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Evaluation of the groundwater quality and hydrogeochemistry characterization using multivariate statistics methods: case study of a hydrographic basin in Brazil

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ABSTRACT

Brazil is a country with different physical and climatic conditions, located in a diverse range of geological structures and abundant in water resources. Among the aquifers present in southern America, the Guarani and Serra Geral aquifer are two of great importance to the population. With the need to improve the quality of groundwater and to present more scientific studies on these groundwater sources, the objective of this study was to use cluster analysis and principal component analysis/factor for hydrogeochemical characterization and groundwater quality and correlate these findings with contaminants from human activities. This study was divided into two steps, hydrogeological characterization, and analysis of some contaminants that cause negative impacts on human health. The study area was a hydrographic basin located within Maringá, Paraná, Brazil. The results demonstrate that the groundwater of this basin has the dominant hydrogeochemical characteristic of calcium bicarbonate type and sodium carbonate type. The hierarchical cluster analysis was effective to the hydrogeological characterization and classified 18 sources in three distinct clusters. It was possible to correlate pollution sources that were contributing to the decline of the quality of this basin. Nitrate and benzene were related to the main pollution originating from the urban area; manganese, chromium, and lead from the old landfill; nickel and copper from electroplating industries; and pesticides atrazine and diuron, were related to the agricultural activities. The present study is of great relevance, because, in addition, to characterize the type of water (hydrogeochemical), it allowed to identifying harmful contaminants to human health in the region by correlating them with their origin.

Keywords: Groundwater; Cluster analysis; Principal component analysis/factor; Hydrogeochemistry characterization; Groundwater contamination

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1. Introduction

Brazil is a country with different physical and climate conditions, located on a diverse range of geological structures. The Brazilian territory is formed by geological structures ranging from the Paleozoic to the Mesozoic, sedimentary characteristics such as the formation of the aquifer Guarani, the Precambrian (Archaeozoic-Proterozoic), crystalline regions such as the formation of the Serra Geral aquifer, and more recent formations which are tertiary and quaternary (Cenozoic), such as the Pantanal basin, western part of the Amazon basin and stretches of the North and South coasts [1,2].

The Serra Geral aquifer and Guarani aquifer are two importants groundwater sources. In Brazil, it plays an important role in public and private water supply, meeting the most varied needs for water in several cities and communities, as well as in autonomous systems in homes, industries, services, agricultural irrigation and pleasure, its ecological role is also essential for the maintenance of flora, fauna, landscaping, and esthetic purposes in surface bodies of water, since the perpetration of the majority of rivers, lakes, and marshes is done through the discharge of aquifers, via the base flow [3,4]. The Guarani aquifer, constituted by sedimentary rocks (sedimentary aquifer), is considered one of the largest reserves of groundwater in the world, has an approximate area of 1.2 million km^2 and is located in the center of the East region of South America, which underlies four Mercosur countries: Argentina, Brazil, Paraguay, and Uruguay. In the South region of Brazil, Serra Geral aquifer is present (crystalline aquifer with 102,000 km^2), constituted by rocks originated by basaltic spills on the formation of the Guarani aquifer. In some regions, as in the state of Paraná, is known that the two aquifers may exist as an integrated system since their waters have connections by means of the fracture rocks of the crystalline aquifer so as by means of water flows from the portion with higher pressure (Guarani aquifer) to the region of lower pressure (Serra Geral aquifer) [5–7].

For this reason, there is a need to increase the number of studies to assess water contamination in the state of Paraná. Among the scarce number of studies conducted, some of them have found concentrations of nitrate, pesticides, and some metals above the limit set by the World Health Organization (WHO). The main difficulty associated with groundwater characterization is the interpretation of information acquired during the studies. In most cases, these studies present a diversified dataset with different groups and varied ranges. Thus, it is necessary to use tools to carry out these interpretations and analysis limitations. These limitations have been overcome with the application of multivariate statistical analysis (MSA), one of the most commonly used MSA and more objective way for the identification of hydrochemical groups in large datasets is the hierarchical cluster analysis (HCA) and principal component analysis (PCA)/factor analysis (FA) [8–11].

HCA is a powerful statistical tool to reduce data when a large number of records are available. By grouping the objects of the study in a cluster, defined by the characteristics present in the selected variables, the records in each cluster show a similar behavior, assigning a new meaning for the objects of each cluster. PCA is designed to transform the original variables into new uncorrelated variables named the principal components. FA is conducted after PCA with the main purpose of reducing the contribution of less significant variables in order to further simplify the data structure deriving from PCA, and to evaluate associations between a wide range of variables in terms of a small number of factors without losing too much information [10–12].

In this context, the goal of the present study was to use HCA and PCA/FA for hydrogeochemical characterization and groundwater quality evaluation and then correlate these findings with possible contaminants sources from human activities. It was conducted in a hydrographic basin located within Maringá limits, Paraná state, in the south region of Brazil.

2. Material and methods

The study was carried out during a 1-year period, between August 2014 and September 2015. The study was divided in two steps: the first step consisted of the hydrogeological characterization (one water sample for each groundwater source), and then the contaminant analysis was realized with six water samples collected at each groundwater source (one water sample in each season of the year: September, December, January, April and August).

2.1. Description of the study area

The municipality of Maringá was founded in 1940. It has a land area of 487,052 km^2, and the population estimate for 2016 was 403,063 inhabitants (Maringá) and 15,000 inhabitants live in Hydrographic Basin of Ribeirão Borba Gato (HBRBG) area. The main economy of the municipality is based on temporary agriculture (sugar cane, maize, and soybean), industries and commerce. According to the classification of Köppen, the climate of the region of Maringá is considered humid subtropical. The average annual precipitation varies from 1,250 to 1,500 mm, with hot and rainy summers, winters with frosts infrequent, without a defined dry season. The rains tend to concentrate in the months of December, January, and February, times in which the temperatures also have high averages. While the months of July to August represent a period of dry season, with precipitations and temperatures much smaller than the other months [13].

The choice of the HBRBG was based on the existence of different activities in the surrounding area, with an industrial area, agricultural areas and urban area and also due to the existence of an urban solid waste site. This landfill did not have adequate systems for pollution control. It was activated in 1974 and deactivated in 2010. Therefore, it is characterized as an environmental liability, with an estimation of having more than 3 million tons of waste [14].

This basin is located within Maringá limits, in Paraná state, in the south region of Brazil, located at 23° 25′ 30″–23° 29′ S latitudes and 53° 56′–52° 00′ W longitudes, covering an area of about 22 km^2 [15] (Fig. 1).

