RADIOLOGICAL AND CHEMICAL CHARACTERIZATION OF DRINKING WATER SUPPLIES OF SERIDO ORIENTAL REGION, RIO GRANDE DO NORTE, BRAZIL.

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ABSTRACT

The presence of natural radioactive anomalies in rocks and soils of the state of Rio Grande do Norte may contribute to an increased exposure of the local population to natural radiation sources. From this region, there is a lack of information on the levels of natural radioactivity in drinking water supplies. Hence, this work focused on the characterization of the radiological and chemical aspects of the drinking water consumed in several municipalities of the Seridó Oriental region. Samples of surface water and groundwater were analysed for gross alpha and beta radioactivity and for the content of $^{226}$Ra. The most important physical and chemical parameters of the water are reported. Most of the monitored water parameter showed values higher than those recommended for a good organoleptic quality of the water. Gross alpha activity, ranging from <0.05 to 1.61 Bq/L, showed values higher than de permissible ones in two samples. Gross beta activity, corrected for $^{40}$K contribution, ranged from 0.22 to 1.67 Bq/L. The activity concentration of $^{226}$Ra ranged from <0.01 to 0.53 Bq/L. Water quality can be considered poor, taking into the high levels of dissolved solids, affecting mainly the organoleptic characteristics of the water. Further investigation is needed to assess the behavior of the radiometric parameter in those samples with values higher than the permissible ones and to extent the study to other municipalities of the region.

1. INTRODUCTION

Water is one of the essential elements for life. Since their consumption takes place throughout the life of the individual, approximately at the rate of 2L per day, the occurrence of acute and/or chronic health effects can occur if the quality of drinking water is not adequate [1]. Therefore, the evaluation of their different characteristics is an important task to ensure their safe
consumption by the population. Constant monitoring to provide sound information about its quality is a relevant aspect of the efforts to improve water quality [2].

Several parameters need to be monitored in the water, including the microbiological, organoleptic, chemical and radiological ones, to validate if the water is suitable for human consumption. For the radiological control of drinking water, reference values for gross alpha (0.5 Bq/L) and gross beta (1.0 Bq/L) activity were established. If these values are exceeded, additional tests must be done to assess the risks to the consumer [3].

The level of the natural radioactivity in water can vary considerably, being generally higher in groundwater due to the strong water/rock interaction process. Radionuclides can be present in the minerals contained in the rocks that are part of the aquifer and can enter the water body by for example weathering processes [4]. This is especially the case if the rocks contain high levels of Natural Occurring Radioactive Materials (NORMs). These materials are characterized by high levels of primordial radionuclides like $^{238}$U and $^{232}$Th and their decay products, as well as $^{40}$K. Regions with high levels of NORMs in the rock mantle may present increased levels of radionuclides in the water, which may increase the exposure to health risks associated with the water consumption.

In the state of Rio Grande do Norte, the presence of elevated levels of natural radioactivity was reported in some municipalities [5, 6]. These regions have geological similarities with the area of the uranium deposit of São José de Espinharas, in the state of Paraíba. Regional studies conducted in the municipalities of Currais Novos, Jardim do Seridó and Parelhas have reported the presence of natural radioactive anomalies containing uranium and thorium [7]. These studies have focused mainly on the radiological characterization of the rocks and soils, and almost no information is available about the impact on water resources. Hence, the main motivation of this work was to investigate the radiological aspects of the drinking water quality in this part of the Northeast region of Brazil.

In this work, the results of the radiological and chemical characterization of five water supply sources in four municipalities of the Eastern Region micro-region are reported. The aims of this study were to evaluate the radiological quality of the water consumed by the inhabitants of the region, as well as to provide information of other quality parameters of interest to the authorities in charge of the water resources management.

2. MATERIALS AND METHODS

2.1. Study área.

Samples were collected from water supply from 4 municipalities, located to the south in the Seridó Oriental micro region, in the state of Rio Grande do Norte. The samples were collected in Parelhas (1), Equador (2), Ouro Branco (1) and Santana do Seridó (1). One of the samples collected in Equador was taken from an artificial basin, the rest from tubular wells. In all cases, the samples corresponded to untreated water, meaning that the water was collected before entering the treatment system. The location of sampling points can be observed in figure 1, the information about coordinates of each sampling point and the type of water collected appears in table 1.
Table 1: Geographical coordinates of sampling points and kind of water collected.

