



**Evaluation of the Quality of Drinking
Mineral Waters Commercialized in Niterói Municipality- RJ**
Avaliação da Qualidade de Águas Minerais Comercializadas no Município de Niterói - RJ

Daniele de Souza Portugal; Camila Rodrigues e Silva;
Daniela Vasconcelos Machado; Luana Alves de Lima & Emmanoel Vieira da Silva-Filho

*Universidade Federal Fluminense, Instituto de Química, Departamento de Pós-Graduação em Geociências (Geoquímica),
Outeiro São João Baptista s/n - Center, 24020-141, Niterói, RJ, Brasil*

E-mails: danieleportugal@id.uff.br; r.s.camila@hotmail.com;

dvasconcelos@id.uff.br; luanalimageol@gmail.com; emmanoelvieirasilvafilho@id.uff.br

Recebido em: 10/04/2019 Aprovado em: 30/05/2019

DOI: http://dx.doi.org/10.11137/2019_2_299_308

Resumo

O consumo de água mineral tem apresentado um crescimento mundial e está associado à preocupação crescente com a qualidade da água, em parte devido à poluição de corpos hídricos superficiais, e a busca por um estilo de vida mais saudável. Segundo o Departamento Nacional de Produção Mineral (DNPM), em 2014, o Brasil permaneceu como 5º maior mercado de água engarrafada do mundo e 8º maior produtor mundial, tendo consumido 19,5 bilhões de litros. Diante da grande procura por uma água de boa qualidade, é necessário o constante monitoramento da água mineral engarrafada comercializada. Este trabalho tem como objetivo averiguar se as características físico-químicas das águas minerais engarrafadas consumidas na cidade de Niterói estão de acordo com o que é apresentado no rótulo das embalagens e com a legislação brasileira. Para atender tal objetivo foram realizadas análises físico-químicas, iônicas e microbiológicas em quatro marcas distintas, num período de quatro meses. As águas analisadas podem ser classificadas como águas bicarbonatadas sódica e cálcica. Os resultados obtidos mostram que as águas minerais estudadas estão em conformidade com os limites estabelecidos pela legislação brasileira, entretanto as concentrações dos íons maiores se mostraram maiores do que o descrito no rótulo, indicando uma possível evolução geoquímica das águas captadas das fontes.

Palavras-chave: água envasada; qualidade microbiológica; metais pesados

Abstract

The consumption of mineral water has grown worldwide and is associated with growing concern about water quality, in part due to the pollution of surface water bodies and the search for a healthier lifestyle. According to the National Department of Mineral Production (DNPM), in 2014, Brazil remained the 5th largest bottled water market in the world and the 8th largest producer in the world, consuming 19.5 billion liters. Faced with the wide demand for good quality water, it is necessary constant monitoring bottled mineral water. This work aims to determine if the physicochemical characteristics of bottled mineral waters consumed in the municipality of Niterói are in accordance with what is presented on the water bottle label and with Brazilian legislation. To attend this objective, physicochemical, ionic, and microbiological analyses were performed in four distinct brands over four months. The analyzed waters can be classified as sodium and calcium bicarbonate. The obtained results show that the mineral waters studied are according to the limits established by the Brazilian legislation. However, the concentrations of the larger dissolved ions were higher than the one described on the label, indicating a possible geochemical evolution of the water collected from the sources.

Keywords: bottled water; microbiological quality; heavy metals

1 Introduction

The mineral waters in Brazil are defined by the Code of Mineral Waters, created in 1945, as those from natural or artificially sources, which have a unique physical and chemical composition, with properties other than common drinking water, and has characteristics that confer some medication properties, such as diuretic and digestive functions, alkaline-bicarbonate waters, and prevention of anemia and hyperthyroidism, as ferruginous mineral waters (Brasil, 1945; Petraccia *et al.*, 2006; Branco, 2016).

The increase in bottled mineral water consumption is a worldwide trend and is associated with growing concern about water quality, in part due to water pollution, and the search for a healthier lifestyle and better wellbeing (Leclerc & Moreau, 2002; ABINAM, 2019). In 2014, it was consumed worldwide 283 billion liters of mineral water, surpassing the soft drink market (Rodwan Jr, 2015; Branco, 2016; DNPM, 2016). Brazilian production has grown gradually, with annual growth close to 20%, being the 8th largest producer of bottled mineral water in the world (ABINAM, 2019).

The exploration of mineral water in Brazil is regulated by the National Department of Mineral Production of the Ministry of Mines and Energy (DNPM). The definition and control of potability are the responsibility of the National Health Surveillance Agency of the Ministry of Health (ANVISA/MS).

The quality of drinking water is evaluated by physicochemical, biological, and organic analyzes. Besides, the mineral water can only be consumed if its content complies with established regulatory limits, considering the maximum daily intake in the long term, the nature of the contaminating agent and its possible degree of toxicity (Petraccia *et al.*, 2006).

The presence of heavy metals in drinking water is a public health problem and is associated with the development of carcinogenic diseases and other harmful effects on health. Although few heavy metals are essential for humans, excess ingestion of these and other non-essential metals can be toxic

(Celere *et al.*, 2007; Badr *et al.*, 2011; Chowdhury *et al.*, 2016). The toxicity level depends on the nature of the metal, its biological function, and the type of organisms that are exposed to it (Sing *et al.*, 2011).

The physicochemical characteristics of the bottled water found in the markets may vary according to the composition of the water sources, the treatment and purification procedures applied, and the environmental factors. Also, changes in the chemical composition of water may occur during storage and transport, especially when the bottles are exposed to direct sunlight (Mihayo & Mkoma, 2012).

As a result, this research aimed to evaluate the quality of the main brands of mineral water commercialized in the Niterói municipality. To achieve this purpose, the analysis of the microbiological and physicochemical parameters were performed, as well as its main cations, anions, and metals present in order to obtain the classification of mineral waters. In addition, the information contained in the product labels were verified and compared with the values obtained in the laboratory, in order to certify if they are in accordance with the limits established in the Brazilian legislation.