The study area is covered by a basaltic to rhyolitic Mesozoic volcanic sequence that belongs to the Serra Geral formation, and the main source of groundwater in this

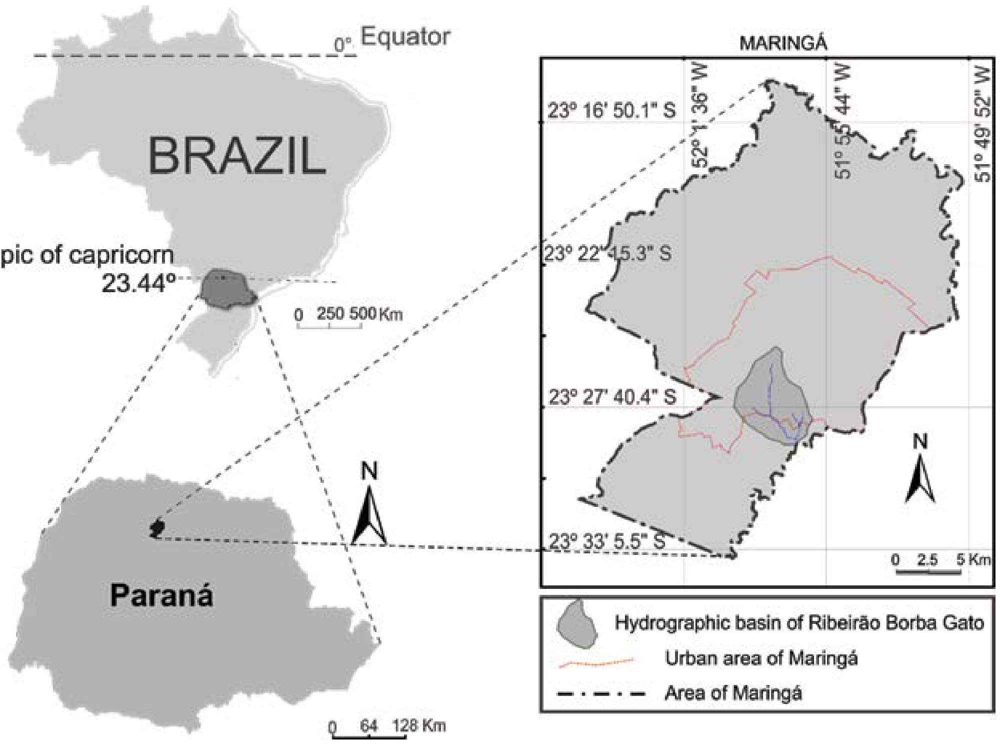


Fig. 1. Localization of Hydrographic Basin of Ribeirao Borba Gato in Brazil, Paraná state, Maringá city [13,15].

region comes from a fractured aquifer, the Serra Geral aquifer system (SGA), which has 61,095.33 km². In the region of Maringá, the average flow of the wells was 9.8 $m^3 h^{-1}$, and the water inlets were associated with geological discontinuities and vesicular zones. Although water inlets were registered up to the depth of 150 m, the highest percentage of cases (80%) occurred in the range between 30 and 90 m, with an average of 70 m depth [2,16].

The Guarani Aquifer (GA) spatial extent and storage potentiality as a transnational aquifer has a preliminarily defined full extension of 1.2 million km². In hydrogeological terms, 90% of the GA area is confined, formed by fluvial-lacustrine sediments from the Triassic period, and aeolian desert sediments from the Jurassic period [17].

2.2. Water samples and analytical methods

The twenty-eight (18) groundwater sources were selected to study in order to obtain the best distribution in the area, it was based on the database of the Waters Institute of Paraná, on the authorization of the groundwater sources owners' and according to Orban et al. [18].

The localization of each source was performed by GPS (Garmin® Etrex 30). The samples were collected according to the National Guide of Collection and Sample Preservation. The wells are active and pumping water daily; however, the removal of at least three well volumes was realized before starting the collection according to literature [19].

The analyses were performed in the Chemical Engineering Laboratory of State University of Maringá.

The parameters and methodologies utilized in the laboratorial analyses are specified in Table 1.

2.3. Statistical analyses

2.3.1. Hydrogeological characterization

The dataset was standardized before starting the statistical treatment. Standardization is mainly justified by three reasons: variables are measured in different units; have very different variances and the variables are of different types. Standardization eliminates the arbitrary effects that nonstandard variables have on the construction of similarity indices, making their contribution to the construction of similarity coefficients more balanced, the calculation was performed according to Eq. (1) [24]:

$$Z = \frac{X - \overline{X}}{S} \tag{1}$$

Z: Z-scores; X: observed value; $\overline{X}$: mean; S: standard deviation.

The physicochemical variables were processed using HCA and PCA/FA, performed by IBM® SPSS v. 22 software [10,25]. The parameters utilized were total dissolved solids, total hardness, bicarbonate alkalinity, carbonate alkalinity, potassium, calcium, fluorine, chloride, sulfate, sodium, magnesium, vanadium, and strontium.

Electrical conductivity and pH are parameters with additive characteristics, for example, impurities such as salts, acids, or bases in the samples provide significant changes in the HCA and PCA/FA, therefore these parameters were excluded from the analysis [10].

The HCA was applied to assemble the groundwater samples in clusters, hydrogeochemistry groups, in order to reveal their intrinsic characteristics based on their similarity,

