Elements concentration analysis in groundwater from the North Serra Geral aquifer in Santa Helena-Brazil using SR-TXRF spectrometer

Gisele C. Justen, Fernando R. Espinoza-Quiñones, Aparecido Nivaldo Módenes and Rosangela Bergamasco

ABSTRACT

In this work the analysis of elements concentration in groundwater was performed using the synchrotron radiation total-reflection X-ray fluorescence (SR-TXRF) technique. A set of nine tube-wells with serious risk of contamination was chosen to monitor the mean concentration of elements in groundwater from the North Serra Geral aquifer in Santa Helena, Brazil, during 1 year. Element concentrations were determined applying a SR-TXRF methodology. The accuracy of SR-TXRF technique was validated by analysis of a certified reference material. As the groundwater composition in the North Serra Geral aquifer showed heterogeneity in the spatial distribution of eight major elements, a hierarchical clustering to the data was performed. By a similarity in their compositions, two of the nine wells were grouped in a first cluster, while the other seven were grouped in a second cluster. Calcium was the major element in all wells, with higher Ca concentration in the second cluster than in the first cluster. However, concentrations of Ti, V, Cr in the first cluster are slightly higher than those in the second cluster. The findings of this study within a monitoring program of tube-wells could provide a useful assessment of controls over groundwater composition and support management at regional level.

Key words | Brazilian aquifer, cluster analysis, groundwater, major elements, SR-TXRF technique

INTRODUCTION

Nowadays, the main factors that lead to the exploitation of aquifers are underground water availability and tube-well productivity. Tube-well drilling activities have undergone uncontrolled growth due to the rising demand for potable water for households. In most cases, lack of sanitary conditions around the well head has led to contamination from surface sources. Besides this factor, other groundwater pollution sources are reported to result from the use of urban, industrial, and agricultural land (Zaporozec & Miller 2000).

In Brazil the use of groundwater has quickly increased in the last decades with thousands of wells built with or without license solicitation or a grant request (Moreira et al. 2006). Groundwater is extensively used for drinking, industrial activities and recreation (thermal swimming pools), with the yields of the wells varying from 10–150 m³ h⁻¹ (phreatic exposed parts) up to 500–1,000 m³ h⁻¹ (confined artesian wells) (Gilboa et al. 1976).

From an earlier work performing 61 water analyses (Bitten-court et al. 2005), groundwater from the North Serra Geral aquifer collected in the basin of the River Piquiri located in the Brazilian state of Paraná was classified as calcium bicarbonate waters containing between 100 and 150 mg L⁻¹ of total dissolved solids, with pH values ranging from 6.6 to 7.2 and hardness of around 40 mg CaCO₃ L⁻¹. In the Brazilian state of São Paulo, groundwater contamination by chromium and lead probably originated from the disposal of several kinds of residues without any control at industrial landfills in the metropolitan area of Campinas has been reported (Moreira et al. 2006).

Analytical methodologies with high elemental sensitivity and accuracy are desirable for environmental monitoring, allowing lower detection limits to be reached as required for trace element analysis as well as to perform a multi-element analysis. Among these methodologies, inductively coupled plasma-mass spectrometry (ICP-MS),...
proton-induced X-ray emission (PIXE) and synchrotron radiation total-reflection X-ray fluorescence (SR-TXRF) have been reported as suitable for several applications, (Rizzutto et al. 2006; Meier et al. 2010; Popp et al. 2010). The ICP-AES (inductively coupled plasma-atomic emission spectroscopy) and ICP-MS methods have been used for the analysis of microsamples, such as in cells, suspended nanoparticles, brain, metalloproteins and dust (Todoli & Mermet 2006). However, as SR-TXRF technique allows detection of metals in the range of a few parts per billion or ng L$^{-1}$, analysis of river water (Rizzutto et al. 2006; Espinoza-Quiñones et al. 2010a), sediments (Espinoza-Quiñones et al. 2010b), plants (Espinoza-Quiñones et al. 2009), and fish (Espinoza-Quiñones et al. 2011) have been reported, highlighting its applicability for the analysis of trace elements. In addition, a monitoring of groundwater by the SR-TXRF technique has become a necessity in order to assess the vulnerability of Brazilian wells by the occurrence of metals originated from anthropogenic activities (Moreira et al. 2006).

The aim of this paper is to assess the monitoring of element concentrations in groundwater samples collected in tube-wells in a small region of the North Serra Geral aquifer, using the SR-TXRF analysis. A cluster analysis was performed in order to detect natural grouping in the data set. In addition, element concentration data were compared with the limits established by the Brazilian Environmental Legislation (BEL).

