



# Combined hydrochemical, isotopic, and multivariate statistics techniques to assess the effects of discharges from a uranium mine on water quality in neighboring streams

Carlos A. De Carvalho Filho<sup>1</sup> · Rubens M. Moreira<sup>1</sup> · Otavio E. A. Branco<sup>2</sup> · Pedro H. Dutra<sup>1</sup> · Elizângela A. Dos Santos<sup>1</sup> · Igor F. S. Moura<sup>3</sup> · Peter M. Fleming<sup>1</sup> · Helena E. L. Palmieri<sup>1</sup>

Received: 29 June 2017 / Accepted: 27 November 2017 / Published online: 16 December 2017  
© Springer-Verlag GmbH Germany, part of Springer Nature 2017

## Abstract

The Caldas Uranium Mine (CUM), located on the Poços de Caldas Plateau in the southeastern region of Brazil, is presently undergoing a decommissioning process. The aim of the present investigation is to identify and characterize the effects of acid mine drainage (AMD) originating from the CUM on surface water quality. To achieve these aims, sampling stations were located at two AMD sources: the retention pond at the foot of waste rock pile#4 (WRP#4) and the settling pond that receives effluents from the tailings dam (TD). Ten additional sampling stations were located along watercourses in the vicinity, both downstream and upstream of the mine. Sampling was performed during the rainy and dry seasons in 2010 and 2011. The water analysis detected significant changes in pH, electrical conductivity, F<sup>-</sup>, Cd, U, Zn, Al, Mn, As, Ca, SO<sub>4</sub><sup>2-</sup>, Pb, <sup>238</sup>U, <sup>226</sup>Ra, <sup>210</sup>Pb, <sup>232</sup>Th, <sup>228</sup>Ra, and Mo in waters downstream of both pond discharge sites. It was demonstrated that the disequilibrium between <sup>226</sup>Ra and <sup>238</sup>U can be used to trace the extent of AMD impacts in nearby streams. Variations in <sup>18</sup>O and <sup>2</sup>H enabled the flow of mining-impacted water to be traced from the ponds to nearby streams. Multivariate analysis yielded a three-factor model: Factor 1 was interpreted as being associated with AMD (from WRP#4) and Factor 2 with a Ca–Mo relationship associated with the chemical constitution of the ore and with the treatment of tailings wastes in the area (from TD); Factor 3 was interpreted as being associated with the natural influence of geogenic processes on water quality in the area. The results of this study provide a scientific basis for recommending appropriate remedial actions during mine decommissioning.

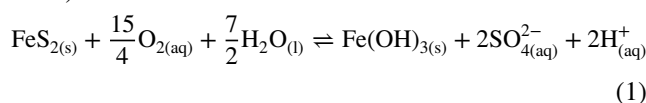
**Keywords** Hydrochemistry · Acid mine drainage · Uranium mine · Isotopes · Multivariate analyses · Water quality

## Introduction

The Caldas Uranium Mine (CUM) is located on the Poços de Caldas Plateau, in Brazil (Fig. 1), inside a 30–35 km diameter alkaline volcanic caldera. Mining at the site started in 1982 and ceased in 1995. The oxidation of sulfide minerals,

mainly pyrite (FeS<sub>2</sub>), in uranium ore and host rocks is responsible for the acid mine drainage (AMD) generation in this mine, mainly in the open pit, in the tailings dam (TD) and in discharges from the waste rock piles (Fernandes et al. 1995, 1996, 1998, 2008; Fernandes and Franklin 2001; Cipriani 2002; Franklin 2007; Campos et al. 2011, Rodgher et al. 2013; De Carvalho Filho et al. 2016).

