HYDROCHEMICAL AND RADIOMETRIC STUDY OF GROUNDWATERS FROM SERRA NEGRA SPA, SÃO PAULO STATE, BRAZIL

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ABSTRACT

This paper presents a novel hydrochemical and radiometric data of groundwater sampled from Serra Negra spa town, São Paulo State, Brazil. Every year, many visitors travel to the municipality, thus, recurrent analyses are recommended and necessary, as the local water is heavily consumed. However, gaps exist in this regard, especially for the groundwater selected for sampling in this paper, since there is no analytical data on its chemical composition. The results obtained were compared with the drinking water standards in relation to the analyzed parameters. The radioactivity of all analyzed samples was below the values established by the World Health Organization of 0.5 and 1 Bq. L^{-1} for gross alpha and beta activities, respectively. In general, the hydrochemical parameters analyzed did not exceed the reference limits established by Brazilian and international legislation, with the exception of pH for one water sample and nitrate for another. The use of Pearson's correlation coefficient reinforced the proportionality between electrical conductivity and dissolved salts. In the chemical aspect, the dominant anion in the waters was bicarbonate, agreeing with the observed pH, while the predominant cation was sodium, possibly suggesting a slightly more evolved hydrogeochemical context. Although the Brazilian legislation does not mention a reference value for the ingestion of silicon in water, in this paper some comments were made about its presence in the analyzed groundwaters.
Keywords: hydrochemistry, potability, radioactivity, Serra Negra spa.

1 INTRODUCTION

Water is probably the most important natural resource on Earth. About 12% of all fresh water available on Earth is present in Brazilian territory, showing its global relevance and need for preservation and maintenance of such resource. Currently, about 80% of the municipalities of the State of São Paulo are fully or partially supplied by groundwater, corresponding to a population of more than 5.5 million inhabitants [1].

Approximately 95% of all groundwater stored in aquifers in the world has residence time of more than 50 years. This indicates a small rate of renewal of underground reservoirs, requiring care in the management of water resources, since their uncontrolled use can cause exhaustion [2], mainly in intensely exploited areas. Therefore, studies aimed at evaluating and characterizing the environmental aspects of these waters are essential. Some of the most common contaminants of water resources are due to agricultural inputs, industrial effluents, and natural and artificial radionuclides. In this way, the hydrochemical and radiological characterization has been carried out by several organizations around the world, owing to the potential dangers caused to human health by the consumption of contaminated water.

The chemical composition of surface water and groundwater is also influenced by rocks with which there was interaction. When a given constituent enters the hydrosphere, it is subject to numerous processes that can affect its concentration, which varies widely, depending on the geochemical conditions of the environment, for instance, ions that can be selectively adsorbed on the minerals surface, ions that can enter in the biosphere as nutrients, noble gases that are released into the atmosphere, or even gases from the atmosphere (e.g. O_2, CO_2, and N_2) that are dissolved in the waters.

The presence of radionuclides in water resources might be linked to several factors, both natural and artificial. This led the World Health Organization (WHO) to propose an extensive list of radionuclides, with their respective reference values for ingestion in potable waters. The radionuclides of natural occurrence on the planet are in much lower number than those of artificial occurrence, for example, ^{3}H and ^{14}C and several others of the decay series of ^{238}U (^{238}U, ^{234}U, ^{230}Th, ^{234}Th, ^{226}Ra, ^{222}Rn, ^{210}Pb, ^{210}Po, ^{210}Bi), ^{235}U (^{235}U, ^{227}Th, ^{231}Th, ^{231}Pa, ^{223}Ra), and ^{232}Th (^{232}Th, ^{228}Th, ^{228}Ra, ^{224}Ra).

Due to the time of analysis, cost, difficulties, and peculiarities of analytical techniques used in the detection of specific radionuclides, WHO [3] recommends initial tests for the characterization of gross alpha and beta activity in waters. Only if the reference values are reached (i.e. 1 Bq. L^{-1} for beta particles and 0.5 Bq. L^{-1} for alpha particles) or exceeded, specific radionuclide analyses shall be performed.

Several countries, including Brazil, adopt reference values for the concentration of various constituents dissolved in the waters, so that they can be classified as adequate for human consumption, thus, justifying the importance of hydrochemical and radiometric studies for such purpose. In this context, the present work has been carried out, focusing on groundwaters of Serra Negra spa town, known for its 'radioactive waters'.

This hydrochemical and radiological investigation was fulfilled taking into account gross alpha and beta radioactivity, as well as important physicochemical and chemical parameters for potable waters, such as hydrogen potential (pH), total dissolved solids (TDS), dry residue (DR), electrical conductivity (EC), alkalinity, and main dissolved anions and cations, establishing relationships among them. This study is relevant in our country because it increases the generation of data related to some parameters, which are scarce in Brazilian waters used for human consumption, especially in this region intensely visited by tourists.

