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Mapping of public water supply in the northeast of the state of São Paulo (Brazil)

Mapeamento da qualidade da água de abastecimento público no nordeste do estado de São Paulo (Brasil)

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ABSTRACT

This paper presents data obtained on microbiological and physico-chemical analysis of 4347 public water supply samples from 88 municipalities in the Northeast region of the state of São Paulo, carried out within a year. In microbiological analysis, 288 samples showed positive results for indicator microorganisms, occurring an increase of 80% in the rainy season compared with the dry period. Physico-chemical analysis: in 1514 samples, lithium concentration was equal to or higher than the detection limit of the method; the nitrate concentration was greater than the maximum value allowed in 17 samples; 1730 samples showed fluoride content out-of-range of drinking pattern; bromate concentration was greater than the maximum value allowed in 16 samples; the pH value was outside the range recommended in 161 samples; 292 samples showed levels of free residual chlorine (FRC) outside the recommended range; 17 samples showed apparent color values above the maximum allowed; 13 samples showed turbidity values above the maximum allowed. By means of principal components analysis, it was possible to discriminate the waters of the region, with the formation of groups of municipalities with similar physico-chemical profiles, generating a mapping based on prominent variables.

KEYWORDS: Water Quality; Mapping; Principal Component Analysis; Sanitary Surveillance

RESUMO

Esse trabalho apresenta dados obtidos em análises microbiológicas e físico-químicas de 4.347 amostras de águas de abastecimento público de 88 municípios da região nordeste do Estado de São Paulo, realizadas no período de um ano. Nos ensaios microbiológicos, 288 amostras apresentaram resultado positivo para microrganismos indicadores, ocorrendo um acréscimo de 80% no período de chuvas em comparação com o período de seca. Nos ensaios físico-químicos: em 1.514 amostras, a concentração de lítio foi igual ou superior ao limite de detecção do método; a concentração de nitrato foi superior ao valor máximo permitido em 17 amostras; 1.730 amostras apresentaram teor de fluoreto fora da faixa do padrão de potabilidade; a concentração de bromato foi superior ao valor máximo permitido em 16 amostras; o valor de pH situou-se fora do intervalo recomendado em 161 amostras; 292 amostras apresentaram teores de cloro residual livre fora da faixa recomendada; 17 amostras apresentaram valores de cor aparente acima do máximo permitido; 13 amostras apresentaram valores de turbidez acima do máximo permitido. Através da análise de componentes principais foi possível discriminar as águas de abastecimento da região, com a formação de grupos de municípios com águas de perfis físico-químicos similares, gerando um mapeamento baseado em variáveis proeminentes.

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

INTRODUCTION

Water is essential to life, but its quality has been impaired by anthropic action on water sources (contamination by waste, domestic and industrial effluents), and by the inadequate production and distribution of drinking water (shortcomings in disinfection and fluoridation, intermittent supply etc.)[1].

According to the World Health Organization (WHO), access to safe drinking water is a basic human right and a component of an effective health protection policy[2]. With that in mind, the National Program for Monitoring Water Quality for Human Consumption (Vigiagua)[3], coordinated by the Health Surveillance Department of the Ministry of Health, carries out surveillance actions to guarantee the population's access to water in sufficient quantity and quality in accordance with the potability standard established by the current legislation[4]. An instrument of the Vigiagua is the Information System for Monitoring the Quality of Water for Human Consumption (Sisagua), created in 2001 to assist in the management of health risks due to water quality. It stores information on alternative supply systems and solutions, as well as data on water quality from surveillance services and utilities[5].

In the State of São Paulo, the Water Surveillance Program for Human Consumption (Proagua) was implemented in 1992. It is coordinated by the Sanitary Surveillance Center of the Coordination of Disease Control of the State Department of Health[6]. Its objectives are aligned with those of Vigiagua, and several actions are planned: collaboration in the management of water resources and in the analysis and interpretation of information on their quality; registration and inspection of systems and alternative solutions for supplying; evaluation of reports; water quality monitoring in the parameters of free residual chlorine (FRC), pH, apparent color, turbidity, fluoride concentration, total coliforms and *Escherichia coli*; analysis of the population epidemiological profile; search for relationships between occurrence of diseases and quality of the water consumed[7].

The present study refers to the public water supply quality of 88 municipalities covered by Proagua, located in the northeast of the state and divided into four Sanitary Surveillance Groups (SSG): Araraquara, Barretos, Franca and Ribeirão Preto. These, in turn, make up the State's Regional Health Care Network n. 13 (RRAS 13). About 3.3 million people live in this region (data from the 2010 census of the Brazilian Institute of Geography and Statistics). For water supply, roughly 70% of the municipalities (corresponding to 62.8% of the population of the region) use groundwater; another 15% of the municipalities (18.6% of the population) use surface water. The remaining municipalities (18.6% of the population) use both sources.

With regard to groundwater, the northeastern region of São Paulo can use water mainly from three aquifers: Bauru, Guarani and Serra Geral[8]. In a report recently published by Companhia Ambiental do Estado de São Paulo (Cetesb)[9], the quality of the groundwater in the state was generally classified as good considering the Groundwater Potability Indicator (IPAS). However, according to the same report, the Serra Geral aquifer continues to show an increase in nitrate concentration while in the Bauru Aquifer the percentage of wells monitored with nitrate concentrations exceeding the maximum permitted value (MPV) by the current legislation (equal to 10.0 mgN-NO_3/L)[4] has remained similar since the 2007-2009 triennium. At the same time, there is a trend to reduce the number of wells with nitrate concentration above 5.0 mgN-NO_3/L (considered as a prevention value by Cetesb). The Guarani aquifer, predominantly of the confined type, occasionally presented some substances that exceeded the organoleptic standards (aluminum, iron and manganese) and the human health risk standards (barium, selenium and vanadium). Furthermore, the nitrate ion was also occasionally quantified above the prevention value, but below the maximum permitted value.