**MATERIAL AND METHODS**

**Study area**

Serra Geral aquifer, which is subdivided into North Serra Geral and South Serra Geral aquifers and formed by basaltic rocks, is one of the principal aquifers in the Brazilian state of Paraná covering an outcrop area of approximately 102,000 km$^2$. The North Serra Geral aquifer is mainly recharged with freshwater coming from rain or river water, corresponding mainly to the basin area of the rivers Ivaí, Piquiri, Paraná, Pirapó, Tibagi, Cinzas, and Paranapanema (see Figure 1). The flow direction and accumulation of groundwater in this aquifer is basically determined by the west of the Brazilian state of Paraná in the basin of the River Paraná. The public water supply source for domestic purposes in rural zones is groundwater obtained from the North Serra Geral aquifer by using tube-wells with an average depth of 107 m. Regarding the high vulnerability of wells to be contaminated via infiltration or percolation of pesticides, fertilizers, domestic sewage, and animal waste through agricultural lands, nine tube-wells with high risk of contamination located in the northern municipality of Santa Helena were chosen for the study, as shown in Figure 1.

**Groundwater sampling**

For sampling, polyethylene bottles were used and were subjected to a cleaning process in accordance with the American Public Health Association (APHA) – Standard Methods for the Examination of Water and Wastewater (APHA 2005). A total of nine tube-wells were considered under study (see Figure 1) during 1 year for element analyses. Groundwater samples were collected from a PVC tap installed at the outlet of the free-flowing and pumped tube-well. The water supply pump was previously put in operation for at least 15 min before collection. In each sampling time and well, three sampling bottles of 200 mL containing groundwater were collected monthly. In order to homogenize samples, replication set of each groundwater collection was mixed, performing 12 annual samplings per well from January to December 2010. After collection, samples were acidified to a pH less than 2, and thus was preserved and maintained under refrigeration for later analyses (APHA 2005).

**Analytical procedure**

SR-TXRF quantitative analysis of the groundwater was performed by an internal standard procedure. One milliliter of sample solution was prepared with an aliquot of 10 $\mu$L of certificated gallium standard solution (1.0 g Ga L$^{-1}$, Acros® Organics) and 990 $\mu$L groundwater sample. A multi-element liquid standard solution (Specsol® MICPG2) containing the following elements: P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Mo, Cd, Sn, Ba, Tl, Pb, and Bi with the same concentration of 100 mg L$^{-1}$ were used in order to obtain the SR-TXRF sensitivity curves. An aliquot of 5 $\mu$L of sample solution was deposited on the central part of a pre-cleaned acrylic sample carrier for later evaporation.
To check the accuracy of the applied analytical method, a Drinking Water Pollutants (DWP) solution (Aldrich) was used as a standard reference material. The proper amount of gallium was added to the right DWP solution volume in order to obtain a Ga concentration of $102.5 \text{ mg L}^{-1}$. Procedural blanks (de-ionized water and all reagents) were included in each sample batch. In order to perform a statistical analysis of the same sample solution, at least three different sample carriers were prepared in this way, while multi-element liquid standard sample carriers were prepared in quintuplicate. The detection limits were set at three times the standard deviation of the procedural blanks.

The SR-TXRF measurements were carried out by using a polychromatic X-ray beam with a beam energy of 2–20 keV from the D09-XRF beam-line at the Brazilian Light Synchrotron Laboratory. A Si(Li) detector with 160 eV FWHM at the Mn-K$_\alpha$ line was used, obtaining SR-TXRF spectra at 100 s acquisition time for groundwater samples, except for...
multi-element standard reference materials, for which they were performed at 500 s. SR-TXRF spectra were analyzed and the element fluorescence intensity (I) was obtained by using the software AXIL (Vekemans et al. 1994), allowing determination of the relative sensitivity yields (S) of the SR-TXRF spectrometer and calculation of the elemental concentrations (C) of the samples, according to Equation (1). The lower limit of detection (LLD) for the SR-TXRF spectrometer is basically related to the background intensity \( I_{BG} \), in agreement with Equation (2):

\[
C_Z = \frac{I_Z}{I_{Ga}} \cdot \frac{C_{Ga}}{S(Z)}
\]

\[
LLD(Z) = \frac{3\sqrt{I_{BG}}}{I_{Ga}} \cdot \frac{C_{Ga}}{S(Z)}
\]

**Statistical analysis**

To determine whether the elemental concentration data from the groundwater samples are normally distributed, the null hypothesis was tested for an alpha level of 0.05 on the basis of the Shapiro–Wilk test. In some sets of element concentration data, a previous normalization of the data by non-linear or linear transformations was required. The analysis of variance (ANOVA) was applied to the elemental concentration data. The Tukey test was also applied for a level of 5%. Furthermore, a cluster analysis was performed in order to show the mutual correlation among elements.

