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Unusual physico-chemical parameters in the public water supply of a town in the northeast of the São Paulo State (Brazil)

Parâmetros físico-químicos incomuns em água de abastecimento público de um município da região nordeste do Estado de São Paulo (Brasil)

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ABSTRACT

Public water supply samples (n = 4347) from 88 municipalities in the northeast of the State of São Paulo (Brazil) were analysed in 21 physico-chemical parameters: temperature, conductivity (by conductimetry), free residual chlorine (colorimetry with N,N-diethyl-p-phenylenediamine), pH (potentiometry), apparent color (spectrophotometry), turbidity (nephelometry), and concentrations of Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, ClO_2^-, BrO_3^-, Cl^-, Br^-, ClO_3^-, NO_3^-, PO_4^{3-}, SO_4^{2-} (ion chromatography). The results were submitted to multivariate data analysis. The principal component analysis of 12 variable medians (pH, conductivity, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, ClO_3^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) from 88 municipalities indicated Ibitinga as the locality with the public water supply having physico-chemical characteristics unique in the region, characterized by higher relative concentrations of sulphate, chloride, lithium, and sodium, and higher values of pH and conductivity. Additionally, Ibitinga was the only municipality that systematically presented bromide in the water composition. A second principal component analysis on 79 samples of Ibitinga has indicated a sample with higher concentrations of chloride and sulphate, and 4 samples where the presence of nitrate was characteristic. Hierarchical cluster analysis exhibited the clustering of these groups produced in two component analysis. Validation of methods based on ion chromatography is also presented.

KEYWORDS: Water Quality; Physico-chemical Analysis; Principal Component Analysis; Sanitary Surveillance

RESUMO

Amostras de águas de abastecimento público (n = 4347) de 88 municípios do nordeste do Estado de São Paulo (Brasil) foram analisadas em 21 parâmetros físico-químicos: temperatura, condutividade (por condutimetria), cloro residual livre (colorimetria com N,N-dietil-p-fenilenodiamina), pH (potenciometria), cor aparente (espectrofotometria), turbidez (nefelometria), e concentrações de Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, ClO_2^-, BrO_3^-, Cl^-, Br^-, ClO_3^-, NO_3^-, PO_4^{3-} e SO_4^{2-} (cromatografia de íons). Os resultados foram submetidos à análise multivariada de dados. A análise de componentes principais das medianas de 12 variáveis (pH, condutividade, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, ClO_3^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) dos 88 municípios indicou Ibitinga como local com água de características físico-químicas únicas, caracterizada pelas concentrações relativas mais altas de sulfato, cloreto, lítio e sódio, e aos valores maiores de pH e condutividade. Em adição, Ibitinga foi o único município que apresentou sistematicamente brometo na composição da água. Uma segunda análise de componentes principais envolvendo as amostras de Ibitinga indicou uma amostra com concentrações mais altas de cloreto e sulfato, e quatro amostras nas quais a presença de nitrato foi característica. Análises de agrupamento hierárquico exibiram a formação dos mesmos grupos produzidos nas duas análises de componentes. A validação dos métodos cromatográficos também é apresentada.

PALAVRAS-CHAVE: Qualidade da Água; Análise Físico-química; Análise de Componente Principal; Vigilância Sanitária

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INTRODUCTION

To collaborate with the promotion and protection of the health of the population, one of the actions provided for in the Drinking Water Surveillance Program of the state of São Paulo (PROAGUA)[1] in Brazil, includes the monitoring of the quality of the public water supply from sample collections, for the analysis of some basic parameters: temperature, pH, free residual chlorine, color, turbidity, fluoride, total coliforms, and *Escherichia coli*. In particular, the northeast region of the state, which is considered to be in the process of industrialization, has 90 municipalities with approximately 3.3 million inhabitants (according to data from the 2010 Brazilian Institute of Geography and Statistics). Approximately 70% of the municipalities (62.8% of the population of the region) use only groundwater for public supply, 15% (18.6% of the population) use only surface water, and 15% (18.6% of the population) use both. Groundwater can be accessed from three aquifers (Bauru, Guarani, and Serra Geral) and an aquiclude (Passa Dois)[2]; while surface water may have a more diverse origin because of the complex regional hydrography that includes the Grande, Sapucaí, Pardo, and Mogi Guaçu rivers[3]. The region is covered by four Regional Health Departments: Araraquara, Barretos, Franca, and Ribeirão Preto (Figure 1), which make up the Health Care Regional Network 13 (RRAS 13) of the state of São Paulo, Brazil. Surveillance includes the respective Health Surveillance Groups in which the 90 municipalities of the region are distributed.

