

# Hydrochemical Assessment of Spring Waters from the Iron Quadrangle Region, Minas Gerais, Brazil

Cláudia A. Ferreira<sup>1,\*</sup>, Helena E. L. Palmieri<sup>2</sup>, Maria Ângela de B. C. Menezes<sup>2</sup>, Lúcia M. L. A. Auler<sup>2</sup>

<sup>1</sup>Pos Graduation in Science and Radiation Technology, Minerals and Materials, (CDTN/CNEN), Belo Horizonte, Minas Gerais, Brazil

<sup>2</sup>Nuclear Technology Development Centre/Brazilian Commission for Nuclear Energy (CDTN/CNEN), Belo Horizonte, Minas Gerais, Brazil

\*Corresponding author: [cferreiraquimica@yahoo.com.br](mailto:cferreiraquimica@yahoo.com.br)

**Abstract** This study deals with the hydrochemical characterization and water quality assessment of springs spread throughout the Iron Quadrangle (IQ) in the state of Minas Gerais, Brazil. In the past these spring waters played an essential and strategic role in supplying towns with potable water. Up to this day water is used by both the local population and tourists who thrust in its quality. A total of forty-four spring water and four artesian well water samples were collected at 26 points in different municipalities of the IQ in two different surveys, March and August 2015, wet and dry seasons, respectively. These water samples were studied for 38 physico-chemical parameters: turbidity (TB), electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), pH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SiO<sub>2</sub>, Fe, Li, V, Cr, Cr (VI), Co, Ni, Cu, As, Ba, Al, Mn, Zn, Sb, Cd, Mo, Se, Tl, Hg and U, as well as thermotolerant coliforms (TC). The pH value of groundwater in the study area ranges from 3.8 to 7.0, indicating the acid nature of most of the spring water samples. In these samples, Ca<sup>2+</sup> and Na<sup>+</sup> are the major cations and HCO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> the dominant anions. As expected, the trace metals presented the following decreasing concentrations: Fe > Ba > Al > Mn > Zn > Ni, since the IQ region is abundant in iron, aluminum and manganese minerals. The chemical relationships in Piper diagram identified mixed-bicarbonate, magnesium-bicarbonate and sodium-bicarbonate as the most prevalent water types. The Gibbs plots of data from the study area indicated that the chemical composition of most spring water samples was controlled primarily by rainfall dominance. Except for some springs, groundwater in the study area are inappropriate for drinking and domestic purposes but good for animal consumption, irrigation and recreation.

**Keywords:** *spring waters, Iron Quadrangle, Minas Gerais-Brazil, hydrochemical assessment, trace elements*

**Cite This Article:** Cláudia A. Ferreira, Helena E. L. Palmieri, Maria Ângela de B. C. Menezes, and Lúcia M. L. A. Auler, "Hydrochemical Assessment of Spring Waters from the Iron Quadrangle Region, Minas Gerais, Brazil." *American Journal of Water Resources*, vol. 5, no. 2 (2017): 29-40. doi: 10.12691/ajwr-5-2-2.

## 1. Introduction

Water is probably the only natural resource which is a primary requirement in all aspects of human civilization, from agricultural and industrial development to cultural and religious values embedded in society [1]. It is an essential element for life, a basic necessity and is the world's most valuable asset in future resources. Therefore, potable water must be provided to all [2]. Although almost two thirds of our planet is covered with water, only a tiny fraction of less than 1% is available to the needs of mankind as pure and healthy freshwater. Almost all available resources are stored underground (about 99%) from where they must be tapped for drinking water supply as well as for agricultural, industrial and environmental purposes. Hosted in various types of aquifers, groundwater appears at the surface in the form of spring feeding streams and wetlands. While still underground, they provide an estimated 25% to 40% of all drinking water on the planet. They may interact with various minerals in the aquifer and become enriched in several

elements, some of which are good for our health but others are less so and some can even be toxic if the critical concentrations are exceeded [3].

The increased and inadequate use of conventional fresh water sources like rivers, reservoirs, lakes, and wells have severely decreased the quality and availability of fresh water resources and have, therefore, intensified the search for alternate sources for meeting potable water requirements worldwide. Spring discharge, rain water harvesting, desalination of sea water, etc., are some of the alternate sources of fresh water in several tropical and subtropical regions [4].

Groundwater quality depends not only on natural factors such as aquifer lithology, groundwater velocity, quality of recharge waters and interaction with other types of water or aquifers, but also on anthropogenic activities, which can alter these fragile systems, either by polluting them or by modifying the hydrological cycle [5].

Toxic inorganic element concentrations are very important for the evaluation of groundwater quality. When these concentrations exceed the maximum permissible limits set by national and international regulations on the quality of water intended for human consumption, adverse health

effects can be expected. Natural or anthropogenic origins may lead to elevated levels of trace elements in groundwaters. The large increase in groundwater consumption has required more rigorous quality controls and a better understanding of naturally occurring groundwater mineralization processes with respect to the trace elements [6].

Several studies have already been carried out on groundwater and spring water resources worldwide. The large number of papers found in the literature reflects the permanent concern for water quality assessment, hydrochemical and hydrogeochemical characterization in mining areas, as well as in legally protected tropical and subtropical areas [4,7,8,9].

The Iron Quadrangle, located in the central-southeast of Minas Gerais state, stands out in the Brazilian scenario for the extraction of gold, iron and manganese. Since the discovery of gold in the late 17<sup>th</sup> century, the region of the IQ has been home to the largest urban concentration of Minas Gerais, with gold, iron and manganese mining, as its main economic activities. However, the intense exploitation of these mineral resources has had a great impact on nature, such as groundwater and soil pollution, biodiversity loss and erosion. Previous studies carried out in different regions of the IQ have shown high levels of arsenic and other toxic metals in soils, sediments, groundwater and stream waters [10,11,12,13,14].

The public supply of water in the IQ is done mainly by water impound of water sheds, but, as today, in some historic towns, like Ouro Preto, Mariana, Congonhas, Sabará, spring waters are still used to supply the fountains located in churches, stately homes, monuments and cobbled streets of these historic towns. These waters are used by the local population and visitors who trust its drinking water quality. Unfortunately, some of the springs have decreased their supply and others have already completely dried up. Springs are important elements in the environment and react to changes that occur in natural ecosystems. A decrease in the number of springs or a drop in their discharge as well as changes in their chemistry and quantity often indicate geological changes in the environment [4,15,16].

As yet there is no data available on the quality of several of the spring waters used by the population in urban and rural areas of the IQ. Therefore, this study was undertaken to document the hydrochemistry, assess the water quality in several spring waters and wells inside and outside the Iron Quadrangle.

## 2. Materials and Methods

### 2.1. General Features of the Area Studied

The Iron Quadrangle (Quadrilátero Ferrífero) covers an area of approximately 7000 km<sup>2</sup> in the central-southeast of Minas Gerais state, Brazil, and is internationally recognized as an important Precambrian terrane with significant mineral resources, particularly gold and iron. The geology of the Iron Quadrangle comprises an Archean greenstone belt sequence, represented by the Rio das Velhas Supergroup, surrounded by Archean granite-gneiss terrains which are overlaid by a Paleoproterozoic

sedimentary succession, i.e., the Minas Supergroup [17].

This region is rich in water resources, hosting the headwaters of the basins of the Rivers Velhas and Doce, two of the main Brazilian watersheds, with wide diversity of biomes, including remnants of the Atlantic Forest, Cerrado stretches and rupestrian fields [17]. The underground water potential in this region has been known since the early occupation of the area due to the abundance and quality of its spring waters. Data available [18] indicate the existence of large reserves of groundwater in various geological formations of the IQ: the hematites and itabirites of the Cauê Formation, the quartzites ferruginous of the Cercadinho Formation, the dolomites of the Gandarela Formation and the quartzites of Moeda Formation. The Cauê aquifer is the main groundwater reservoir in the IQ, with a high storage capacity.

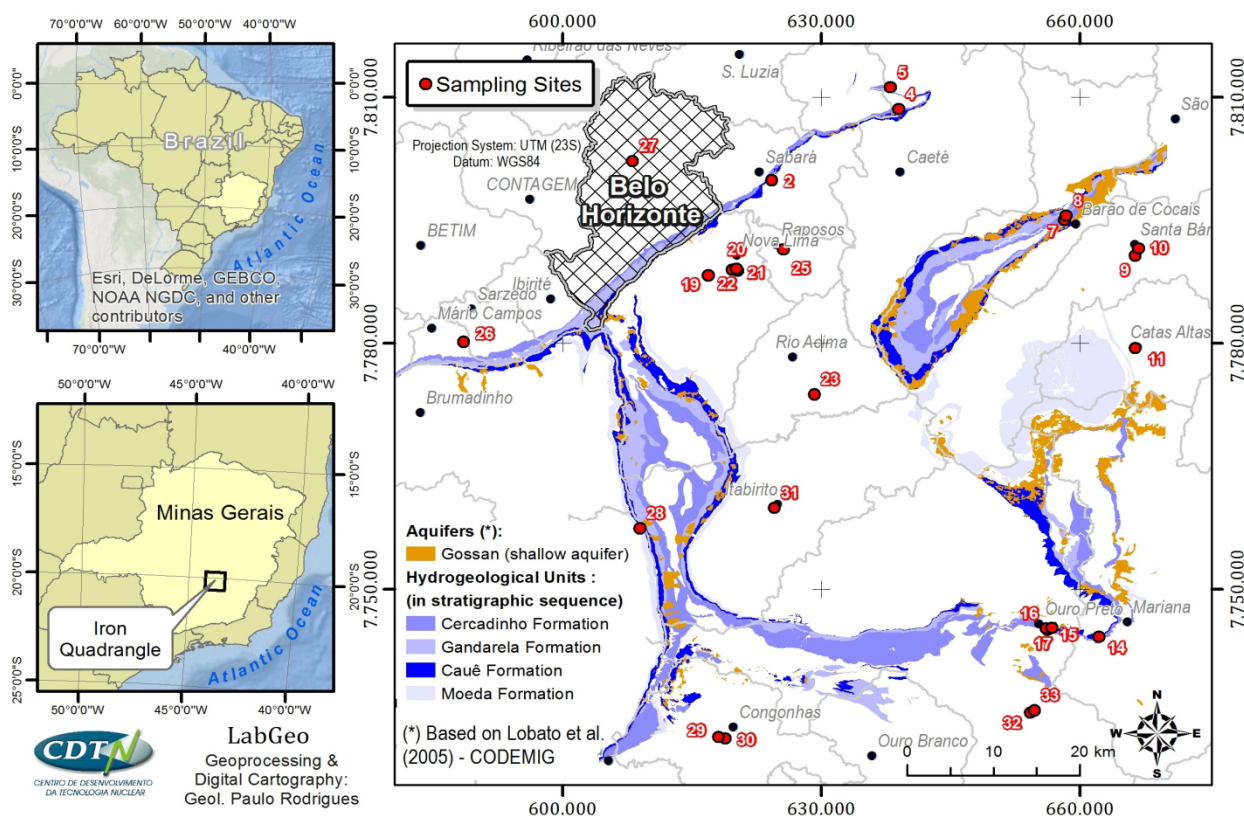
Forty-four spring water samples were collected in the municipalities of Sabará, Caeté, Barão de Cocais, Santa Bárbara, Catas Altas, Mariana, Ouro Preto, Congonhas, Moeda, Nova Lima, Rio Acima, Raposos, Itabirito, Mário Campos and four artesian well water samples in the municipalities of Santa Bárbara and Belo Horizonte. Figure 1 shows the sample sites in the various municipalities as well as the main aquifers in the Iron Quadrangle region. The geoprocessing program used was the ArcGIS (ESRI), version 10.2.2, [19]. Six sampling sites (4, 5, 7, 8, 16 and 17) fell into the Cercadinho Formation (quartzitic ferruginous aquifer), one (14) in the Cauê Formation (aquifer in iron formations) and one (28) in the Moeda Formation (quartzitic aquifer).