**RESULTS AND DISCUSSION**

As both the Kα line of low atomic number elements (15 < Z < 40) and the Lα line of high atomic number elements (40 < Z < 83) are in the 1–20 keV energy range, detected elements in all samples could be simultaneously identified. In order to build the sensitivity curve of the SR-TXRF spectrometer, the known concentration values (100 mg L\(^{-1}\)) of P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Se, Sr, and Mo as well as their corresponding background-subtracted areas of Kα X-ray peaks were used to obtain the relative-to-gallium experimental sensitivity points \( S_K \) for the Kα X-ray series. Similarly, by using the known concentration values (100 mg L\(^{-1}\)) of Ag, Cd, Sn, Te, Ba, TI, Pb, and Bi and their corresponding Lα X-ray peak intensities the relative-to-gallium sensitivity curve \( S_L \) for the Lα X-ray series was also obtained. Exponential-type functions depending on the atomic number (Z) of the chemical element were chosen as suitable to reproduce relative-to-gallium fluorescence sensitivity data for the Kα and Lα X-ray series according to Equations (3) and (4). The obtained results showed a good statistical fit \( (r^2 = 0.9981 \text{ and } r^2 = 0.9568 \text{ for Kα and Lα X-ray series, respectively}) \):

\[
S_K(Z) = \exp \left[ -25.624 \times Z - 0.0257 \times Z^2 \right]
\]

\[
S_L(Z) = \exp \left[ -22.42 + 0.516 \times Z - 0.003 \times Z^2 \right]
\]

Considering the intention of monitoring both groundwater pollution and agricultural contaminants occurring in this area, we have reported the quantitative analysis of only eight elements found in the groundwater samples: K, Ca, Ti, V, Cr, Fe, Cu, and Zn. The accuracy of the measurements was determined by analysis of one reference material (DWP). The calculated concentrations of 9.40±0.65 mg L\(^{-1}\) Cr, 9.50±0.47 mg L\(^{-1}\) As, and 4.65±0.37 mg L\(^{-1}\) Se are in agreement with the certified values of Cr (9.09±0.45 mg L\(^{-1}\)), As (9.09±0.45 mg L\(^{-1}\)), and Se (4.54±0.23 mg L\(^{-1}\)) within approximately 5%. The element concentration results of all groundwater samples collected from nine tube-wells in the North Serra Geral aquifer, the detection limits and the maximum tolerance limits recommended by the BEL for groundwaters (Brazil 2008) are shown in Table 1.

Testing the null hypothesis, the p-values of the Shapiro–Wilk test were greater than 0.05 for all elements in the nine analyzed tube-wells, indicating that the elemental concentration data show a normal distribution. In addition, when the F-ratio test was applied within the ANOVA framework, all element concentrations in the nine tube-wells showed a statistical significance of 95%.

As can be seen from Table 1, of all the constituents of groundwater that were quantified, a low spatial variability of Cr and Zn concentrations was observed in the nine studied wells with mean distributions of 0.03 and 0.08 mg L\(^{-1}\), respectively. However, when the concentrations of the elements K, Ca, Ti, V, Fe, and Cu in the nine studied wells were compared, differences between the concentration values among the nine wells above 20% were observed with mean distributions of 1.2, 30, 0.09, 0.11, 0.17, and 0.04 mg L\(^{-1}\), respectively. Performing a comparative analysis of the mean concentrations of the elements of interest, the mean K concentration in Well 8 showed a significant difference with respect to Wells 2, 3, and 4,
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High concentrations of calcium ions in groundwater could be attributed to the easy removal of this cation from the basaltic rock by the interaction with water and its release into the groundwater. Bittencourt et al. reported lower concentrations of calcium ions in groundwater samples from a region close to the one investigated in this study, high spatial variability in the Ca concentration; however, it has not been yet established as an important micronutrient for humans (Bishayee et al. 2010).

Analyzing results of Ca, the mean concentrations showed high variations between analyzed wells. In addition, the mean Ca concentration (47.8 mg L⁻¹) in Well 5 was at least three times higher than that measured in Well 4. High concentrations of calcium ions in groundwater could be attributed to the easy removal of this cation from the basaltic rock by the interaction with water and its release into the groundwater. Bittencourt et al. (2005), who performed an analysis from the databases of the Superintendence of Water Resources Development and Environmental Sanitation of the Brazilian state of Paraná (SUDERHSA) and the Sanitation Company of Brazilian state of Paraná (SANEPAR), reported lower concentration values of Ca (9.78 mg L⁻¹) and K (0.81 mg L⁻¹) in groundwater samples from the North Serra Geral aquifer. In the present work, the mean Ca distribution is almost twice as much as that (15.15 mg L⁻¹) reported in the Water Resources Atlas of the Brazilian Paraná State (Brazil 1998), whereas the mean K and Fe distributions are similar (1.44 and 0.29 mg L⁻¹, respectively). Furthermore, in studies on the water typology of samples collected from a region close to the one investigated in this study, high spatial variability in the Ca concentration values, ranging from 0.8 to 33.7 mg L⁻¹, was also reported by Athayde et al. (2007). Possible causes of abrupt variations in the element concentration values in the nine studied wells