<table>
<thead>
<tr>
<th>Municipality</th>
<th>Id</th>
<th>Coordinates</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parelhas</td>
<td>M1</td>
<td>S 06°40'45.1&quot; W 036°42'16.5&quot;</td>
<td>Groundwater. Tubular well</td>
</tr>
<tr>
<td>Equador</td>
<td>M2</td>
<td>S 06°57'00.2&quot; W 036°43'07.3&quot;</td>
<td>Groundwater. Tubular well</td>
</tr>
<tr>
<td></td>
<td>M3</td>
<td>S 06°54'59.5&quot; W 036°44'05.4&quot;</td>
<td>Surface water. Artificial basin</td>
</tr>
<tr>
<td>Ouro Branco</td>
<td>M4</td>
<td>S 06°42'34.3&quot; W 036°57'00.8&quot;</td>
<td>Groundwater. Tubular well</td>
</tr>
<tr>
<td>Santana do Seridó</td>
<td>M5</td>
<td>S 06°46'11.0&quot; W 036°44'00.2&quot;</td>
<td>Groundwater. Tubular well</td>
</tr>
</tbody>
</table>

In general, the Seridó Oriental region is characterized by hot and semi-arid climate, with an average annual rainfall of 500 mm and a mean temperature of 27 °C, ranging from 18 to 33 °C, and relative humidity around 64% [8]. The vegetation of the region includes the Caatinga Hyperxerophilous and Caatinga Subdesértica of Seridó.

The soils are of Eutrophic Litolics type, with medium texture, stony and rocky phase. There are also Bruno non calcium soils, with sandy/clayey texture. They both are shallow, very eroded and very well drained soils [9, 10]. The region has a pre-Cambrian geological structure, with igneous and metamorphic rocks, such as pegmatites, granite and gneiss, with contains
radioactive minerals. Secondary minerals of uranium are also common (uraninite, meta-
autunite, fosfouraninite, gadolininite) [6, 7, 11].

The region of Seridó Oriental is totally inserted in the domains of the Piranhas-Açu watershed,
with more than 45 main tributaries and some dozens of tributaries. The municipalities included
in this study are in the basins of the subsidiary rivers of the River Piranhas-Açu. The water
courses in the area have an intermittent flow regime and a drainage pattern of the dendritic type
[10].

2.2. Determination of anions and cations

The content of $\text{SO}_4^{2-}$ and $\text{NO}_2^-$ was determined using the Flow Injection Analysis technique.
The analytical system was a FIALab 2500 and samples were analyzed according to the
methodologies described by the manufacturer [12]. The standard method 4500-Cl-B [13] was
used for the quantification of the chlorides, based on the titration of the ions with silver nitrate
and by using potassium chromate as indicator of the end of the reaction.

The determination of Na and K was performed in a flame photometer. Inductively Coupled
Plasma Optical Emission Spectrometry (Optima 8300 ICP-OES spectrometer, Perkin Elmer)
was used to determine the contents of Ca, Mg, Ba, Al, Fe, Mn, Zn and Cu in the water samples.

2.3. Gross alpha beta analysis.

The water samples were processed according to the methodology described in Standard
Methods SMWW 7110 B [14], which is based on the slow evaporation, until dryness, of a
sample volume and its measurement in a proportional counter. This method requires the
determination of the content of the total dissolved solids (TDS). This allow the estimation of
the volume of water sample resulting in a mass residue that would yield a source with mass
thickness not greater than 5 mg/cm$^2$ for gross alpha measurements.