Results of the hydrochemical data were subjected to graphical evaluation using Piper diagram [20] to classify and compare the different water types based on the ionic composition of the different spring water samples, and Gibbs plot [21] was used to evaluate the functional sources of the dissolved ions in the groundwaters.

### 2.2. Sampling and Analysis

Natural spring waters and artesian well waters samples were collected in two different surveys, i.e., March 2015 (wet season) and August 2015 (dry season). The well samples were included in our study due to the fact that these waters were also used for human consumption.

Electric conductivity (EC) and total dissolved solids (TDS) were measured in the field using a multiparameter (Myron L Company Ultrameter) and water turbidity (TB) was measured using HACH 2100Q (HACH, USA). Bicarbonate was determined by acid-base titration and total hardness (TH) was estimated by EDTA titrimetric method using eriochrome black-T as indicator. Thermotolerant coliform (TC), also known as fecal coliforms due to their role as fecal indicators was evaluated according to the methodology established by (Standard Methods – SM-9222 D) [22]. Coliform density was computed in terms of the Most Probable Number (MPN)/100 mL. Total mercury was determined by cold vapor atomic absorption spectrometry (CVAAS) using a Perkin Elmer flow-injection mercury system, FIMS 400. Chromium (VI) was determined colorimetrically by reaction with diphenylcarbazide in acid solution (Standard Methods – 3500-Cr D) [22].



**Figure 1.** Map of the study area with the sample sites in the various municipalities and the main aquifers in the Iron Quadrangle region

Samples for anions, cations and trace element analysis were collected into washed polyethylene narrow-mouth bottles with screw cap. Before sample collection, the bottles were rinsed with spring water filtered through 0.45  $\mu\text{m}$  membrane (mixed cellulose esters-Merck Millipore). The samples for laboratory element trace analysis were immediately acidified to  $\text{pH} < 2$  with ultrapure nitric acid and then stored at  $4^{\circ}\text{C}$  before analysis. The anions, fluoride, chloride, nitrite, nitrate, sulfate, and the cations, sodium, potassium and ammonium were determined by high performance ionic liquid chromatography (HPLC) using a Shimadzu chromatographic system with a CDD-6A conductivity detector. Concentrations of the trace elements, including Li, V, Cr, Co, Ni, Cu, As, Ba, Al, Mn, Zn, Ca, Mg, Si, P, Fe, Sb, Cd, Mo, Se, Tl and U were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin-Elmer Elan DRCe). Ultra-pure water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ) obtained from a Milli Q Element System (Millipore, Belford, MA, USA) and ultrapure  $\text{HNO}_3$  69.5% (w/w) (Fluka) were used for the preparation of all standard solutions and for the preservation of the samples. Multi-element Standard 3 PerkinElmer N9301720 solution (STD 3) containing Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn ( $10.0 \text{ mg L}^{-1}$ ) was used for preparing the calibration curves. All solutions and samples were prepared in 1%  $\text{HNO}_3$  for ICP-MS.

Since the samples to be analyzed were primarily groundwaters, the elements of interest were calibrated at levels typical of the samples analyzed. Germanium (Aldrich 356247) and holmium (Perkin Elmer N9300123) were used as internal standards at a concentration of  $100 \mu\text{g L}^{-1}$  (Ge) and  $20 \mu\text{g L}^{-1}$  (Ho) in 2% (v/v) nitric acid. The internal standards were added on-line to standards and

samples using a separate feeding tube on the peristaltic pump (Trident Internal Standard Kit - PerkinElmer). Standards and samples were aspirated into the ICP-MS using  $1 \text{ mL min}^{-1}$  carrier flow and the isotopes selected were measured using the experimental conditions established by [23].

The standard reference materials, SRM 1640a, trace elements in natural water from the National Institute of Standards and Technology (NIST) and the synthetic water SPS- SW1 Batch 116 from Spectra pure Standards (Oslo, Norway) were used for recovery and precision studies. The recovery obtained for the elements Mg, Ca, Li, V, Cr, Co, Ni, Cu, As, Ba, Al, Mn, Zn and Si, using the SRM 1640a, was 100%, 91%, 107%, 98%, 101%, 101%, 101%, 94%, 103%, 103%, 106%, 104%, 89% and 95%, respectively. Iron recovery, using the SRM SPS-SW1, was 106%. To obtain phosphorus recovery, a secondary standard produced by the Minas Gerais metrological network (RMMG) was used and the value obtained was 96%. The relative standard deviation (RSD,  $n=3$ ) used to assess the precision of the selected elements were smaller than 10%.

### 3. Results and Discussion

#### 3.1. Hydrochemical Characteristics and Spring Water Quality

The quality of the spring and well samples was monitored based on guidelines set by the World Health Organization (WHO), [24] and by the Brazilian Environment Council (CONAMA) 396/2008 [25]. The latter lists the maximum permitted values (MPV) for

inorganic (Al, Sb, As, Ba, Be, B, Cd, Pb, CN, Cl<sup>-</sup>, Co, Cu, Cr, Cr (VI), Fe, F<sup>-</sup>, Li, Mn, Hg, Mo, Ni, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Ag, Se, Na, TDS, SO<sub>4</sub><sup>2-</sup>, U, V, Zn), organic, pesticides and microorganisms parameters that might occur in groundwater, for use of human and animal consumption, irrigation and recreation. Table 1 and Table 2 summarize the measured parameters and their units, the minimum and maximum values found in each survey during the wet and dry seasons in March and August 2015, respectively, and the MPV established by [24] and [25]. The parameters Sb, Cd,

F, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Cr (VI), Hg, Mo, Se, and U were not included in Table 1 and Table 2 because their concentrations were close to the detection limit. As can be seen in Table 1 and Table 2, parameters such as pH, turbidity, Fe, Mn, Al, As, NO<sub>3</sub><sup>-</sup> and TC in some samples presented concentrations above MPV. A correlation matrix was carried out to find the relation among the parameters used for characterization and evaluation of the water quality. Table 3 presents the Pearson correlation coefficients matrix for a 95% confidence level.

Table 1. Water quality parameters of spring and well samples collected in March 2015