With regard to surface water, the northeast of the state can use water from Grande, Sapucaí, Pardo and Mogi-Guaçu rivers, but the region hydrography is complex with several smaller rivers, streams and creeks. Another recent report by Cetesb[10] shows that information on surface water in the region is influenced by the limited number of sampling points: of the 501 points of Cetesb in the state only 43 are distributed in 30 municipalities of the Regional Health Care Network - RRAS 13, and only one point coincides with catchment for public supply (Córrego Rico, in Jaboticabal). However, it is worth highlighting that in terms of Water Resource Management Units (UGRHI), it was verified that the Water Quality Index (WQI) was classified as poor in 25% of the monitoring points of the UGRHI 12 - Baixo Pardo/Grande, where municipalities like Bebedouro and Colômbia are located, in 17% of the UGRHI 4 - Pardo monitoring points (for example, Santa Rosa de Viterbo and Cássia dos Coqueiros), and 11% in the UGRHI 9 – Mogi-Guaçu (for example, Porto Ferreira and Santa Rita do Passa Quatro). These results contrast to the index obtained in the UGRHI 8 - Sapucaí Grande (Franca and Batatais, for example), in which none of the points presented poor quality, while 7% and 86% were classified as excellent or good quality, respectively.

The RRAS13 springs, both groundwater and superficial, are currently undergoing a process of increasing anthropic pressure not only because of urbanization but also because of increasing industrialization: Cetesb, for example, classifies the aforementioned region as a "region under industrialization"[9]. In view of this process and in order to obtain a more detailed characterization of the water quality for human consumption in the region and contribute to the surveillance of situations involving health risk factors that require preventive or corrective actions, in 2014 we began a study in our laboratory that provided for the analysis of samples of public water supply for a year. For Proagua samples the number of investigated parameters rose from eight to 23: in addition to those previously mentioned, conductivity measurements and the concentrations of 14 ions were included (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, ClO_2^-, BrO_3^-, Cl^-, Br^-, ClO_3^-, NO_3^-, PO_4^{3-} e SO_4^{2-}). The data acquisition started in May 2015 and ended in April 2016, totaling the analysis of 4,347 samples of public water supply. This work presents a description of the data obtained in the period.

METHOD

Sampling plan

The "National guideline sampling plan of environmental health surveillance related to the water quality intended for human consumption"[11,12] establishes sampling plans that must be followed by the Municipal Sanitary Surveillance (VISA-M), responsible for collecting samples, preliminary temperature, FRC and pH measurements, and for sending the samples to the laboratory for further analysis. However, we found initially that it would not be possible to analyze the total samples delivered by the VISA-Ms, due to the time required to process each sample mainly for anion analysis by chromatography (approximately 38 minutes per sample). We therefore decided to carry out a second sampling on the VISA-M collections observing some conditions:

- The minimum number of samples per municipality and per collection was 2, with a minimum ratio of 1/10,000 being sought between the number n_m of samples per month and the number of inhabitants n_h of the municipality ($n_m/n_h \geq$ 1/10,000, or $n_m/n_h \geq 1.10^{-4}$);

- Samples were selected from locations with the greatest distance between themselves whenever 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).

It should be noted that the municipalities of Franca and Motuca are not included in this study since Franca carries out the analyses in its own laboratory, and Motuca did not send samples in the period of this study - the reasons for this fact are not known to us. Thus, the work presented here includes water samples from 88 municipalities of RRAS 13, corresponding to the supply of approximately 3 million inhabitants.

Methods and equipment

The collection, packaging and transportation of drinking water samples followed the guidelines of the Ministry of Health[13].

For the microbiological analysis, 100 mL of the water samples were collected in plastic bottles or in *Thio Bags* by VISA-M agents. Both containers (bottles and bags) were sterile and disposable, with the capacity of 120 mL. They contained sodium thiosulfate for neutralization of residual chlorine. Determination of the presence or absence of total coliforms and *Escherichia coli* was carried out by the chromogenic and fluorogenic method (Colilert Test Kit, *Idexx Laboratories*/USA).

For the physico-chemical analysis, public water supply samples were collected in clean plastic bottles (capacity between 250 and 1,000 mL) by VISA-M agents who measured temperature, pH and FRC at the time of collection.

All reagents used in the laboratory (Sigma-Aldrich and Merck) were of analytical grade. All aqueous solutions were prepared with Type I water obtained from a Millipore Milli-Q Direct 8 purification system. Apparent color was determined by spectrometry using Merck Spectroquant Nova 400 spectrophotometer. Turbidity was determined using Micronal B250 turbidimeter. Conductivity was determined on Metrohm 912 conductometer. Cations chromatography was performed on Metrohm 930 Compact IC Flex Deg ion chromatograph under the following conditions: eluent, HNO_3 1.7 mmol/L solution containing 0.7 mmol/L dipicolinic acid; flow rate, 0.9 mL/min; room temperature; Metrohm Metrosep C4 150/4.0 column. Anions chromatography was carried out on Metrohm 930 Compact IC Flex Oven/SeS/PP/Deg ion chromatograph under the following conditions: eluent, solution of Na_2CO_3 3.6 mmol/L; suppressor, solution of H_2SO_4 100 mmol/L; flow rate, 0.8 mL/min; temperature, 45°C; Metrohm Metrosep A Supp 7 250/4.0 column. Prior to the chromatographic analysis, all samples were filtered on 0.45 µm filters.

