed on the thermal springs of San Diego de Alcalá ($45^\circ$C), located in the same water basin, the $^{226}$Ra activity concentration reported was of 5.6 Bq/L in the water [7]; corroborating the presence of radium in water. Thus, the presence of rock types, sulfated salts, high $T$, suboxic conditions, and environmental evaporation rate of the study area may be influencing the presence of radium in the spring waters. These results indicate the need to evaluate the radium contents in the water of the springs under study.

On the other hand, temperature plays an important role in the presence of radon in water; at higher temperatures, radon concentrations decrease [2,3]. In the present study, the concentration of $^{222}$Rn in the analyzed water showed a tendency to decrease with an increase in temperature ($r = 0.74$), in agreement with the literature (Figure 5). In Table 5, a comparison is shown of $^{222}$Rn concentrations in spring waters reported in the literature, taking into account water $T$ and the characteristic rocks of every study place.

![Figure 5. Correlation of $^{222}$Rn concentrations with T.](image)

In general, $^{222}$Rn concentrations evaluated in the present study are around the same levels as those presented by other authors (Table 5). However, in comparison to similar $T$ ranges, published works showed lower $^{222}$Rn concentrations (<50 Bq/L) than those found here [45–47]. According to this work, the authors found a slight trend towards lower radon concentration with increasing temperature in water [48]. Conversely, there are several studies that show high concentrations of $^{222}$Rn at high water temperatures. It can be observed that the concentrations have a higher dependency on rock...
type and its contents of $^{238}$U and $^{226}$Ra than on temperature. For instance, the authors found $^{222}$Rn concentrations of up to 576 Bq/L at temperatures above 50 °C [49] (see Table 5). Moreover, in calcium and sodium carbonate waters (>90 °C), radon concentrations of 292 Bq/L were reported [50]. Thus, high $^{222}$Rn concentrations in groundwater (measured in spring and wells) were attributed to rock types and their contents of radon progenitors ($^{238}$U and $^{226}$Ra) in rocks and water [49,51–53].

Table 5. $^{222}$Rn concentration in spring waters in relation to temperature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$^{222}$Rn (Bq/L)</th>
<th>Temperature (°C)</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>[47]</td>
<td>3.3–10.7</td>
<td>21–26</td>
<td>Jordan</td>
</tr>
<tr>
<td>[47]</td>
<td>3.2–5.5</td>
<td>30–48</td>
<td>Jordan</td>
</tr>
<tr>
<td>[49]</td>
<td>0.1–0.42</td>
<td>27</td>
<td>Venezuela</td>
</tr>
<tr>
<td>[49]</td>
<td>1–576</td>
<td>34–78</td>
<td>Venezuela</td>
</tr>
<tr>
<td>[46]</td>
<td>0.46–49.6</td>
<td>25–30</td>
<td>Lebanon</td>
</tr>
<tr>
<td>[50]</td>
<td>53.4–292.5</td>
<td>40–90</td>
<td>China</td>
</tr>
<tr>
<td>[54]</td>
<td>2.1–93.8</td>
<td>nm *</td>
<td>Croatia</td>
</tr>
<tr>
<td>[55]</td>
<td>1.4–105</td>
<td>11.3–18.1</td>
<td>Spain</td>
</tr>
</tbody>
</table>

This study 52–380 27–31 Mexico

<table>
<thead>
<tr>
<th>Reference</th>
<th>$^{222}$Rn (Bq/L)</th>
<th>Temperature (°C)</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>[56]</td>
<td>&lt;1–3</td>
<td>14–20</td>
<td>Mexico</td>
</tr>
<tr>
<td>[57]</td>
<td>8–25</td>
<td>40–43</td>
<td>Mexico</td>
</tr>
<tr>
<td>[45]</td>
<td>0.5–22</td>
<td>28–34</td>
<td>India</td>
</tr>
<tr>
<td>[58]</td>
<td>0.14–20.33</td>
<td>nm</td>
<td>Australia</td>
</tr>
<tr>
<td>[53]</td>
<td>2–129</td>
<td>10–15</td>
<td>Romania</td>
</tr>
<tr>
<td>[52]</td>
<td>4.2–1703</td>
<td>nm</td>
<td>Poland</td>
</tr>
<tr>
<td>[48]</td>
<td>&lt;1–10.8</td>
<td>1.7–145</td>
<td>Iceland</td>
</tr>
<tr>
<td>[48,59]</td>
<td>&lt;1–67.4</td>
<td>nm</td>
<td>Saudi Arabia</td>
</tr>
<tr>
<td>[51]</td>
<td>153–291</td>
<td>6.5–12</td>
<td>Hungary</td>
</tr>
</tbody>
</table>

* not mentioned.