To obtain a more detailed characterization of the quality of the drinking water in the region, in view of the occurrence of significant nitrate contamination in one of its municipalities[4], a study was started in the Regional Laboratory Center, Adolfo Lutz Institute of Ribeirão Preto VI (São Paulo) in 2014, increasing the number of parameters evaluated, in addition to the aforementioned ones, with the concentrations of 14 ions (ammonium, bromate, bromide, calcium, chlorate, chloride, chlorite, phosphate, lithium, magnesium, nitrate, potassium, sodium, and sulphate) also being determined, as well as conductivity measurements. Thus, the total physicochemical parameters investigated were increased from six to 21. Since the importance of the basic parameters evaluated by PROAGUA is widely described in the pertinent literature[3,5-7], it was important to consider the ones included in this study, based mainly on a document from the World Health Organization[6] (the maximum allowed value (MAV) is indicated when established by Ordinance No. 2,914, of December 12, 2011[8]):

Figure 1. Region to which this study refers, which includes the Regional Health Departments of Araraquara, Barretos, Franca, and Ribeirão Preto, Brazil.

- Ammonium (NH_4^+) or ammonia (NH_3) – originates in the environment as a result of metabolic, agricultural, and industrial processes, as well as when chloramine is used in the process of water disinfection. On the other hand, ammonium can react with free chlorine, producing chloramines, nitrogen trichloride, and nitrite, compromising the efficiency of the disinfection process[5]. The MAV for ammonia is 1.5 mg L^{-1}.

- Bromate (BrO_3^-) – is not normally found in water, but can be formed by the conversion of the bromide ion by the disinfection during ozonation, which depends on the organic matter present, pH, and temperature, among other factors. Sodium or potassium bromide ($NaBrO_3$ or $KBrO_3$) are oxidizing agents that can be used, for example, in dyeing fabrics. Similar to trihalomethanes and dichloro- and trichloroacetic acids, bromate is a probable carcinogen in humans and it is considered mutagenic (MAV = 0.01 mg L^{-1}).

- Bromide (Br^-) – an ion commonly found in nature next to chloride, because of its similar chemical properties, but in lower amounts. Industrial sewage can contribute to increasing its concentration in springs. It can participate in the reaction between chlorine and natural organic matter, which forms trihalomethanes and halogenated acetic acid (the rate of trihalomethane formation increases as a function of the concentrations of chlorine and humic acids, temperature, pH, and concentration of the bromide ion).

- Calcium (Ca^{2+}) and magnesium (Mg^{2+}) – although referred as “total hardness” and often associated with problems in distribution systems and industries (precipitation of soaps, corrosion, and deposition in treatment plants, distribution networks, and tanks), these ions are essential nutrients to human health. Intake amounts of these ions have been recommended at national and international level, but the needs are different for different individuals. On the other hand, concentrations in drinking water can vary greatly from one source to another – mineral-rich waters, for example, can contribute substantially to the daily needs of these nutrients in some populations or subgroups. In addition, water treatment may also affect the concentrations of both. The MAV for total hardness is 500 mg L^{-1}.

- Chlorate (ClO_3^-) and chlorite (ClO_2^-) – are secondary ionic products from the use of chlorine dioxide (ClO_2) as a disinfecting agent or as an odor and taste control agent in water. The ClO_2 is also used as a bleach in the paper, flour, and oil industries, and as a cleaning agent in the leather industry. Sodium chlorite ($NaClO_2$) is used in the paper, textile, and straw industries and in the manufacture of waxes, varnishes, and enamels. Uses of sodium chlorate ($NaClO_3$) include the leather industry and as a herbicide and defoliant. The chlorite and chlorate ions can also be formed during the slow decomposition of sodium hypochlorite (NaClO) solutions. The main concern with chlorite and chlorate intake is the oxidative damage to red blood cells. High doses of chlorate may interfere with thyroid functions. The MAV for chlorite is 1 mg L^{-1}.

- Chloride (Cl^-) – a byproduct, in supply water, of chlorination by Cl_2 or hypochlorite (ClO^-) solutions, and it may originate from natural sources, sewage, and industrial wastewater. When excess is present (MAV = 250 mg L^{-1}), it increases the corrosion rate of metals in the distribution system (depending on the pH of the water), which can lead to an increase in the concentration of metals in the water supply.

- Orthophosphate (PO_4^{3-}) – phosphorus (P) is a nutrient essential to human health and can occur in natural waters, mainly as organic phosphates and orthophosphates, as polyphosphates tend to hydrolyze and form orthophosphates. The presence in water occurs from the discharge of domestic sewage and industrial wastewater (industries of fertilizers, pesticides, canned foods, slaughterhouses, dairies, etc.), as well as the drag caused by rains in fertilized agricultural areas. Because it is a nutrient for biological processes, excess phosphorus can lead to water eutrophication[3].

- Lithium (Li^+) – in medicine, lithium salts are effective in the treatment of bipolar disorder and unipolar depression, and are used in suicide prevention[9]. As a natural element occurring in low amounts, lithium is transported from rocks and soil by rain, reaching springs, and, in some regions, concentrations can reach up to 5.2 mg L^{-1}, corresponding to a daily intake of up to 10 mg[10]. Although daily doses of this magnitude are considerably lower than those used therapeutically[11], studies have shown negative correlations between levels of lithium in drinking water and suicide mortality[10,12,13].