The main features of AMD are low pH (generally lower than 4), high Fe, SO<sub>4</sub><sup>2-</sup> concentrations, and varying concentrations of toxic metals (US Environmental Protection Agency-USEPA 1994; Drever 1997, Williams 1975; Canovas et al. 2007). The full pyrite oxidative dissolution process can be summed up by the equation (Appelo and Postma 1999):

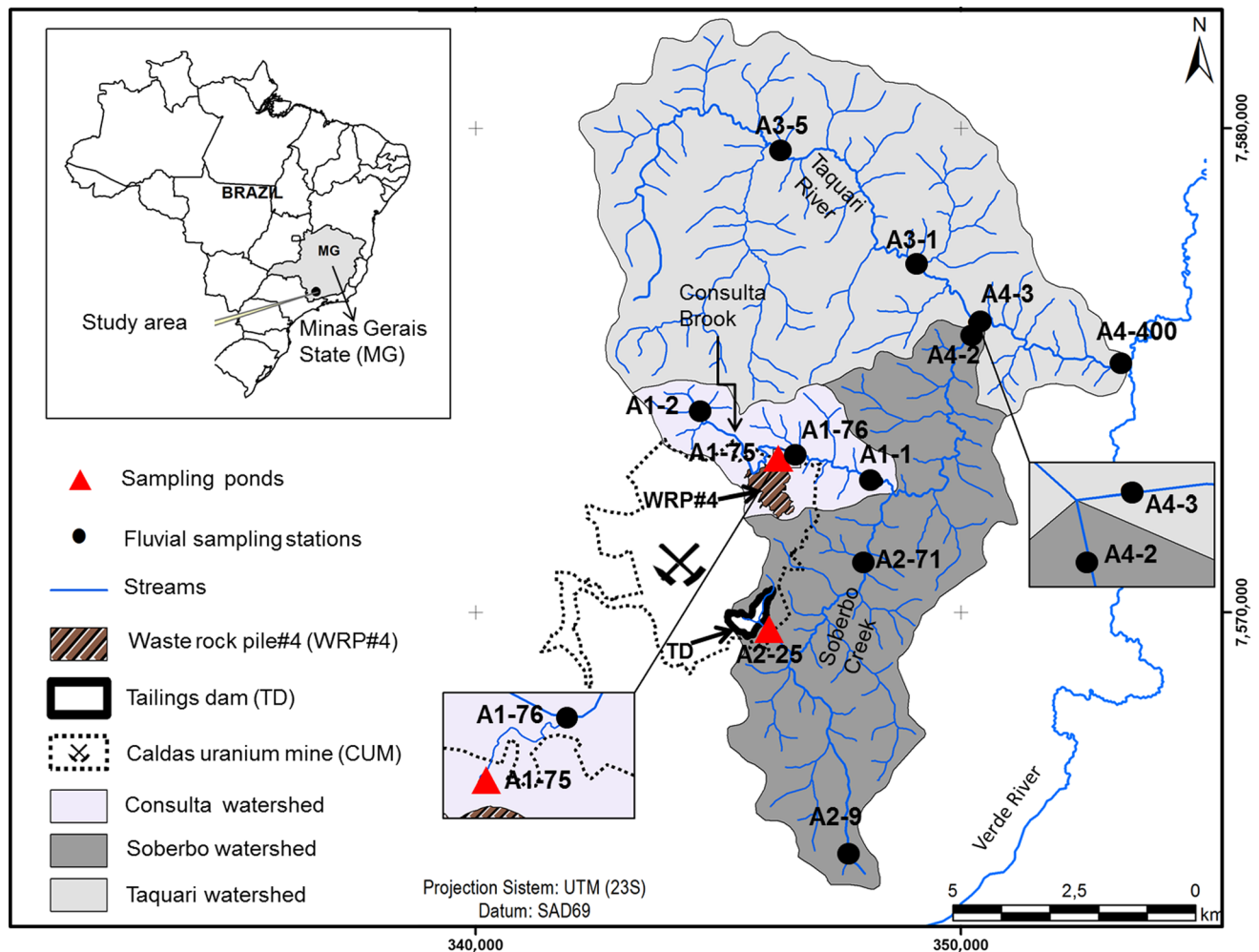


✉ Carlos A. De Carvalho Filho  
cacf@cdtn.br

<sup>1</sup> Nuclear Technology Development Center (CDTN/CNEN), Av. Presidente Antônio Carlos 6627, Pampulha, Belo Horizonte, Minas Gerais 31270-901, Brazil