2 Materials and Methods

2.1 Study Area and Sampling

The study was carried out in the city of Niterói (22°52'51" S, 43°6'15" W), located in the state of Rio de Janeiro, in southeastern Brazil. Currently, the population of the city is estimated at 511 thousand inhabitants in an area of 134 km², according to IBGE (2017).

The research was limited to evaluating four leading bottled mineral water brands available in supermarkets located in the districts of Centro, Ingá and São Domingos, where four lots of each brand (between June and October 2017) were obtained, totaling 16 samples of mineral water. To maintain the anonymous brands, the samples were labeled A, B, C, and D and from 1 to 4 for the respective batches. Brand A has several sources from Brazil, but in this work, the sources Yguaba (A1) and Ipiranga, for samples A2, A3, and A4 were analyzed. The waters

of brands B, C, and D come from sources: Levíssima, Água Santa, and Santo Antônio, respectively.

The four brands analyzed showed in their labels pH, electrical conductivity (EC) and calcium, magnesium, sodium, potassium, chloride, bicarbonate, barium, and strontium concentrations. However, elements such as fluoride, nitrate, sulfate, and phosphate were not reported on all labels.

2.2 Geological Context

The waters of brand A studied came from two sources, Yguaba and Ipiranga. The Yguaba source, belonging to lot 1, is located in Mogi das Cruzes in the state of São Paulo and located between two lithological border units. One of them is part of the Southeast Eastern Shield formed by mylonite and metaultraphic rocks, rich in iron and magnesium. The other unit refers to the São Paulo Formation that contains sedimentary rocks, coarse sandstones, and conglomerates. The Ipiranga source, relative to samples A2 to A4, is located in Ribeirão Preto, also in São Paulo, and forms part of the Serra Geral Formation formed by basaltic rocks related to volcanic lava where iron and magnesium-rich minerals predominate, rhyolitic rocks, acid volcanic rocks predominant in silicic minerals, rich in sodium and potassium, and also composed of diabásicas rocks composed of calcium plagioclase and mafic minerals, rich in sodium, calcium and iron and magnesium (Pessoa *et al.*, 1980; CETESB, 2019).

The Água Santa source, corresponding to samples from brand C, is located in Campos do Jordao in São Paulo, and is part of Varginha Unit - Guaxupé composed of paragneiss migmatites with rock types of biotite gneiss consisting of potassium feldspar, plagioclase, quartz and biotite where iron and aluminum predominant, metamargas rocks that are sedimentary rocks of carbonated classes and calcissilictic rocks, rich in calcium and silica (Pessoa *et al.*, 1980; CETESB, 2019).

The sources Levíssima and Santo Antônio, referring to samples of brands B and D, respectively, are located in Petrópolis, RJ, and are part of the Santo Aleixo Unit - Suite Serra dos Órgãos composed

of foliar granitoids that originate from magmatic rocks containing feldspar (rich in calcium and sodium) and silica, orthogneiss type I, calc-alkaline of high and medium content of potassium (Valladares *et al.*, 2012).

2.3 Laboratory Tests

The microbiological quality of the waters was evaluated by quantification of total and thermotolerant coliforms (*Escherichia coli*) using the Colilert Test, in which the samples were placed in appropriate 100 mL vessel, the chromogenic substrate (defined substrate technology) added and then transferred to Quanti-Tray/2000 cartons and incubated at 36° C for 24 hours. After the incubation period, the NMP (Most Likely Number) was obtained for total coliforms and, with the aid of an ultraviolet chamber, the NMP for thermotolerant coliforms was obtained. This analysis was performed immediately after opening the bottles.

The pH was determined by a portable probe (Hanna Instruments Model HI 98183) calibrated with buffer solutions of pH = 4.0; 7.0 and 10.0. The electrical conductivity was obtained using a bench glass electrode (Hanna Instruments, Model HI 255), calibrated with a solution of 1413 $\mu\text{S cm}^{-1}$ and the concentration of total dissolved solids (TDS) was determined empirically from the conductivity (EC), based on Equation 1:

$$\text{TDS} = 0,68 \times \text{EC} \quad (1)$$

Alkalinity was determined by titration with a standard solution of hydrochloric acid (0.01 N) as the titrant, following the model proposed by Grasshoff *et al.* (1983). From the concentration of total alkalinity and pH, the bicarbonate (HCO_3^-) concentrations were estimated for each sample by Equation 2:

$$\text{HCO}_3^- = \frac{(\text{Total alkalinity} \div 50) + 10^{3-\text{pH}} - 10^{\text{pH}-11} \times 61,02}{9,38 \times 10^{\text{pH}-11}} \quad (2)$$

The phosphate (PO_4^{3-}) and silica (SiO_2) ions were analyzed in the spectrophotometer (Instrutherm, Model UV-2000A) using the colorimetric method described by Grasshoff *et al.* (1983), where the absorbance values (at wavelengths 880 nm and 810 nm, respectively) are determined and subsequently converted to concentrations in mg L^{-1} .

The ionic chromatography (Metrohm, compact model 850 Professional IC) was used to determine the ions calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), nitrate (NO₃⁻) and sulfate (SO₄²⁻). Finally, an aliquot of each sample was separated and acidified to 2% with nitric acid (HNO₃) and analyzed in the X-Series 2 inductively coupled plasma mass spectrometer (ICP-MS), in order to obtain the metals: antimony (Sb), arsenic (As), barium (Ba), lead (Pb), strontium (Sr), iron (Fe) and manganese (Mn).

2.4 Data Processing

The results obtained in the laboratory were compared to the values presented in the Brazilian legislation, to certify if they agree with the limits allowed for human consumption. In this work, the standards established by Ordinance of the Ministry of Health n° 2914 of December 12, 2011, which establishes water quality standards for human consumption and Resolution of the Collegiate Board of Directors (RDC) n° 274 of September 22, 2005, of ANVISA, that establishes on the technical regulation of the minimum characteristics of quality that must obey the mineral waters, natural and added of salts, packaged for human intake.