March Samples	TB	EC	TDS	pH	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	TH	SiO <sub>2</sub>
	(NTU)	(µS cm <sup>-1</sup> )	(mg L <sup>-1</sup> )		(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )
M2 - Sabará	0.11	109	51.4	5.7	3.87	3.60	6.51	2.68	10.5	2.30	15.4	21.2	28.9	8.66
M4 - Caeté	3.30	13.8	6.42	6.1	0.43	0.65	1.07	0.31	0.71	0.10	9.20	0.29	5.10	5.86
M7 - Barão de Cocais	0.96	92.2	43.5	4.6	1.00	3.00	6.44	2.23	7.69	1.37	4.10	29.2	15.2	9.37
M8 - Barão de Cocais	3.09	137	64.5	6.8	8.68	10.1	0.19	0.11	0.12	0.24	70.8	0.64	71.1	10.8
M 9 - Sta. Bárbara	0.18	125	59.1	5.2	0.68	7.16	9.68	1.81	8.82	6.40	26.7	18.5	30.5	5.94
M10 - Sta. Bárbara	0.64	114	54.2	6.0	3.45	7.82	5.98	2.04	0.53	0.64	58.5	0.70	44.7	38.9
M11 - Catas Altas	0.44	5.58	2.68	5.8	0.36	0.79	0.21	0.14	0.24	0.37	3.10	0.25	3.10	3.22
M14 - Passagem de Mariana	0.09	23.5	11.0	4.8	0.32	0.88	0.80	0.75	1.13	1.81	4.10	5.27	5.10	3.23
M15 - Ouro Preto	0.19	7.39	3.56	5.5	0.32	0.78	0.24	0.22	0.50	0.63	7.20	0.76	3.10	3.85
M16 - Ouro Preto	0.33	16.3	7.64	3.9	0.25	0.96	0.80	0.35	1.69	0.55	4.10	3.29	3.10	6.49
M17 - Ouro Preto	0.25	16.1	7.53	4.8	0.24	0.91	0.80	0.34	1.52	0.63	3.10	3.49	4.10	6.77
M19 - Nova Lima	9.48	60.6	28.5	6.3	4.08	3.36	1.80	0.16	0.48	0.59	32.8	0.61	30.5	17.7
M20 - Nova Lima	0.10	251	120	6.4	11.5	17.5	5.65	0.30	10.9	1.41	101	17.1	115	41.0
M21 - Nova Lima	0.12	351	169	6.5	18.7	23.4	5.91	0.29	22.0	1.33	120	35.4	164	33.4
M22 - Nova Lima	0.30	53.5	35.0	5.8	3.08	2.75	2.55	0.08	1.21	1.02	20.5	4.69	20.3	16.4
M23 - Rio Acima	8.09	32.9	15.4	6.7	4.19	2.19	1.70	0.61	0.13	0.47	18.5	0.39	15.2	13.8
M26 - Mário Campos	0.55	20.1	9.31	4.5	0.27	0.16	1.69	0.54	1.16	<0.05	4.10	4.22	3.10	6.39
M27 - Belo Horizonte	0.66	98.8	54.0	6.5	2.15	4.65	9.84	2.18	1.47	0.27	46.2	1.46	27.9	46.5
M28 - Moeda	4.04	6.70	3.30	4.8	0.10	0.60	0.25	0.06	0.36	0.27	5.10	0.05	1.00	2.38
M29 - Congonhas	14.4	24.6	11.5	6.9	1.01	1.05	1.73	0.81	0.22	0.35	14.4	0.54	11.2	15.9
M30 - Congonhas	0.78	295	141	5.4	11.1	6.08	24.7	2.65	43.7	7.20	28.2	55.0	71.1	22.4
M31 - Itabirito	2.39	28.5	13.3	6.3	1.02	0.90	2.22	0.31	2.98	1.66	9.20	0.67	11.2	9.11
M32 - Lavras Novas	0.65	19.8	9.27	3.8	0.05	0.15	1.32	0.47	1.73	0.12	4.10	4.04	2.00	5.71
M33 - Lavras Novas	0.24	29.4	13.8	4.2	0.21	0.69	1.68	1.28	3.30	1.02	5.10	2.94	5.10	4.08
Mín.	0.09	5.58	2.68	3.8	0.05	0.15	0.19	0.06	0.12	<0.05	3.10	0.05	1.00	2.38
Máx.	14.4	351	169	6.9	18.7	23.4	24.7	2.68	43.7	7.20	120	55.0	164	46.5
CONAMA 396/2008 (mg L <sup>-1</sup> )	-	-	1000	-	-	-	200	-	250	250	-	44.3	-	-
WHO (2011) (mg L <sup>-1</sup> )	5 NTU	-	<600	6.5 - 8.5	-	-	200	-	250	250	-	50	500	-
March Samples	Fe	PO <sub>4</sub>	Li	V	Cr	Co	Ni	Cu	As	Ba	Al	Mn	Zn	TC
	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )	MPN/100 mL
M2 - Sabará	22.6	29.5	1.81	<0.03	0.23	0.04	13.4	<0.50	1.97	55.1	<2.0	0.86	8.98	<1
M4 - Caeté	41.4	19.0	0.87	0.06	0.16	0.06	0.62	0.70	<0.08	10.5	7.95	6.44	3.47	55
M7 - Barão de Cocais	46.5	20.8	1.16	0.05	0.20	5.33	6.56	1.22	<0.08	67.0	230	266	15.9	<1
M8 - Barão de Cocais	17.3	49.6	1.97	0.18	0.49	<0.01	0.54	<0.50	0.24	10.7	<2.0	<0.50	<2.0	<1
M 9 - Sta. Bárbara	14.0	22.2	1.00	0.11	0.30	0.24	0.68	<0.50	<0.08	61.3	71.8	101	7.41	<1
M10 - Sta. Bárbara	11.9	166	8.77	2.05	0.55	0.04	0.49	2.30	0.64	20.8	<2.0	<0.50	12.2	<1
M11 - Catas Altas	16.0	12.1	0.38	0.09	0.35	0.06	1.59	0.89	0.89	4.40	19.5	<0.50	4.72	39
M14 - Passagem de Mariana	11.7	17.5	0.34	0.05	0.55	0.18	0.71	<0.50	1.34	7.27	30.4	25.6	28.5	<1
M15 - Ouro Preto	4.25	21.4	0.38	<0.03	0.34	0.07	1.49	<0.50	12.0	8.91	10.1	5.50	4.67	<1
M16 - Ouro Preto	16.5	<1.6	0.15	<0.03	0.14	0.23	0.55	1.69	0.44	6.12	14.1	9.01	5.04	<1
M17 - Ouro Preto	17.5	<1.6	0.14	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	9.91	25.6	9.67	4.04	<1
M19 - Nova Lima	21.6	22.4	0.72	0.40	0.61	0.17	<0.11	0.55	<0.08	9.56	<2.0	13.8	7.19	<1
M20 - Nova Lima	35.4	82.7	2.80	3.04	<0.06	0.06	1.22	<0.50	2.35	4.97	<2.0	<0.50	14.7	<1
M21 - Nova Lima	43.8	69.2	1.95	2.42	1.48	0.08	1.25	0.53	1.25	5.78	<2.0	<0.50	13.0	<1
M22 - Nova Lima	3.87	25.8	1.43	0.21	0.42	0.06	5.08	1.98	<0.08	14.4	<2.0	<0.50	23.1	<1
M23 - Rio Acima	484	21.4	1.94	0.45	1.37	1.55	2.05	0.89	0.63	8.97	40.3	65.1	5.01	<1
M26 - Mário Campos	<1	32.3	0.72	<0.03	0.21	0.56	1.71	1.13	<0.08	15.8	24.6	34.9	27.8	<1
M27 - Belo Horizonte	13.2	227	6.64	0.82	1.30	0.08	1.50	2.01	<0.08	99.4	<2.0	1.64	99.9	<1
M28 - Moeda	8.20	26.7	0.14	<0.03	0.10	0.26	0.68	0.53	<0.08	3.87	22.9	2.34	9.16	16
M29 - Congonhas	605	<1.6	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	0.72	19.2	88.1	16.7	3.72	250
M30 - Congonhas	26.1	78.4	3.40	0.25	1.04	0.17	2.82	0.69	2.06	241	3.00	11.9	11.6	<1
M31 - Itabirito	365	<1.6	1.08	0.13	0.37	0.10	0.67	<0.50	0.39	8.85	54.1	10.2	11.3	<1
M32 - Lavras Novas	2.64	<1.6	0.24	<0.03	0.20	0.62	1.39	2.44	<0.08	27.5	53.7	27.8	24.2	<1
M33 - Lavras Novas	6.60	<1.6	0.29	<0.03	0.25	0.33	0.74	<0.50	<0.08	25.4	63.5	35.9	11.1	<1
Mín.	<1	<1.6	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	3.87	<2.0	<0.50	<2.0	<1
Máx.	605	227	8.77	3.04	1.48	5.33	13.4	2.44	12.0	241	230	266	99.9	250
CONAMA 396/2008 (mg L <sup>-1</sup> )	0.3	-	-	0.05	0.05	-	0.02	2	0.010	0.7	0.2	0.1	5	Absent/100 mL
WHO (2011) (mg L <sup>-1</sup> )	-	-	-	-	0.05	-	0.07	2	0.010	0.7	0.2	0.1	-	-

Table 2. Water quality parameters of spring and well samples collected in August 2015