- Nitrate (NO_3^-) – the toxicity of nitrate in humans is mainly attributed to its reduction into nitrite by microbiological action in the gastrointestinal tract, including the mouth, where commensal bacteria on the surface of the tongue reduce approximately 20% of the nitrate present in the saliva (approximately 25% of the ingested nitrate is transported up to the saliva). The correlation between high levels of nitrate and the occurrence of methemoglobinemia (mainly in children up to three months of age) is well established, but a possible correlation between the risk of cancer development and endogenous nitrosation caused by high nitrate and/or nitrite intake and by nitrosatable compounds is still under investigation. Both surface and groundwater are accessible to the ion because of agricultural activity, disposal of wastewater without treatment, and oxidation of animal and human excreta. Nitrate concentrations can vary rapidly in surface waters, but the variations are generally slow in groundwater[4] (MAV = 10 mgN-NO_3 L^{-1}).

- Potassium (K^+) – is an essential element in humans and is widely distributed in the environment. Found in low concentrations in natural waters, it rarely reaches levels that may be considered a human health risk (adverse effects may occur in susceptible individuals). Potassium salts are widely used in the industry and in fertilizers for agriculture; industrial and agricultural land discharges can raise their concentrations in springs.

- Sodium (Na^+) – all natural waters contain sodium in different proportions (it is a necessary element of living organisms). While in surface waters the levels are usually well below 50 mg L^{-1}, concentrations above 50 mg L^{-1} are frequent in groundwater. An increase in sodium content is mainly associated with the release of domestic sewage and industrial wastewater into springs. There is no correlation confirming the association between sodium content in water and hypertension, but concentrations above 200 mg L^{-1} can result in flavor (MAV = 200 mg L^{-1}).

- Sulfate (SO_4^{2-}) – occurs naturally in many minerals and is mainly used by the chemical industry. In water, the highest concentrations are found in underground springs. The main anthropogenic sources are domestic sewage and industrial wastewater, and the use of coagulants in water treatment contributes to an increase in sulfate concentration. The existing data do not identify a concentration level from which this ion can be considered to cause adverse effects in humans, except at very high concentrations (1,000–1,200 mg L^{-1}) in which a laxative action can be observed (MAV = 250 mg L^{-1}).

- Conductivity – is the capacity of water to conduct electric current and depends on the concentrations of ions, their respective mobility and valence, and temperature. By indicating the amount of salts present in the water, it represents an indirect measure of the concentration of pollutants (generally, waters with conductivities greater than 100 S cm^{-1} are considered to be impacted)[3].

This study gathered data for one year (May 2015 to April 2016). A preliminary analysis of the physicochemical data, based on the hierarchical analysis of clusters and the principal component analysis, indicated the existence of a municipality (Ibitinga) whose samples had a unique physicochemical profile in the region[15,16]. This work presents the final analysis of the results obtained for this municipality. In addition, considering that the 15 ions involved in the study (the basic fluoride parameter and the 14 above, summarized briefly) correspond to most of the information obtained from the analyses performed, a summary of the validation of the chromatographic methods used is also presented. In this respect, we highlight that ion chromatography was introduced in this laboratory because of this study and, although standard methods exist for the determinations performed[17,18], some conditions were changed in relation to these standard methods (such as eluents, columns, and concentration ranges of the standard solutions, for example), and we had to confirm that the methods were appropriate to the intended uses[19].

METHOD

Sampling

The Municipal Health Surveillances have their own sampling plans for PROAGUA, based on the "National Guideline of Sampling Plan of the Environmental Health Surveillance Related to the Quality of Drinking Water"[20]. Therefore, we initially decided not to change these plans. However, we found that the chromatography system was not able to analyze the total number of samples delivered to the laboratory, because of the time required to perform each chromatographic analysis, especially in relation to the analysis of anions (approximately 38 minutes per sample). Thus, we decided to make a second sampling of the surveillance collections in such a way that some conditions were observed: (i) the minimum number of samples per municipality per collection was two, in order to maintain a minimum ratio of 1/10,000 between the n_m number of samples per month and the n_h number of inhabitants of the municipality ($n_m/n_h \geq 1/10{,}000$, or $n_m/n_h \geq 1.10^{-4}$); (ii) samples were selected from different locations those given by the municipal surveillances when possible (for example, in the case of two samples from the same municipality in the same collection: a sample from the central urban area and another from a peripheral neighborhood or district). Of the 90 municipal surveillances, only two of them did not send samples for analysis in this laboratory from May 2015 to April 2016. In this way, the results presented here include samples of water supply from 88 municipalities of the RRAS 13, corresponding to approximately three million inhabitants.

Methods and equipment

The 4,347 water samples analyzed were collected in clean plastic bottles (with a capacity varying between 250 and 1,000 mL) by agents of the 88 Municipal Health Surveillances who determined temperature, pH, and free residual chlorine at the time of collection. The samples, after collection, were refrigerated and immediately sent to the laboratory, where they were analyzed on the same date of collection.