Table 1
Parameters and methodologies used in the laboratorial analyses

Parameter	Methodology/equipment	Reference	Step
pH	Potentiometric method, equipment: Thermo® Scientific Orion Versa Star (Waltham, Massachusetts, U.S)	By handbook of equipment	Hydrogeological characterization and Contaminations characterization
Calcium, magnesium, sodium, potassium (mg L^{-1})	Spectrometric method. Atomic absorption spectroscopy, equipment Varian® SpectrAA 10 Plus (Palo Alto, California)	[20]	Hydrogeological characterization
Fluorine, sulfate and chloride (mg L^{-1})	Chromatography method. Ionic chromatography, equipment Metrohm® Professional IC 850 (Herisau, Switzerland)	[21]	Hydrogeological characterization
Total dissolved solids (mg L^{-1}) (TDS)	Gravimetric method	[20]	Hydrogeological characterization and contaminations characterization
Carbonate alkalinity and bicarbonate alkalinity (mg L^{-1} as $CaCO_3$)	Volumetric method	[20]	Hydrogeological characterization
Total hardness (mg L^{-1} as $CaCO_3$)	Volumetric method	[20]	Hydrogeological characterization
Electrical conductivity (EC) (μS cm^{-1}) and pH	Potentiometric method, equipment: Thermo® Scientific Orion Versa Star (Waltham, Massachusetts, U.S)	By handbook of equipment	Hydrogeological characterization
Inorganic carbon (mg L^{-1})	Combustion catalytic oxidation method (at 680°C). Equipment TOC-L cph Shimadzu® (Kyoto, Japan)	By handbook of equipment	Hydrogeological characterization
Atrazine and diuron (mg L^{-1})	Chromatography method. High-performance liquid chromatography Equipment: Varian®, model LC-920; (Palo Alto, California) Column used: Microsorb-MV 100-5 C18, 250 × 4.6 mm × 1/14″ at 25°C	[22]	Contaminations characterization
Benzene (μg L^{-1})	Chromatography method. Gas chromatography with mass detection (Static headspace analysis)	[23]	Contaminations characterization
Lead, nickel, arsenic, vanadium, copper, manganese, chromium, cadmium and strontium (mg L^{-1})	Spectrometric method. Total reflection X-ray fluorescence (TXRF)	[5]	Contaminations characterization
Escherichia coli (CFU in 100 mL)	Count plates for *E. coli* (3M™ Petrifilm™)	[20]	Contaminations characterization
Nitrate	Spectrometric method wavelength 205 nm	[20]	Contaminations characterization

performed by Ward's method and using Euclidean distance as a measure of similarity. PCA/FA was used to determine the main factors corresponding to chemical variables in the dataset in which all variables were standardized, and the number of components was based on the Kaiser criterion, for which only the components with eigenvalues of 1.0 or greater are considered significant [26], equal number of varifactors (VFs) was obtained through FA performed on the principal components, and finally the Varimax normalized rotation was applied [27]. Graphical representations to classify and interpret the geochemical data were used, such as scatter plots of chemical parameters, and plot of factor scores.

2.3.2. PCA and FA to determine main pollutants in the study area

PCA and FA were utilized to determine the main factors corresponding to chemical variables from the dataset of the year, according to the same proceedings of hydrogeological characterization previously described. The choice of variables was determined according to possible groundwater pollutants in the region: atrazine, diuron, nitrate, benzene, lead, nickel, copper, manganese, chromium, *Escherichia coli*. Arsenic was not used because this heavy metal is mobilized predominantly from young volcanic rocks and from their weathering products (natural sources).

For MSA, it is required numerical values for each input parameter, values reported as "zero" or as "below the detection limit" need to be renamed or otherwise need to be discarded from the MSA. For "zero" values, these should be set equal to the detection limit. Among the selected input parameters, vanadium and strontium presented zero values above the 5% of the entire dataset. For these two parameters, no detection limit was reported for the zero values in the database analysis and, consequently zero values were substituted by a value of the lowest value in the dataset (generally a value very close to zero); values below the detection limit were substituted by a value of half the detection limit, as the detection limits are typically very low and the influence on statistical analysis is expected to be small [11,28,29]. All statistical analysis performed in this study were conducted using the IBM® SPSS v. 22 software.

3. Results

3.1. Hydrogeological characterization

A total of 576 laboratorial analyses were carried out (16 parameters, 18 sources, in duplicated), and the chemical analyses were tested for charge balance to be less than or equal to 5% errors [10,30,31]. If alkalinity is not measured in the field, it is very likely that precipitation of a carbonate mineral will occur in the sampled bottle. This is particularly true for groundwaters in carbonate terrains that are typically supersaturated with respect to calcite and/or dolomite [10].

The statistics of the physicochemical analyses is summarized in Table 2.

The largest variations observed among the parameters were the total dissolved solids, electrical conductivity, pH, total hardness considered between soft and moderately hard (1–94.6 mg L^{-1} as $CaCO_3$), bicarbonate and carbonate alkalinity, calcium, sodium, and nitrate. These variations can be related to the mixture of waters of the unconfined aquifer of SGA with the GA waters (aquifer below SGA), a phenomenon that occurs through rocks fractures and pressures differences. The results corroborate the researches of Athayde et al. [32] and Portela Filho et al. [17].

Two processes of HCA and PCA/FA were performed. In this dataset, both processes according to the dominant chemical composition and the chemical constituents in the PCA/FA remained the same, and therefore all groundwater samples (18 samples) were used. According to HCA, the groundwater samples were classified in three main clusters, which are shown in Fig. 2.

Table 2
Range, mean, and standard deviation of physicochemical parameters in groundwater samples

Physicochemical parameters	Range	Mean	Standard deviation
Total dissolved solids (mg L^{-1})	92.000–310.000	213.444	61.132
Electrical conductivity (μS cm^{-1})	76.050–400.000	258.083	92.617
Total hardness (mg L^{-1} as $CaCO_3$)	1.000–94.625	41.097	27.483
Bicarbonate alkalinity (mg L^{-1} as $CaCO_3$)	29.000–169.000	86.527	39.270
Carbonate alkalinity (mg L^{-1} as $CaCO_3$)	0.010–155.000	19.507	43.758
pH	6.160–10.079	7.500	1.242
Potassium (mg L^{-1})	0.204–4.567	1.570	0.973
Calcium (mg L^{-1})	2.480–33.813	20.067	11.427
Fluorine (mg L^{-1})	0.050–0.410	0.113	0.094
Chloride (mg L^{-1})	1.440–19.100	7.779	5.194
Sulfate (mg L^{-1})	0.180–9.270	1.894	2.365
Sodium (mg L^{-1})	3.350–95.550	20.230	28.164
Magnesium (mg L^{-1})	0.050–9.310	4.152	2.980
Vanadium (mg L^{-1})	0.005–0.135	0.022	0.030
Strontium (mg L^{-1})	0.005–0.181	0.064	0.061
Inorganic carbon (mg L^{-1})	4.290–20.771	11.926	4.495