August Samples	TB	EC	TDS	pH	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	TH	SiO <sub>2</sub>
	(NTU)	( $\mu\text{S cm}^{-1}$ )	( $\text{mg L}^{-1}$ )		( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )	( $\text{mg L}^{-1}$ )
AG2 - Sabará	0.12	109	53.9	5.9	3.76	3.49	5.50	2.65	11.2	2.30	16.0	22.1	30.0	9.32
AG4 - Caeté	0.68	14.6	7.07	6.3	0.48	0.73	0.99	0.37	1.03	0.27	9.30	1.13	6.00	7.15
AG5 - Caeté	0.41	10.8	5.22	5.3	0.74	0.17	0.24	0.28	0.67	0.26	7.20	0.75	7.00	9.13
AG7 - Barão de Cocais	0.11	86.4	42.5	4.5	0.87	2.73	5.60	2.23	6.70	1.30	4.10	24.6	14.0	9.06
AG8 - Barão de Cocais	0.09	130	64.1	7.0	8.39	9.94	0.21	<0.05	0.20	0.35	71.1	0.82	71.5	11.8
AG10 - Sta. Bárbara	0.50	110	54.1	6.2	1.38	2.98	5.20	2.04	0.72	0.55	56.7	0.93	44.0	14.0
AG11 - Catas Altas	0.55	17.9	8.68	6.5	1.69	0.68	0.21	<0.05	0.40	0.43	11.3	0.58	11.0	5.63
AG14 - Passagem de Mariana	0.08	22.5	10.9	4.6	0.30	0.86	0.74	0.80	1.16	1.71	3.10	6.00	5.00	3.37
AG15 - Ouro Preto	0.15	6.09	2.95	6.9	0.21	0.28	0.19	0.24	0.46	0.55	5.20	0.78	3.00	3.86
AG16 - Ouro Preto	0.25	14.2	6.52	4.9	0.15	0.40	0.71	0.33	1.38	0.49	4.10	3.07	3.00	6.81
AG17 - Ouro Preto	0.59	14.2	6.56	5.4	0.39	0.63	0.75	0.18	1.35	0.48	7.20	2.60	5.00	7.02
AG20 - Nova Lima	0.08	238	118	6.6	10.0	16.9	4.40	0.26	8.80	1.20	100	18.5	113	30.5
AG21 - Nova Lima	0.15	341	170	6.5	18.4	24.0	5.10	0.17	19.9	1.40	119	42.0	162	30.0
AG22 - Nova Lima	0.22	47.9	23.5	6.0	3.01	2.32	2.10	<0.05	1.12	1.00	20.6	4.90	24.0	17.3
AG23 - Rio Acima	1.50	37.3	18.3	6.5	3.06	1.34	1.44	0.09	0.07	0.52	22.7	0.71	19.0	12.3
AG25 - Raposos	2.66	36.1	17.6	6.0	2.27	2.95	0.21	<0.05	0.06	0.60	20.6	0.39	21.0	9.48
AG26 - Mário Campos	0.34	17.8	8.23	4.7	0.20	0.11	0.87	0.20	0.35	<0.05	5.20	3.00	4.00	6.03
AG27 - Belo Horizonte	0.24	88.4	41.4	6.3	2.21	4.64	7.30	1.97	1.72	0.26	46.4	2.30	27.0	45.5
AG28 - Moeda	2.68	5.55	2.70	5.3	0.01	0.05	0.15	<0.05	0.25	0.12	4.10	0.05	2.00	3.33
AG29 - Congonhas	18.1	26.6	12.3	6.4	1.22	1.13	1.88	0.66	0.34	0.30	16.5	0.60	11.0	16.2
AG30 - Congonhas	0.11	270	128	6.0	10.3	5.73	21.2	2.80	37.8	5.80	25.8	60.3	69.0	21.2
AG31 - Itabirito	0.88	19.1	9.25	6.2	1.12	0.61	1.11	0.31	0.98	0.70	9.30	1.20	9.00	7.88
AG32 - Lavras Novas	0.10	41.1	20.1	4.3	0.03	0.09	1.02	0.19	1.70	0.06	4.10	3.20	2.00	5.10
AG33 - Lavras Novas	0.12	30.6	14.2	4.8	0.24	0.68	1.88	1.60	4.20	0.74	6.20	4.71	5.00	3.51
Mín.	0.08	5.55	2.70	4.3	0.01	0.05	0.15	<0.05	0.06	<0.05	3.10	0.05	2.00	3.33
Máx.	18.1	341	170	7.0	18.4	24.0	21.2	2.80	37.8	5.80	119	60.3	162	45.5
CONAMA 396/2008 ( $\text{mg L}^{-1}$ )	-	-	1000	-	-	-	200	-	250	250	-	44.3	-	-
WHO (2011) ( $\text{mg L}^{-1}$ )	5 NTU	-	<600	6.5 - 8.5	-	-	200	-	250	250	-	50	500	-
August Samples	Fe	PO <sub>4</sub>	Li	V	Cr	Co	Ni	Cu	As	Ba	Al	Mn	Zn	TC
	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	MPN/100 mL
AG2 - Sabará	3.81	29.9	1.70	<0.03	0.22	<0.01	12.4	0.66	1.82	50.7	<2.0	0.97	10.1	<1
AG4 - Caeté	34.1	14.7	0.68	<0.03	<0.06	0.03	0.44	0.82	<0.08	6.43	12.6	4.13	3.16	2
AG5 - Caeté	3.61	22.5	1.55	0.06	0.26	0.43	2.59	<0.50	0.18	7.32	8.51	5.51	4.86	<1
AG7 - Barão de Cocais	28.7	13.4	1.10	<0.03	0.15	5.01	6.45	1.34	<0.08	62.2	227	256	5.13	<1
AG8 - Barão de Cocais	18.2	34.0	1.95	0.16	0.45	0.05	0.55	<0.50	0.25	5.70	<2.0	<0.50	2.88	<1
AG10 - Sta. Bárbara	5.14	65.5	3.29	0.83	0.25	<0.01	0.30	5.69	0.29	5.86	<2.0	<0.50	5.91	<1
AG11 - Catas Altas	17.1	21.3	0.43	<0.03	4.75	0.06	2.05	11.3	0.20	1.74	9.83	1.43	13.6	13
AG14 - Passagem de Mariana	<1	20.0	0.26	<0.03	0.42	0.16	0.69	0.69	1.57	3.73	16.5	25.5	9.20	<1
AG15 - Ouro Preto	8.54	14.2	0.35	<0.03	0.42	0.02	1.03	<0.50	12.5	4.97	4.07	2.26	3.61	<1
AG16 - Ouro Preto	47.6	<1.6	0.12	<0.03	<0.06	0.16	0.45	4.24	0.86	3.26	14.1	10.2	10.4	<1
AG17 - Ouro Preto	41.5	<1.6	0.21	<0.03	<0.06	0.09	0.36	<0.50	0.25	2.40	5.56	7.01	9.03	<1
AG20 - Nova Lima	34.2	75.0	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	0.24	1.93	<2.0	<0.50	8.66	<1
AG21 - Nova Lima	43.6	68.7	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	2.19	<2.0	<0.50	2.85	<1
AG22 - Nova Lima	6.65	22.4	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	10.1	<2.0	<0.50	19.7	<1
AG23 - Rio Acima	34.5	26.6	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	3.15	2.42	2.44	9.55	<1
AG25 - Raposos	73.3	23.4	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	4.00	<2.0	1.41	5.28	<1
AG26 - Mário Campos	45.4	22.9	0.55	<0.03	<0.06	0.35	1.37	0.67	<0.08	10.3	18.5	28.4	14.9	<1
AG27 - Belo Horizonte	12.8	207	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	93.2	<2.0	1.28	411	<1
AG28 - Moeda	61.7	26.4	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	<1.1	22.0	4.71	4.39	29
AG29 - Congonhas	526	39.4	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	13.4	46.2	14.9	3.25	120
AG30 - Congonhas	14.7	64.8	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	219	<2.0	7.13	9.32	<1
AG31 - Itabirito	94.9	16.2	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	0.10	3.35	19.3	1.79	3.59	<1
AG32 - Lavras Novas	1.50	20.0	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	0.12	21.0	51.1	25.6	4.28	<1
AG33 - Lavras Novas	6.71	22.1	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	0.11	30.4	87.2	42.1	4.42	<1
Mín.	<1	<1.6	<0.03	<0.03	<0.06	<0.01	<0.11	<0.50	<0.08	<1.1	<2.0	<0.50	2.85	<1
Máx.	526	207	3.29	0.83	4.75	5.01	12.4	11.3	12.5	219	227	256	411	120
CONAMA 396/2008 ( $\text{mg L}^{-1}$ )	0.3	-	-	0.05	0.05	-	0.02	2	0.010	0.7	0.2	0.1	5	Absent/100 mL
WHO (2011) ( $\text{mg L}^{-1}$ )	-	-	-	-	0.05	-	0.07	2	0.010	0.7	0.2	0.1	-	-

The pH value of groundwater in the study area ranges from 3.8 to 7.0, indicating the acid nature of most of the spring water samples, which could enhance the dissolution of some elements present in the soils or bedrock. Only 11 samples showed pH values within the recommended standards (6.5 - 8.5) for drinking water (Table 1 and Table 2). Although pH usually has no direct impact on human health, it shows close relations with some chemical constituents of water [26]. Total hardness (TH) and pH show positive correlations with HCO<sub>3</sub><sup>-</sup> (r = 0.946, r = 0.542, respectively), whereas pH and TH are also positively correlated (r = 0.450), Table 3. These positive correlation values are an indication of the interdependency and control of pH in the CO<sub>2</sub> dissolution process in the groundwater system of the study area [27].

Turbidity (TB) was measured in nephelometric turbidity units (NTU). Of the four samples that showed turbidity above the VMP, three samples from Nova Lima (M19), Rio Acima (M23) and Congonhas (M29) (Figure 1) were collected in the rainy season and only one sample (AG 29 - Congonhas) in the dry season. Samples M29 and AG29 presented close values in March and August, whereas the same was not observed in M23 and AG23 (Table 1 and Table 2). Therefore, it may be concluded that the turbidity of M23 was influenced by mud and silt resulting from the rainy season. The turbidity of points 23 and 29 may also have been influenced by the high iron content found in these samples. This was confirmed by the high positive correlation between turbidity and iron (r = 0.826), (Table 3).

In this study, Fe and Mn concentrations ranged between <1 - 605 µg L<sup>-1</sup> and <0.50 - 266 µg L<sup>-1</sup>, respectively. Four samples in the study area presented iron concentrations above the VMP (0.3 mg L<sup>-1</sup>), being that the samples from Rio Acima (M23), Congonhas (M29) and Itabirito (M31) were collected in the rainy season and (AG29) in the dry season. Three samples collected in Barão de Cocais (M7/AG7) and Santa Bárbara (M9) presented manganese concentration above the VMP (0.1 mg L<sup>-1</sup>). It was observed that these samples as well as the other spring waters, points (14, 26, 32, 33), presented high Mn concentrations and low pH values, confirming the solubility of Mn in low pH waters (Table 1 and Table 2).

The correlation between Mn and pH was (r = -0.377), Table 3. The strong correlation between Mn and Al (r = 0.935) showed that these ions could be derived from the same source.

Water with concentrations close to 0.3 mg L<sup>-1</sup> Fe and 0.05 mg L<sup>-1</sup> Mn has its color, odor and taste altered and usually causes aesthetic problems to water consumers. At these concentrations, however, the health risk of dissolved Fe and Mn in drinking water is insignificant. Although Mn is essential for human health, it may act as an environment contaminant when its concentration in groundwater exceeds the VMP. The most common sources of iron and manganese in groundwater are due to the weathering of iron and manganese bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute to the increased Fe and Mn levels in local groundwater [28].

High values of aluminum were detected in spring waters from Barão de Cocais (M7/AG7), Passagem de Mariana (M14/AG14), Santa Bárbara, Ouro Preto, Rio Acima, Congonhas, Itabirito and Lavras Novas, (M9, M17, M23, M29, M31, M32/M33, respectively), but the Al concentrations were relatively higher in the former, exceeding the VMP (0.2 mg L<sup>-1</sup>), since bauxite is one of the main minerals extracted in the Iron Quadrangle. These spring waters showed also low pH values. A negative correlation between Al and pH (r = -0.401) was found (Table 3), indicating the aggressiveness of the acidic media towards soil and host rocks, increasing de Al concentration at those points. According to [29] Al in groundwater is strongly pH dependent. Aluminum is not soluble in water under normal circumstances. In surface and groundwaters, at low pH, Al occurs as free Al<sup>3+</sup> and at pH>6, it may form the highly insoluble Al(OH)<sub>3</sub> solid (gibbsite). In acidic waters (pH<5) Al can be mobilized by dissolution of gibbsite and the accelerated weathering of both clay minerals (e.g. kaolinite) and rock-forming minerals. However, Al concentrations are still very low in natural waters due to the extreme low solubility of Al-bearing minerals. Elevated aluminum concentrations are also mostly linked to acidic conditions e.g. rainfall acidity, acid mines drainage. Health effects of Al have been linked to Alzheimer disease [30].