High values of mass thickness strongly affect the gross alpha determination, due to the self-
absorption effect of alpha radiation in the residue. The self-absorption also affects the beta
radiation but to a lesser extent [15]. Therefore, it is important to determine the self-absorption
factor for different residue masses. To correct for this effect, self-absorption alpha and beta
curves were obtained by measuring several sources prepared by evaporating known volumes
of a synthetic solution (with composition similar to the samples), containing the major ions
($\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Cl}^-$, $\text{HCO}_3^-$, $\text{CO}_3^{2-}$ and $\text{SO}_4^{2-}$) and spiked with known activities of $^{241}\text{Am}$
and $^{137}\text{Cs}$, respectively. The composition of the synthetic solution was derived from the results
of the anion and cation determinations on the water samples.

Samples and standards were measured in a Canberra's Tennelec S5 APC low background
continuous flow proportional counter, which has a 2.5 cm diameter gaseous detector with an
ultra-fine window, and a mass thickness of 80 $\mu$g/cm$^2$. The counting time was 900 minutes.
Sources were measured immediately after finishing the treatment of each sample, to avoid the
effect of increasing the activity due to by the accumulation of the $^{226}\text{Ra}$ decay products.
2.4 Determination of $^{226}\text{Ra}$.

Radium determination was performed using a methodology based on the coprecipitation of $^{226}\text{Ra}$ with barium sulphate. The method is a modification of the one reported by Khan [16] and uses high resolution gamma spectrometry for the measurements of the samples. The Canberra spectrometric system included a hyperpure Germanium detector with beryllium window (HPGe-Be), 4.54 cm diameter and active volume of 41.1 cm$^3$, with energetic resolution of 1.8 keV for the energy 1332 keV of the $^{60}\text{Co}$ and nominal efficiency of 25%.

Approximately four liters of water were measured and then heated to reduce the volume to about 3 L. Five milliliters of a Ba carrier solution was added and then 20 mL of sulfuric acid (18 N) was used to precipitate BaSO$_4$ while stirring the solution. The precipitate was allowed to stand overnight and the next day it was filtered to recover the insoluble material. The filter was air dried and weighed to calculate the yield of the precipitation. After three weeks, the precipitated was measured by gamma spectrometry for 86 400 s. The determination of $^{226}\text{Ra}$ was made indirectly, through the 352 keV and 609 keV photopeaks of $^{214}\text{Pb}$ and $^{214}\text{Bi}$.

The efficiency of the system was calculated from a synthetic solution, doped with known $^{226}\text{Ra}$ activity, which was processed following the same procedure described above. A similar solution, without the addition of the radioisotope, was used as a blank to evaluate the contribution of the reagents to the sample spectrum and to determine the minimum detectable activity.

3. RESULTS AND DISCUSSION

3.1 Chemical characterization.

The results of the determination of chemical and physical parameters of the samples are included in table 2. The maximum permissible values (MPV) established in the Ordinance are also included to facilitate the evaluation of the results. Although the alkalinity and the content of K, Ca and Mg are not parameters regulated in the drinking water standard, their analysis is of interest to know the composition of the water and, in the case of potassium, to determine the proportion of $^{40}\text{K}$, based on the isotopic abundance of this element.

The water samples M3 and M4 presented the lower mineralization levels among all the water samples, with lower values for most of the monitored parameters. In the case M3, this is not surprising as this sample was collected from a surface water reservoir and therefore, less water/rock interaction processes are expected compared to the rest of the samples that originated from groundwater. All the monitored parameters in the sample M3 were below the MPVs and therefore the water can be considered to have good quality.

In the rest of the samples, it is possible to find at least two parameters, whose values do not comply with the requirements of the Ordinance. The sample M1 is the one with the greatest quantity of alterations, six in total, although the altered parameters only influence the organoleptic quality of the water. The calculated Fe, Mn and Al content was approximately one order higher than the maximum permissible value, the Na value and the dissolved solids
were approximately 4 times higher while the chloride content exceeded almost three times the reference value.