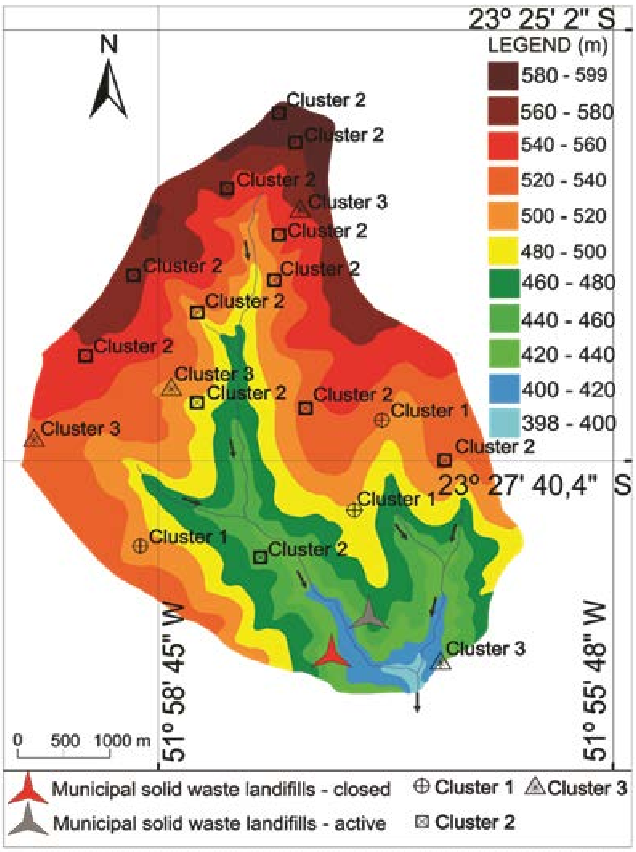


Fig. 2. Distribution of sources in the HBRBG and the classification by HCA.

The black arrows represent the groundwater flow direction.

In Fig. 2, the majority of the sources belong to cluster 2 (C2) (61%); 17% belong to cluster 1 (C1) and 22% belong to cluster 3 (C3). We can see in Fig. 2 that the groundwater sources of C3 were constituted of water with the influence of the Guarani Aquifer, according to data from the Paraná water institute, responsible for the wells, these sources are constituted with the deepest water abstraction. In the three wells located between altitudes 500 and 560, the depth is 100–150 m, while the well located downstream of the basin is 80 m deep. It is important to note that the latter, through the difference in the level of the mouth of the well have drawn water approximately the same depth, concluding that the wells of C3 draw water at depths higher than the others.

The other wells have depths ranging from 70 to 100 m. C1 formation in cluster analysis may be related to similar fractures. In this case, for future research suggests the performance of a salt tracer test, as was done by Robert et al. [33] with the objective of identifying possible hydraulic connections in the aquifer. In Table 3, the mean concentrations in the three clusters produced by HCA are presented.

In Table 3, the differences between the clusters are evident: cluster 1 (C1) includes samples with low ionic concentration, indicated by TDS (125.33 mg L^{-1}) and electrical conductivity (113.53 µS cm^{-1}), the main ions showed the following order: $HCO_3^- > Ca^{2+} > Na^+ > Cl^- > Mg^{2+} > K^+ > SO_4^{2-} > F^- > CO_3^{-2}$.

Table 3
Mean concentrations of physicochemical characteristics each cluster produced by HCA

Chemical parameters	C1	C2	C3
Total dissolved solids (TDS) (mg L^{-1})	125.33	211.18	285.75
Electrical conductivity (µS cm^{-1})	113.53	270.71	331.76
Total hardness (mg L^{-1} as $CaCO_3$)	25.25	59.21	2.75
Bicarbonate alkalinity (HCO_3^-) (mg L^{-1} as $CaCO_3$)	45.33	111.68	13.13
Carbonate alkalinity (CO_3^{-2}) (mg L^{-1} as $CaCO_3$)	0.01	0.01	53.54
pH	6.62	7.00	9.53
Potassium (k$^+$) (mg L^{-1})	1.20	1.60	1.74
Calcium (Ca^{2+}) (mg L^{-1})	9.60	28.33	5.81
Fluorine (F^-) (mg L^{-1})	0.11	0.08	0.20
Chloride (Cl^-) (mg L^{-1})	3.16	10.66	3.36
Sulfate (SO_4^{2-}) (mg L^{-1})	0.28	2.65	1.00
Sodium (Na^+) (mg L^{-1})	3.64	9.40	62.24
Magnesium (Mg^{2+}) (mg L^{-1})	2.86	5.95	0.17
Vanadium (V) (mg L^{-1})	0.008	0.01	0.06
Strontium (Sr) (mg L^{-1})	0.03	0.09	0.008
Inorganic carbon (mg L^{-1})	10.86	12.40	11.39

Note: Mean values of electrical conductivity and pH are also shown.

Cluster 2 (C2) samples present the largest concentrations of total hardness, bicarbonate alkalinity, calcium, chloride, and magnesium; the average values of total dissolved solids, electrical conductivity, and pH are intermediate between C1 and C3. The order of the main ions is similar to C1: $HCO_3^- > Ca^{2+} > Cl^- > Na^+ > Mg^{2+} > SO_4^{2-} > K^+ > F^- > CO_3^{-2}$. Clusters 1 and 2 have a similar order of their main ions and show the presence of strontium, magnesium, calcium, and pH is lower than 7. These clusters are related with the Serra Geral aquifer's waters, in conformity with studies [6,31,32].

Cluster 3 (C3) includes samples with the largest concentrations of TDS, EC, pH, and Na^+, in comparison with C1 and C2. According to studies conducted in the Paraná state [7,17], the presence of vanadium, soft water, pH above 9 and high TDS values are characteristic of water from Guarani aquifer. The order of the main ions is $CO_3^{-2} > Na^+ > HCO_3^- > Ca^{2+} > Cl^- > K^+ > SO_4^{2-} > F^- > Mg^{2+}$.

One can see in Table 3 that C3 waters are nearly depleted in bicarbonate, which is expectable considering its high mean pH (9.53). According to carbonate, speciation rules at these pH values the dominant carbonate species is "carbonate". Consequently, C3 water type is sodium carbonate.

The PCA results showed significant correlation among the variables (KMO statistics and Bartlett's test result in Table 4) and yielded two principal components with eigenvalues >1. Corresponding varifactors (VFs), variable loadings, and explained variance are presented in Table 4.