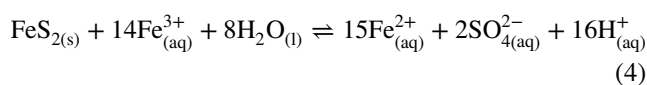
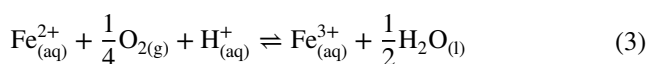
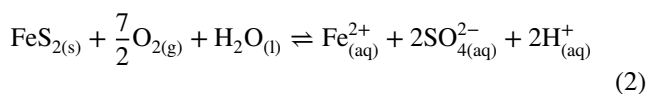
<sup>2</sup> Federal University of Juiz de Fora (UFJF), Juiz de Fora, Brazil

<sup>3</sup> Federal University of Minas Gerais (UFMG), Belo Horizonte, Brazil



**Fig. 1** General study area location and the sampling stations

The complete oxidation process involves the oxidation of both sulfur and iron (Eq. 1). Often, this process is developed in steps (Appelo and Postma 1999; Lottermoser 2010, 2017; Langmuir 1997), e.g., the initial step is S oxidation by  $O_2$  (Eq. 2); then,  $Fe^{2+}$  is oxidized by  $O_2$  to  $Fe^{3+}$  which may precipitate as  $FeOOH$  in a medium at  $pH > 3$  (Eq. 3). Then,  $Fe^{3+}$  oxidizes pyrite (Eq. 4), producing more  $Fe^{2+}$ , and the cycle is reproduced.



CUM is controlled by Nuclear Industries of Brazil (INB) and is currently undergoing a decommissioning process. A recovery plan for degraded areas was prepared in support of the selection and evaluation of closing alternatives for various components of the mine site. The present investigation is part of a larger project which has the aims of identifying the environmental impacts caused by CUM, as well as proposing remediation strategies. Related to this project, one can cite the works by Abreu et al. (2011), Gomes et al. (2012), Ferreira et al. (2012), Silva et al. (2014), De Carvalho Filho (2014), and De Carvalho Filho et al. (2016).

The objective of the present investigation is to identify and characterize changes in surface water quality caused by treated effluents from TD and by non-treated effluents from waste rock pile #4 (WRP#4). Hydrochemical and isotopic data from watercourses and from two ponds were obtained and evaluated. Some of these hydrochemical data were subjected to multivariate statistical analysis in order to substantiate the mentioned evaluations.

## The study area and the Caldas Uranium Mine

The study area is about 100 km<sup>2</sup> and partially encompasses the Caldas mine premises, as well as three watersheds: the Taquari River, the Soberbo Creek, and the Consulta Brook (Fig. 1). The annual average temperature in the region is 19 °C, varying between 1 and 36 °C. The average annual rainfall is around 1700 mm, with 80% of the precipitation concentrated between October and March each year (Franklin 2007).

The area is underlain by a suite of alkaline volcanic and plutonic rocks belonging to the Poços de Caldas alkaline complex (PCAC). Various alkaline rocks in vicinity of the Caldas mine were affected by a large hydrothermal event (enriched K-S solutions), which led to pyritization and potassium metasomatism in the pre-existing rocks and the primary mineralization of uranium. Intense weathering, associated with downward migrating oxidizing groundwater, has resulted in a secondary supergene enrichment of uranium along redox fronts (Fraenkel et al. 1985; Lapido Loureiro and Dos Santos 1988; Schorscher and Shea 1992; Waber et al. 1992).