Table 3. Pearson correlation coefficient matrix for water samples

Variables	TB	TDS	pH	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	TH	Fe	SiO <sub>2</sub>	PO <sub>4</sub>	As	Ba	Al	Mn	Zn
TB	1.000																			
TDS	-0.194	1.000																		
pH	0.317	0.328	1.000																	
Mg <sup>2+</sup>	-0.093	<b>0.935</b>	0.458	1.000																
Ca <sup>2+</sup>	-0.148	<b>0.897</b>	0.412	<b>0.922</b>	1.000															
Na <sup>+</sup>	-0.143	<b>0.675</b>	0.073	0.463	0.316	1.000														
K <sup>+</sup>	-0.132	0.321	-0.113	0.051	0.015	<b>0.736</b>	1.000													
Cl <sup>-</sup>	-0.189	<b>0.793</b>	0.044	<b>0.677</b>	0.486	<b>0.880</b>	<b>0.504</b>	1.000												
SO <sub>4</sub> <sup>2-</sup>	-0.178	<b>0.531</b>	-0.048	0.344	0.226	<b>0.832</b>	<b>0.574</b>	<b>0.808</b>	1.000											
HCO <sub>3</sub> <sup>-</sup>	-0.085	<b>0.832</b>	<b>0.542</b>	<b>0.869</b>	<b>0.953</b>	0.253	-0.018	0.346	0.086	1.000										
NO <sub>3</sub> <sup>-</sup>	-0.227	<b>0.809</b>	-0.011	<b>0.675</b>	<b>0.538</b>	<b>0.823</b>	<b>0.536</b>	<b>0.953</b>	<b>0.766</b>	0.364	1.000									
TH	-0.136	<b>0.944</b>	<b>0.450</b>	<b>0.968</b>	<b>0.978</b>	0.412	0.060	<b>0.592</b>	0.294	<b>0.946</b>	<b>0.615</b>	1.000								
Fe	<b>0.826</b>	-0.144	0.346	-0.053	-0.102	-0.100	-0.086	-0.120	-0.103	-0.076	-0.154	-0.096	1.000							
SiO <sub>2</sub>	0.015	<b>0.654</b>	0.477	<b>0.599</b>	<b>0.654</b>	<b>0.476</b>	0.275	0.330	0.104	<b>0.737</b>	0.310	<b>0.650</b>	0.033	1.000						
PO <sub>4</sub>	-0.113	0.449	0.347	0.336	0.406	0.466	0.421	0.202	0.067	<b>0.526</b>	0.163	0.395	-0.147	<b>0.868</b>	1.000					
As	-0.115	-0.071	0.143	-0.046	-0.053	-0.059	-0.058	0.003	0.025	-0.076	-0.028	-0.059	-0.084	-0.123	-0.071	1.000				
Ba	-0.115	0.450	-0.052	0.249	0.054	<b>0.934</b>	<b>0.741</b>	<b>0.786</b>	<b>0.758</b>	-0.010	<b>0.717</b>	0.156	-0.103	0.306	0.385	-0.039	1.000			
Al	0.111	-0.147	<b>-0.401</b>	-0.281	-0.192	0.014	0.303	-0.040	0.039	-0.313	0.133	-0.249	0.200	-0.244	-0.260	-0.136	0.098	1.000		
Mn	-0.024	-0.032	<b>-0.377</b>	-0.182	-0.096	0.122	0.366	0.043	0.145	-0.226	0.245	-0.153	0.034	-0.169	-0.170	-0.112	0.173	<b>0.935</b>	1.000	
Zn	-0.096	0.027	0.101	-0.038	0.020	0.168	0.244	-0.052	-0.085	0.109	-0.070	-0.010	-0.088	<b>0.498</b>	<b>0.636</b>	-0.076	0.249	-0.094	-0.061	1.000

In only one point studied (M15/AG15 - Lajes - Ouro Preto) the level of arsenic was above the limit of  $0.010 \text{ mg L}^{-1}$  established by the legislations (Table 1 and Table 2). In this region of the Iron Quadrangle, As has been found closely associated with sulfide-rich gold-bearing rocks [31]. Previous studies have shown high levels of arsenic [32,33] in aquatic and terrestrial environments in different regions of the IQ. According to [32], such high amounts of arsenic in water, soils, and sediments in the IQ is related to natural causes as well as to past and recent mining activities.

Silica ( $\text{SiO}_2$ ) and phosphous ( $\text{PO}_4^-$ ) in the samples ranged from  $2.38 - 46.5 \text{ mg L}^{-1}$  and  $<1.6 - 227 \mu\text{g L}^{-1}$ , respectively. High levels of  $\text{SiO}_2$  and  $\text{PO}_4^-$  were found in the well samples of Santa Bárbara and Belo Horizonte, points (10, 27), as well as in the spring waters, points (19, 20, 21, 22, 30), Table 1 and Table 2. There was a strong correlation between  $\text{SiO}_2$  and  $\text{PO}_4^-$  ( $r = 0.868$ ), as well as between  $\text{SiO}_2^-$  and  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Zn}$  ( $r = 0.599$ ,  $r = 0.654$ ,  $r = 0.737$ ,  $r = 0.476$ ,  $r = 0.498$ , respectively), (Table 3) indicating that these ions could originate from the common source. The high  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{SiO}_2$  concentrations in these samples result from the reaction between carbonic acid ( $\text{H}_2\text{CO}_3$ ) and reactive silicate in the aquifer matrix [34]. Sixty percent of the Earth's crust is composed of silicate minerals, and therefore constitutes the bulk of common rocks, soils, clays and sands. Water that drains deposits high in silicate minerals, particularly feldspars, often contains high contents of silica [35]. There are several water soluble forms of silica referred collectively to as silicic acid (ortho, meta, di, and tri-silicates), which are present in surface and well waters in the range of  $1 - 100 \text{ mg L}^{-1}$ . Silica is essential for human health and has myriad beneficial effects. Its deficiency induces deformities in skull and peripheral bones, poorly formed joints, reduced contents of cartilage, collagen and disruption of mineral balance in the femur and vertebrae [36].

Barium was monitored because it is associated with a potential health concern. The short-term or acute problems include gastrointestinal disturbance and muscular weakness and the long-term impacts are associated with high blood pressure. It has also been suggested to cause kidney damage and problems with the nervous system [24]. In this study barium concentrations ranged from less than  $<1.1 \mu\text{g L}^{-1}$  to  $241 \mu\text{g L}^{-1}$  and presented association to  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  ( $r = 0.934$ ,  $r = 0.741$ ,  $r = 0.786$ ,  $r = 0.758$ ,  $r = 0.717$ , respectively), Table 3. The highest levels of Ba were found in the samples (M2/AG2, M7/AG7, M9, M27/AG27, M30/AG30), but at levels below the VMP ( $0.7 \text{ mg L}^{-1}$ ). At these points, pH was below 6.6, which may enhance Ba concentration, once the solubility of Ba compounds increases as the pH level decreases. Barium in water comes primarily from natural sources. Acetate, nitrate and halides are soluble in water, but the carbonate, chromate, fluoride, oxalate, phosphate and sulfate are quite insoluble [24].

Zinc is an essential element in all living organisms, but may be toxic at higher concentrations. In natural surface waters, the concentration of zinc is usually below  $10 \mu\text{g L}^{-1}$ , and in groundwaters,  $10 - 40 \mu\text{g L}^{-1}$  [24]. In this work zinc concentrations ranged from less than  $<2.0 \mu\text{g L}^{-1}$  to  $411 \mu\text{g L}^{-1}$  and presented association with  $\text{SiO}_2$  and

$\text{PO}_4^-$  ( $r = 0.498$  and  $r = 0.636$ , respectively), Table 3. Zinc is known to occur in small amounts in almost all igneous rocks. The principal zinc ores are sulfides ( $\text{ZnS}$ ), calamine ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2$ ), smithsonite ( $\text{ZnCO}_3$ ), franklinite ( $\text{Zn, Mn}(\text{Fe}_2\text{O}_4)$ ) [37].

Nitrate in samples under investigation ranged from  $0.05$  to  $60.3 \text{ mg L}^{-1}$ . Nitrate occurred in many samples: Sabará (M2/AG2), Barão Cocais (M7/AG7), Santa Bárbara (M9), Passagem de Mariana (M14/AG14), Nova Lima (M20/AG20; M21/AG21), however at levels below the VMP ( $44.3 \text{ mg L}^{-1}$ ) for drinking water. Only the Congonhas (M30/AG30) sample exceeded the VMP established by WHO and CONANA [24,25] (Table 1 and Table 2). Nitrate is found naturally in the environment and is an important plant nutrient. It is present in all plants at varying concentrations and is part of the nitrogen cycle. Nitrite ( $\text{NO}_2^-$ ) is not usually present in significant concentrations except in a reducing environment, as nitrate is the more stable oxidation state. Nitrate can reach both surface water and groundwater as a consequence of agricultural activity, from wastewater disposal and from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks [24]. Other main potential sources of naturally occurring nitrate in groundwaters are bedrock nitrogen and nitrogen leached from natural soils [24]. The guideline values for nitrate and nitrite ions to protect against methaemoglobinaemia in bottle-fed infants (shot-term exposure) are  $44.3 \text{ mg L}^{-1}$  and  $3 \text{ mg L}^{-1}$ , respectively [24].

Bacteriological analysis reveals the presence of thermotolerant coliforms in the spring waters from Caeté, Catas Altas, Moeda and Congonhas (M4/AG4, M11/AG11, M28/AG28; M29/AG29, respectively) in the samples collected in the two surveys with the highest values observed in the rainy season (March). Spring waters 4 and 28, located along the roads are generally used by by-passers and also animals. Therefore these spring waters sources are not well protected nor wisely used or managed and susceptible to contamination. The depth of ground water occurrence and the extent of anthropogenic activities in the spring catchment areas, as well as climatic conditions, soil and geologic characteristics may contribute to the presence and survival of coliform bacteria in spring discharges [4].

### 3.2. Mechanism Controlling Groundwater Chemistry

Total dissolved solids (TDS) indicate the salinity behavior of groundwater and, in the study area, varied from  $2.68 - 170 \text{ mg L}^{-1}$ . The classification of the groundwaters on the basis of TDS, according to [38] establishes: up to  $500 \text{ mg L}^{-1}$  (desirable for drinking);  $500 - 1000 \text{ mg L}^{-1}$  (permissible for drinking) and up to  $3000 \text{ mg L}^{-1}$  (useful for agricultural purposes). Based on this classification, all the water samples studied are of the fresh water type.

The highest TDS values were found in the spring waters in Nova Lima and Congonhas, points (20, 21, and 30), Table 1 and Table 2. The values of TDS, EC and hardness of these samples suggest that these points are the most mineralized groundwater systems in this study area. Strong correlations exist among the major cations,  $\text{Mg}^{2+}$ ,

Ca<sup>2+</sup>, Na<sup>+</sup>, and TDS (r = 0.935, r = 0.897, r = 0.675, respectively), Table 3, which is a clear indication of the contribution of these ionic components to the overall mineralization [39].

In this study the natural or anthropogenic presence of nitrate, sulfate and chloride in the spring waters was also evaluated. The variation of EC and TDS in the groundwater is dependent on the geochemical processes, but may also be related to anthropogenic activities. Ions such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Na<sup>+</sup> may also originate from agricultural fertilizers, animal waste and industrial and municipal sewage. The correlation of these ions with TDS can be used to indicate the influence of human activities

on the water chemistry [40]. In this work the chemical variables (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and nitrate show a strong correlation (r = 0.675, r = 0.538, r = 0.823, r = 0.536, r = 0.953, r = 0.766, respectively). The major anions, (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>), also have positive correlations with TDS (r = 0.793, r = 0.531, r = 0.832, r = 0.809, respectively), Table 3, suggesting that these ions present in the groundwater system of the study area mostly derived from geogenic sources. A low correlation between TDS and (NO<sub>3</sub><sup>-</sup> + Cl<sup>-</sup>)/Na<sup>+</sup> as well as between TDS and (NO<sub>3</sub><sup>-</sup> + Cl<sup>-</sup>)/HCO<sub>3</sub><sup>-</sup> (Figure 2 a, b) molar ratios, also confirm geogenic input of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> into QF spring waters [40].