All reagents used in the laboratory were of analytical grade (Sigma-Aldrich and Merck) and all aqueous solutions were prepared with type I water obtained from a Millipore purification system, Milli-Q Direct 8 model. Apparent color was determined by spectrometry using Merck equipment, Spectroquant NOVA 400 model. Turbidity was determined by nephelometric method using Micronal equipment, B250 model. Conductivity was determined using Metrohm equipment, 912 model. Cation chromatography for Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} was carried out on Metrohm equipment, 930 COMPACT IC FLEX DEG model, under the following conditions: eluent, solution of HNO_3 1.7 mmol L^{-1} containing 0.7 mmol L^{-1} dipicolinic acid; flow, 0.9 mL min^{-1}; room temperature; Metrohm column, Metrosep C4 150/4.0 model. Anion chromatography for F^-, ClO_2^-, BrO_3^-, Cl^-, Br^-, ClO_3^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} was carried out on Metrohm equipment, 930 Compact IC Flex Oven/SeS/PP/Deg model, under the following conditions: eluent, solution of Na_2CO_3 3.6 mmol L^{-1}; suppressor, solution of H_2SO_4 100 mmol L^{-1}; flow, 0.8 mL min^{-1}; temperature, 45 °C; Metrohm column, Metrosep A Supp 7 250/4.0 model. Prior to the chromatographic analysis, all samples were filtered in 0.45 μm filters.

The validation of the chromatographic methods for the ions was carried out following a guideline document of the General Coordination of Accreditation of the Brazilian Institute of Metrology, Quality, and Technology[19], the ISO[21-24] standards, and the recommendations of the *International Union of Pure and Applied Chemistry*[25]. The validation parameters investigated were: selectivity, homogeneity of variances, linearity, limit of detection (LD), limit of quantification (LQ), reliability of measurement, and accuracy. In the evaluation of these last two parameters, the Fluka certified standards (cations, lot BCBL7990V; anions, lot BCBM5733V) and the certified reference materials (CRMs) BURTAP-05 (lot 0313) of *Environment Canada* were used, and the analyses were conducted in triplicate. In assays with standard additions, each addition was also performed in triplicate.

In the data processing, we used the *software Microsoft Excel*® 2013, *Origin*® 9.1Pro, and *The Unscrambler*®X 10.3.

RESULTS AND DISCUSSION

Validation of ion chromatography

In the validation of the chromatographic methods by external calibration, we initially observed that, while the chromatogram of the cation standard solution (Figure 2A) had satisfactorily separated peaks, the bromide and chlorate peaks occurred with significant overlap in the chromatogram of the anion standard solution (Figure 2B). Selectivity was checked by chromatography of individual standard solutions, in which each ion was identified by its respective retention time recorded in the peak area produced. A preliminary exploratory analysis of 320 water samples from RRAS 13 indicated that only samples from the municipality of Ibitinga indicated the presence of bromide and absence of chlorate in their composition, which was confirmed during the 12 months of data acquisition. Thus we decided to treat the analytical curves of these two ions individually, using the addition of standard to confirm the identity of the analyte when analyzing the water samples from Ibitinga (Figure 2C). If one sample had bromide and chlorate simultaneously, multivariate calibration would have been used[26].

The concentration ranges for the ions were initially established based on reports from the Environmental Company of the State of São Paulo – *Companhia Ambiental do Estado de São Paulo* (CETESB) for surface and underground springs in the State of São Paulo[27,28]. Using preliminary curves obtained from the data of five standard solutions (simple linear regression), the 320 public water supply samples mentioned above were analyzed. Based on these results, the concentration ranges were adjusted so that the highest concentration of the analytical curve was higher than the 90th percentile value of the concentrations estimated in the analyses of the 320 samples for each of the 15 ions, and we used five standard solutions for the construction of analytical curves.

In order to define the best fit of the calibration function, we obtained analytical signals (peak areas, µS cm^{-1} min) for 10 true replicates, that is, each series of five standard solutions was prepared 10 times, and the peak areas were measured for each ion in each of the 50 solutions. The Shapiro-Wilk test ($n = 10$, $\alpha = 0.05$) indicated normal distribution for all ions for each of their five concentrations. The homogeneity test of variance applied according to ISO 8466-1[21] indicated homoscedasticity only for the lithium and potassium data. On the other hand, the linearity test, applied according to the same standard for analytical curves constructed with the averages ($n = 10$) of the peak areas of each concentration, indicated that a non-linear function should be used in the calibration in the case of fluoride, chlorite, bromate, chlorate, and phosphate (in these cases, second-order polynomials were used for adjustment).

The LD was calculated from the estimate of its respective analytical signal (y_{LD}) expressed by Equation 1:

$$y_{LD} = intercept + 3.s_{SP1} \qquad \text{(Equation 1)}$$

where: *intercept* = intercept of the calibration function obtained by the regression of the averages of the peak areas ($n = 10$) of five standard solutions; s_{SP1} = standard deviation of the analytical signals of the standard solution of lower concentration.

The signal y_{LD} was converted into concentration from the adjusted calibration function for each particular ion, obtaining the respective LD.