In the data processing, we used *Microsoft Excel®* 2013, *Origin®* 9.1Pro and *The Unscrambler®*X 10.3. As part of the pre-treatment of the data for the multivariate analysis, initially the number of samples representing each municipality was reduced by the respective series of medians in the 21 physico-chemical 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).

RESULTS AND DISCUSSION

Sampling

From May/2015 to April/2016, VISA-M sent 7,587 public water supply samples, of which 4,347 (57%) were investigated for 21 physico-chemical parameters and two microbiological parameters (total coliforms and *Escherichia coli*): 2,167 samples were analyzed between May and October/2015, and 2,180 samples were analyzed between November/2015 and April/2016. The $n_m/n_h \geq 1.10^{-4}$ ratio could not be reached for three municipalities: Ribeirão Preto (144 analyzed samples, $n_m/n_h = 2.10^{-5}$), Araraquara (148 analyzed samples, $n_m/n_h = 5.9.10^{-5}$) and São Carlos (165 analyzed samples, $n_m/n_h = 6.2.10^{-5}$). The insufficient number of samples sent to this laboratory was the determining factor for not reaching the target for the three municipalities with the highest population among those included in this study: Ribeirão Preto sent 234 samples (which would produce a ratio of $n_m/n_h = 3.2.10^{-5}$ if all the samples had been analyzed, still lower than the objective). Moreover, contributing to an additional decrease in the n_m/n_h ratio of that municipality, a significant part of the samples came from alternative solutions (outside the scope of the study) and, therefore, they were not analyzed. Araraquara and São Carlos sent 168 and 172 samples, respectively, which, if they had all been analyzed, would lead to ratios of n_m/n_h equal to $6.7.10^{-5}$ and $6.5.10^{-5}$, respectively. However, it should be emphasized that the total numbers of samples analyzed for each of these municipalities are among the five highest achieved in this study, together with those of Sertãozinho (156 analyzed samples, $n_m/n_h = 1.2.10^{-4}$) and Barretos (145 analyzed samples, $n_m/n_h = 1.1.10^{-4}$). Trabiju was the municipality for which the highest ratio ($n_m/n_h = 1.7.10^{-3}$) was obtained, with 31 samples analyzed.

General analysis: microbiology

Of the 4,347 samples analyzed, 288 (6.6%) presented indicator microorganisms (256 contained total coliforms and 32 contained *E. coli* and total coliforms). In the comparison between the results from the first half of the study (May to October 2015, considered here as the dry season) and the results from the second half (November 2015 to April 2016, the rainy season), we observed that the number of cases increased from 103 (13 *E. coli*) to 185 (19 *E. coli*), which corresponds to an increase of 80% (if we consider only *E. coli*, this increase is 46%). This seasonal variation in fecal contamination of water for human consumption (increase in the number of occurrences due to the rainy season) is already described in the literature[14] and attributed to a greater amount of fecal contaminants (of human or animal origin) transported by rainfall from soil saturated with these microorganisms, after a period of drought, towards the water catchment areas for the public supply[15].

Of the 288 samples with indicator microorganisms, 126 (44%) were collected at the SSG of Araraquara which includes 24 municipalities. Of those 126 samples in the SSG of Araraquara, 15 (12%) were collected in the same municipality (Santa Lúcia, 26 samples analyzed, $n_m/n_h = 2{,}6.10^{-4}$). Of these 15 samples from Santa Lúcia, ten contained *E. coli*. These ten samples account for 31% of the total *E. coli* cases in RRAS 13. The difference between the halves for Santa Lúcia was lower: there were seven cases (four *E. coli*) in the first half and eight positives (six *E. coli*) in the second which suggests difficulties in the water disinfection process either during the dry season or during the rainy season.

The physico-chemical parameters will be discussed in the next item but it is worth mentioning those that may be related to this difficulty in improving the microbiological quality of the water in Santa Lúcia: (i) the median FRC values of the water of this municipality in the 12 months of data acquisition is equal to the minimum acceptable value established by current legislation (equal to 0.2 mg/l)[4] and lower than the median for RRAS 13 (equal to 0.7 mg/l). There is no difference between the values of the medians of the first and second halves; (ii) the median values of apparent color and turbidity of the water of that municipality in the same period (equal to 3.5 uH and 0.6 uT, respectively) are higher than the medians determined for RRAS 13 (less than 2 uH and lower 0.5 uT, respectively). The values between the halves presented only a small variation (apparent color ranged from 4 to 3 uT and turbidity, from 0.5 to 0.7 uT).

General analysis: physical and chemical (relevant occurrences)

Table 1 shows a summary of the data obtained in the 12 months for the 21 physico-chemical variables investigated in 4,347 samples.

In 1,514 samples (34.8% of the total) the lithium concentration was equal to or greater than the detection limit of the method (0.002 mg/L). Lithium salts have been used in the treatment of bipolar disorder, unipolar depression and suicide prevention[16], and some studies report a negative correlation between lithium concentrations in water for human consumption (similar to those found in this study for RRAS 13) and suicide-related deaths[17,18,19]. Epidemiological studies may be conducted to investigate the possible existence of this negative correlation. The mapping (next item) indicates more details about the presence of lithium.

Table 1. Description of the physico-chemical data obtained in the analysis of 4,347 public water supply samples from RRAS 13 during 12 consecutive months.