The uranium deposit was defined by U-Th-Zr-Mo-REE (rare earth elements) mineralization, made up mostly of uranium black oxides (uraninite and pitchblende—UO<sub>2</sub>) which is occasionally accompanied by coffinite ((U<sup>4+</sup>,Th)(SiO<sub>4</sub>)<sub>1-x</sub>(OH)<sub>4x</sub>). The uranium ore also includes sulfide minerals (mainly pyrite (FeS<sub>2</sub>) and rarely galena (PbS) and sphalerite (ZnS)); zirconium minerals (generally zircon—Zr(SiO<sub>4</sub>)); Mo-bearing minerals (mostly jordisite (MoS<sub>2</sub>) and ilsemanite (Mo<sub>3</sub>O<sub>8</sub>·nH<sub>2</sub>O)); fluorite (CaF<sub>2</sub>); and REE phases (Fraenkel et al. 1985; Lapido Loureiro and Dos Santos 1988; Schorscher and Shea 1992; Waber et al. 1992). The ore has an average grade of about 1000 ppm for uranium (Franklin 2007) and maximum grades of 15,000 ppm for zirconium, 1500 ppm for molybdenum and 200 ppm for thorium (Fraenkel et al. 1985).

The uranium mineralization has been emplaced in various host rocks including volcanic and subvolcanic phonolites, nepheline syenites, and volcanic breccia pipes. The ore host rocks are constituted mainly of orthoclase (KAlSi<sub>3</sub>O<sub>8</sub>), nepheline (NaAlSi<sub>3</sub>O<sub>8</sub>), albite (NaAlSi<sub>3</sub>O<sub>8</sub>), and aegirine-augite (Ca,Na)(Fe<sup>3+</sup>,Mg,Fe<sup>2+</sup>)Si<sub>2</sub>O<sub>6</sub>. The uranium deposit has been covered by a thick regolith composed of weathered rock and soil, constituted mainly of kaolinite Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, illite (K<sub>0.65</sub>Al<sub>2.0</sub>[Al<sub>0.65</sub>Si<sub>3.35</sub>O<sub>10</sub>](OH)<sub>2</sub>), gibbsite (Al(OH)<sub>3</sub>), Fe(Mn)-hydroxide, greenockite (CdS), and ilsemanite (Waber et al. 1992).

The ore was extracted from an open pit and then sent for physical and chemical processing where the uranium was produced in the form of ammonium diuranate (yellow cake). One facility was originally built for the production

of calcium molybdate. However, the recovery of molybdenum only occurred during the initial phase of the mining operations. After being treated with limestone (CaCO<sub>3</sub>) and lime (CaO), the solid and liquid effluents from chemical processing were deposited in the TD. Subsequently, the effluents leaving the TD are treated with barium chloride (BaCl<sub>2</sub>) for radium precipitation in the A2-25 settling pond in the form of sulfate phases including (Ba,Ra)SO<sub>4</sub>. Thereafter, the treated liquid effluent is released to the Soberbo Creek (Fig. 1).

Most of the mining wastes were stored in two main waste rock piles (WRP) which are named as waste rock pile number 4 (WRP#4) and number 8 (WRP#8). Only WRP#4 is inside the study area and in the Consulta Brook watershed (Fig. 1). It consists of overburden (soil and weathered rock covering the ore deposit, trace amounts of the uranium ore, and radioactive decay products), low-value ores and barren rock bereft of ore.

Most of the acidic water (pH 3–4) that has percolated through WRP#4 is collected in the A1-75 effluent retention pond (Fig. 1) and is then pumped to the acid water treatment unit. In this facility, the effluent is neutralized with calcium-rich material, producing a precipitate that until 1998 was pumped to the TD, and since then, it is being discharged to open pit.