2 STUDY AREA

The study area is located in the city of Serra Negra, in the countryside of the State of São Paulo, Brazil (Fig. 1). The municipality belongs to an area known as 'Circuíto das Águas Paulista' (i.e. a region that has many mineral water springs), including the spa towns of Águas de Lindóia, Amparo, Holambra, Jaguariúna, Lindóia, Monte Alegre do Sul, Pedreira, and Socorro.
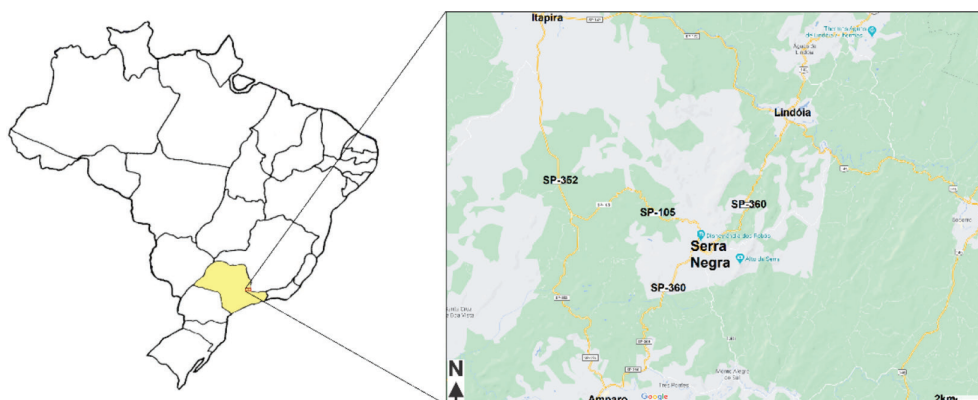

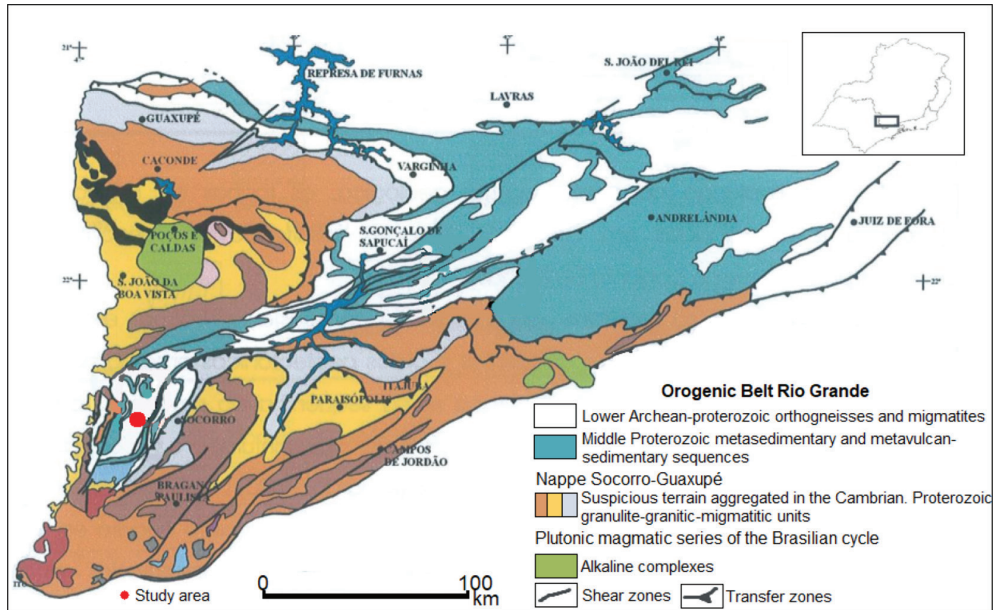Figure 1: Location of the study area.

Figure 2: Geologic map of the study area. (Source: Campos Neto, 1990)

Geologically, the city of Serra Negra is located in the Orogenic Belt Rio Grande, a Meso-proterozoic tectonic unit marginal to the São Francisco Craton with Archean and Paleoproterozoic fragments reworked during the Brasiliano Cycle [4, 5]. In its southern part, the orogenic belt has N–S orientation with inflection to NE–SW as it moves northeast of the unit. This range of foldings is bounded by faults and shear zones by the Guaxupé Complex to the northwest and the Socorro Complex to the south [5] (Fig. 2).

The oldest units, Archean and Neoproterozoic, are the Amparo and São Gonçalo do Sapu-caí Complexes. The study area is mainly located at the Amparo Complex, which is found in the SW of the orogenic belt and is characterized by stromatic and phlebitic migmatites exhib-iting intense deformation, cut by amphibolite biotite dykes, in addition to orthogneisses affected by anatexis [6]. Structurally, the region underwent polyphasic and polycyclic evolu-tion with events dating back to the Upper Proterozoic [6].