Parameter	Minimum	1st Quartile	Median	3rd Quartile	Maximum
Lithium (mg/L)	< 0.002	< 0.002	< 0.002	0.002	0.028
Sodium (mg/L)	< 0.06	2.7	5.3	10.9	152.4
Ammonium (NH_3, mg/L)	< 0.008	< 0.008	< 0.008	< 0.008	0.119
Potassium (mg/L)	< 0.1	1.6	2.8	3.8	9.8
Calcium (mg/L)	< 0.09	4.1	8.6	18.5	62.8
Magnesium (mg/L)	< 0.06	1.1	1.8	3.1	12.6
Fluoride (mg/L)	< 0.008	0.52	0.66	0.74	8.3
Chlorite (mg/L)	< 0.005	< 0.005	< 0.005	< 0.005	0.126
Bromate (mg/L)	< 0.002	< 0.002	< 0.002	< 0.002	0.03
Chloride (mg/L)	< 0.08	0.97	2	4.8	39.9
Bromide (mg/L)	< 0.002	< 0.002	< 0.002	< 0.002	0.087
Chlorate (mg/L)	< 0.002	< 0.002	0.085	0.147	3.34
Nitrate ($N\text{-}NO_3$, mg/L)	< 0.05	< 0.05	0.23	1.07	20
Phosphate ($P\text{-}PO_4$, mg/L)	< 0.05	< 0.05	0.066	0.12	2.9
Sulfate (mg/L)	< 0.12	0.17	0.36	1.31	122.2
Temperature (°C)	11.9	24	26	28	38.4
CRL (mg/L)	0*	0.5	0.7	1	10
pH	0.6	6.8	7.2	7.8	10.6
Apparent color (Hz)	< 2	< 2	< 2	2	107
Turbidity (uT)	< 0.5	< 0.5	< 0.5	< 0.5	96
Conductivity (µS/cm)	7.1	68.9	123.1	179.8	710

*Undetermined detection limit.

The concentration of nitrate was higher than the maximum permitted value (10mgN-NO_3/L)[4] in 17 samples (0.4% of total) from the municipalities of Guaraci (one sample with concentration > MPV, 28 samples analyzed, n_m/n_h=2,3.10^{-4}), Monte Azul Paulista (two samples with concentrations > MPV, 76 samples analyzed, n_m/n_h = 3,4.10^{-4}) and Severínia (14 samples with > concentrations > MPV, 60 samples analyzed, n_m/n_h = 3,2.10^{-4}). While groundwater contamination in Monte Azul Paulista is already known, the high number of samples contaminated with nitrate in Severínia (which also makes exclusive use of groundwater) caused this laboratory to contact the SSG of Barretos to inform the situation. Similar to the approach used in the case of Monte Azul Paulista[20], technical meetings were held in Severínia involving staff of this laboratory, VISA-M, SSG Barretos, the City Hall, the Autonomous Water and Sewage Service of Severínia (SAAE), Cetesb and the Department of Water and Electricity of the State of São Paulo (DAEE), in order to investigate the contamination for preventive or corrective actions. The contamination in the case of Guaraci appears to be localized, since the municipality makes use of a surface spring and a principal component analysis indicated that the concentration of magnesium is also an important variable for discrimination of this sample. This is similar to what we observed in contaminated samples from Monte Azul Paulista[21]. Also with regard to nitrate, 122 samples (2.8% of the total) showed concentrations between 5 and 10 mgN-NO_3/L. The value of 5mgN-NO_3/L is considered by Cetesb as a prevention value (PV) to determine preventive actions and rules for the application of residues in agricultural soil, environmental licensing and inspection processes while the value of 10 mgN-NO_3/L is considered the guiding value of intervention for the management of contaminated areas[9]. The 122 samples were collected in 20 municipalities and we can highlight Altair (22 samples with concentration > PV, 33 samples analyzed, n_m/n_h = 7,2.10^{-4}), Severínia (19 samples with concentration > PV), Dobrada (13 samples with concentration > PV, 28 samples analyzed, n_m/n_h = 2,9.10^{-4}), Taiaçu (nine samples with concentration > PV, 33 samples analyzed, n_m/n_h = 4,7.10^{-4}) and Monte Azul Paulista (nine samples with concentration > PV).

Ibitinga (79 samples analyzed, n_m/n_h = 1,2.10^{-4}) was the only municipality that systematically presented bromide in the water samples. We also verified through principal component analysis (see next item) that Ibitinga is the municipality whose water supply differs from the rest of the region because it presents higher levels of sulfate, chloride, lithium and sodium, in addition to higher values of pH and conductivity [22]. The situation was described in detail in a recently published article[23].

As for the fluoridation quality it might be observed that: (i) 2,617 samples (60.2%) had fluoride content within the range of 0.6 to 0.8 mg/L, i.e. according to the drinking pattern established by Resolution SS-250[24]; (ii) 1,313 samples (30.2%) presented fluoride content of less than 0.6 mg/L; (iii) 417 samples (9.6%) presented fluoride content higher than 0.8 mg/L. In addition to this classification between "adequate" (within the drinking pattern) and "inadequate" (outside the drinking pattern), the Collaborating Center in Oral Health Surveillance of the Ministry of Health suggested another more detailed approach to public water supply according to fluoride content, which considers both the benefit of cavity prevention and the risk of producing dental fluorosis. This classification applied to RRAS 13 samples is shown in Table 2. In this table one can see that the best benefit-risk combination is in the range of 0.55 to 0.84 mg/L in which we could classify 2,760 samples (63.5% of the total).

Bromate is considered by the WHO as mutagenic and potentially carcinogenic[2]. The current Brazilian legislation establishes an MPV equal to 0.010 mg/L in water for public supply[4]. This ion was quantified in 42 samples (1% of the total), and in 16 samples (0.36%) the concentration was higher than the MPV. In this case, Ribeirão Preto (144 analyzed samples, n_m/n_h = 2.10^{-5}) should be highlighted: bromate was present in 19 water samples from that municipality (seven samples with levels above the MPV). These results, especially those obtained in Ribeirão Preto, must be confirmed in further investigations in view of the impact in health related to the presence of bromate in the water.