Table 2: Values of the chemical-physical parameters of water samples together with recommended values.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sample</th>
<th>MPV1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
</tr>
<tr>
<td>pH</td>
<td>7.66±0.02</td>
<td>7.47±0.02</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>155±14</td>
<td>127±11</td>
</tr>
<tr>
<td>chloride (mg/L)</td>
<td>683±34</td>
<td>52±4</td>
</tr>
<tr>
<td>STD (mg/L)</td>
<td>2200±154</td>
<td>3460±252</td>
</tr>
<tr>
<td>Alkalinity (mg CaCO3/L)</td>
<td>355±21</td>
<td>755±37</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>243±17</td>
<td>79±5</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>106±5</td>
<td>260±12</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>8.8±0.3</td>
<td>60.4±2.8</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>614±23</td>
<td>152±6</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>2.71±0.14</td>
<td>0.012±0.001</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>1.32±0.04</td>
<td>0.003±0.001</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>1.74±0.01</td>
<td>0.05±0.01</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>0.18±0.01</td>
<td>0.004±0.001</td>
</tr>
<tr>
<td>Ba (mg/L)</td>
<td>0.33±0.02</td>
<td>1.07±0.08</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.06±0.01</td>
<td>0.011±0.001</td>
</tr>
<tr>
<td>nitrite (mgN/L)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

1: Maximum permissible values, according to Ordinance MS n° 2.914 (2011).

The large variation in the chemical parameters of the waters are explained by the different origin of the samples and therefore the different composition of the rocks locally. The mineralization of the water is also influenced by the low levels of precipitation and the intense evapotranspiration in the investigated region [17]. Total dissolved solids and Fe and chloride content were the parameters that showed the highest incidence of alterations in the analyzed samples. Of the parameters considered as health risk (Ba, Cu and nitrite content), only Ba is exceeded in sample M2.

From the analysis of these results, it can be reached the conclusion that the organoleptic quality of the groundwater is affected. In fact, it is reported that the region's water is of the brackish type [17], therefore, for the consumption of the population as drinking water, their treatment is required to decrease the content of dissolved solids, without considering the treatments necessary to achieve the appropriate microbiological quality.

3.2 Radiological characterization.

Table 3 shows the results of determination of the gross alpha and beta activity, as well as the activity concentration of $^{226}$Ra. Values are reported with their counting uncertainty. The activity concentration values due to potassium $^{40}$K are also included.
Table 3: Values for radiological parameters of water samples.

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>SAMPLES</th>
<th>MPV&lt;sup&gt;1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
</tr>
<tr>
<td>Gross alpha (Bq/L)</td>
<td>1.61±0.56</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Gross beta (Bq/L)</td>
<td>0.48±0.10</td>
<td>2.37±0.07</td>
</tr>
<tr>
<td>&lt;sup&gt;40&lt;/sup&gt;K (Bq/L)</td>
<td>0.26±0.01</td>
<td>1.81±0.08</td>
</tr>
<tr>
<td>Gross beta corrected for &lt;sup&gt;40&lt;/sup&gt;K (Bq/L)</td>
<td>0.22±0.10</td>
<td>0.56±0.11</td>
</tr>
<tr>
<td>&lt;sup&gt;226&lt;/sup&gt;Ra (Bq/L)</td>
<td>0.53±0.02</td>
<td>0.06±0.01</td>
</tr>
</tbody>
</table>

<sup>1</sup>: Maximum permissible values, according to Ordinance MS n° 2.914 (2011).

Malanca et al. [18] analyzed several water samples from different municipalities of Rio Grande do Norte, reporting values for gross alpha and beta activity in the range of 0.0028-0.354 Bq/L and 0.0505-0.580 Bq/L, respectively. Although the area covered in their research did not include municipalities considered in our work, the results are useful by way of comparison, considering that the different municipalities of the region have similar hydrogeological characteristics.

As can be seen in table 3, the gross alpha and beta activities found in our study were in the range of <0.05-1.61 Bq/L and 0.48-1.79 Bq/L, respectively, being in some samples higher than those reported by Malanca et al. [18]. In the samples M1, the gross alpha activity was significantly higher than the MPV of 0.5 Bq/L. In the case of M5, the gross alpha slightly exceeded the MPV, but the result has a large uncertainty. The gross alpha activity may be due, in a large extent, to the presence of the uranium radionuclides <sup>238</sup>U and <sup>234</sup>U [19].