In order to compare the values and concentrations obtained in the laboratory with those presented

by the respective brands, the percentage difference (PD) calculation, given by $PD = (L - A) / L$, was used on the bottle label, where L represents the value shown on the label of the bottle and A is the average of values determined in the laboratory.

3 Results and Discussion

3.1 Water Quality Parameters

From the bacteriological point of view, all samples analyzed showed an absence of total coliforms and thermotolerant coliforms (E. coli), as required by the legislation. The pH presented values between 5.6 and 7.9, with an average of 6.9. EC and TDS presented values between 53.4 and 165.0 µS cm⁻¹ with a mean of 92.7 µS cm⁻¹ and 36.3 to 112.2 mg L⁻¹ with a mean of 63.1 mg L⁻¹, respectively. The total alkalinity presented values from 17.0 to 89.0 mgCaCO₃ L⁻¹ with a mean of 42.0 mgCaCO₃ L⁻¹.

Waters intended for human consumption, according to Brazilian legislation, Ordinance n° 2914/2011, must have pH values between 6.0 and 9.5 (Brasil, 2011). Among the analyzed samples, B4 and D4 were the only ones that were below the minimum limit allowed by the legislation, with pH equal to 5.6 and 5.9 respectively. About the TDS, all the samples are within the allowed limit of 1000 mg L⁻¹.

Brand	Batches	Parameters (mg L ⁻¹)										
		Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	F ⁻	NO ₃ ⁻	PO ₄ ³⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	SiO ₂
A	1	0.6	1.8	108.6	0.9	0.1	0.77	35.4	2.3	1.6	8.4	38.0
	2	1.4	0.2	22.0	0.1	2.2	0.87	0.1	0.6	0.9	6.4	26.5
	3	1.4	0.4	23.0	0.1	2.2	0.53	0.1	0.4	0.8	5.6	25.7
	4	1.5	0.4	28.1	0.1	2.3	0.51	0.1	0.4	0.9	6.3	26.4
B	1	1.1	1.8	23.4	0.1	0.1	0.03	0.3	0.1	0.5	6.4	15.1
	2	1.0	1.8	26.9	0.1	0.2	0.03	3.2	0.9	1.1	7.3	16.2
	3	1.1	1.9	25.7	0.1	0.2	0.09	0.3	0.2	0.5	6.8	16.4
	4	1.1	1.8	30.7	0.1	0.1	0.07	2.8	1.0	1.1	8.5	16.2
C	1	0.1	0.2	106.1	0.1	nd	0.03	0.9	0.8	10.9	21.9	22.9
	2	0.1	0.2	104.8	0.1	0.1	0.03	0.9	0.9	8.3	16.5	21.9
	3	0.1	0.2	108.6	0.1	0.1	0.08	1.1	1.2	10.6	22.1	22.2
	4	0.1	0.2	102.5	0.1	0.1	0.05	1.1	1.1	8.1	20.6	21.9
D	1	0.0	1.5	25.7	0.1	0.1	0.03	2.6	0.7	0.9	6.8	15.3
	2	1.1	1.7	20.8	0.1	0.2	0.03	0.3	0.1	0.5	6.1	16.2
	3	1.1	1.8	33.0	0.1	0.2	0.10	2.5	0.9	1.0	7.8	15.8
	4	1.1	1.9	39.1	0.1	0.2	0.05	3.4	1.0	1.4	10.2	16.4
Ord. 518/2004		250,0	250,0	-	1.5	10,0	-	200,0	-	-	-	-

Table 1 Ionic analyzes of bottled mineral waters.

Total alkalinity is the sum of different forms of alkalinity. Inorganic carbon species, bicarbonate ions (HCO_3^-), carbonates (CO_3^{2-}) and hydroxides (OH^-), the main constituents of alkalinity in natural waters, and predominance of one of the ions are directly related to the pH of the environment, where values between 4.4 and 8.3 occur the predominance of bicarbonate ion. In the bottled mineral water samples analyzed, the measured pH range is within the bicarbonate range.

Table 1 shows the results obtained from the chemical species evaluated and the respective maximum limits established by Ordinance 2914/2011 (Brasil, 2011). Among the main anions analyzed, HCO_3^- presented the highest concentration, followed by sulfate and chloride, with averages of 51.8 mg L^{-1} , 1.1 mg L^{-1} , and 0.8 mg L^{-1} respectively. Among the cations, calcium had the highest concentration, followed by sodium, magnesium, and potassium, where the mean concentrations were 10.5 mg L^{-1} , 3.4 mg L^{-1} , 3.1 mg L^{-1} , and 0.8 mg L^{-1} respectively. All concentrations are within limits permitted by the Brazilian laws for water consumption.

The waters brand A presented high concentrations of phosphate in comparison to the other brands, and in the case of silica, brands A and C presented the highest concentrations. These results are validated by the local geology of each source. The A samples came from a sedimentary type aquifer system

and the C samples came from a fractured aquifer, formed by igneous rocks and metamorphic, both rich in feldspars that are one of the most important sources of Si for the water (Riccomini & Coimbra, 1992; Yassuda *et al.*, 1992; Dantas *et al.*, 2005; CETESB, 2013; Bulia & Enzweiler, 2016).

On the other hand, it should be noted that the high phosphate concentrations in brand A (Mogi das Cruzes – A1 and Ribeirão Preto in São Paulo state) probably are associated with a strong presence of agriculture in that region. Mogi das Cruzes is the largest polo producer in vegetables, mushrooms, persimmon, orchids, and loquats in Brazil, while Ribeirão Preto has a prominent role in sugar cane plantation. Donadio *et al.* (2005) in a study developed in the Rico stream watershed, located in the northeastern region of the State of São Paulo, administrative region of Ribeirão Preto, evidenced the influence of PO_4^{3-} concentration on the deterioration of water quality associated with agriculture.