Hydrologically, the city of Serra Negra belongs to the Water Resources Management Unit (UGRHI) No. 9 – Mogi Guaçu, which is composed of 38 municipalities, 58% of which use partial or totally groundwater for public supply. Serra Negra is inserted in the Pre-Cambrian Aquifer System (SAC), which has an average flow rate ranging from 3 to 23 $m^3.h^{-1}$, being free or semi-confined [7]. This aquifer is characterized by crystalline rocks, fractured-type, with a hydrogeological potential in the region from weak to medium [8], with recharge areas limited to topographically higher areas and with circulation that can reach up to 2,000 m deep [9].

3 MATERIALS AND METHODS

In this study, 24 samples of groundwater were collected at different sites in the municipality of Serra Negra (Table 1). There is no previous record of hydrochemical analyses or measure-ment of gross alpha and beta radioactivity. pH and EC measurements were performed *in situ,*

Table 1: Location of the groundwater sampling points.

Sample no.	Coordinates	Sampling date	Sampling time	Name	Property	District
1	22º36'35.5"S 46º42'37.2"W	11/08/2019	13:00	Fonte Vila Nhozinho	-	Bairro das Palmeiras
2	22º35'25.3"S 46º41'52.7"W	11/08/2019	16:20	Mina 'de baixo'	Sítio Sta. Terezinha	Belo Horizonte
3	22º35'28.7"S 46º41'54.0"W	11/08/2019	16:30	Mina 'de cima'	Sítio Sta. Terezinha	Belo Horizonte
4	22º37'54.7"S 46º43'35.1"W	24/08/2019	15:00	Fonte Nossa Sra. de Lourdes	Parque Represa Dr. Jovino Silveira (Barragem)	Bairro das Posses
5	22º35'14.2"S 46º41'19.1"W	24/08/2019	15:50	Mina 'de baixo'	Hotel Fazenda Vale do Sol	Bairro das Palmeiras
6	22º34'14.0"S 46º39'01.9"W	30/08/2019	6:50	Mina Angelina	Sítio Shanday	Ramalhada
7	22º35'14.3"S 46º41'16.9"W	28/08/2019	15:00	Mina 'de cima'	Hotel Fazenda Vale do Sol	Bairro das Palmeiras
8	22º35'15.1"S 46º41'23.5"W	28/08/2019	15:15	Mina 'casa de baixo'	Hotel Fazenda Vale do Sol	Bairro das Palmeiras
9	22º36'19.5"S 46º42'25.1"W	08/09/2019	10:00	Fonte Sant'Ana do Sonho Verde	-	Centro
10	22º36'15.3"S 46º44'13.1"W	23/09/2019	13:45	Fonte Leão	Condomínio Parque das Vertentes	Vertentes
11	22º36'16.1"S 46º44'10.3"W	23/09/2019	14:00	Fonte Busto	Condomínio Parque das Vertentes	Vertentes
12	22º36'19.0"S 46º44'05.6"W	23/09/2019	14:10	Fonte dos Namorados	Condomínio Parque das Vertentes	Vertentes
13	22º34'11.4"S 46º39'03.9"W	24/10/2019	15:50	Mina DAE	Sítio Rubiara	Ramalhada
14	22º34'10.7"S 46º38'56.2W	24/10/2019	16:05	Mina Dona Maria	Sítio São João	Ramalhada
15	22º34'23.5"S 46º38'58.2W	24/10/2019	16:15	Mina São José da Laje de Pedra	Sítio São José da laje de pedra	Ramalhada
16	22º36'50.8"S 46º42'13.0"W	24/10/2019	17:10	Mina Glória	Casa da Glória Perondini	Centro

Continued

Table 1: *Continued*

Sample no.	Coordinates	Sampling date	Sampling time	Name	Property	District
17	22°38'16.5"S 46°43'46.9"W	25/10/2019	15:00	Fonte Santanario	Água Mineral Vida & Legítima Fonte Verônica	Parque das Cachoeiras
18	22°36'14.6"S 46°42'36.1"W	25/10/2019	16:30	Fonte Ariadne Mittestainer	-	Bairro das Palmeiras
19	22°36'50.9"S 46°44'39.1"W	16/01/2020	10:00	Mina Fran	Condomínio Monte Samkhya	Bairro dos Macacos
20	22°37'00.4"S 46°41'58.0"W	17/01/2020	18:00	Mina Nancy	Casa da Nancy Marchi	Centro
21	22°36'42.2"S 46°41'55.1"W	18/01/2020	10:00h	Fonte Radio Hotel	Radio Hotel Resort	Centro
22	22°37'29.5"S 46°41'20.0"W	18/01/2020	10:30	Mina 'de cima'	Sítio Santa Rosa (Café Santa Serra)	Barrocão
23	22°37'29.5"S 46°41'20.0"W	18/01/2020	10:40	Mina 'pé abacate'	Sítio Santa Rosa (Café Santa Serra)	Barrocão
24	22°37'29.5"S 46°41'20.0"W	18/01/2020	10:50	Mina 'muita água'	Sítio Santa Rosa (Café Santa Serra)	Barrocão