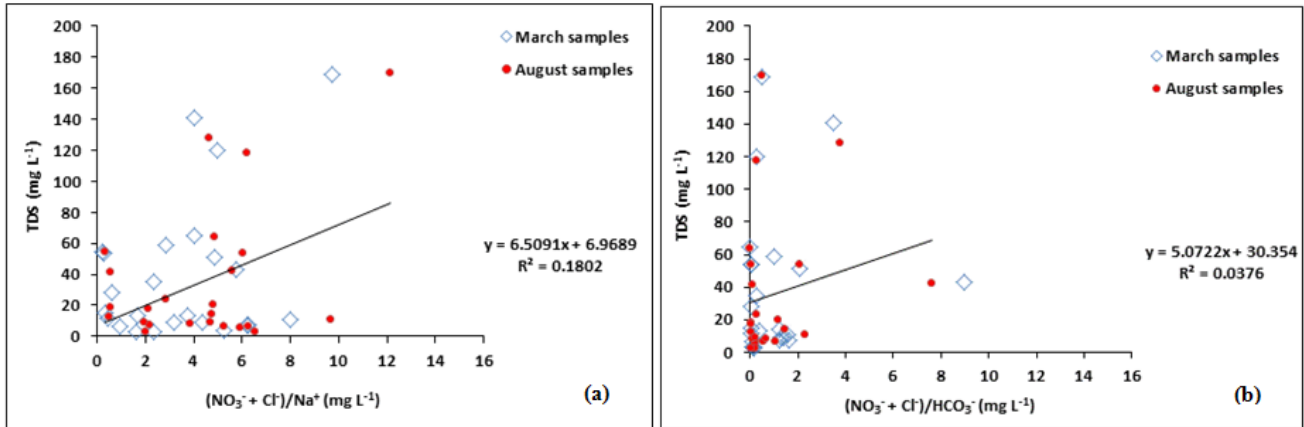


Figure 2. Plots showing variations of (a) TDS versus (NO<sub>3</sub><sup>-</sup> + Cl<sup>-</sup>)/Na<sup>+</sup> and (b) (NO<sub>3</sub><sup>-</sup> + Cl<sup>-</sup>)/HCO<sub>3</sub><sup>-</sup> for waters from the study area

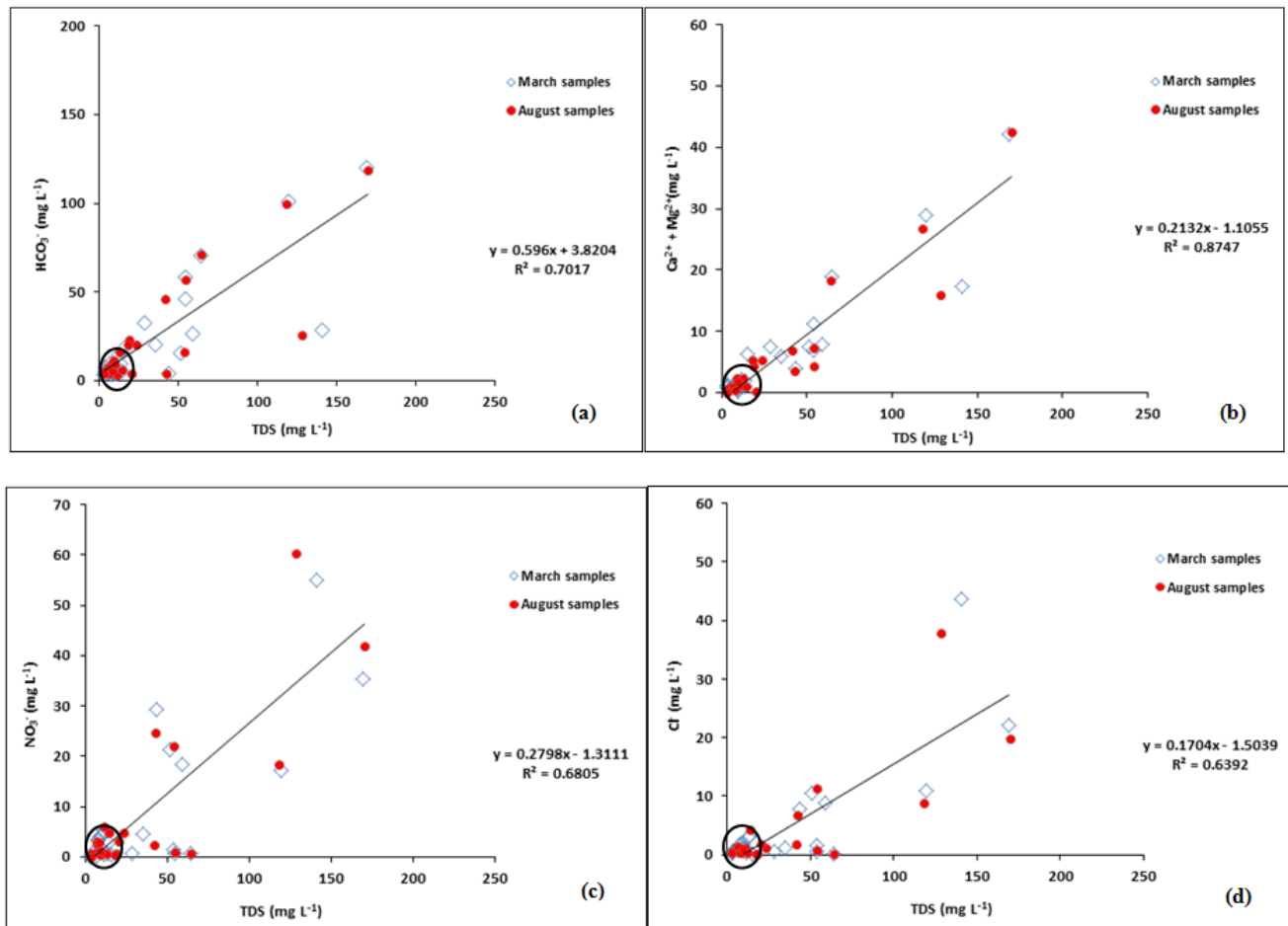


Figure 3. Relationship among TDS and anions/cations in spring waters from the study area



The plots of the spring water ionic parameters in the study area, (Figure 3 a-d) show a distinct group of samples with very low TDS (2.68 -10.0 mg L<sup>-1</sup>). The very low TDS in the groundwater system of these samples was a reflection of the general characteristics of groundwater in basement terrain. It is assumed that some of these springs may have been originated from aquifers located beneath outcrops of ferruginous rocks (cangas) and iron formation, common in the Iron Quadrangle, such as the well-known outcrop of the Serra do Rola Moça State Park, located at 1400 m altitude. The cangas act as important areas of water recharge and due to the huge amount of pores, cracks, channels and cavities in these soils, function as real sponges, effectively

transferring rainwater into the mountains [41]. Low ion values in the spring waters are a reflection of meteoric source water with limited migratory history [39]. The chemical character of groundwater is influenced by the minerals and gases reacting with the water in its relatively slow passage through the rocks and sediments of the Earth's crust. Many variables cause extensive variation in the quality of groundwater, even in local areas. In general, groundwater increases in mineral content as it moves along through the pores and fracture openings in rocks. This is why deeper, older waters can be highly mineralized. At some point, the water reaches an equilibrium, which prevents it from dissolving additional substances [37].

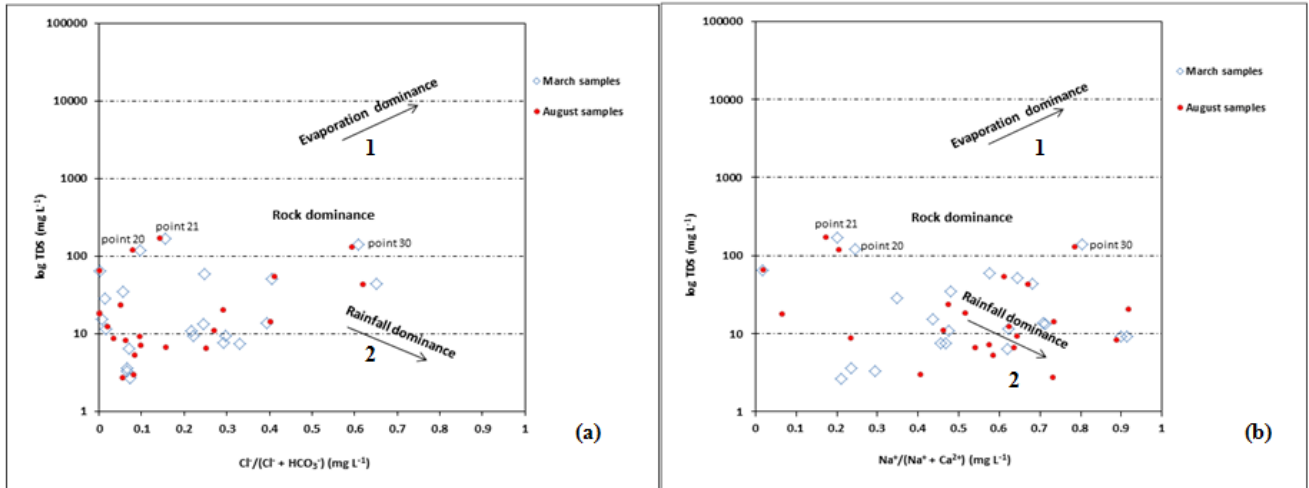


Figure 4. Gibb's Plot Controlling mechanisms for spring waters quality in the study area. 1- Evaporation dominance; 2- Rainfall dominance