Besides this, the sample A1 comes from a different source from the other batches of that brand and based on Table 1 it is noted that it presents the highest concentrations of the bicarbonate, sodium and silica ions, and a high concentration of total solids dissolved in this sample, 108.1 mg L^{-1} . In the other brands, no significant discrepancies were observed in the total of ions between the lots, as shown in Figure 1.

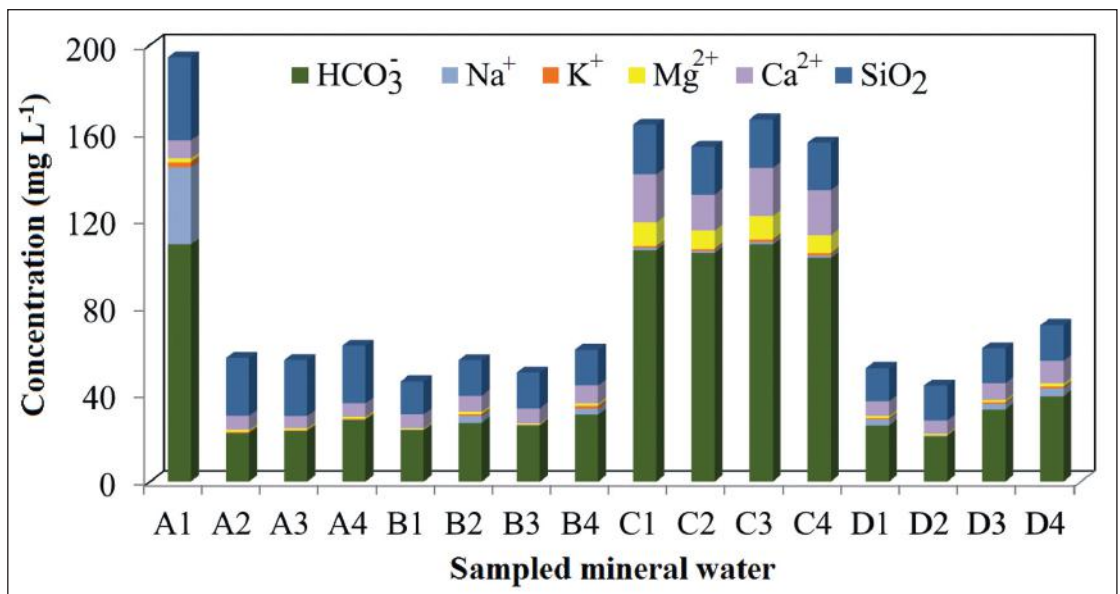


Figure 1 Total concentration of major elements present in sampled bottled waters.

The bicarbonate appears as the main component in all samples, and based on Figure 2, it is observed that its concentration represents between 47 and 66% of the total dissolved. Following the bicarbonate, there is in brand A, the abundance on crescent order of SiO_2 (30%) > Na^+ (9%) > Ca^{2+} (7%) for brand C, SiO_2 (14%) > Ca^{2+} (13%) > Mg^{2+} (6%). However, B and D brands had dominant concentrations of SiO_2 > Ca^{2+} > Na^+ with 29 and 27% of silica, 13% of calcium and 3 and 4% of sodium, respectively. Brands B and D present their sources within the same geological context showing similarity in the dominant concentrations, reflecting the local lithotypes.

Since the host rocks of the studied mineral waters do not contain significant amounts of carbonates, sulfates or haloids, bicarbonate, the main anion found, is the product of the dissociation of carbonic acid dissolved in water from atmospheric carbon dioxide or produced in the soil. This acid will produce HCO_3^- and H^+ , the latter being consumed in the dis-

solution reaction of the host rock minerals (Freeze & Cherry, 1979; Bertolo *et al.*, 2007; Bulia & Enzweiler, 2016).

From the average concentrations of bicarbonate, chloride, sulfate, sodium, potassium, calcium, and magnesium ions, it was possible to classify the hydrochemical types through the Piper diagram, shown in Figure 3. Based on the figure, it is possible to compare the water classification obtained with the bottle label information and experimentally. It is noted that the samples are in the field of calcium bicarbonate waters, except sample A1, classified as sodium bicarbonate waters, in (Figure 3A), however, according to the labels (Figure 3B) the mineral waters would be classified as sodium bicarbonate (brands A1 and B) and calcium bicarbonate (all other brands sampled).

This may be happening due to ion exchange of the Ca^{2+} ion by the Na^+ ion in this aquifer. According to Apello & Postma (2005), high Ca^{2+} contents