using *Digimed* DM-2P and *Analion* model C-702 meters, respectively. These samples were stored in polyethylene recipients of 2.5 L properly sealed, labeled, and transported to LABI-DRO – Isotopes and Hydrochemistry Laboratory of the Geology Department of the Institute of Geosciences and Exact Sciences of UNESP, campus of Rio Claro, for hydrochemical and radiometric analysis.

The determination of Na^+ and K^+ was conducted in a *Benfer* flame photometer model BFC-300. The constituents Ca^{2+}, Mg^{2+}, NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, PO_4^{3-}, and SiO_2 were determined by colorimetry, employing the spectrophotometer *Hach* model DR/2000, adopting as reference the analytical procedures described in Hach [10]. Regarding alkalinity, the data were obtained by sulfuric acid titration [10]. The TDS were obtained by summing the concentration of the analyzed constituents and the DR through the total evaporation of 1 L of each water sample.

For radiometric analyses, two different spectrometers were used to quantify the gross alpha and beta activity in the water samples. For the acquisition of beta activity data, a gamma spectrometric system using a 3" × 3" NaI(Tl) scintillation detector was used, coupled to a 2048-channel multi-channel analyzer, controlled by the MAESTRO software from EG&G ORTEC. The calibration adopted provided direct information on the presence of

radionuclides emitting β^- from gamma emissions occurring during radioactive decays by this process, according to the analytical procedure described by Bonotto *et al.* [11].

For the acquisition of alpha spectrometric data, four Si(Au) surface barrier detectors were used, with a depletion depth of 0.1 mm and a surface area of 450 mm². The data were stored in four 1024-channel multi-channel analyzers, controlled by the MAESTRO software from EG&G ORTEC. Data were obtained from the calibration of the spectrometric system in activity based on the analytical procedure described by Bonotto *et al.* [11].

For the radiometric analysis of the samples, the aliquot of 1 L was separated from each beaker. The water contained in the beaker was subjected to evaporation under infrared lamps until a final volume of 12 mL, which was introduced into a suitable vial for insertion in the NaI(Tl) well-type crystal, aiming to get the gross beta activity. After this reading, the remaining volume of 12 mL was fully evaporated on aluminum disks for the reading in the alpha spectrometer to obtain the gross alpha activity.

4 RESULTS AND DISCUSSION

4.1 Gross alpha and beta activity

According to the WHO [3], the reference values for the gross alpha and beta activities for the consumption of potable waters correspond to 0.5 and 1.0 Bq. L^{-1}, respectively, which are also in force in Brazil, according to Ordinance No. 2914 of 12/12/2011 of the Brazilian Ministry of Health [12].

From the results of the readings obtained in the gamma (gross beta) and alpha spectrometers, it was possible to calculate the activities for the analyzed water samples (Table 2). The values were obtained from the calibration factors described by Bonotto *et al.* [11], and the net counting rate (cps) is determined by subtracting the total counting rate (cps) from the background value (BG).

The results indicated that the employed techniques produced satisfactory results, and no water sample analyzed presented values above the recommended by WHO [3], both in gross alpha and beta. Gross beta radioactivity ranged from values below the detection limit (0.03 Bq. L^{-1}) up to 0.78 Bq. L^{-1} (Table 2). Gross alpha radioactivity varied between the detection limit (0.001 Bq. L^{-1}) and 0.0388 Bq. L^{-1} (Table 2).

The highest gross beta activity value (0.78 Bq. L^{-1}) was obtained in sample 7, collected at the 'Hotel Fazenda Vale do Sol' being considered the most radioactive water source analyzed in this work (Table 2). However, it does not present any risk for consumption in relation to radioactivity. Regarding the gross alpha activity, the sample 12, collected at 'Fonte dos Namorados' in 'Condomínio Parque das Vertentes' exhibited the highest value, corresponding to 0.0388 Bq. L^{-1} (Table 2).

4.2 Hydrochemical parameters

The pH of the samples ranged from 5.40 to 6.75 (Table 3), being mildly acid (average 6.50). With the exception of sample No. 24, all other pH values are inserted in the interval between 6.0 and 9.5, as established by [12] on the potability standard for public water supply.

Alkalinity values range from 2 to 60 mg. L^{-1} (average 31 mg. L^{-1}) for the 24 samples (Table 3). Only bicarbonate ions were characterized, which is consistent with the measured pH values. As for TDS, the values are between 59 mg. L^{-1} (sample 23) and 157 mg. L^{-1}

Table 2: Gross alpha and beta activity values.