The first varifactor (VF1) explains 53% of the total variance contained in the original variables, with loadings in bold (between 0.496 and 0.849). This factor is associated with the chemical constituent bicarbonate alkalinity, total

Table 4
Factor analysis results of variables under study

Variables	Principal components	
	VF1	VF2
Total dissolved solids (TDS)	0.339	**0.812**
Carbonate alkalinity (CO_3^{-2})	–0.322	**0.917**
Bicarbonate alkalinity (HCO_3^-)	**0.786**	–0.244
Total hardness	**0.849**	–0.437
Calcium (Ca^{2+})	**0.825**	–0.386
Vanadium (V)	–0.261	**0.776**
Strontium (Sr)	**0.809**	–0.204
Fluorine (F^-)	–0.345	**0.467**
Chloride (Cl^-)	**0.818**	–0.198
Sulfate (SO_4^{2-})	**0.637**	–0.019
Sodium (Na^+)	–0.320	**0.895**
Magnesium (Mg^{2+})	**0.834**	–0.418
Inorganic carbon (IC)	**0.496**	0.113
% Explained variance	53	16
Cumulative % variance	53	69
Eigenvalue	6.8	2.2

Extraction method: Principal components analysis.
Rotational method: Varimax with Kaiser normalization.
KMO: 0.582; Bartlett's test: *p*-value ≈ 0.000.

hardness, Ca^{2+}, Sr, Cl^-, SO_4^{2-}, Mg^{2+}, and IC. VF2 explains 16% of the total variance, which is associated with variables TDS, CO_3^{-2} alkalinity, V, F^-, and Na^+ showing loading between 0.467 and 0.917. For a better understanding of these components there follows a presentation by scatter plot of loadings and a plot of factor scores with the groundwater clusters in Fig. 3.

In Fig. 3a, in observation to the x-axis (parameters of VF1), carbonate alkalinity, V, F^-, and Na^+ are inversely proportional to the bicarbonate alkalinity, total hardness, Ca^{2+}, Sr, Cl^-, SO_4^{2-}, Mg^{2+}, TDS, and inorganic carbon. Otherwise, the observations of y-axis (parameters of VF2), the inorganic carbon and SO_4^{2-} little influence on correlations (VF2 with VF1), the correlations of carbonate alkalinity, V, F^-, Na^+, TDS are inversely proportional to the bicarbonate alkalinity, total hardness, Ca^{2+}, Sr, Cl^-, and Mg^{2+}.

It can be seen in Fig. 3b that groups 1 are the samples that are least influenced by the selected parameter loads (VF1 and VF2). This behavior is observed in Tables 3 and 4, making it clear that this group shows lower concentrations of ions in the medium, compared with the other groups. Group 2 has a higher influence of VF1 parameters than VF2 influence, while C3 shows a different behavior, presented by parameters located in the upper left quadrant, greater influence of VF2 and lower influence of VF1.

Based on the physical–chemical composition, the bicarbonate ion is the most abundant, and all clusters are plotted within the HCO_3^- water area. This characteristic is directly influenced by balance system: CO_2–H_2O, current in recharge areas. The SGA is an unconfined aquifer, and therefore during the water infiltration process by atmospheric precipitations occurs generation and dissociation of carbonic acid ($H_2CO_3^-$).

Based on the physical–chemical characterization, the groundwater samples of cluster 1 and cluster 2 are classified as calcium bicarbonate type, and the samples of cluster 3 as sodium carbonate type. The dominant hydrogeochemical type is calcium bicarbonate type, that is, the same classifications obtained by Justen et al. [34]. Cluster 2 samples showed higher concentrations of calcium and magnesium that are associated with the rocks of the Serra Geral formation, which have mainly plagioclase and ferromagnesian in the basalt composition. Cluster 1 has waters with lower ionic concentrations and together with cluster 2 is classified as calcium bicarbonate.

Groundwater classified as sodium carbonate type can be associated with deep sources (80–150 m), because these waters are in contact with the rocks of Serra Geral formation

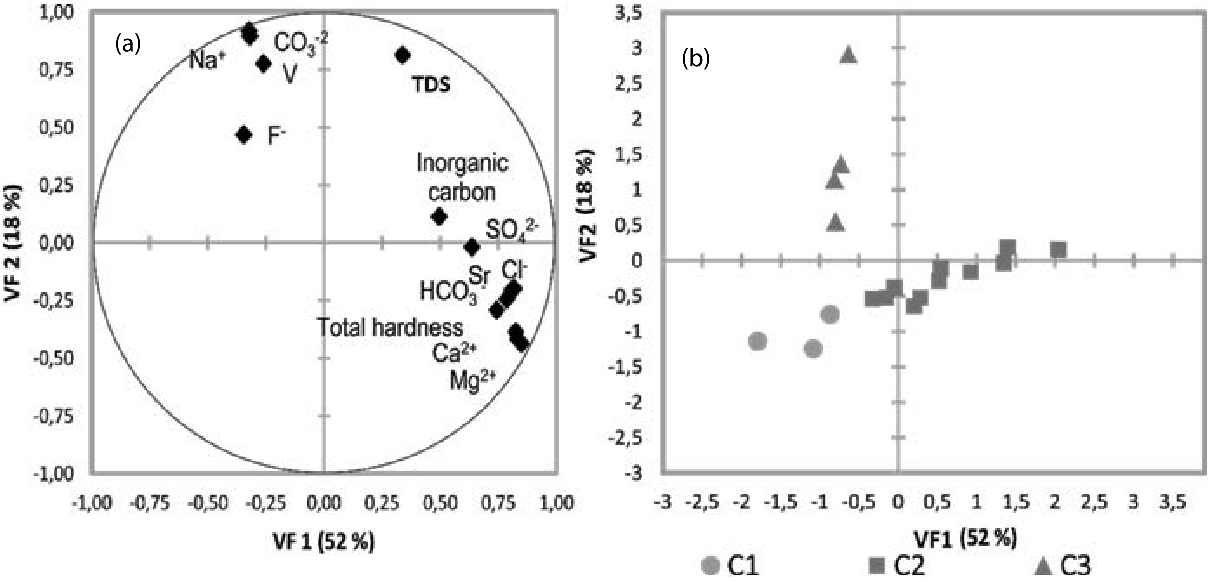


Fig. 3. Scatter plot of loadings (a) and a plot of factor scores with the groundwater clusters (b).

and they have totally distinct characteristics. This behavior can be explained by the alkaline environment, since sodium and magnesium are virtually insoluble. Thus, as suggested by Athayde et al. [7], the SGA is constantly recharged by groundwater from GA accessed by means of basaltic fractures.

Calcium bicarbonated water occurs in wells with less than 100 m depth. This water may result from the weathering of calcium plagioclase and calcite. The bicarbonate character is directly influenced by the equilibrium of CO_2–H_2O system in the areas close to the water recharge and also by hydrolysis reactions of the silicates in the extrusive rocks. The field of calcium carbonate waters has a lithochemistry control, already that its chemical characteristics are related to weathering processes that act on the volcanic rocks [35,36].