The LQ was calculated similarly, using Equation 2 to estimate its analytical signal (y_{LQ}):

$$y_{LQ} = intercept + 6.s_{SP1} \qquad \text{(Equation 2)}$$

For the cations Li^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}, reliability of measurement and accuracy were evaluated using the certified standard: we obtained percentage relative errors ranging from -1.1% (magnesium) to +0.3% (sodium) and relative standard deviations between 0.4% (Li^+) and 1.9% (Na^+). In the case of NH_4^+, we added the standard to the CRMs (BURTAP-05) at three concentration levels (0.10, 0.50, and 0.80 mg L^{-1}), obtaining recoveries of 101.3%, 100.8%, and 100.3%, respectively, with relative standard deviations of 2.3%, 0.4%, and 0.7%, respectively. In addition, the analysis of this CRM also showed that the percentage relative errors for the ions Na^+, K^+, Ca^{2+}, and Mg^{2+}, declared in the certificate, varied between -1.3% (K^+) and +0.4% (Na^+), with relative standard deviations between 0.6% (Mg^{2+}) and 2.0% (Na^+).

In the certified standard analysis of the anions fluoride, chloride, bromide, nitrate, phosphate, and sulfate, we obtained the percentage relative errors between -0.5% (chloride) and +0.3% (sulfate), and relative standard deviations between 0.5% (nitrate) and 1.5% (chloride). In the case of chlorite, bromate, and chlorate, the addition of the standard at three concentration levels to water samples without these analytes resulted in recoveries ranging from 95% (chlorate at 0.020 mg L^{-1}) to 102% (chlorite at 0.010 mg L^{-1}), with relative standard deviations between 0.8% (chlorate at 0.20 mg L^{-1}) and 14% (chlorate at 0.020 mg L^{-1}). The analysis of the CRMs (BURTAP-05) indicated relative percentage errors of +4.7%, -0.6%, and -1.1% for fluoride, chloride, and sulfate, respectively, with relative standard deviations of 0.4%, 3.0%, and 0.4%, respectively.

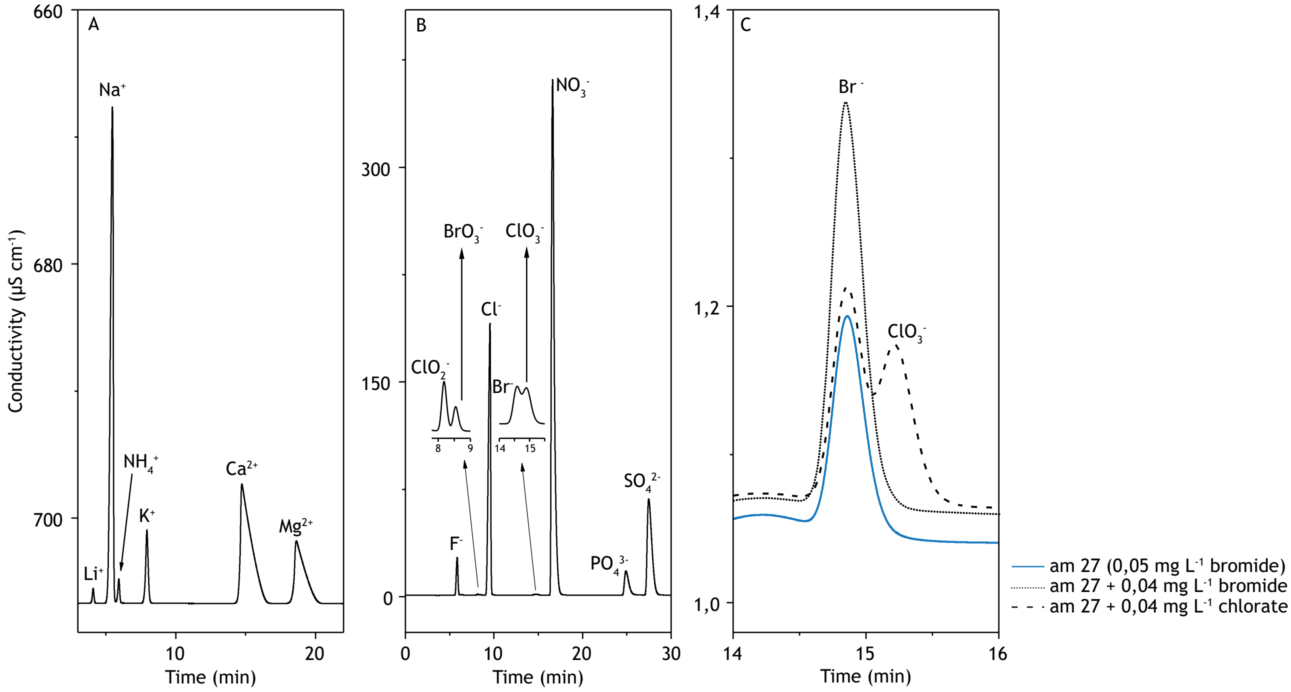

Figure 2. A) Chromatogram of the cation standard solution. B) Chromatogram of the anion standard solution. C) Fractions of chromatograms of sample 27 from Ibitinga (0.05 mg L^{-1} of bromide) without and with adding the standards (0.04 mg L^{-1} of bromide and 0.04 mg L^{-1} of chlorate).