## Methodology

### Sample collection and chemical analyses

A total of 98 surface water samples were collected from 12 sampling stations in the wet and dry seasons in 2010 and 2011 (Fig. 1). In order to hydrochemically characterize the potential sources of contamination, two sampling stations were located inside the effluent ponds: station A1-75 at the WRP#4's effluent retention pond and station A2-25 at the effluent settling pond immediately downstream of the TD. Four sampling stations were positioned upstream of the mine: A1-2 at the Consulta Brook, A2-9 at the Soberbo Creek, A3-1 and A3-5 at the Taquari River. The remaining stations were located downstream of the mine.

Eh (redox potential), pH, and EC (electrical conductivity) were measured in situ, using an Ultrameter II multiparameter handheld meter (Myron L Company). Water samples for isotopic analyses were collected in clean glass flasks (100 mL) provided with polyseal caps. For other determinations, the water samples were collected in properly clean polyethylene bottles (500 mL). The samples (except those for isotopic analyses) were filtered through 0.45 μm membranes, and the samples for metal and cation analyses were acidified with HNO<sub>3</sub> (pH < 2). The flasks were duly packed in thermally

insulated cases ( $\pm 4$  °C) and dispatched as soon as possible to the laboratory.

Calcium, aluminum, and iron were determined by inductively coupled plasma optical emission spectrometry (ICP-OES); sulfate and chloride by ionic chromatography; fluoride by ion-selective electrode (ISE); arsenic, lead, cadmium, manganese, molybdenum, uranium, thorium, and zinc by ICP-MS. All the above-mentioned analyses were carried at the Nuclear Technology Development Center (CDTN/Brazil).

Radiochemical procedures described by Godoy et al. (1994) were used to measure  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{210}\text{Pb}$  activity concentrations at the Poços de Caldas Laboratory (LAPOC/Brazil).  $^{238}\text{U}$  and  $^{232}\text{Th}$  concentrations were estimated to be 12.3 Bq per mg of uranium mass and 4.1 Bq per mg of thorium mass.

### Ponds and fluvial hydrochemistry

Hydrochemical data were organized by descriptive statistics. The maximum, minimum, and median values of each parameter were plotted in graphs for each sampling station to portray their spatial distribution and identify water quality changes in the receiving watercourses caused by the discharge of the mine effluents. The water quality was assessed by comparing the results with the limits established by existing water quality and effluents guidelines: MS (2011) and WHO (2011) for radionuclides; CONAMA (2005, 2011) for the others parameters, including limits for effluent discharge.

### Environmental isotopes

The stable isotope composition of a water sample is expressed in terms of its deviation from the Vienna Standard Mean Ocean Water (VSMOW). The delta notation ( $\delta$ ) (Clark and Fritz 1997), as shown in Eqs. 5 and 6, is used.

$$\delta^{18}\text{O}(\text{‰}) = \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} - 1 \right] \times 10^3 \quad (5)$$

$$\delta^2\text{H}(\text{‰}) = \left[ \frac{(^2\text{H}/^1\text{H})_{\text{sample}}}{(^2\text{H}/^1\text{H})_{\text{standard}}} - 1 \right] \times 10^3 \quad (6)$$

Isotopic analyses were used to evaluate the isotopic composition of water and effluents and detect changes in the stable isotopic signature of water that had been affected by mine-related discharges. Hence, stable isotopes were determined in 12 samples collected during the season in 2011 and measured by isotope-ratio mass spectrometry (IRMS) at the University of Queensland (Australia).

### Multivariate statistical methods

Many hydrochemical studies have demonstrated the power of multivariate analysis to help identify different factors that control water quality, e.g., Yu et al. (2010), Wu and Wang (2007), Krishna et al. (2009), Bahar and Reza 2010, Najjar and Khan (2012), Obeidat et al. (2013), Adamu et al. (2014), and Rebelo et al. (2015). Multivariate statistics have been used to identify spatial variations in water quality and to determine whether the physicochemical characteristics of the water are derived from anthropogenic or from geogenic sources.