<table>
<thead>
<tr>
<th>Element</th>
<th>BEL (mg L⁻¹)</th>
<th>LOQ (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Ti</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>V</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Zn</td>
<td>0.05</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 1 | Mean value and standard deviation of element concentrations in groundwater samples, corresponding to 12 annual samplings per well. Maximum tolerance limits recommended by BEL for groundwaters (Brazil 2008) and LLD values are reported.
could be the mixture of groundwaters from the North Serra Geral aquifer and a nearby aquifer and due to the groundwater geochemistry. From the concentration results, heterogeneity in the element spatial distribution was found to be characteristic of the groundwater from the studied wells in the North Serra Geral aquifer.

A hierarchical clustering based on Ward’s method was applied to detect natural grouping in the element concentration data of nine tube-wells. As appropriated metric, squared Euclidean distance was chosen, allowing to group wells by similarity of the elements composition. Two of the nine wells were grouped in a first cluster, while the other seven were grouped in a second cluster, as shown in Figure 2. The first cluster is formed by the Wells 3 and 4, while the second cluster is formed by the Wells 1, 2, 5, 6, 7, 8, and 9. Performing a descriptive analysis of these groupings (see Table 2), calcium was the major element in all wells, with higher Ca concentration in the second cluster than that in the first cluster. However, concentrations of Ti, V, Cr in the first cluster are slightly higher than those in the second cluster. As can be seen in Figure 1, wells that belong to the first cluster are adjacently located (around 4 km), suggesting that there is an enrichment of some metals, such as V and Ti, as consequence of their presence in the basaltic rocks and the groundwater geochemistry in this region.

In order to confirm the results given herein, further evaluations should be conducted at other wells, or at the same wells, with other variables, focusing other factors such as geochemical characterization of soil, basaltic rocks and water, among other factors, and the anthropogenic contamination on the vulnerability of the North Serra Geral aquifer in the region of the municipality of Santa Helena.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Descriptive analysis of clusters for analyzed groundwater samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Annual mean element concentration in clusters (mg L(^{-1}))</td>
</tr>
<tr>
<td>K</td>
<td>0.98±0.06</td>
</tr>
<tr>
<td>Ca</td>
<td>13.9±4.2</td>
</tr>
<tr>
<td>Ti</td>
<td>0.055±0.078</td>
</tr>
<tr>
<td>V</td>
<td>0.334±0.018</td>
</tr>
<tr>
<td>Cr</td>
<td>0.019±0.026</td>
</tr>
<tr>
<td>Fe</td>
<td>0.145±0.032</td>
</tr>
<tr>
<td>Cu</td>
<td>0.042±0.011</td>
</tr>
<tr>
<td>Zn</td>
<td>0.095±0.006</td>
</tr>
</tbody>
</table>

**CONCLUSION**

The SR-TXRF method is appropriated to determine simultaneously elements in very low and high concentrations in groundwater. In the municipal area of Santa Helena, it was possible to perform the quantitative analysis in groundwater samples, verifying the presence of elements: K, Ca, Ti, V, Cr, Fe, Cu, and Zn with concentration values ranging from 0.05 to 50.0 mg L\(^{-1}\). High spatial variations were observed for K, Ca, Ti, V, Fe, and Cu with mean distributions of 1.2, 29.8, 0.09, 0.11, 0.17, and 0.04 mg L\(^{-1}\), respectively. Only in one tube-well vanadium and iron concentration values slightly exceed the maximum tolerance limits recommended by the BEL. Based on a cluster analysis, it was possible to group wells into two clusters. Calcium was the major element in both clusters. It can be noticed that annual mean Ca concentration in the second cluster (Wells 1, 2, 5, 6, 7, 8 and 9) is higher than that in the first cluster (Wells 3 and 4). However, annual mean concentrations of Ti, V, Cr in the first cluster are slightly higher than those in the second cluster.
than those in the second cluster. Finally, the monitoring program of groundwater should be continued in the same wells and extended to others of the North Serra Geral aquifer, detecting elements or substances that could be associated to anthropogenic source of contamination, controlling better the groundwater supply quality as well as providing information about the vulnerability of groundwater on several Brazilian municipal districts that are provisioning by groundwater.

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