Sample no.	Gross alpha (Bq. L^{-1})	Gross beta (Bq. L^{-1})	Sample no.	Gross alpha (Bq. L^{-1})	Gross beta (Bq. L^{-1})
1	0.0070	0.05	13	0.0086	<0.03
2	0.0232	<0.03	14	0.0160	0.24
3	0.0053	<0.03	15	0.0133	0.15
4	0.0364	<0.03	16	0.0077	<0.03
5	<0.001	<0.03	17	0.0126	<0.03
6	0.0109	<0.03	18	0.0057	<0.03
7	0.0034	0.78	19	0.0151	<0.03
8	0.0158	0.01	20	0.0043	<0.03
9	0.0368	<0.03	21	0.0028	<0.03
10	0.0251	<0.03	22	0.0198	<0.03
11	0.0192	<0.03	23	0.0027	<0.03
12	0.0388	<0.03	24	0.0051	<0.03

(sample 1). All waters were classified as freshwater, since none of them exceeded the guide-line value of 1000 mg. L^{-1} for this category (Table 3). For DR, the variation was from 12.6 to 130.3 mg. L^{-1}, while EC was from 60 to 307 µS. cm^{-1} (Table 3).

Table 4 shows the results obtained in other hydrochemical analyses. Due to the chemical composition of the rocks found in the region, it was expected to find higher Na$^+$ (maximum of 17 mg. L^{-1} for sample 19) and Ca^{2+} (maximum 11 mg. L^{-1} for sample 1) levels when com-pared to other constituents. The Cl$^-$ concentration in sample No. 1 (30.8 mg. L^{-1}) is highlighted, possibly related to an *in situ* contamination of the 'Fonte Vila Nhozinho' caused by animal waste, once the spring is located in a rural agricultural and pasture region.

EC is generally used as an indicator of salinity, as the presence of dissolved salts in water is directly related to this parameter, since they provide electrical charges due to the movement of ions. Therefore, it has been frequently described in the literature a significant number of correlations between EC and TSD, as well as between EC and concentration of several ions in solution such as Na$^+$, Ca^{2+}, Mg^{2+}, HCO$_3^-$, Cl$^-$, and SO$_4^{2-}$ [13–18]. Some of the differences found between the parameters considered have been attributed to soil type, texture, presence of carbonate and gypsum, organic matter content, method used for the sample preparation for analysis, proportion of exchangeable cations, and chemical composition of salinity [18–21].

Thus, in order to verify whether there is a linear relationship between the EC values and the dissolved salts concentration in the analyzed samples, statistical tests were performed involving the determination of the Pearson's correlation coefficient (r). The value of this parameter ranges from 1 to −1, so that 1 indicates a perfect direct significant correlation between the two variables, while −1 suggests a perfect inverse correlation between the varia-bles. All anions and cations analyzed in this work were submitted to the test, and significant values were found in the following situations: EC vs. TDS ($r = 0.55$); EC vs. DR ($r = 0.53$); EC vs. Cl$^-$ ($r = 0.87$); EC vs. Na$^+$ ($r = 0.56$); and EC vs. Ca^{2+} ($r = 0.84$). Therefore, a trend of positive linear relationship between EC and these parameters is confirmed, emphasizing the strongly significant values observed for the anion Cl$^-$ and cation Ca^{2+}.

Table 3: Hydrochemical data obtained in this study.

Sample no.	pH	Alkalinity (mg. L^{-1})	TDS (mg. L^{-1})	DR (mg. L^{-1})	EC (μS. cm^{-1})
1	6.40	44	157.4	43.8	307
2	6.25	14	87.6	70.1	130
3	6.50	22	85.4	48.5	105
4	6.55	38	108.2	22.4	108
5	6.70	26	85.2	12.6	68
6	6.70	34	87.9	15.7	76
7	6.60	56	127.2	19.2	129
8	6.70	26	83.5	28.8	62
9	6.50	38	106.5	30.4	91
10	6.50	38	106.7	61.2	91
11	6.60	34	101.2	49.0	94
12	6.50	60	135.2	55.7	138
13	6.75	26	88.0	26.7	60
14	6.60	24	76.8	22.3	81
15	6.65	30	77.2	13.8	74
16	6.60	26	98.7	20.7	118
17	6.55	34	104.7	22.3	104
18	6.60	42	119.2	37.8	102
19	6.60	36	123.2	37.8	131
20	6.45	18	102.4	107.2	183
21	6.55	38	99.5	19.7	102
22	6.40	24	98.2	130.3	206
23	6.25	14	58.9	71.7	131
24	5.40	2	61.7	80.2	126

4.3 Hydrochemical diagrams

Regarding the chemical composition of the studied water samples (Tables 3 and 4), for better evaluation of their main characteristics, two types of diagrams were chosen, Piper and Schoeller, which allow the graphical visualization of the ionic distribution of the waters and identification of the differences and similarities between the samples.