Selected data in this study were subjected to three multivariate statistical techniques: cluster analysis (CA), principal component analysis (PCA), and factor analysis (FA). These techniques were applied to two sets of data. The first one considered all the collected samples, while the second one excluded the samples from the ponds.  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ , and  $^{228}\text{Ra}$  were not used in the multivariate analysis because they exhibited many activity concentrations below the detection limits. The Minitab<sup>®</sup> computer program was used in all statistical analyses.

### Results and discussion

The hydrochemical results are reported in Table 1 and displayed in Figs. 2 and 3. In the case of results below the limit of detection (LOD), this limit was adopted in graphic representations.

#### Pond hydrochemistry

In pond A1-75, the measured values of pH and sulfate concentration (Table 1) are characteristic of AMD. Another indication of AMD in pond A1-75 is the relatively high concentrations found for all elements and radionuclides analyzed (except Fe and Mo), at levels of potential environmental concern for many of them, as shown in Table 1 and Figs. 2 and 3. Certainly, this chemical composition of water in this pond reflects the WRP#4 geochemistry and mineralogy.

The low iron concentration in the A1-75 pond is due to  $\text{Fe}^{2+}$  being oxidized to  $\text{Fe}^{3+}$  and the subsequent precipitation of Fe(III) oxyhydroxide phases. This could be visually verified at the studied site by the characteristic brownish-yellowish-reddish hue of the sludge (rich in  $\text{Fe}^{3+}$  oxide-hydroxides) known as “yellow boy” that colors the A1-75 pond banks (De Carvalho Filho et al. 2016).

Acid drainage in this area has caused intensive leaching of mine wastes, resulting in a plume enriched in metals which, after percolating downwards through waste materials in WRP#4 discharges into the A1-75 pond. The high EC value

**Table 1** Median values (number of samples  $N = 4$ ) of the analyzed parameters and their standards for effluent discharge (SE) and water quality (SW)