Sodium carbonate waters occur in wells with water intakes predominantly greater than 100 m. These waters are in marked imbalance what would be expected for a supported aquifer by typical basaltic rocks. They are waters with probably influenced by an external environment Serra Geral aquifer. Thus, these waters can present the existence of structural conditioners that would be responsible for the mixing of aquifer waters, mainly the Guarani aquifer. Another possibility is portrayed by the depletion of the amount of calcium and dissolved magnesium, thus increasing the relative sodium is one of the consequences that can result in carbonated sodium water [36].

3.2. Characterization of the main contaminants that cause negative impacts on human health and natural resources

A total of 2,808 laboratorial analyses were carried out (13 parameters, 18 sources, 6 campaigns, in duplicated), and the results were validated according to the methodology for each parameter (Table 1) in order to include all the results within the calibration curve of each analysis (except the microbiological one). The results of the physicochemical and microbiological characterization are presented in Table 5.

As shown in Table 5, during the six campaigns throughout a 1-year period in the study area, benzene, *Escherichia coli*, chromium, cadmium, copper, and turbidity do not exceed the maximum value recommended by the WHO (diuron limits are not indicated by WHO). Lead (Pb) was the only parameter whose mean value exceeded the WHO recommendations; this heavy metal has also been found by others researchers in the region, in groundwater, surface waters, sewerage, and in percolated liquid produced at the sanitary landfill [37,38].

In Fig. 4, it is possible to view and compare the frequency of parameters that were detected and the physicochemical analysis of frequencies greater than the WHO recommendations in the period of the study.

According to Fig. 4, the parameters pH, nitrate, Pb, Ni, Mn, As, and atrazine resulted in values above WHO's recommendations. Benzene, Cu, and Cr did not exceed the limits but are present in groundwater, as well as diuron, which is not stated by the WHO. It is important to highlight that nitrate was detected in concentrations between 10 and 50 mg L^{-1}, which is indicative of contamination.

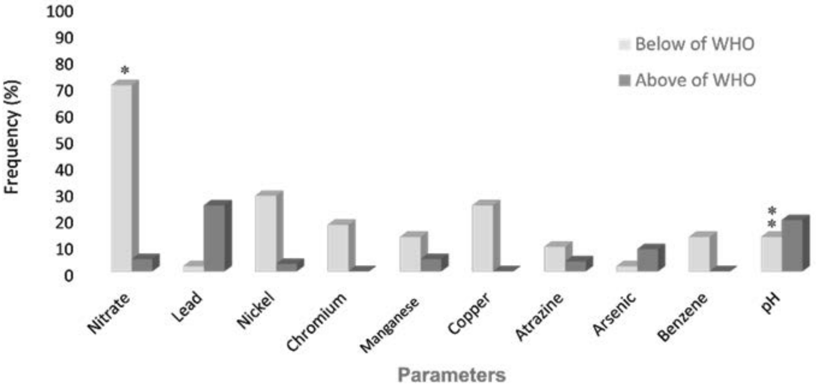
The presence of Ni, Cu, and Cr can be related with the metallurgical industry and liquid percolated from the sanitary landfill that is present within the basin. Atrazine and diuron are related with the agriculture practices in the region.

The pH variation and the presence of arsenic are related with the geomorphological compositions. The frequency of pH less than 6.5% (WHO) was 17.5% (20 samples), but there were also values greater than 8.5% in 18.4% of the samples (21 samples). Values less than 6.5 were taken in sources belonging to cluster 1 and were classified as calcium bicarbonate type (Serra Geral aquifer) [39], while samples with values greater than 8.5 were taken in sources belonging

Table 5
Physical-chemical and microbiological characterization of groundwater samples

Chemical parameters	Range	Mean	Standard deviation	WHO recommendations
Nitrate (mg L^{-1})	1.893–77.430	39.6615	15.387	50.000
Atrazine (mg L^{-1})	<0.01*–0.130	0.017	0.022	0.100
Diuron (mg L^{-1})	<0.01*–0.130	0.014	0.016	–
Benzene (μg L^{-1})	<0.50*–1.500	0.535	0.139	10.00
Toluene (μg L^{-1})	<0.50*	–	–	170
Ethylbenzene (μg L^{-1})	<0.50*	–	–	200
Xylenes (μg L^{-1})	<0.50*	–	–	300
Escherichia coli (CFU in 100 mL)	**	**	0	0.00
Chromium (Cr) (mg L^{-1})	<0.005*–0.041	0.008	0.008	0.050
Manganese (Mn) (mg L^{-1})	<0.005*–1.420	0.055	0.211	0.400
Nickel (Ni) (mg L^{-1})	<0.005*–0.090	0.011	0.015	0.070
Copper (Cu) (mg L^{-1})	<0.005*–0.130	0.011	0.018	2.000
Arsenic (As) (mg L^{-1})	<0.005*	–	–	0.010
Cadmium (Cd) (mg L^{-1})				
Lead (Pb) (mg L^{-1})	<0.005*–0.920	0.060	0.166	0.010

*Below detection limit; – = Not indicated by OMS; ** = not detected; CFU = colony forming unit.



*Concentration of nitrate between 10 mg L^{-1} to 50 mg L^{-1} of NO_3^-
**pH less than WHO's recommendations (6.5)

Fig. 4. Frequency of parameters detected in groundwater samples with possible health risks for the human population.

to cluster 3 and were classified as sodium carbonate type (Guarani aquifer) [40].

The presence of arsenic resulted in values above the WHO's recommendations: 9% (10 samples), with low frequency during all study, 1% (1 sample); these samples were taken in sources belonging to clusters 2 and 3. This heavy metal is mobilized predominantly from young volcanic rocks and from their weathering products. In Latin America, the problem of arsenic contamination in water is known in 14 out of 20 countries (including Brazil) [41].

The frequency of manganese above WHO's recommendations was 4% (5 samples), and the presence of this ion was 15% (17 samples). As well as arsenic, the presence of this parameter is related with the geomorphological aspects, but sources of contamination, especially percolated liquid from the sanitary landfill, can also contribute to the presence of this heavy metal in the regional groundwater.

The presence of lead was observed in values greater than the WHO's recommendations, with a frequency of 26% (30 samples). In the past, the use of lead-acid batteries was common in the region. These batteries and solutions were discarded without any control in the soil of the companies of this segment in the HBRBG. In addition, the first water distribution system in the city used pipes made of lead, and until 1986 lead was used in gasoline.

Benzene was not detected in values greater than the WHO's recommendations, but was detected in 13% of the samples (15 samples). The frequency of nitrate was in values between 10 and 50 mg L^{-1} were observed more frequently, with 67% (76 samples), and 4% (5 samples) presenting values greater than the WHO's recommendations. Values greater than 50 mg L^{-1} were 54–77.43 mg L^{-1} of NO^{3-}.