In general, the Piper diagram (Fig. 3) suggests that the water samples analyzed exhibited relatively similar results, most of which were enriched in bicarbonate and sodium, and depleted in the other constituents. According to the diagram, in relation to dissolved cations, the vast majority of samples (75%) were classified as sodic water and the rest as mixed water. In terms of the dissolved anions, the diagram indicates that most samples (79%) are classified as bicarbonated water, 17% as chlorinated water and only one of them (4%) as mixed water. Thus, the following classification was obtained according to the predominance of the ions: 62% are sodium bicarbonated type (15 samples); 17% are mixed bicarbonate type (4 samples); 12% are sodium chloride type (3 samples); 4% is mixed chloride type (1 sample); and 4% is mixed type (1 sample).

Table 4: Chemical composition (mg. L^{-1}) of the groundwater samples. PS – Potability Standard according to Brazilian Ministry of Health [12].

Sample no.	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	SiO$_2$	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	NO$_2^-$	PO$_4^{3-}$
1	16.10	3.21	11.00	0.67	43.2	30.8	5	3.3	0.005	0.12
2	9.89	1.88	8.50	0.69	37.2	5.1	<1	10.2	0.005	0.09
3	9.43	1.72	5.25	0.95	36.5	3.2	1	5.2	0.005	0.12
4	9.20	2.66	6.83	0.82	46.9	1.7	1	0.9	0.005	0.18
5	7.36	1.99	4.16	1.50	41.8	0.8	1	0.5	0.006	0.14
6	7.13	1.99	5.16	0.94	37.9	0.4	<1	0.3	0.005	0.06
7	10.35	1.68	9.50	0.60	45.7	1.4	1	0.8	0.006	0.21
8	7.13	1.84	2.83	1.33	42.3	0.8	<1	1.2	0.005	0.10
9	9.20	2.23	5.83	2.00	47.2	0.5	<1	1.3	0.007	0.25
10	12.19	0.90	5.16	1.83	46.0	1.2	1	0.3	0.006	0.14
11	11.73	1.72	4.50	1.83	41.6	3.8	1	0.9	0.004	0.09
12	10.81	2.15	8.00	0.52	49.9	1.3	1	1.4	0.005	0.17
13	9.66	1.72	1.54	0.28	47.6	0.5	<1	0.3	0.005	0.44
14	4.83	1.29	5.33	0.91	35.6	1.7	<1	3.1	0.006	0.04
15	4.60	2.19	4.00	0.87	34.4	0.7	<1	0.3	0.006	0.19
16	14.69	3.32	5.00	0.98	41.3	4.4	2	0.9	0.005	0.15
17	9.66	2.70	6.33	0.72	48.8	1.5	<1	0.7	0.009	0.30
18	11.04	2.03	6.00	0.79	54.7	0.9	<1	1.4	0.021	0.33
19	17.02	1.33	6.87	0.70	45.7	3.5	10	1.9	0.005	0.16
20	13.34	3.99	10.87	0.65	36.0	5.0	<1	14.4	0.005	0.11
21	10.12	2.15	6.50	0.83	39.7	1.6	<1	0.4	0.005	0.18
22	9.20	2.89	10.50	0.99	41.3	6.5	<1	2.6	0.006	0.20
23	7.13	3.28	7.16	0.70	16.5	5.3	3	1.7	0.006	0.08
24	9.20	5.71	4.66	0.69	23.8	5.1	<1	10.4	0.006	0.16
PS	200	-	500	500	-	250	250	10	1	-

These chemical facies of the waters point to a geochemical evolution based mainly on the dissolution of silicates (rocks of the Amparo Complex), as demonstrated by the sodium predominance. They are also compatible with a hydrogeochemical evolution from younger waters (bicarbonate) to more evolved waters (chlorinated).