Station	F <sup>-</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	U (mg L <sup>-1</sup> )	Al (mg L <sup>-1</sup> )	Fe (mg L <sup>-1</sup> )	Mn (mg L <sup>-1</sup> )	Cd (mg L <sup>-1</sup> )
A1-2	0.04	0.31	0.0003	0.17	0.93	0.10	0.00007
A1-75	123.00	1300.96	8.8765	157.50	0.84	75.00	0.03600
A1-76	4.93	71.35	0.2125	6.50	0.81	3.88	0.00116
A1-1	1.67	21.80	0.0680	2.25	0.39	2.28	0.00049
A2-9	0.06	0.32	0.0001	0.13	1.31	0.35	0.00006
A2-25	3.79	405.12	0.0027	0.54	0.15	0.57	0.00053
A2-71	0.17	16.25	0.0001	0.23	0.23	0.10	0.00002
A4-2	0.28	11.95	0.0057	0.25	0.16	0.36	0.00008
A3-5	0.09	0.40	0.0001	0.42	0.66	0.12	0.00002
A3-1	0.09	0.32	0.0003	0.43	0.89	0.11	0.00002
A4-3	0.20	5.72	0.0027	0.38	0.33	0.19	0.00004
A4-400	0.19	5.14	0.0021	0.39	0.52	0.17	0.00004
SW	1.4 <sup>a</sup>	250 <sup>a</sup>	0.02 <sup>a</sup>	0.1 <sup>a</sup>	0.3 <sup>a</sup>	0.1 <sup>a</sup>	0.001 <sup>a</sup>
SE	103	ND	ND	ND	153	13	0.23
LOD <sup>e</sup>	0.001	0.05	0.0001	0.002	0.01	0.0005	0.00001
Station	Mo (mg L <sup>-1</sup> )	<sup>228</sup> Ra (Bq L <sup>-1</sup> )	Pb (mg L <sup>-1</sup> )	Ca (mg L <sup>-1</sup> )	pH	EC (μS cm <sup>-1</sup> )	<sup>232</sup> Th (Bq L <sup>-1</sup> )
A1-2	0.0003	< LOD	0.0019	0.5	6.06	20.1	0.0005
A1-75	0.0001	0.47	0.0251	80.0	3.65	1788.5	0.9376
A1-76	0.0004	0.05	0.0045	6.7	4.59	158.2	0.0024
A1-1	0.0003	0.04	0.0015	3.2	4.83	80.6	0.0006
A2-9	0.0002	< LOD	0.0007	2.1	6.23	36.4	0.0004
A2-25	0.1269	< LOD	0.0006	164.5	6.14	792.2	0.0006
A2-71	0.0021	< LOD	0.0007	6.0	6.53	59.6	0.0004
A4-2	0.0009	< LOD	0.0011	3.7	6.30	45.4	0.0004
A3-5	0.0002	< LOD	0.0007	1.1	6.19	19.5	0.0006
A3-1	0.0002	< LOD	0.0007	1.2	6.42	18.3	0.0005
A4-3	0.0005	< LOD	0.0008	2.1	6.42	31.5	0.0004
A4-400	0.0005	< LOD	0.0008	2.1	6.64	30.2	0.0006
SW	ND <sup>f</sup>	0.1 <sup>d</sup>	0.01 <sup>a</sup>	ND	6–9 <sup>a</sup>	ND	1 <sup>a</sup>
SE	ND	ND	0.5 <sup>c</sup>	ND	5–9 <sup>c</sup>	ND	ND
LOD <sup>e</sup>	0.0001	0.02	0.0001	0.001	0.01	0.1	0.0001
Station	Zn (mg L <sup>-1</sup> )	<sup>238</sup> U (Bq L <sup>-1</sup> )	<sup>226</sup> Ra (Bq L <sup>-1</sup> )	<sup>210</sup> Pb (Bq L <sup>-1</sup> )	As (mg L <sup>-1</sup> )	SO <sub>4</sub> /Cl (meq L <sup>-1</sup> )	
A1-2	0.03	0.003	< LOD	< LOD	0.0004	1.1	
A1-75	16.69	109.172	0.49	0.70	0.0329	415.7	
A1-76	0.74	2.614	0.04	0.02	0.0044	186.0	
A1-1	0.30	0.836	0.04	0.02	0.0020	64.8	
A2-9	0.02	0.002	< LOD	< LOD	0.0002	0.9	
A2-25	0.04	0.033	< LOD	< LOD	0.0003	108.6	
A2-71	0.03	0.002	< LOD	< LOD	0.0001	35.0	
A4-2	0.07	0.070	< LOD	< LOD	0.0003	35.5	
A3-5	0.03	0.002	< LOD	< LOD	0.0001	1.2	
A3-1	0.04	0.004	< LOD	< LOD	0.0001	1.0	
A4-3	0.05	0.034	< LOD	< LOD	0.0002	17.0	
A4-400	0.04	0.025	< LOD	< LOD	0.0002	16.2	
SW	0.18 <sup>a</sup>	10 <sup>b</sup>	1 <sup>d</sup>	0.1 <sup>b</sup>	0.01 <sup>a</sup>		
SE	5 <sup>c</sup>	ND	ND	ND	0.5 <sup>c</sup>		
LOD	0.0001	0.001	0.02	0.02	0.0001		

<sup>a</sup>CONAMA (2005); <sup>b</sup>WHO (2011); <sup>c</sup>CONAMA (2011); <sup>d</sup>MS (2011); <sup>e</sup>limit of detection; <sup>f</sup>Not defined