Reliability of measurement and accuracy were considered satisfactory in both cases (cations and anions).

Table 1 summarizes the data related to the analytical curves and the values of LD and LQ. It should be noted that the weighting in heteroscedastic cases was performed by the inverse of the squared concentration ($1/x^2$). The quality of the adjustment was considered satisfactory (adjusted coefficient of determination, $R^2_{adj} \geq 0.9997$).

Sampling data

Of the 7,587 samples received, 4,347 (57%) were analyzed for 21 physicochemical parameters. The monthly ratio of $n_m/n_h \geq 1.10^{-4}$ could not be reached for only three municipalities: Ribeirão Preto (144 samples analyzed, $n_m/n_h = 2.10^{-5}$), Araraquara (148 samples analyzed, $n_m/n_h = 5.9.10^{-5}$), and São Carlos (165 samples analyzed, $n_m/n_h = 6.2.10^{-5}$). These three municipalities have the largest population in the region and the ratio was not reached because of the insufficient number of samples sent to the laboratory. Ribeirão Preto sent 234 samples (which would produce a ratio of $n_m/n_h = 3.2.10^{-5}$ if all the samples were analyzed, still below the objective); moreover, contributing to an additional decrease in the n_m/n_h ratio of Ribeirão Preto, a significant portion of the samples submitted were samples of alternative solutions (outside the scope of the study). Araraquara and São Carlos sent 168 and 172 samples, respectively, which would lead to n_m/n_h ratios equal to $6.7.10^{-5}$ and $6.5.10^{-5}$, respectively if they were all analyzed (still below the objective). However, it should be noted that the total numbers of samples analyzed for each of these municipalities are among the five highest achieved in this study, together with Sertãozinho (156 samples analyzed, $n_m/n_h = 1.2.10^{-4}$) and Barretos (145 samples analyzed, $n_m/n_h = 1.1.10^{-4}$). In particular, 79 water samples from Ibitinga were analyzed, and we obtained $n_m/n_h = 1.2.10^{-4}$.

Principal component analysis (RRAS 13)

As part of the data preprocessing, initially the number of samples was reduced representing each municipality as the respective series of medians in the 21 variables measured for the water samples analyzed in the period (one year). Thus, the initial 4,347 x 21 data matrix was transformed into an 88 x 21 matrix (88 municipalities x 21 medians in each variable). To carry out the multivariate analysis, the variables ammonium, chlorite, and bromate were initially excluded, since the respective medians of all municipalities showed a zero value, which means, in analytical terms, a value that is lower than the LD. The variable bromide was also excluded, since only Ibitinga showed a median other than zero (and equal to 0.028 mg L^{-1}). The analysis of the correlation matrix among the remaining 17 variables indicated that 12 variables had the most significant correlations: lithium, sodium, potassium, calcium, magnesium, chloride, chlorate, nitrate, phosphate, sulfate, pH, and conductivity.

The data of the 88 x 12 matrix were centered by the median and scaled by the interquartile range, and were then submitted to a principal component analysis, calculating the score and loading matrices using the NIPALS (*Non-linear Iterative Partial Least-Squares*) algorithm with four principal components. The PC1/PC2 score plot obtained (Figure 3A) showed Ibitinga as a unique sample in relation to three other groups; the analysis of the respective loading plot (Figure 3B) revealed that the unique nature of the composition of the water supply of Ibitinga is due to higher relative concentrations of sulfate, chloride, lithium, and sodium and higher values of pH and conductivity, in addition to "bromide presence" (bromide was not included in this model). In fact, the comparison between the medians of the 12 variables of Ibitinga with the respective medians of RRAS 13 (excluding the data from that municipality), indicates that the greatest positive differences are actually those observed in

Table 1. Data of the analytical curves used in the cation and anion chromatography and respective limits of detection and quantification.

Analyte	Concentrations of standard solutions (mg L^{-1})					Model	Adjustment	R^2_{aj}	LD	LQ
	SP 1	SP 2	SP 3	SP 4	SP 5					
Ammonium[1]	0.05	0.25	0.5	0.75	1	$y = a + bx$	WLS[4]	0.9997	0.008	0.016
Bromate	0.008	0.04	0.08	0.12	0.16	$y = a + bx + cx^2$	WLS	0.99999	0.002	0.004
Bromide	0.01	0.05	0.1	0.15	0.2	$y = a + bx$	WLS	0.99994	0.002	0.004
Calcium	2	10	20	30	40	$y = a + bx$	WLS	0.99999	0.09	0.18
Chlorate	0.01	0.05	0.1	0.15	0.2	$y = a + bx + cx^2$	WLS	0.99998	0.002	0.004
Chloride	1	5	10	15	20	$y = a + bx$	WLS	0.99998	0.08	0.16
Chlorite	0.01	0.05	0.1	0.15	0.2	$y = a + bx + cx^2$	WLS	0.99995	0.005	0.01
Fluoride	0.07	0.35	0.7	1.05	1.4	$y = a + bx + cx^2$	WLS	0.99997	0.008	0.016
Phosphate[2]	0.2	1	2	3	4	$y = a + bx + cx^2$	WLS	0.9997	0.05	0.1
Lithium	0.01	0.05	0.1	0.15	0.2	$y = a + bx$	OLS[5]	0.99997	0.002	0.005
Magnesium	0.5	2.5	5	7.5	10	$y = a + bx$	WLS	0.99998	0.06	0.12
Nitrate[3]	1	5	10	15	20	$y = a + bx$	WLS	0.99997	0.05	0.09
Potassium	0.5	2.5	5	7.5	10	$y = a + bx$	OLS	0.99999	0.1	0.2
Sodium	2	10	20	30	40	$y = a + bx$	WLS	0.99999	0.06	0.12
Sulfate	1	5	10	15	20	$y = a + bx$	WLS	0.99999	0.12	0.23