In most countries, nitrate levels in natural groundwater and surface water do not exceed 10 mg L^{-1} of NO^{3-}; levels above those are indicative of contamination, especially by domestic sewage. In the study area, higher nitrate concentrations were obtained at the sources belonging to cluster 2, followed by cluster 1 and cluster 3. Therefore, the results from the nitrate analyses indicated that samples collected in sources from cluster 3 have less influence of contamination; however, one source from cluster 3 showed nitrate concentrations higher than 10 mg L^{-1} [42–44].

The PCA/FA was applied to the dataset and the results are presented in Table 6.

Table 6 shows that component 1 (VF1) explained 22.4% of the total variance occurring in the original variables. The loadings (in bold) had a variance between 0.683 and 0.705 (the closer to 1 the greater the correlation between the parameters; the closer to 0 the lower the correlation). That component was associated with chrome, lead, and manganese. Among the sources of contamination in which the presence of these three metals is common, leachate is discarded from landfills.

Component 2 (VF2) explained 13.8% of the total variance. The loadings had a variation ranging from 0.693 to 0.874, and this component was associated with copper and nickel. These heavy metals are common in industrial effluents, especially in the metallurgical industry which are common in HBRBG.

Table 6
Factor analysis results of the variables under study

Parameters	Principal components			
	VF1	VF2	VF3	VF4
Nitrate	0.245	–0.097	**0.687**	–0.209
Atrazine	–0.015	–0.110	–0.127	**0.583**
Diuron	–0.011	0.019	0.084	**0.844**
Benzene	–0.212	0.130	**0.756**	0.094
Manganese (Mn)	**0.705**	–0.110	–0.146	–0.095
Chromium (Cr)	**0.683**	0.131	–0.043	0.021
Nickel (Ni)	0.481	**0.693**	0.120	0.015
Copper (Cu)	–0.082	**0.874**	–0.024	–0.129
Lead (Pb)	**0.687**	0.119	0.326	0.027
% Explained variance	22.4	13.8	12.4	12
Cumulative % variance	22.4	36.2	48.6	60.6
Eigenvalue	2.0	1.2	1.1	1.0

Extraction method: principal components analysis.
Rotational method: varimax with Kaiser normalization.
KMO: 0.553 and Bartlett's test: p-value ≈ 0.000.

Component 3 (VF3) was represented by nitrate and benzene, and explained 12.4% of the total variance. The loadings (in bold) had variance ranging from 0.687 to 0.756. Benzene was not detected in higher values than those recommended; however, it was detected in 15 samples. According to the WHO [45], the main sources of this organic compound are atmospheric depositions and petroleum or other petroleum products spills, for example, effluents from mechanical repairs, fuel tanks leaks, and the like.

The frequency of nitrate in values greater than 10 mg L^{-1} was observed in 81 samples. In most countries, nitrate levels in natural groundwater do not exceed 10 mg L^{-1} of NO^{3-}. Nitrate contamination in groundwater is mainly associated with domestic sewage [46,47,48]. In the study area, the highest nitrate concentrations were obtained in the sources belonging to cluster 2, followed by clusters 1 and 3. Nitrate and benzene were found in sources located in the urban area where residencies, gas stations, and mechanic workshops are present. Therefore, with the association of these parameters, it suggests the joint contamination by infiltration in the soil by the mentioned sources. The nitrate contamination in agricultural areas is strongly linked to the use of chemical agents (e.g., pesticides), the intensive agricultural activity is an important factor that interferes in groundwater quality due to N leaching from soils to groundwater [49].

Component 4 (VF4) was represented by the contaminants atrazine and diuron, and explained 12% of the total variance, with loadings ranging from 0.583 to 0.844. These contaminants were associated with agricultural contamination caused by the pesticides used in the region.

The loadings of the variables were illustrated using graphical representations (Table 6). It was observed that the closer to 1, the stronger the association between the variable and the component, whereas a loading close to zero allowed concluding that this variable little contributed to the formation of the component. Fig. 5 shows the distribution of loadings comparing the four components obtained using the PCA.

Fig. 5 shows the component VF1 compared with VF2, VF3, and VF4. It was observed that when there was manganese, lead, and chromium contamination, there was also nickel contamination, little influence of nitrate and benzene (inversely proportional to nitrate) in the medium, very low contribution of copper, and almost no influence of pesticides This behavior may have been related to the infiltration of effluents from the landfill because the simultaneous presence of these four metals is common in this type of effluent.

However, the analysis of the y-axis in VF1 × VF2 and, also, the x-axis of the diagrams VF2 × VF3 and VF2 × VF4 indicated that when there was copper and nickel contamination (strongly correlated), the other contaminants had very low or almost no contribution. Copper and nickel are common in effluents from electroplating and frequent in industrial areas.

People in contact with these metals by oral ingestion or dermal contact for an extended time have the accumulation of these compounds in muscle, liver, and brain that can damage the central nervous system. Of most concern is the lead with the highest concentrations recorded; the consequences of this metal is deterioration of the nerve connection, inhibits the enzymatic function and causes many chronic diseases such as hypertension, kidney failure, tiredness, irritability, etc. [50,51].

The analysis of the y-axis in diagrams VF1 × VF3 and VF2 × VF3, as well as the x-axis in diagram VF3 × VF4 indicated that, when there was nitrate and benzene contamination, there was also lead and very low contribution of other contaminants. Thus, as mentioned previously, as well as the contamination by benzene (from mechanical workshops and fuel stations), nitrate contamination is common in urban areas (domestic sewage). In addition to lead being common in effluent from landfills, the results indicate that this metal is also associated with contamination in urban areas, which, for example, is produced by battery recovery workshops and used in the past in gasoline.

Benzene has considerable solubility in water and may cause mutagenic, carcinogenic effects, neurological disorders, changes in endocrine system function, and damage to the kidney and liver in humans. Nitrate concentration level in groundwater is normally within the low range of 0–80 mg L^{-1} and contaminated drinking water can potentially cause health problems such as blue-baby syndrome or methemoglobinemia in infants and can still increase the risk of cancer because nitrate is endogenously reduced to nitrite and subsequent reactions of nitrosation give rise to *N*-nitroso compounds, highly carcinogenic compounds and can act systemically [52,53].

The comparison of the y-axes (contaminants atrazine and diuron) in diagrams VF1 × VF4, VF2 × VF4, and VF3 × VF4 indicated that pesticides had no influence of other contaminants, except nitrate that was lightly inversely proportional. In this way, it is suggested that the main source of pesticides contamination was the agricultural area. In fact, these compounds are especially related to maize and sugarcane, which were the common plantations in the region.