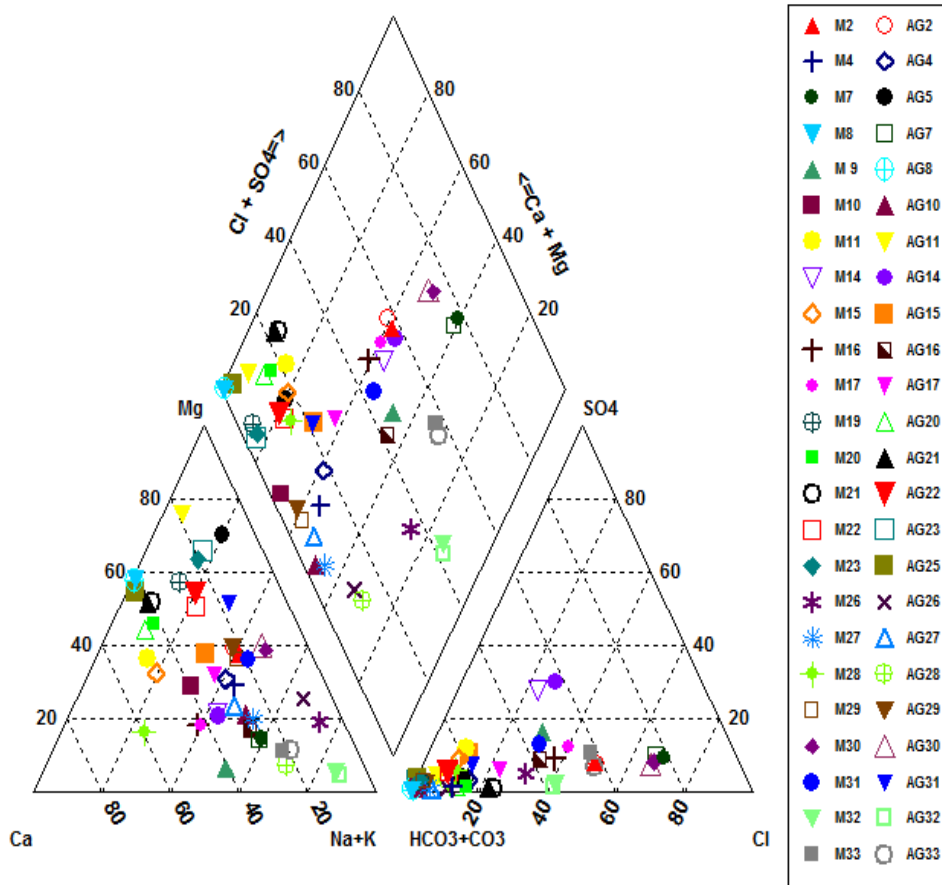


Figure 5. Water type classification using the Piper trilinear diagram

A plot of TDS versus  $(\text{Na}^+/\text{Na}^+ + \text{Ca}^{2+})$  for cations and TDS versus  $(\text{Cl}^-/\text{Cl}^- + \text{HCO}_3^-)$  for anions, referred to as Gibbs plot [21], illustrate the natural mechanism controlling groundwater chemistry, including rainfall, rock weathering, and evaporation-precipitation dominance. The Gibbs plot of data from the study area (Figure 4 a, b) indicate that the chemical composition of most spring water samples was controlled primarily by rainfall dominance. Only three points (20, 21 and 30) may have been influenced by rock weathering reaction. The interaction between rocks and water results in ion leaching into the groundwater system, thereby influencing the water chemistry [34].

### 3.3. Geochemical Classification and Relationships

The chemical composition of groundwater is primarily dependent on the geology as well as on the geochemical processes and anthropogenic activities which take place within the aquifer system [34]. Normally the classification of groundwater is based on the concentration of various predominant cations and anions and on the interrelationships of ions. Results of the hydrochemical data of the spring water samples were graphically evaluated through the Piper diagram using the AquaChem program 2011.1 of Schlumberger Water Services. Based on this diagram (Figure 5), the spring waters were classified into eight types: mixed-bicarbonate (29.2%), magnesium-bicarbonate

(27.1%), sodium-bicarbonate (18.8%), mixed-chloride (8.3%), sodium-chloride (6.3%), mixed-water (6.3%), calcium-bicarbonate (2%) and sodium-mixed (2%), Table 4.

## 4. Conclusion

A total of forty-four spring water and four artesian well water samples were collected at 26 points in different municipalities of the IQ in two different surveys, March and August 2015. These samples have been assessed for water quality and hydrochemical characterization. The average of the values obtained from the analyzed water samples revealed  $\text{Ca}^{2+}$  and  $\text{Na}^+$  as the major cations followed by  $\text{Mg}^{2+}$  and  $\text{K}^+$ , with concentrations ranging from 0.05 - 24.0, 0.15 - 24.7, 0.01 - 18.7 and  $<0.05$  - 2.80  $\text{mg L}^{-1}$ , respectively. The dominant anions are  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  followed by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , with concentrations ranging from 3.10 - 120, 0.05 - 60.3, 0.06 - 43.7,  $<0.05$  - 7.20  $\text{mg L}^{-1}$ , respectively. As expected, the trace metals present the following decreasing concentrations:  $\text{Fe} > \text{Ba} > \text{Al} > \text{Mn} > \text{Zn} > \text{Ni}$ , since the IQ region is abundant in iron, aluminum and manganese minerals. The presence of iron in the samples also influenced the turbidity of the samples. The pH value of groundwater ranges from 3.8 to 7.0, indicating the acid nature of most of the spring water samples. It was observed that the acid nature in some springs enhanced the dissolution of mainly Al, Mn and Ba present in the soils or bedrock.

Table 4. Type of water samples in the study area

Samples	Hydrochemical facies	Water types
M2; AG2	Mg-Na-Ca-Cl-HCO <sub>3</sub>	Mixed-chloride
M4; AG4	Na-Mg-Ca-HCO <sub>3</sub>	Mixed-bicarbonate
AG5; AG11; AG23	Mg-HCO <sub>3</sub>	Magnesium-bicarbonate
M7; AG7	Na-Ca-Cl	Sodium-chloride
M8; AG8; M19; M23; AG25	Mg-Ca-HCO <sub>3</sub>	Magnesium-bicarbonate
AG15	Mg-HCO <sub>3</sub>	Mixed-bicarbonate
M20	Mg-Ca-HCO <sub>3</sub>	Mixed-bicarbonate
M9; AG16	Na-Ca-HCO <sub>3</sub> -Cl	Sodium-bicarbonate
M10	Ca-Mg-Na-HCO <sub>3</sub>	Mixed-bicarbonate
AG10, AG28	Na-HCO <sub>3</sub>	Sodium-bicarbonate
M11; M15; AG20	Ca-Mg-HCO <sub>3</sub>	Mixed-bicarbonate
M14; AG14	Ca-Na-Mg-HCO <sub>3</sub> -SO <sub>4</sub> -Cl	Mixed-water
M16	Ca-Na-HCO <sub>3</sub> -Cl	Mixed-bicarbonate
M17	Ca-Na-HCO <sub>3</sub> -Cl	Mixed-water
AG17	Na-Mg-Ca-HCO <sub>3</sub> -Cl	Mixed-bicarbonate
M21; AG21	Mg-Ca-HCO <sub>3</sub> -Cl	Magnesium-bicarbonate
M22; AG22	Mg-Ca-Na-HCO <sub>3</sub>	Magnesium-bicarbonate
M26	Na-Mg-HCO <sub>3</sub> -Cl	Sodium-bicarbonate
M31	Na-Mg-HCO <sub>3</sub> -Cl	Mixed-bicarbonate
AG26	Na-Mg-HCO <sub>3</sub>	Sodium-bicarbonate
M27	Na-Ca-Mg-HCO <sub>3</sub>	Sodium-bicarbonate
AG27	Na-Ca-Mg-HCO <sub>3</sub>	Mixed-bicarbonate
M28	Ca-HCO <sub>3</sub>	Calcium-bicarbonate
M29; AG29	Mg-Na-Ca-HCO <sub>3</sub>	Mixed-bicarbonate
M30; AG30	Na-Mg-Cl-HCO <sub>3</sub>	Mixed-chloride
AG31	Mg-Na-HCO <sub>3</sub>	Magnesium-bicarbonate
M32; AG32	Na-HCO <sub>3</sub> -Cl	Sodium-bicarbonate
AG33	Na-Cl-HCO <sub>3</sub>	Sodium-chloride
M33	Na-Cl-HCO <sub>3</sub>	Sodium-mixed

Based on Piper Trilinear diagram method, the spring waters were classified into eight types: mixed-bicarbonate (29.2%), magnesium-bicarbonate (27.1%), sodium-bicarbonate (18.8%), mixed-chloride (8.3%), sodium-chloride (6.3%), mixed-water (6.3%), calcium-bicarbonate (2%) and sodium-mixed (2%). These different kinds of waters are a reflection of the diversity of minerals and lithological types present in the Iron Quadrangle.

A distinct group of samples with very low TDS ( $2.68 - 10.0 \text{ mg L}^{-1}$ ) was observed in this region. It is assumed that these springs may have been originated from aquifers located beneath outcrops of ferruginous rocks (cangas) and iron formation, common in the Iron Quadrangle. The cangas act as important areas of water recharge and due to the huge amount of pores, cracks, channels and cavities in these soils, function as real sponges, effectively transferring rainwater into the mountains. Low ion values in the spring waters are a reflection of meteoric source water with limited migratory history. The Gibbs plot of data confirm that the chemical composition of most spring water samples was controlled primarily by rainfall dominance. Only three points (20, 21 and 30) may have been influenced by rock weathering reaction.

In this study the natural or anthropogenic presence of nitrate, sulfate and chloride in the spring waters was also evaluated. The high positive correlations obtained between the major anions, ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ) and TDS and the low correlation between TDS and  $(\text{NO}_3^- + \text{Cl}^-)/\text{Na}^+$  as well as between TDS and  $(\text{NO}_3^- + \text{Cl}^-)/\text{HCO}_3^-$  induces geogenic input of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  into QF spring waters.

A comparison of spring water quality in relation to drinking water quality standards [24,25] revealed that the parameters: turbidity at points (19, 23, 29), iron at points (29, 31), manganese at points (7, 9), aluminum at point 7, arsenic at point 15, nitrate at point 30, and the presence of thermotolerant coliforms at points (4, 11, 28, 29) exceeded the VMP. Therefore these waters are not suitable for human consumption, but can be used for animal watering, irrigation and recreation [25]. Although the following spring waters (2, 4, 5, 10, 11, 14, 16, 17, 20, 22, 25, 26, 27, 28, 32, and 33) showed pH and TC values outside the permissible limits, these waters can be used for drinking purpose, provided pH correction and proper disinfection are carried out prior to its end use.

One important lesson can be drawn from this study: if society does not protect and preserve all spring waters sources, future generations run the risk of not enjoying these nature's gifts.

## Acknowledgements

The authors thank Nuclear Technology Development Center (CDTN), Brazilian Nuclear Energy Commission (CNEN) and Research Support Foundation of the State of Minas Gerais (FAPEMIG) for their financial support (APQ-02575-13) and PhD scholarship. The authors also thank Dr. Paulo Rodrigues for the map elaboration.