As for pH, in 161 samples (3.7% of the total) the pH value was outside the range 6.0-9.5 established by the legislation[4]. Seventy-three samples (1.7%) exhibited pH > 9.5; of which 66 were collected in Ibitinga (79 samples analyzed, n_m/n_h 1,2.10^{-4}). Eighty-eight samples (2%) exhibited pH < 6.0 with highlights to the municipalities of Dobrada (20 samples with pH < 6.0, 28 samples analyzed, n_m/n_h = 2,9.10^{-4}) and São Carlos (15 samples with pH < 6.0, 165 samples analyzed, n_m/n_h = 6,2.10^{-5}). pH values were not determined in 173 samples (4.0% of the total) - note that there was no pH measuring during the period for the municipalities of Rincão (26 samples analyzed, n_m/n_h =2,1.10^{-4}) and Santa Ernestina (30 analyzed samples, n_m/n_h = 4,5.10^{-4}).

With regard to the FRC content established by the legislation[4], seven samples (0.16% of the total) presented values above the MPV (equal to 5 mg/L). A total of 215 samples (4.9%) presented values below the minimum 0.2 mg/L - in this case, highlights to the municipalities of Rifaina (20 samples with FRC < 0.2 mg / L, 26 samples analyzed, n_m/n_h = 6,3.10^{-4}), Rincão (20 samples with FRC < 0.2 mg/L, 26 samples analyzed, n_m/n_h = 2,1.10^{-4}), and Gavião Peixoto (17 samples with FRC < 0.2 mg/L, 29 samples analyzed, n_m/n_h = 5,5.10^{-4}); 4,055 samples (93.3%) presented FRC

Table 2. Classification of the public water supply of Regional Health Care Network n. 13 according to the classification of the Collaborating Center in Oral Health Surveillance of the Ministry of Health [25].

Fluoride content (mg/L)	Benefit	Risk	N. of samples	%
Below 0.44	Insignificant	Insignificant	821	18.9
Between 0.45 and 0.54	Minimum	Low	370	8.5
Between 0.55 and 0.84	Maximum	Low	2760	63.5
Between 0.85 and 1.14	Maximum	Moderate	323	7.4
Between 1.15 and 1.44	Questionable	High	40	0.9
Above 1.45	Harm	Very high	33	0.8

levels within the recommended range (0.2 to 2.0 mg/L). The determination of FRC was not performed in 11 samples (0.25%).

With regard to the apparent color (MPV = 15 uH) and turbidity (MPV = 5 uT)[4], 17 (0.39%) and 13 samples (0.30%) presented values above the MPV, respectively.

Mapping by principal component analysis

In the previous item we analyzed the water supply of RRAS 13 in general, focusing attention on parameters in which relevant results were obtained, individually considering each parameter. Here we present a multivariate approach to view the data in order to identify patterns in the water supply of RRAS 13. The initial specific objective was to recognize municipalities whose physico-chemical profiles of their water supply had some degree of similarity with the water supplied to Monte Azul Paulista, a municipality that currently has its groundwater catchment limited by a DAEE ordinance[26] due to contamination by nitrate[20]. In practical terms we intended to identify municipalities in which preventive or corrective actions could be planned with respect to this contamination using the case of Monte Azul Paulista as a reference.

In order to perform the multivariate analysis of the 88 x 21 data matrix (88 municipalities x 21 medians in each variable) initially constructed, the variables of ammonium, chlorite and bromate were excluded since the respective median concentrations of all municipalities presented a zero value which means, in analytical terms, a value lower than the limit of detection. The bromide variable was also excluded since only Ibitinga presented a median concentration different from zero for this variable. Analysis of the correlation matrix between the 17 remaining variables indicated that 12 variables exhibited the most significant correlations: lithium, sodium, potassium, calcium, magnesium, chloride, chlorate, nitrate, phosphate, sulfate, pH and conductivity. These variables were chosen for the multivariate analysis.

The data of the 88 x 12 matrix was centered by the median and scaled by the interquartile range. It was then subjected to a principal component analysis (PCA), calculating the matrices of scores and loadings using the Nipals algorithm (Non-linear Iterative Partial Least-Squares) with four principal components. The variance explained by PC1 and PC2 was 56% and 19%, respectively. The PC1/PC2 score plot shows Ibitinga as a single sample (as already mentioned in the previous item) compared to three other groups. Due to the high influence of this sample in the description (visualization) of the others, we decided to remove it from the set and analyze it separately. This analysis was described in the recently published and previously cited article[23].

To the new matrix 87 (municipalities) x 12 (variables) identical treatment was applied (median centralization, interquartile range scaling, ACP/Nipals/4PCs). The variances explained by each PC were: PC1, 50%; PC2, 18%; PC3, 10%; PC4, 6% (total variance explained = 84%). By the PC1/PC2 score plot (Figure 1A) we can observe the initial formation of three groups (the groups were coincident with those obtained through the hierarchical clustering analysis by the *Ward* method): the first group of eight municipalities in magenta in Figure 1A extends along the axis defined by PC1, which has "sulfate" as the variable with the highest loading (Figure 1B) - the municipalities of Santa Rosa de Viterbo (39 samples analyzed, n_m/n_h =1.4.10^{-4}) and Cássia dos Coqueiros (26 analyzed samples, n_m/n_h = 8.2.10^{-4}) have the highest PC1 scores; the position of the second group of four municipalities (light blue, Figure 1A) is mainly defined by the scores in PC2 in which the sodium and lithium variables, followed by conductivity and pH, presented the highest contributions (Figure 1B) - this group comprises the municipalities of Guará (39 samples analyzed, n_m/n_h= 1.6.10^{-4}), Itápolis (65 analyzed samples, n_m/n_h=1.4.10^{-4}), Pitangueiras (52 analyzed samples, n_m/n_h = 1.2.10^{-4}) and Borborema (39 samples analyzed, n_m/n_h=2.2.10^{-4}); the third group (in green, Figure 1A) can be broken down into 2 if we use the PC1/PC3 score plot (Figure 1C) - in this case, the red group includes 14 municipalities (including Monte Azul Paulista and Severínia) mainly determined by scores in PC3 that exhibits nitrate, magnesium, chloride, and conductivity as relevant loadings (Figure 1D). Finally, in the PC1/PC4 score plots (Figure 1E) it is possible to visualize the formation of a fifth group due mainly to the chloride variable (Figure 1F), with the municipalities of Jaboticabal (104 samples analyzed, n_m/n_h = 1.2.10^{-4}), Porto Ferreira (78 analyzed samples, n_m/n_h = 1.3.10^{-4}) and Santa Rita do Passa Quatro (43 analyzed samples, n_m/n_h = 1.4.10^{-4}). Figure 1G indicates these 5 groups in the PC1/PC2/PC3 space (the green group, located near the origin, was denominated "typical" because it does not present any prominent variable in that model).