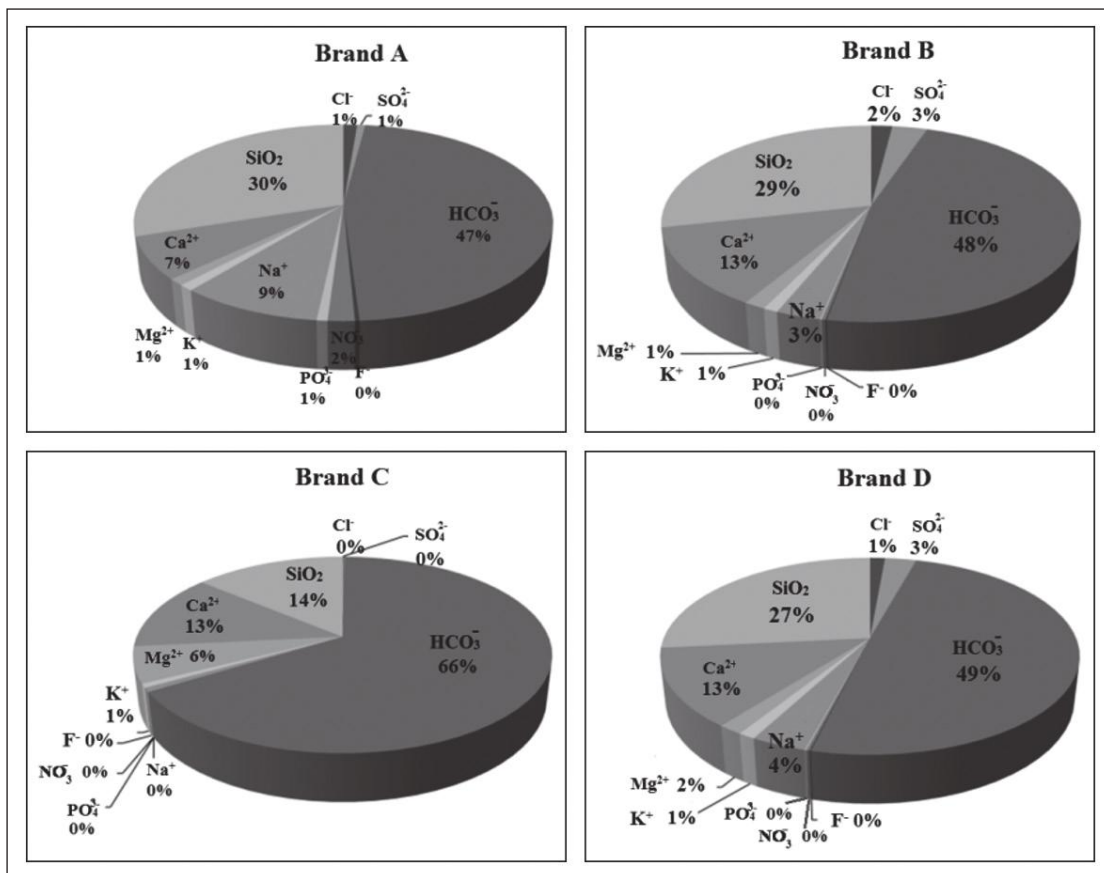


Figure 2
Abundance in percentage (%) of the main elements present in the bottled mineral waters.

that equilibrate with the HCO_3^- ion indicate that the cation exchange may be influencing the composition of the waters, which shows a possibility of their geochemical evolution.

3.2 Metals

Figure 4 and Table 2 are presented the total concentrations of the metals in the bottled mineral water samples. The total concentration of metals in samples A1 and A2 was approximately two times higher than the other samples. The B brand presented the highest concentrations of Sr, and among the batches of brand C, lot 2 presented the highest Fe concentration, which made the total metals for this sample to stand out over the others. The same can be observed for lot 1 of brand D.

Strontium does not have a limit value in Brazilian legislation. However, this element may represent a potential threat to human health due to its role in abnormal skeletal development and bone calcification (Langley *et al.*, 2009). The average concentration of strontium was $43.4 \mu\text{g L}^{-1}$, and the samples of the brand C showed the lowest levels of this element.

Iron and manganese when present in high concentrations in the water give it a characteristic flavor, also, manganese is associated with the devel-

opment of neuropsychiatric diseases and behavioral disorders (Dobson *et al.*, 2004). The mineral water samples have an average of $40.9 \mu\text{g L}^{-1}$ and $4.2 \mu\text{g L}^{-1}$ for Fe and Mn, respectively. The Fe concentrations varied largely among the samples of the same brand. In samples A4 and C3, the concentrations were below the detection limit, and in sample A1, the highest concentration ($216.6 \mu\text{g L}^{-1}$) was measured. The maximum limit established is $300 \mu\text{g L}^{-1}$; all samples were within the permitted limits. Mn did not exceed values of $10 \mu\text{g L}^{-1}$, with the highest concentration found in sample B3 ($9.4 \mu\text{g L}^{-1}$). Samples A3, A4, C3, and C4 did not show concentrations of Mn, and all others were in the legislation ($< 500 \mu\text{g L}^{-1}$).

Antimony can occur associated with arsenic, in addition to being found in PET plastic packaging. Arsenic has high toxicity, and all its soluble compounds are poisonous (Lafuente, 1981). Thus, their concentrations need to be limited to human consumption purposes. Brazilian legislation determines maximum concentrations of $10 \mu\text{g L}^{-1}$ and $5.0 \mu\text{g L}^{-1}$ for As and Sb, respectively. All the samples analyzed presented concentrations within limits allowed by law, and again, in sample A1, the highest concentration of both elements was found ($4.6 \mu\text{g L}^{-1}$ for As and $0.7 \mu\text{g L}^{-1}$ for Sb). The mean concentrations obtained were $0.8 \mu\text{g L}^{-1}$ for As and $0.3 \mu\text{g L}^{-1}$ for Sb.