A completely different situation was observed for the gross beta activity. Except for the M1 and M3 samples, all the water samples showed activities that exceeded significantly the MPV. Notably, the sample M2 showed a value of 2.37±0.07 for the gross beta activity, almost 2.5 times higher than the MPV.

The activity concentration of <sup>40</sup>K was calculated from the potassium content in the samples, according to the [20] criterion. In sample M2 the <sup>40</sup>K content is very high and represents more than 70% of the beta activity of the sample. Also in samples M1 and M3, the presence of this radionuclide is responsible for approximately half of the gross beta activity, however, in samples M4 and M5 the contribution decreases, barely reaching 6 and 25%, respectively. After correcting for the contribution of <sup>40</sup>K, elevated gross beta activities, still above the MPV, were only observed in samples M4 and M5. In these samples, the gross beta activity may be due to the presence of short-lived radioisotopes of the <sup>238</sup>U decay chain (e.g. <sup>234</sup>Th and <sup>234</sup>mPa) in water [19]. The gross beta activity in the samples M2 and M3 shows values below 1 Bq/L after correcting for the contribution of <sup>40</sup>K and, together with the sample M1, complies with the requirement for this radiological parameter.

For the determination of gross alpha and beta activities, it is recommended to use 5.0 cm diameter counting pans, which allows to work with sample residues of up to 200 mg and therefore to use larger volumes of sample, thus improving the sensitivity of the method [21].
However, the instrument used in this work has a detector of reduced diameter (2.5 cm) and is designed to work with counting pans of corresponding size. Because of this, the mass of salts to be deposited in the counting pans and the volume of sample to be used is significantly restricted. To compensate for this limitation and to obtain good counting statistics, the samples were measured for 900 minutes. Under these conditions, the Minimum Detectable Activity (MDA) for the gross alpha determination is 0.05 Bq/L, an order less than the maximum allowable value. In the case of the gross beta activity, an MDA value of 0.2 Bq/L was obtained.

Despite the considerable increase in counting time, the number of counts recorded during the measurement was relatively low, increasing the uncertainty of the results. This is because high levels of total dissolved solids in the samples prevented the use of sufficient sample volume. This limitation can be obviated by applying a precipitation procedure like the SMWW 7100 C methodology from Standard Methods [22], which allows working with samples with high salt levels.

On the other hand, the presence of $^{226}$Ra was detected in two samples. The activity concentration of this radioisotope in sample M1 was $0.53 \pm 0.02$ Bq/L, which already had values of gross alpha activity higher than the maximum allowed value. The level of $^{226}$Ra in this sample represents 30% of the total alpha activity. $^{226}$Ra was also present in sample M2, but at a much lower value of 0.06 Bq/L. In the remainder samples, the concentration activity values were lower than the MDA value of the method.

Although several samples showed values of total alpha and beta activity above the MPV, it should be considered that they are the result of the analysis of raw water, obtained directly from the source. This water constitutes the feed water of the treatment plants and the effect of the treatment on the values of the parameters studied is unknown.

4. CONCLUSIONS

In this paper, the results of the analysis of water samples from sources of supply of some municipalities of the Seridó Oriental region in Rio Grande do Norte are reported. The chemical information collected indicates that the organoleptic quality of the water is quite affected by the presence of high levels of dissolved solids although the chemical parameters evaluated, considered of health risk, were within the permissible values.

The values of gross alpha and beta activity also proved to be higher than the maximum allowable value in some samples. The presence of $^{226}$Ra was also detected in two samples. Considering the set of all parameters studied, the sample of groundwater collected in the municipality of Parelhas (M1) presented the highest number of alterations compared to what was established in the drinking water standard.

On the other hand, the results obtained are a starting point indicating that a deeper investigation is necessary, carrying out new analyzes in later dates to evaluate the behavior of alpha and beta activity levels and to extend the radionuclide characterization by analyzing other radioisotopes of interest ($^{238}$U, $^{234}$U, $^{210}$Pb, $^{210}$Po and $^{228}$Ra), which will allow to evaluate the dose received by the population due to the consumption of water from these sources. It is also recommended to analyze the waters that result from the treatment of raw water, to evaluate their effect on the values of the different parameters.
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