Figure 2 shows the location of the municipalities grouped by the hierarchical clustering analysis and the PCA, emphasizing the municipalities of Ibitinga (unusual physico-chemical parameters), Severínia and Monte Azul Paulista (nitrate contamination). The location of the municipality of Santa Lúcia (which presented differentiated microbiological results) is also shown. This figure suggests a classification of the water supply of RRAS 13 through the grouping of municipalities according to the variable(s) responsible for the discrimination. For example, the nitrate group includes 14 municipalities and their public health interest is due to the occurrence of methemoglobinemia and a possible correlation with cancer onset when the drinking water is rich in nitrate[2]. If the water in the sulfate and chloride groups does not require immediate attention from the surveillance, in the municipalities of the sodium and lithium group epidemiological studies for the presence of lithium may be developed, as already mentioned in the general data analysis. In these studies, Ibitinga can be included since lithium is one of the important variables for the discrimination of this municipality - in this case (a group of a single element), studies should be conducted in order to verify if the rich composition of its water (in comparison with the waters of the region) does not include other analytes of interest in Public Health but not researched in this work, such as heavy metals[23]. The case of Santa Lúcia (another group of a single element) should also be

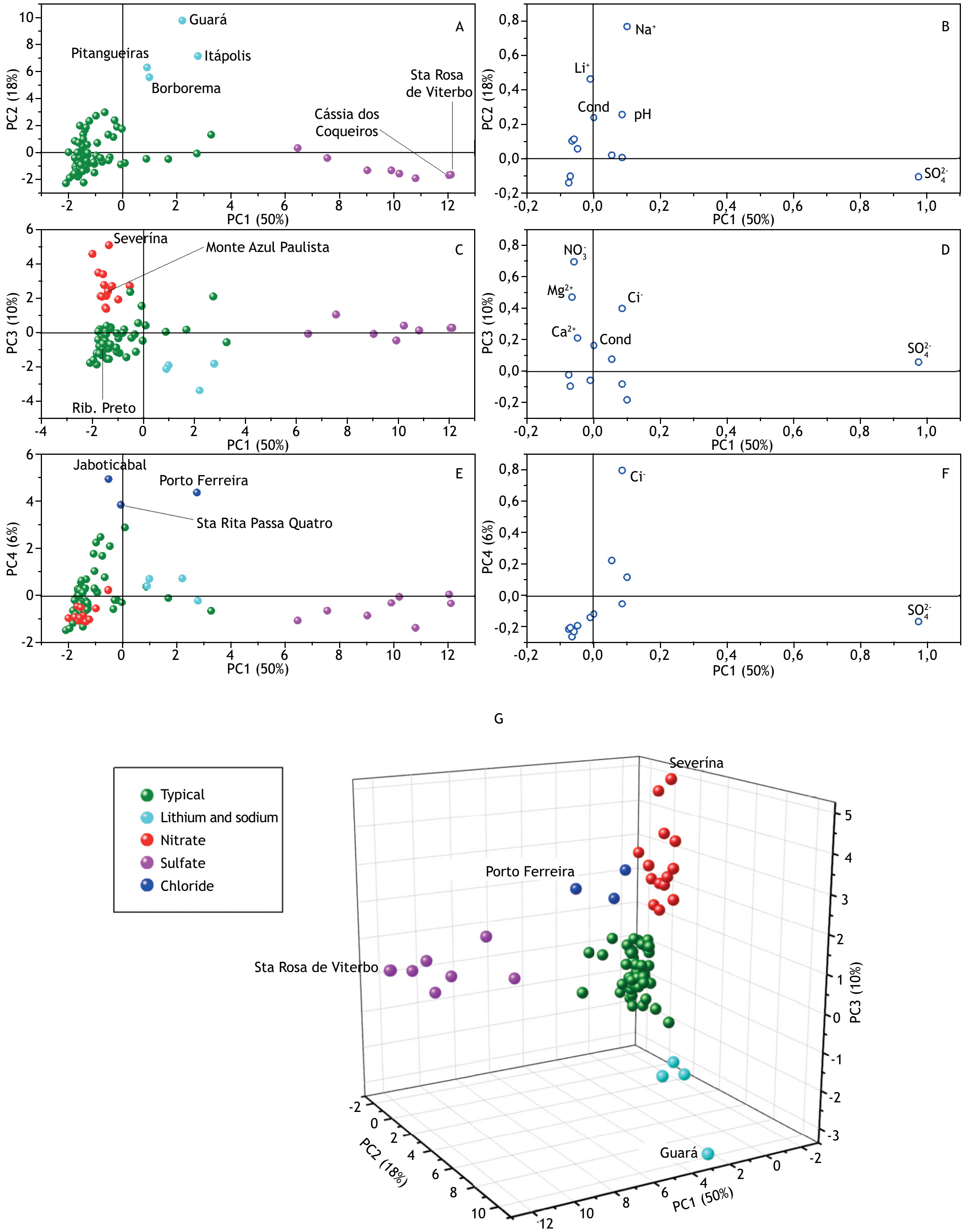

Figure 1. Principal component analysis of 87 samples (municipalities) and 12 physico-chemical variables. The groups in score plots A, C and E are interpreted by the respective loading plots B, D and F: the group in magenta in score plot A is defined mainly by the sulfate variable indicated in B; the light blue group (A) is defined by sodium and lithium (B) variables; the red group (C) is defined by the nitrate variable (D); the dark blue group (E) is defined primarily by the chloride variable (F). Score plot G shows the position of the five groups in the PC1/PC2/PC3 three-dimensional space, where we can see that the green group (typical group) does not have any prominent variables in this model since it is close to the origin.

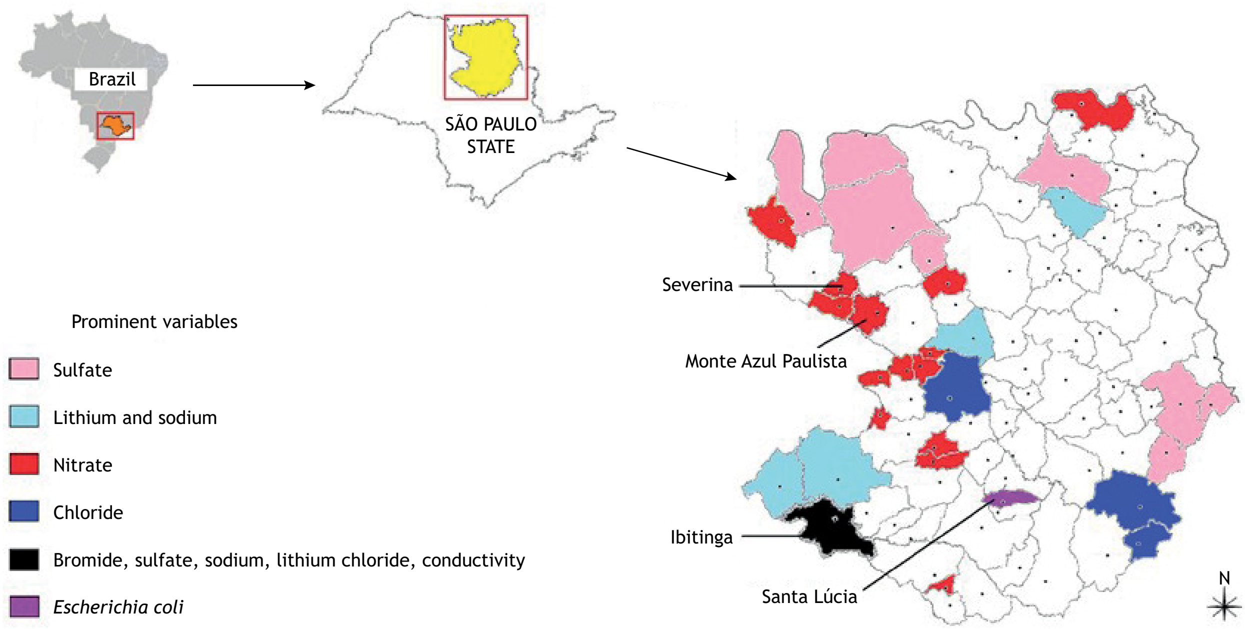

Figure 2. Illustration of the region covered by this study indicating the most significant variables characterizing the water supply (cities not colored in the illustration to the right indicate absence of prominent variables in the model).