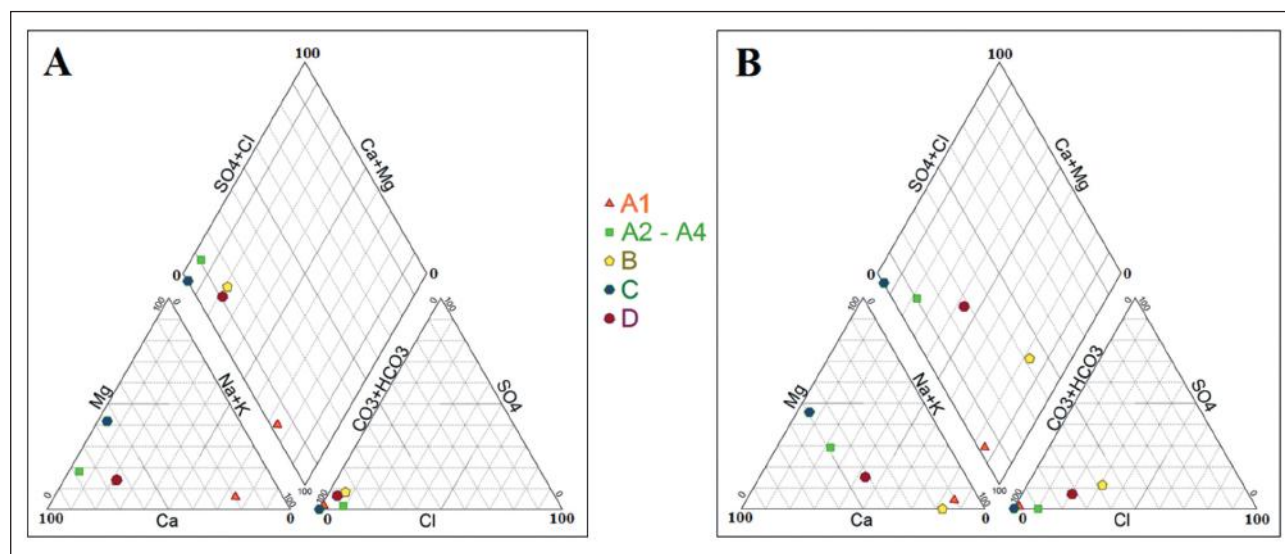


Figure 3 (A) Piper diagram of mineral waters analyzed in laboratory (B) Piper diagram of results presented on bottle labels.

Evaluation of the Quality of Drinking Mineral Waters Commercialized in Niterói Municipality- RJ

Daniele de Souza Portugal; Camila Rodrigues e Silva; Daniela Vasconcelos Machado; Luana Alves de Lima & Emmanoel Vieira da Silva-Filho

		Parameters ($\mu\text{g L}^{-1}$)								
Brand	Batches	Fe	Ba	Sr	As	Cu	Sb	Mn	Pb	Cr
A	1	216.60	136.70	45.82	4.60	0.73	0.66	0.54	0.23	0.29
	2	174.80	117.90	50.95	0.58	0.97	0.21	1.24	0.48	1.86
	3	1.03	103.20	43.33	0.83	0.00	0.22	< DL	< DL	1.97
	4	< DL	108.50	45.91	0.64	0.04	0.20	< DL	< DL	2.01
B	1	4.80	15.06	49.36	0.03	0.21	0.32	6.54	< DL	0.57
	2	12.67	14.83	54.89	0.02	1.72	0.32	8.35	< DL	0.51
	3	0.78	14.07	54.55	0.58	0.01	0.28	9.37	< DL	0.63
	4	1.30	13.59	56.45	0.46	< DL	0.42	8.05	< DL	0.61
C	1	3.78	15.09	47.85	< DL	< DL	0.34	7.16	< DL	0.31
	2	92.32	26.14	22.12	0.02	0.18	0.39	0.44	0.02	0.64
	3	< DL	23.48	19.76	1.36	< DL	0.27	< DL	< DL	0.32
	4	2.05	24.90	20.92	1.28	< DL	0.28	< DL	< DL	0.39
D	1	132.10	21.55	15.61	< DL	0.04	0.36	0.14	0.01	0.67
	2	11.87	15.54	49.41	0.03	0.75	0.39	8.56	1.04	0.72
	3	0.96	14.24	58.82	0.54	1.72	0.39	9.07	< DL	0.67
	4	0.30	13.91	58.38	0.48	0.06	0.46	7.00	< DL	0.64
Legislation		300.0	700.0	-	10.0	2000.0	5.0	100.0	10.0	50.0

Table 2 Concentration of the metals analyzed in comparison with the potability standards of the Ministry of Health and ANVISA. DL = Detection Limit.

According to Feitosa *et al.* (2008), high levels of lead can cause intoxication, causing brain damage or death in extreme cases, however, even at low concentrations, this element can inhibit enzymes associated with hemoglobin synthesis leading to anemia (Silvany-Neto *et al.*, 1996). By law, drinking water must have a maximum concentration of $10 \mu\text{g L}^{-1}$. Concentrations of Pb were detected only in 5 samples: A1, A2, C2, D1 and D2, the latter being the highest concentration equal to $1.0 \mu\text{g L}^{-1}$.

3.3 Comparison with the Bottle Label

Figure 5 shows the percentage difference (PD) between the mean values found in the laboratory and the values described on the label of each brand, expressed as a percentage (%). Negative values indicate that the mean values found in the analyzes were higher than the values indicated on the bottle labels. In contrast, positive values show averages lower than those indicated by the brand. The closer to zero,

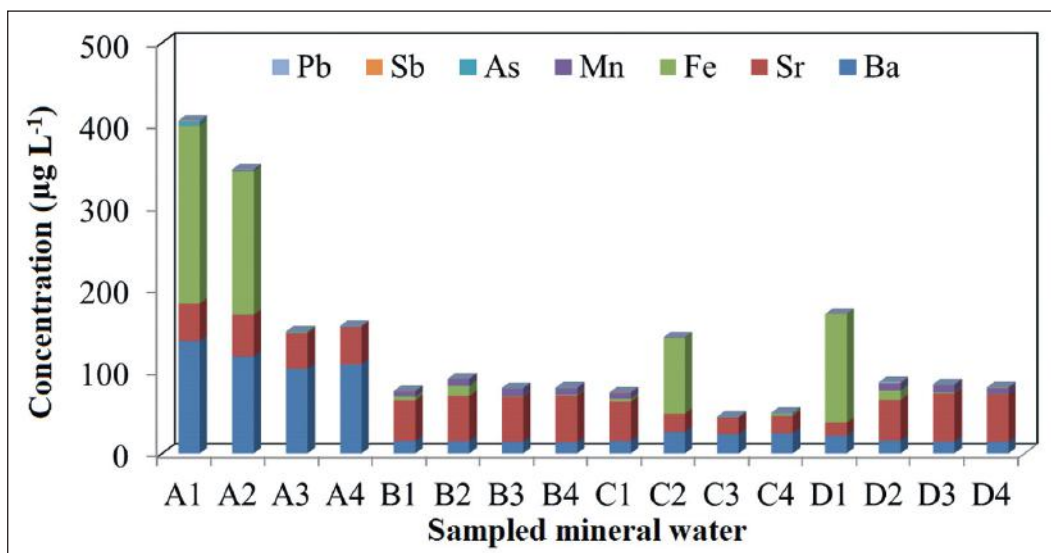


Figure 4 Concentration of the main metals present in the bottled mineral water analyzed.

the smaller the difference between the analysis and the bottle label. For mark A, lot 1 was analyzed separately because of the difference in the source.