The Schoeller diagram (Fig. 4) provides another visualization of the hydrochemical data, allowing to identify which samples are more (or less) sodic, chlorinated, bicarbonated, etc. Similar trends (water families) were observed, indicating a main trend in which bicarbonate and sodium ions predominate, as well as low values of magnesium, chloride, sulfate, and nitrate (Fig. 4). However, some of the samples are not adherent to this main trend, for instance: sample No. 1 – there is a higher predominance of the anions chloride and sulfate; sample No. 19 – has more sulfate than other samples; sample No. 13 – shows lower concentration of calcium and magnesium; sample No. 24 – presents bicarbonate concentration far
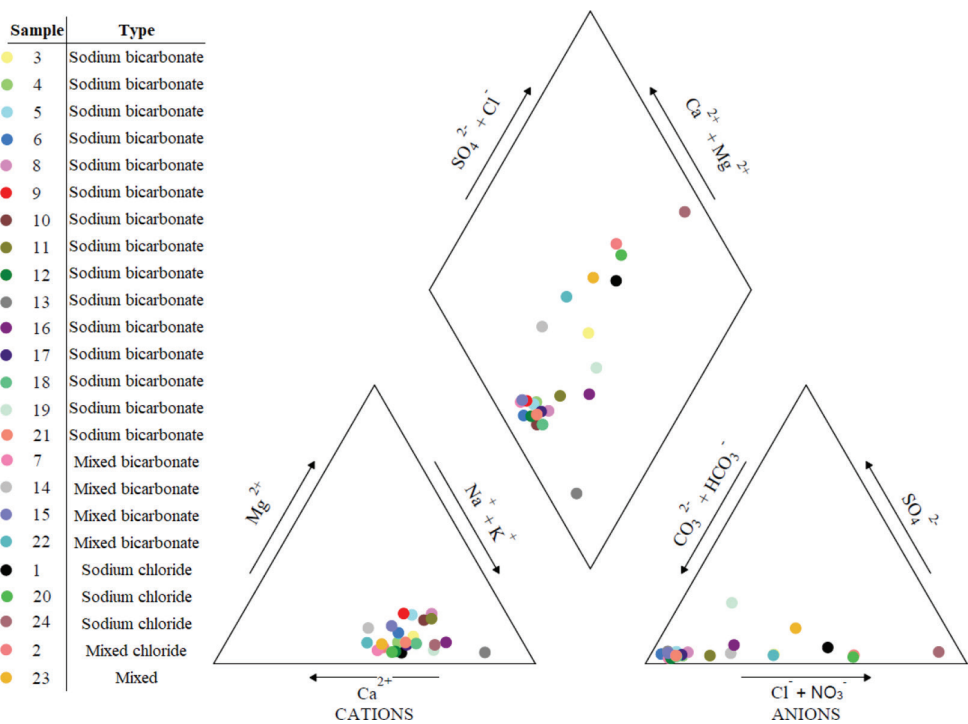
Figure 3: Insertion of the hydrochemical data in a Piper diagram.

below than other samples, as well as higher nitrate concentration, as also observed in samples No. 2 and 20.

4.4 Hydrochemistry and potability

According to the organoleptic potability standard of Brazilian Ministry of Health [12], the concentrations of chloride, sulfate, calcium + magnesium, and sodium did not reach the established guideline reference values (Table 4), and therefore do not present a risk to consumption in relation to these parameters. Also, according to Brazilian Ministry of Health [12], there are reference values for several other constituents that pose a risk to human health, among them nitrate and nitrite ions. For nitrite ion, none of the water sample presented concentration close to the limit of 1 mg. L^{-1}. For nitrate ion, the maximum allowed value for its intake in potable waters is 10 mg. L^{-1}, which exceeded for three samples analyzed (Table 4): sample No. 2 – 10.2 mg. L^{-1}; sample No. 20 – 14.4 mg. L^{-1}, and sample No. 24 – 10.4 mg. L^{-1}. According to WHO [3], the reference value for this ion is slightly higher (11.3 mg. L^{-1}), so that in conformity to this standard only sample No. 20 ('Casa da Nancy Marchi' – 14.4 mg. L^{-1}) presents possible risk to consumption.

For silica, there is no standard of potability in Brazil, neither by the Ministry of Health, nor by any other Brazilian legislation. However, according to international potability standards, this constituent is an important controlling agent of the toxic biological availability of aluminum in the waters, besides presenting several health benefits. Thus, internationally, the dietary recommendation between 35 and 45 mg.day^{-1} of silicon is recognized as important to avoid
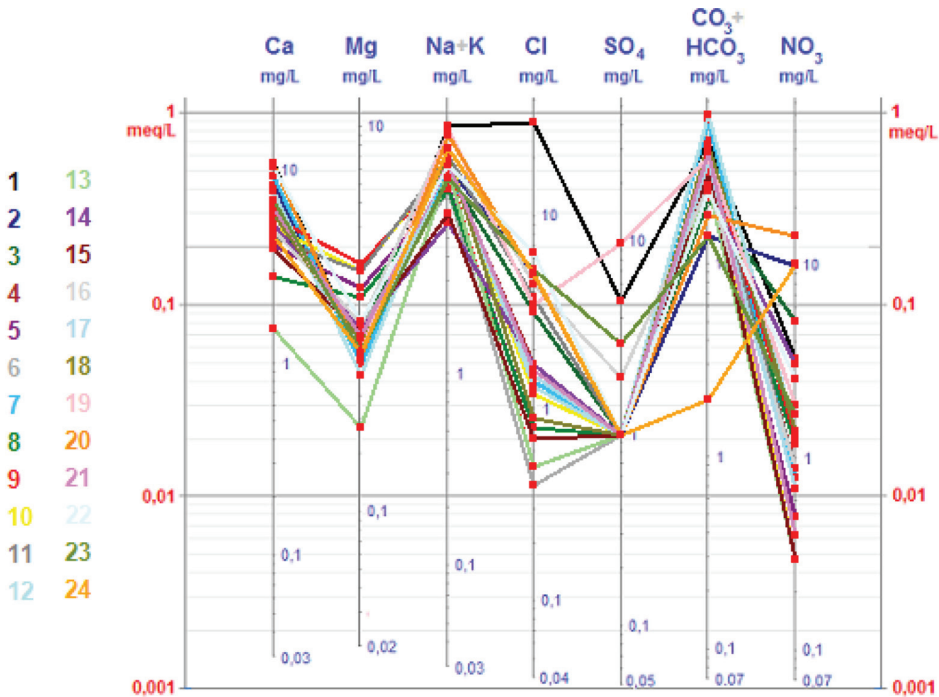
Figure 4: Insertion of the hydrochemical data in a Schoeller diagram.