Settlements of less than 200 inhabitants can be found close to the region of El Granero [60]. Due to the arid conditions in the area, these settlements are located around the springs which are their main water supply, for both use and human consumption. Taking into account the existing regulations for water use and human consumption, the levels of Ca in sampling point P6 exceed the acceptable limit of 75 ppm for human consumption established by the Environmental Protection Agency (EPA). Moreover, the springs of sampling points P5 and P6 can be considered unsuitable for human consumption (Table 2) because the levels of fluorides, sulfates, and TDS exceed the levels proposed in Mexican regulations [18]. In contrast, the calculated values for hardness are below the limits considered in national and international regulations. Similarly, the authors found the contents of TDS, sodium, sulfates, and hardness above the allowable limits in 60% of the groundwater samples in this aquifer [14]. They concluded that only 13% of sampling sites have optimal conditions for domestic and/or potable use.

The acceptable amount of radioactive substances present in drinking water is established by the Environmental Protection Agency [20], United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) [21], and the Europe Union (EU) [22]. Considering the maximum acceptable limit values (Table 3), 100% of the spring waters in this study exceed the allowed limit set by the EPA and UNSCEAR, while sampling points P4, P5, and P6 showed radon concentrations above the acceptable limit for drinking water proposed by EU. Radon and its progeny result in human exposure through ingestion and inhalation of the dissolved gas in water. It can be ingested by direct consumption of water or when it is liberated from water into indoor air, causing exposure through inhalation. The annual effective dose that inhabitants receive from this spring water may reach up to 79.8 µSv/y, which is high in comparison to results for dissolved radon of several countries presented in Table 5. On the contrary, this annual effective dose is lower than that calculated in Poland. The consumption of water that contains $^{222}$Rn exceeding the established limit can result in a growing risk of cancer, mainly of both the lung and stomach [20]. Finally, there have been no levels identified at
which TDS in water can have a negative health impact [19]. Nevertheless, high TDS concentrations in water can produce an unpleasant taste. Likewise, high concentrations of fluorides can lead to staining of the teeth, and, in severe cases, skeletal fluorosis [61]. There exist no established levels for sulfates at which they present serious health risks to those who consume them, but they may provoke laxative effects. Because the water from the springs is not directly piped for distribution to the community, there is a low risk of radon ingestion. However, radium concentrations present in this water may be a true cause of natural contamination, and consequently an important source of human exposure.

5. Conclusions

In the present study, the composition of the major ions and radon concentrations dissolved in spring waters were obtained. The spring waters with the highest concentrations of sulfates, fluorides, and total dissolved solids had the highest radon concentrations. It is suggested that anions and cations are leaching from the geological substrate towards the spring waters. Because of this, the origin of fluorine in these spring waters is attributed to leaching from fluorite present in silicates contained in the rocks in the study area. In addition, the salts that the water contains are mainly calcium fluorides, as well as sulfates of both calcium and magnesium.

Although the region of El Granero does not present conditions of uranium mineralization, the high radon concentrations that were found can be attributed to the content of \(^{226}\text{Ra}\) present in the groundwater.

Several parameters analyzed in these spring waters exceed the reference values of the Mexican regulations and the EPA. Furthermore, the water of all the springs evaluated showed values of \(^{222}\text{Rn}\) that exceeded the maximum acceptable limit for water for use and human consumption. More studies are essential in order to increase the knowledge on the geochemical behavior of radioisotopes. These studies should be considered highly relevant because the water in this area is used and consumed by the local inhabitants.

It is recommended that authorities are notified about the quality of the water that is consumed by inhabitants of small settlements, because these populations, in most cases, present a high rate of marginalization due to their location that is difficult to access. The implementation of environmental education strategies for the local population and technologies to remove the contaminants from the water are essential in order to reduce the health risk for these inhabitants.

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Author Contributions: Marusia Rentería-Villalobos participated in the whole process of conducting the research, sampling collection, sample processing, spectra analysis, results interpretation, discussion, and article writing. Alejandro Covarrubias participated in the spectra analysis, results interpretation, and statistical data processing. Alfredo Pinedo-Alvarez participated in the results interpretation, statistical data processing, and discussion of the results. Guillermo Manjón-Collado contributed to the interpretation and the discussion of the results.

Conflicts of Interest: The authors declare no conflict of interest.

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