Atrazine is 1-chloro-3-ethylamino-5-isopropylamino 2,4,6-triazine. It is used as a herbicide to control the growth of weeds and grasses in agriculture. Atrazine is one of the most widely used pesticides in the world, in some countries the use of this compound is prohibited, but in Brazil it is legalized. Exposure to atrazine may cause a variety of symptoms, such as low weight, cardiac defect, and premature deliveries. Diuron is 3-(3,4-dichlorophenyl)-1,1-dimethylurea, it is designed to inhibit photosynthesis and is used as a herbicide. High level of exposure to diuron can cause central nervous system depression after entering the human body by ingestion or inhalation [53].

The present study made it possible to correlate pollution sources that were contributing to the decline in the quality of this basin groundwater. Nitrate and benzene parameters were related to the main pollution originating from the urban area, manganese, chromium, and lead from the old landfill, nickel and copper from electroplating industries. Pesticides atrazine and diuron were related to the agricultural area and, possibly, to vegetable producers of the region.

The use of CA and PCA for hydrogeochemical characterization was relevant, because it allowed for more parameters, such as strontium and vanadium, which were indicative of the types of common groundwaters in the region. In addition, we used piper diagram for the

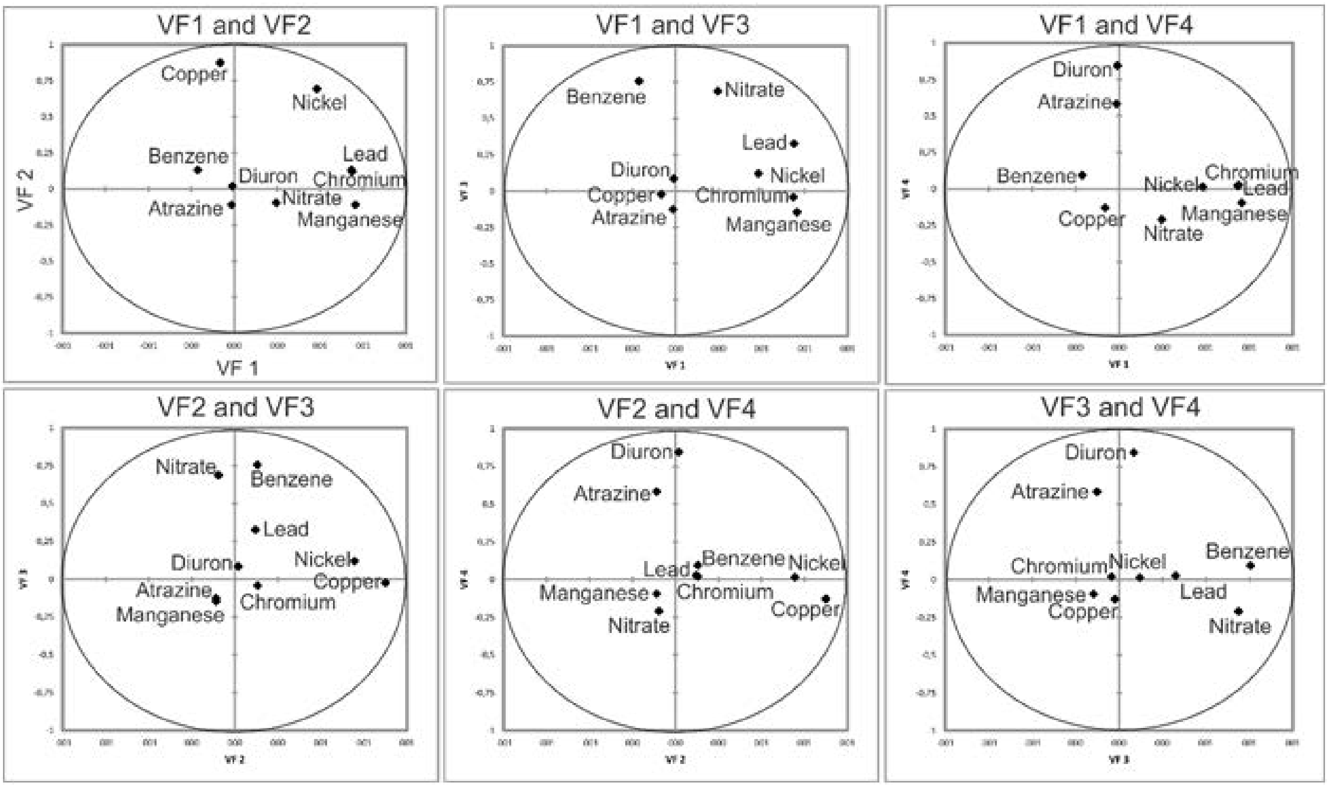


Fig. 5. Scatter plot with the respective loadings of the four components.

classification of the main ions in these waters, which were calcium bicarbonated and sodium carbonated types.

For future researches we suggest the performance of a salt tracer test with the objective of identifying possible hydraulic connections in the aquifer and thus associate the location of the polluting sources with the underground flow in HBRBG.

4. Conclusions

The results demonstrate that the waters collected in the hydrographic basin of Ribeirão Borba Gato present the dominant hydrogeochemical calcium bicarbonate type and sodium carbonate type.

HCA was effective for the hydrogeological characterization, because this method classified 18 sources in 3 distinct clusters, C1 that presents sources of calcium bicarbonate type, with low minerals concentrations; C2 with sources of calcium bicarbonate type with greater concentrations of minerals, that were associated with waters from the Serra Geral aquifer, and C3 with sources of sodium carbonate type that were associated with waters from the Serra Geral aquifer that are under the influence of the water from the Guarani aquifer.

With the use of PCA/FA, it was possible to check two varifactors in the hydrogeological dataset that were associated with the two groundwater types (calcium bicarbonate and sodium carbonate types).

From characterization of the main contaminations by anthropogenic process four varifactors were checked in the dataset: first, Cr, Pb, and Mn (percolated from sanitary landfill); second, copper and nickel (industrial contaminations); third, nitrate and benzene (in the urban area); and fourth, atrazine and diuron (pesticides used in all the region's agriculture).

The present study is of great relevance, because, in addition to characterize the type of water (hydrogeochemical), it made it possible to identify harmful contaminants to human health in the region by correlating them with their origin (agricultural, industrial, urban, and natural). This way, this study can promote the improvement of monitoring and decision-making relating to conscious use of groundwaters.

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