investigated because of the municipality's difficulties in producing microbiologically adequate water.

Investigation of the nitrate group through principal component analysis

In order to obtain more information on the nitrate group, a PCA was performed involving four variables correlated with nitrate: chloride (r = 0.17), conductivity (r = 0.30), calcium (r = 0.31) and magnesium (r = 0.58). In this situation, Ibitinga did not present an unusual profile and, therefore, was not excluded from the analysis. Thus, to the 88 (municipalities) x 5 (variables) data matrix, the same treatment was applied (centering by the median, scaling by the interquartile range, PCA/NIPALS/4PCs) and the explained variances were: PC1, 48%; PC2, 29%; PC3, 15%; PC4, 6% (total variance explained = 98%).

The PC1/PC2 score plot (Figure 3A) indicated the formation of three groups: (i) the smallest group (three municipalities, corresponding to 4.5% of the total population of RRAS 13, which mainly use surface water) has its position defined essentially by the chloride concentration (Figure 3B) - these municipalities are the same as previously defined as the "chloride group" (Figures 1E and 2): Jaboticabal, Porto Ferreira and Santa Rita do Passa Quatro; (ii) the largest group (71 municipalities corresponding to 91.2% of the RRAS 13 population) is located near the origin of the score plot (Figure 3A) mainly in the negative parts of PC1 e PC2 showing a small scattering of the Group towards PC2 positive direction – on the other hand, the variable of greatest loading in PC1 is nitrate (Figure 3B) and, therefore, the main feature of this group in this model are the low concentrations of this ion in the water supply; (iii) a group of 14 municipalities (including Monte Azul Paulista and Severínia, indicated in Figures 1C and 2) corresponding to 4.3% of the population of RRAS 13, which use groundwater for public supply, extends over PC1 with Severínia presenting the highest score (5.6) - this positive direction of PC1, strongly influenced by the nitrate and magnesium variables (Figure 3B), is currently being investigated in this laboratory in order to develop predictive models that may inform the decision-making process regarding nitrate contamination of the water (preliminary results of models based on linear discriminant analysis and *Soft Independent Modeling of Class Analogy* [Simca] have already been reported[22]).