[1] Expressed as N-NH3; [2] Expressed as P-PO4; [3] Expressed as N-NO3; [4] Weighted least squares (1/x2, x = concentration); [5] Ordinary least squares.
LD: limits of detection; LQ: limits of quantification

these six variables (Table 2). The hierarchical clustering analysis (Ward's method) showed the formation of the same four groups (considering Ibitinga as a group consisting of only one sample).

Principal component analysis (Ibitinga)

In order to make a preliminary mapping of the water quality of Ibitinga, a principal component analysis was carried out on the 79 samples analysed in this municipality, using the same variables previously used under the same conditions, but replacing chlorate with bromide (79 x 12 matrix). The score plot obtained (Figure 3C) showed that one sample ($^{\#}$ 72) differed from the others mainly because of higher concentrations of chloride and sulphate (Figure 3D), while four samples were distributed in the negative side of PC1 ($^{\#}$ 1, 28, 34, and 35) in which the concentrations of nitrate, calcium, and magnesium were prominent (Figure 3D). In fact, these samples had nitrate levels equal to 5.1, 4.6, 5.1, and 2.0 mg L^{-1}, respectively, and it should be noted that: (i) samples 1 and 34 were collected at the same address, but with an interval of four months – the proximity of their positions in the score chart indicates that the profile of the 12 variables of both samples remained similar, despite the time interval, (ii) no bromide was detected in any of these four samples, and (iii) sampling sites 1, 34, and 28 are located in the same neighborhood, while sample site 35 is in a neighborhood close to the other three samples. Hierarchical clustering analysis (Ward's method) indicated the formation of the same three groups, with sample 72 being a group with only one sample.

Ibitinga is supplied by underground and shallow springs. Information obtained from the website of the Autonomous Water and Sewage Service of the municipality (http://www.saaeibitinga.sp.gov.br) indicates that most of the water collection is from underground springs (approximately 90%), and the supply of the central urban area is complemented with treated water from the Água Quente stream. The data suggest that nitrate-contaminated samples originate from a well (underground source), not only because of the presence of nitrate but also taking into account the high correlations of this ion with those of calcium (r = 0.92) and magnesium (r = 0.97) from the composition of the soil of the region, as already observed in previous studies carried out in the municipality of Monte Azul Paulista[15]. The absence of bromide in these samples reinforces the hypothesis that they are samples from a source with characteristics different from the other sources used by the municipality for the supply. On the other hand, the sample with a high content of chloride and sulphate must also originate from a source with different characteristics from most: in fact, the collection point of this sample is located in an area far from the central urban area. We highlight that this sample presented with the maximum value of conductivity (710 μS cm^{-1}) in the municipality.

Unfortunately, we could not compare the results obtained for Ibitinga with data from recent reports by CETESB[3,7], since there is no groundwater monitoring point in the municipality and the closest surface water monitoring point analyzes water from the Jacaré-Guaçu river (point with code JCGU03900, away from the urban area[3]).