symptoms of its deficiency [22]. The main guidelines and legislations from other countries to classify silicate mineral waters suggest the following minimum levels of Si needed in the waters [23]: 17.9 mg. L^{-1} in Japan; 23.4 mg. L^{-1} in Russia; 25.3 mg. L^{-1} in Poland; 14.1 mg. L^{-1} in Spain; 18.7 mg. L^{-1} in Cuba; and 45.1 mg. L^{-1} in the USA. Thus, according to these countries, the range of variation for silicon is from 14.1 to 45.1 mg. L^{-1}. The water samples analyzed in this work exhibited silica concentrations ranging from 16.5 to 54.7 mg. L^{-1}, practically equivalent to what has been considered suitable for human consumption due to beneficial therapeutic properties.

5 CONCLUSION

This work is a contribution to the survey of new physicochemical, chemical, and radiometric data of groundwater occurring in Serra Negra, State of São Paulo, Brazil, which are extremely important for the municipality because its potable waters are generally consumed by a large number of visitors. The results obtained indicated that, in general, the analyzed waters are suitable for human consumption, considering the parameters analyzed. The sample No. 24 is slightly acidic, whose pH = 5.4 is lower than the minimum recommended by the WHO [3] and Brazilian Ministry of Health [12] for potable waters (pH = 6). However, this pH value is equivalent to that often found in rainwater (pH = 5.5).

   The water sample No. 20 ('Casa da Nancy Marchi') presented nitrate concentration above the reference value in Brazil and abroad, recommending the need of a greater control in its use for human consumption and also the realization of complementary analyses to better evaluate its quality. Since there are few and rare nitrogen-based minerals, the geological

framework would hardly alter nitrate levels in the waters. However, this ion is commonly found in groundwater. In areas of heavy use of chemical fertilizers or animal waste, nitrate concentration is significant and may represent an anthropic polluting source. Thus, because the study area is a coffee growing region, with significant fracturing due to its lithological characteristics, it is believed that this nitrate accumulation should be associated with the use of NPK fertilizers, very commonly utilized in the cultivation of this grain.

As seen in this work, aquifers in Serra Negra city are fractured, free to semi-confined. Thus, according to processes of hydrogeochemical evolution of the waters, in the unconfined parts we usually see the presence of calcium bicarbonate waters that evolve to sodium bicarbonated waters due to ion exchange processes in the deepest parts of the aquifers. Therefore, most of the collected waters should be in this transition to a more evolved phase, based on the predominance of sodium in 75% of the samples. The main anion present in the groundwater samples is bicarbonate (HCO_3^-), probably due to the entry of CO_2 dissolved in rainwater during recharge, and secondarily as a function of carbonate (CO_3^{2-}), a product of the geochemical evolution of the carbonate system, since in an open system, the degradation of organic matter makes the pH acidic (<6.3), with greater abundance of H_2CO_3.

The results obtained from the statistical analysis based on the Pearson's correlation coefficient (r) involving EC, TDS, DR, and the ions Cl^-, Na^+ and Ca^{2+} agreed with others reported in the literature. Regarding water radioactivity, the combined gamma–alpha spectrometric technique used in this study proved to be applicable and reliable to provide important data on the gross alpha and beta activity of potable waters. The results obtained, in general, show that the methodology adopted in the study allowed estimates of values below the critical detection levels corresponding to 0.001 Bq. L^{-1} (gross alpha) and 0.03 Bq. L^{-1} (gross beta). Furthermore, none of the water sample exhibited activity concentration greater than 1 and 0.5 Bq. L^{-1} for gross beta and alpha, respectively, as recommended by WHO [3]. Therefore, the studied water sources are suitable for drinking purposes, based on these radiological parameters.

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