CONCLUSIONS

In view of the objective of this work and of the related project, two municipalities that required corrective actions have been identified: Santa Lúcia (which presented a relatively high percentage of samples with *Escherichia coli*) and Severínia (water contamination by nitrate). If in the first case an investigation should be conducted, in the case of Severínia the actions have already begun with the holding of Technical Meetings. It should be stressed that the municipality of Monte Azul Paulista is already undergoing a period of corrective actions. The bromate contamination of the Ribeirão Preto water samples is less obvious requiring confirmation and, if possible, mapping.

With regard to preventive actions, the municipalities classified in the nitrate group (with the exception of Monte Azul Paulista and Severínia which are currently undergoing corrective actions) stand out. Studies on these 12 municipalities will soon be published along with the prediction models mentioned above, in

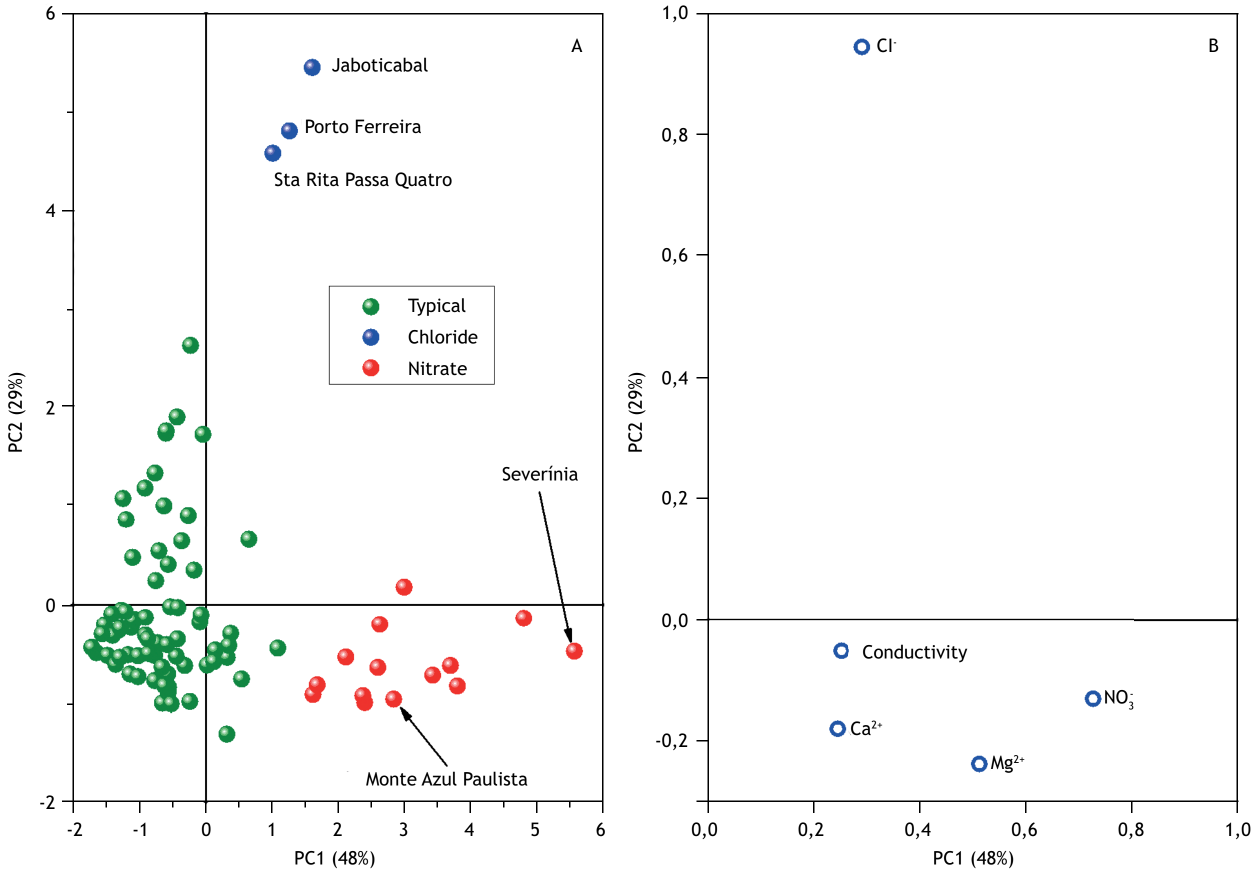

Figure 3. Principal component analysis of 88 samples (municipalities) and five variables. The positions of the groups in the score plot (A) are mainly influenced by the loading of the variables of nitrate and magnesium (in the case of the nitrate group), and chloride (in the case of the chloride group), indicated in the loading plot (B). The typical group does not present any prominent variables in this model since it is close to the origin of the score plot.

order to establish priorities based on the physico-chemical profile of each municipality and its similarity with the profiles of Monte Azul Paulista and Severínia.

Finally, we highlight two interesting situations identified in this study that, at first, do not require preventive or corrective actions but draw attention to their peculiarities: (i) Ibitinga which requires a more complete analysis of its water supply; (ii) the municipalities in the sodium and lithium group (Guará, Itápolis, Pitangueiras and Borborema) which may be the subject of epidemiological studies in view of the presence of lithium - in this particular case, Ibitinga could also be included in these studies since lithium is one of the variables that differentiate the water of this municipality from the rest of RRAS 13.

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Conflict of Interest

Authors have no potential conflict of interest to declare, related to this study's political or financial peers and institutions.