## References

- [1] Omar, Y.Y., Parker, A., Smith, J.A. and Pollard, S.J.T, "Risk management for drinking water safety in low and middle income countries - cultural influences on water safety plan (WSP) implementation in urban water utilities", *Science of the Total Environment*, 576. 895-906. 2017.
- [2] Singh, V.B. and Tripathi, J.N, "Identification of Critical Water Quality Parameters Derived from Principal Component Analysis: Case Study from NOIDA Area in India", *American Journal of Water Resources*, 4(6). 121-129. 2016.
- [3] Peh, Z., Šorša, A. and Halamić, J, "Composition and variation of major and trace elements in Croatian bottled waters", *Journal of Geochemical Exploration*, 107. 227-237. 2010.
- [4] Nair, H.C., Padmalal, D. and Joseph, A, "Hydrochemical assessment of tropical springs - a case study from SW India", *Environ. Monit. Assess.*, 187(48). 1-24. 2015.
- [5] Helena, B., Pardo, R., Vega, M., Barrado, E., Fernandez, J.M. and Fernandez, L, "Temporal Evolution of Groundwater composition in an alluvial aquifer (Pisuerga river, Spain) by Principal Component Analysis", *Water Research*, 3(34). 807-816. 2000.
- [6] Kilchmann, S., Waber, H.N., Parriaux, A. and Bensimon, M, "Natural tracers in recent groundwaters from different Alpine aquifers", *Hydrogeology Journal*, 12. 643-661. 2004.
- [7] De Carvalho, A.M., Duarte, M.C. and Ponezi, A.N, "Quality assessment of sulfurous thermal waters in the city of Poços de Caldas, Minas Gerais, Brazil", *Environmental Monitoring Assessment*, 187(563). 1-11. 2015.
- [8] Hao, X., Wang, D., Wang, P., Wang, Y. and Zhou, D, "Evaluation of water quality in surface water and shallow groundwater: a case study of a rare earth mining area in southern Jiangxi Province, China", *Environmental Monitoring Assessment*, 188. 1-24. 2016.
- [9] Jang, C.S., Chen, J.S., Lin, B.U. and Liu, W.C, "Characterizing hydrochemical properties of springs in Taiwan based on their geological origins", *Environmental Monitoring Assessment*, 184. 63-75. 2012.
- [10] Borba, R.P., Figueiredo, B.R. and Matschullat, J, "Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil", *Environmental Geology*, 44. 39-52. 2003.
- [11] Deschamps, E. and Matschullat, J, *Arsênio antropogênico e natural: um estudo em regiões do Quadrilátero Ferrífero*, Fundação Estadual do Meio Ambiente (FEAM), Belo Horizonte, 2007, 330pp.
- [12] Gonçalves, J.A.C., Lena, J.C., Paiva, J.F., Nalini, H.A.Jr., and Pereira, J.C, "Arsenic in the groundwater of Ouro Preto (Brazil): Its temporal behavior as influenced by hydric regime and hydrology", *Environmental Geology*, 53. 785-794. 2007.
- [13] Matschullat, J., Borba, R.P., Deschamps, E., Figueiredo, B.R., Gabrio, T. and Schwenk, M, "Human and environmental contamination in the Iron Quadrangle, Brazil". *Applied Geochemistry*, 15. 181-190. 2000.
- [14] Varejão, E.V.V., Bellato, C.R., Fontes, M.P.F. and Mello, J.W.V, "Arsenic and trace metals in river water and sediments from the southeast portion of the Iron Quadrangle, Brazil", *Environmental Monitoring Assessment*, 172. 631-642. 2011.
- [15] Singh, A.K., Raj, B., Tiwari, A.K. and Mahato, M.K, "Evaluation of hydrogeochemical processes and groundwater quality in the Jhansi district of Bundelkhand region, India," *Environmental Earth Sciences*, 70 (3). 1125-1247. 2013.
- [16] Song, S.R., Chen, Y.L., Liu, C.M., Ku, W.Y., Chen, H.F., Liu, Y.J., Kuo, L.W., Yang, T.F., Chen, C.H., Liu, T.K. and Lee, M, "Hydrochemical changes in spring waters in Taiwan: implications for evaluating sites for earthquake precursory monitoring," *TAO*, 16(4). 745-762. 2005.
- [17] De Azevedo, U.R., Machado, M.M.M., Castro, P. de T.A., Renger, F.E., Trevisol, A. and Beato, D.A.C, *Quadrilátero Ferrífero (MG). Geoparques do Brasil. Propostas*, CPRM – Serviço Geológico do Brasil. Vol. I, Cap. 7, 2012, 748pp.
- [18] Silva, A.B., Sobreiro-Neto, A.F. and Bertachini, A.C, "Potencial das águas subterrâneas do Quadrilátero Ferrífero", in *VIII Congresso Brasileiro de Águas Subterrâneas*, Recife. Associação Brasileira de Águas Subterrâneas-ABAS, 1994, 264-273.
- [19] Lobato, L.M., Baltazar, O.F., Reis, L.B., Achtschin, A.B., Baars, F.J., Timbó, M.A., Berni, G.V., Mendonça, B.R.V. de, Ferreira, D.V, *Projeto Geologia do Quadrilátero Ferrífero - Integração e Correção Cartográfica em SIG com Nota Explicativa*, Belo Horizonte: CODEMIG. CD-ROM. 2005.
- [20] Piper, A.M, "A graphic procedure in the geochemical interpretation of water analyses", *Trans. Am. Geophys. Union*, 25. 914-928. 1944.

- [21] Gibbs, R.J. "Mechanisms controlling world water chemistry," *Science*, 170. 1088-1090. 1970.
- [22] Rice, E.W., Bard, R.B., Eaton, A.D. and Clesceri, L.S, *Standard methods for the examination of water and wastewater*, 22 ed. Ed. American Public Health Association, 2012.
- [23] Palmieri, H.E.L., Knupp, E.A.N., Ferreira, C.A. and Windmoller, C.C, "Direct quantification of trace element concentrations in spring waters by ICP-MS." *Brazilian Journal of Analytical Chemistry - BrJAC* (Print), 3. 451-459. 2013.
- [24] World Health Organization (WHO), *Guidelines for Drinking Water Quality*, Vol. 1: Recommendations (4rd ed.), Geneva: Switzerland, 2011, 541pp.
- [25] Conselho Nacional do Meio Ambiente (CONAMA), *Resolução nº 369 de 3 de abril de 2008. Dispõe sobre a classificação e diretrizes ambientais para o enquadramento das águas subterrâneas e dá outras providências*, Brasil, 2008, 13pp.
- [26] Pitt, R., Clark, S. and Field, R, "Groundwater contamination potential from storm water infiltration practices", *Urban Water*, 1. 217-236. 1999.
- [27] Talabi, A.O. and Tijani, M.N, "Hydrochemical and stable isotopic characterization of shallow groundwater system in the crystalline basement terrain of Ekiti area, southwestern Nigeria", *Appl. Water Sci.*, 3.229-245. 2013.
- [28] Abd El-Salam, M.M. and Abu-Zuid. G.I, "Impact of landfill leachate on the groundwater quality: A case study in Egypt", *Journal of Advanced Research*, 6.579-586.2015.
- [29] Nordstrom, D.K, "The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system  $Al_2O_3$ - $SO_3$ - $H_2O$  at 298 K", *Geochim. Cosmochim. Acta*, 46.681-692.1982.
- [30] Ferreira, P.C., Piai, K.de.A., Takayanagui, A.M. and Segura-Muñoz, S.I, "Aluminum as a risk factor for Alzheimer's disease", *Rev. Latino-am Enfermagem*, 16 (1). 151-157. 2008.
- [31] Mello, J.W.V.de., Roy, W.R., Talbott, J.L. and Stucki, J.W, "Mineralogy and arsenic mobility in arsenic-rich Brazilian soils and sediments," *Journal of Soils and Sediments*, 6.9-19.2006.
- [32] Deschamps, E., Ciminelli, V.S.T., Lange, F.T., Matschullat, J., Raue, B. and Schmidt, H, "Soil and sediment geochemistry of the Iron Quadrangle, Brazil: The case of arsenic," *Journal of Soils and Sediments*, 2 (4). 216-222. 2002.
- [33] Palmieri, H.E.L, *Distribuição, Especificação e Transferência de Hg e As para a Biota em Áreas do Sudeste do Quadrilátero Ferrífero, MG, Ouro Preto, Tese (Doutorado) – Universidade Federal de Ouro Preto*, 2006. 169pp.
- [34] Kamtchueng, B.T., Fantong, W.Y., Wirmvem, M.J., Tiodjio, R.E., Takounjou, A.F., Ndam Ngoupayou, J.R., Kusakabe, M., Zhang, J., Ohba, T., Tanyileke, G., Hell, J.V. and Ueda, A, "Hydrogeochemistry and quality of surface water and groundwater in the vicinity of Lake Monoun, West Cameroon: approach from multivariate statistical analysis and stable isotopic characterization," *Environ. Monit. Assess.*, 188 (9). 524. 2016.
- [35] Day, B.A., Nightingale, H.I, "Relationships between Ground-water Silica, Total Dissolved Solids, and Specific Electrical Conductivity," *Groundwater*, 22 (1). 80-85. Jan-Feb.1984.
- [36] Martin, K.R, "The chemistry of silica and its potential health benefits," *J. Nutr. Health Aging.*, 11 (2). 94-98. 2007.
- [37] Feitosa, F.A.C., Filho, J.M., Feitosa, E.C. and Demetrio, J.G.A, *Hidrogeologia: conceitos e aplicações*, 3 ed., Rio de Janeiro, RJ: CPRM, 2008, 812pp.
- [38] Davis, S.N. and De Wiest, R.J.M, *Hydrogeology*. Vol. 463, New York: John Wiley & Sons, 1966.
- [39] Talabi, A.O, "Hydrogeochemistry and Stable Isotopes ( $\delta^{18}O$  and  $\delta^2 H$ ) Assessment of Ikogosi Spring Waters", *American Journal of Water Resources*, 1 (3). 25-33. 2013.
- [40] Jalali, M, "Geochemistry characterisation of ground-water in an agricultural area of Razan, Hamadan, Iran," *Environmental Geology*, 56 (7). 1479-1488. 2009.
- [41] Carmo, F.F.do., Carmo, F.F.do., Campos, I.C. and Jacobi, C.M, "Cangas - Ilhas de ferro estratégicas para conservação", *Ciência Hoje*, 295. August. 2012.