For pH, F-, PO₄³⁻ and Ba, the PD was very close to zero, indicating conformity between the label and the results obtained. All brands presented positive PD for Cl⁻, NO₃⁻, PO₄³⁻ and K⁺, indicating a lower concentration of these ions than indicated by the brands. The opposite occurs with SO₄²⁻ and Ca²⁺, where for all brands PD was negative, indicating higher values than indicated on the label. The results obtained in the analyzes of HCO₃⁻, Ca²⁺ and Sr for the B and D marks were much higher than those indicated on the label. The D mark, in general, was the one that presented more distinct and higher values in the analyzes than the values indicated by the manufacturer.

5 Conclusions

The results obtained from the analysis of the bottled mineral waters carried out in the laboratory were mostly, close to or below the values described on the bottle labels for all brands except calcium, bicarbonate, sulfate and magnesium ions whose ionic contents were higher than those reported. This fact may be related to the groundwater geochemical evolution originated from the studied sources that become more mineralized.

With the exception of samples B4 and D4, which diverged from the acceptable pH standard of potable water, all other samples from the four brands, even in divergence between the values found

and those labeled, were in accordance with the recommended physicochemical and microbiological standards for in the case of this work, Ordinance n° 2914 of December 12, 2011 and Resolution of the Collegiate Board of Directors (RDC) n° 274 of September 22, 2005, of the National Agency of Sanitary Surveillance (ANVISA).

6 Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Financial Code 001.

7 References

Apello, C.A.J. & Postma, D. 2005. *Geochemistry, groundwater and pollution*. Balkema Publishers, Amsterdam, 649p.

Associação Brasileira de Indústria de Água Mineral (ABINAM). 2019. Água Mineral: uma fonte de benefícios para a saúde. Available in: <http://www.abinam.com.br/lermais_materias.php?cd_materias=398&friurl=AguaMineral: uma fonte de beneficios-para-a-saude-:#topo>. Accessed on: Feb, 3, 2019.

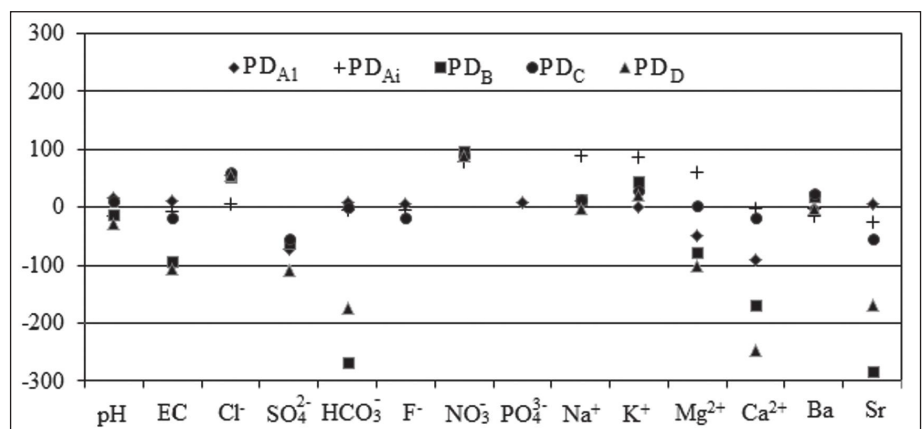
Badr, E.A.E.; Agrama, A.A.E. & Badr, S.A.E. 2011. Heavy metals in drinking water and human health, Egypt. *Nutrition & Food Science*, 41(3): 210-217.

Bertolo, R.; Hirata, R. & Fernandes, A. 2007. Hidrogeoquímica das águas minerais envasadas do Brasil. *Revista Brasileira de Geociências*, 37(3): 515-529.

Branco, P.M. 2016. Coisas que você deve saber sobre a água. Companhia de Pesquisa de Recursos Minerais – Serviço Geológico Do Brasil. Available in: <<http://www.cprm.gov.br/publique/Redes-Institucionais/Rede-de-Bibliotecas---Rede-Ametista/Canal-Escola/Coisas-que-Voce-Deve-Saber-sobre-aAgua1084.html#mineral>>. Accessed on: Mar, 10, 2019.

Brasil. 1945. *Código de Águas Minerais*. Decreto-Lei n° 7.841 de 8 de agosto de 1945. Diário Oficial da União de

Figure 5 Percentage difference (PD) between the mean values found in the laboratory and the values described on the label of each brand, expressed as a percentage (%). Ai = average between A2, A3, and A4.