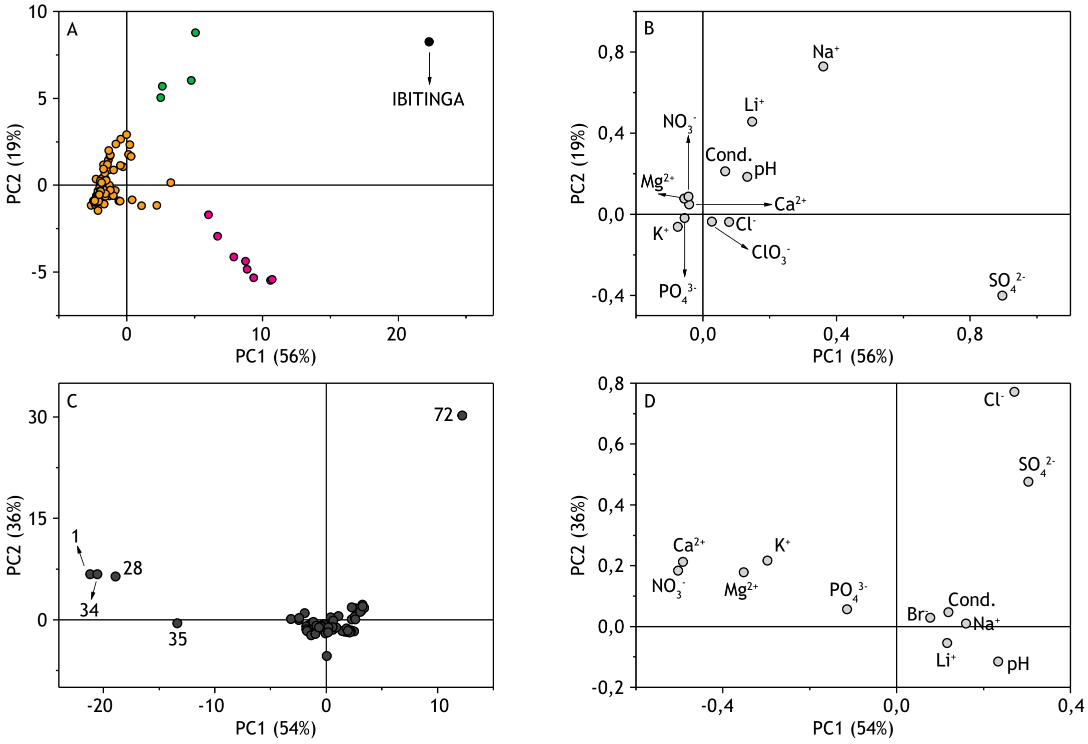

Figure 3. A) Score plot of principal component analysis of 88 samples and medians of 12 variables from each municipality. B) Loading plot related to A. C) Score plot of principal component analysis of the 79 samples from Ibitinga (12 variables, replacing chlorate with bromide). D) Loading plot related to C.

Table 2. Medians of the physico-chemical variables: comparison between samples from Ibitinga and RRAS 13 (87 municipalities).

Variable	Medians[1]	
	Ibitinga	RRAS 13[2]
Lithium (mg L^{-1})	0.016	0
Sodium (mg L^{-1})	104.4	5.6
Potassium (mg L^{-1})	0.66	2.75
Calcium (mg L^{-1})	1.7	9.1
Magnesium (mg L^{-1})	0.37	1.84
Chloride (mg L^{-1})	7.79	1.97
Chlorate (mg L^{-1})	0	0.087
Nitrate (mg L^{-1})	0.2	0.22
Phosphate (mg L^{-1})	0.06	0.071
Sulfate (mg L^{-1})	16.6	0.34
pH	9.7	7.2
Conductivity (μS cm^{-1})	440.2	121.5

[1] Zero indicates value lower than limits of detection; [2] Excluded the data from Ibitinga.

Finally, we must also consider as relevant the presence of lithium in the supply waters of Ibitinga, whose levels ranged from 0.003 to 0.028 mg L^{-1} (in fact, this variable was also important in the definition of another group of four municipalities, as shown in Figure 3A). As stated in the introduction, research studies have been reporting a negative correlation between lithium levels in drinking water and suicide mortality. In these studies, lithium concentration ranges are similar to those found in Ibitinga – for example, in a study involving 18 municipalities in Japan, whose ion concentrations in drinking water ranged from 0.0007 to 0.059 mg L^{-1}, Ohgami et al.[12] suggested that lithium, even at low concentrations, may contribute to reduce suicide mortality rates.

CONCLUSIONS

Although the results do not indicate a level of attention for the analyzed parameters, except for the samples with nitrate levels between 4.6 and 5.1 mg L^{-1} (5 mg L^{-1} is considered by CETESB as a prevention value, in the sense of defining preventive actions and rules for the application of residues in agricultural soils, environmental licensing and inspection processes[7]), the fact that the waters of Ibitinga are the only ones in the region to systematically present bromine, associated with the characteristics of high conductivity, high pH, and high relative concentrations of lithium, sodium, chloride, and sulfate (which represent a unique profile in the region), points to issues that should be addressed in the future to verify if the composition of this water includes analytes not researched in this study, such as heavy metals, for example. We also emphasize that if the presence of bromide is not significant from the point of view of the regulatory or public health (a MAV was not established by Ordinance No· 2,914, of December 12, 2011[8]), its role as a bromate precursor in the disinfection of water in the ozonation process[29] requires attention, as bromate is considered a mutagen and a probable carcinogen[6], with a MAV equal to 0.010 mg L^{-1} in drinking water[8]. As stated earlier, according to the World Health Organization, the main source of bromate in drinking water is actually its formation from bromide during the ozonation process, but the amount formed depends on factors other than the concentration of bromide, such as the level of ozone, pH, and dissolved organic carbon. For example, Gonçalves et al.[29] report that bromide concentrations as low as 0.05 mg L^{-1} are sufficient to produce bromate, but there are no considerations about the conditions under which the reaction is conducted. Thus, a possible use of the ozonation in the supply water of Ibitinga should be carefully evaluated.

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Conflict of interest

The authors report that there is no potential conflict of interest with peers and institutions, political or financial, in this study.