- 20/08/1945, Brasília, Distrito Federal.
- Brasil. 2011. *Portaria nº 2914, de 12 de dezembro de 2011*. Legislação para águas de consumo humano e padrão de potabilidade. Diário Oficial [da] República Federativa do Brasil, Brasília, Distrito Federal.
- Bulía, I.L. & Enzweiler, J. 2016. Hidrogeoquímica de águas minerais envasadas para o estado de São Paulo. In: CONGRESSO BRASILEIRO DE ÁGUAS SUBTERRÂNEAS, 19, São Paulo, 2016. Anais, São Paulo.
- Celere, M.S.; Oliveira, A.S.; Trevilato, T.M.B. & Segura-Muñoz, S.I. 2007. Metals in landfill leachate in Ribeirão Preto, São Paulo State, Brazil, and its relevance for public health. *Caderno de Saúde Pública*, 23(4): 939-947.
- Chowdhury, S.; Mazumder, M.A.J.; Al-Attas, O. & Hunsai, T. 2016. Heavy metals in drinking water: Occurrences, implications, and future needs in developing countries. *Science of the Total Environment*, 569-570: 476-488.
- Companhia Ambiental do Estado de São Paulo (CETESB). 2013. *Qualidade das águas subterrâneas do estado de São Paulo 2010-2012*, State Secretary for the Environment, 242p.
- Companhia Ambiental do Estado de São Paulo (CETESB). 2019. Águas subterrâneas. Available in: <<https://cetesb.sp.gov.br/aguas-subterraneas/programa-demonitoramento/consulta-por-aquiferos-monitorados/>>. Accessed on: Mar, 10, 2019.
- Dantas, M.E.; Goulart, D.R.; Jacques, P.D.; Almeida, I.S. & Krebs, A.S.J. 2005. Geomorfologia aplicada à gestão integrada de bacias de drenagem: bacia do rio Araranguá (SC), zona carbonífera sul-catarinense. In: LIVRO DE RESUMOS, João Pessoa, 2005, 74p.
- Departamento Nacional de Produção Mineral (DNPM). 2016. *Sumário Mineral*, Ministry of Mines and Energy, 146p.
- Dobson, A.; Erikson, K.M. & Aschner, M. 2004. Manganese Neurotoxicity. *Annals of the New York Academy of Sciences*, 1012: 115-129.
- Donadio, N.M.M.; Galbiatti, J.A. & de Paula, R.C. 2005. Qualidade da água de nascentes com diferentes usos de solo na bacia hidrográfica do córrego Rico, São Paulo, Brasil. *Engenharia Agrícola*, 25(1):115-125.
- Feitosa, F.A.C.; João, M.F.; Feitosa, E.C. & Demetrio, J.G. 2008. *Hidrogeologia: Conceitos e Aplicações*. Rio de Janeiro, CPRM, 812p.
- Freeze, R.A. & Cherry, J.A. 1979. *Groundwater*. Prentice Hall, Englewood Cliffs, 604p.
- Grasshoff, K.; Ehrhardt, M. & Kremling, K. 1983. *Methods of seawater analysis*. Weinheim, Verlag Chemie, 634p.
- IBGE. 2017. Instituto Brasileiro de Geografia e Estatística. Available in: <<https://cidades.ibge.gov.br/>>. Accessed on: Feb, 3, 2019.
- Lafuente, J.C. 1981. *Química del agua*. Madrid, Bellisco, 423p.
- Langley, S.; Gault, A.G.; Ibrahim, A.; Takahashi, Y.; Renaud, R.; Fortin, D.; Clark, I.D. & Ferris, F.G. 2009. Sorption of Strontium onto Bacteriogenic Iron Oxides- *Environmental Science & Science*, 43(4): 1008-1014.
- Leclerc, H. & Moreau, A. 2002. Microbiological safety of natural mineral water. *FEMS Microbiology Reviews*, 26(2): 207-222.
- Mihayo, I.Z. & Mkoma, S.L. 2012. Chemical water quality of bottled drinking water brands marketed in Mwanza city, Tanzania. *Research Journal of Chemical Science*, 2(7): 21-26.
- Pessoa, M.D.; Mente, A. & Leal, O. 1980. Províncias hidrogeológicas adotadas para o mapa hidrogeológico do Brasil na escala 1:2.500.000. In: CONGRESSO BRASILEIRO DE ÁGUAS SUBTERRÂNEAS, 1, Pernambuco, 1980. Anais, Pernambuco.
- Petraccia, L.; Liberati, G.; Masciullo, S.G.; Grassi, M. & Fraioli, A. 2006. Water, mineral waters and health. *Clinical Nutrition*, 25: 377-385.
- Riccomini, C. & Coimbra, A.M. 1992. Geologia da Bacia Sedimentar de São Paulo. In: SOLOS DA CIDADE DE SÃO PAULO, 1992.
- Rodwan Jr., J.G. 2015. Bottled Water 2014: Reinvigoration. *Bottled Water Reporter*, 55(4): 10-20.
- Silvany-Neto, A.M.; Carvalho, F.M.; Tavares, T.M.; Guimarães, G.C.; Amorim, C.J.B.; Peres, M.F.T.; Lopes, R.S.; Rocha, C.M. & Raña, M. 1996. Evolução da intoxicação por chumbo em crianças de Santo Amaro, Bahia - 1980, 1985 e 1992. *Boletín de la Oficina Sanitaria Panamericana*, 120(1): 11-22.
- Sing, S.; Lal, S.; Harjit, J.; Amlathe, S. & Kataria, H.C. 2011. Potential of metal extractants in determination of trace metals in water sample. *Advanced Studies in Biology*, 3(5): 239-246.
- Valladares, C.S.; Gontijo-Pascutti, A.; da Silva, T.M.; Heilbron, M.; de Almeida, J.C.H.; Duarte, B.P.; Tupinambá, M.; Nogueira, J.R.; Valeriano, C.M.; Silva, L.G.E.; Schmitt, R.; Ragatky, C.D.; Geraldles, M.; Valente, S.C.; André, J.L.F.; Corval, A.; Viana, S.M.; da Mota, G.S.; Menezes, P.T.L.; Mane, M.A.; Palermo, N.; Melo, R.P.; Guimarães, P.V. & da Silva, F.L. 2012. *Geologia e recursos minerais da folha Três Rios SF.23-Z-B-I, estado do Rio de Janeiro escala 1:100.000*, Ministry of Mines and Energy, CPRM, 136p.
- Yassuda, C.T.; Hori, K. & Rocha, H.C. 1992. Água do subsolo. In: MESA REDONDA - SOLOS DA CIDADE DE SÃO PAULO, ABMS/ABEF, 4, São Paulo, 1992.