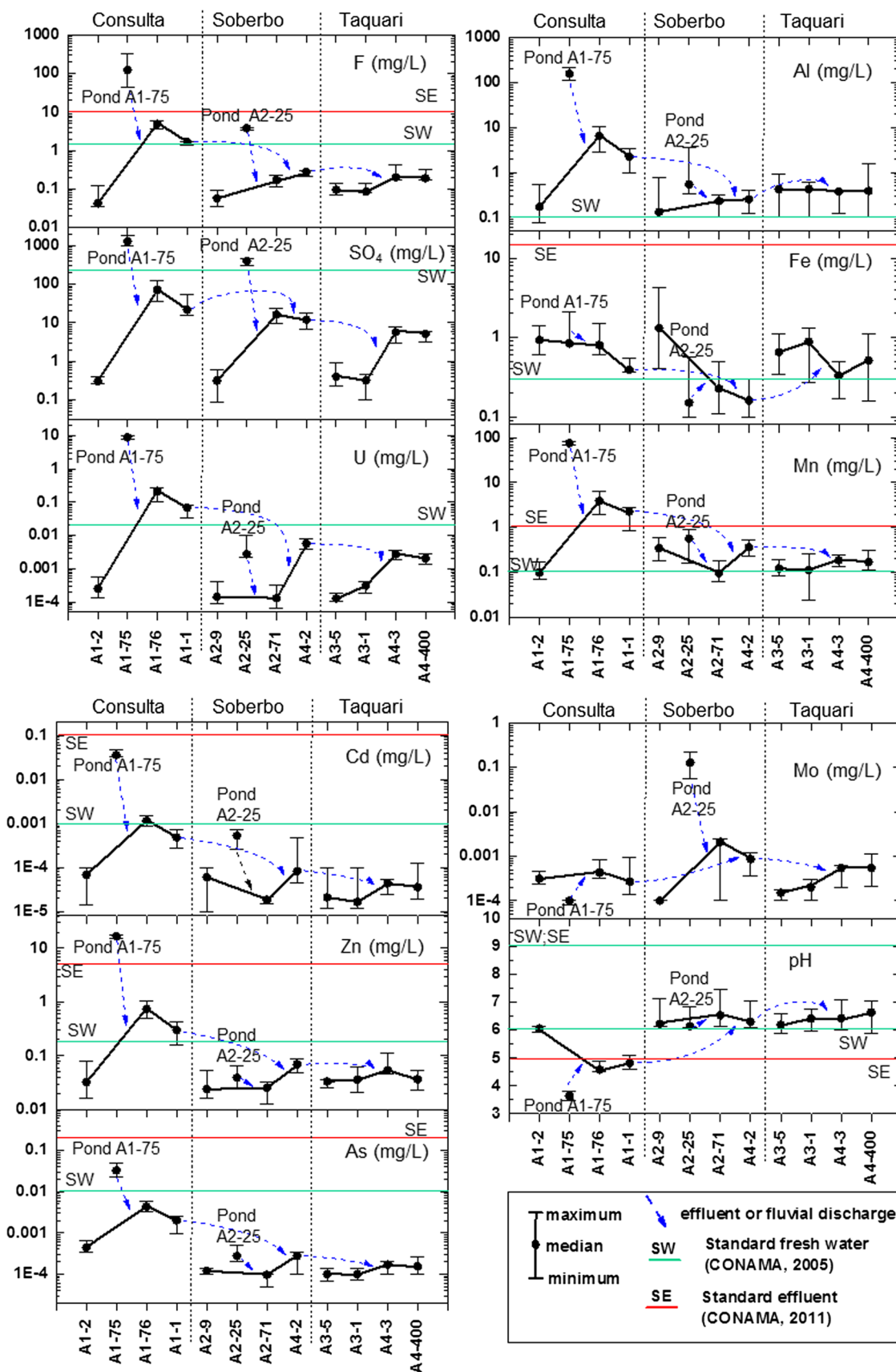


Fig. 2 Spatial variation of monitored parameters (concentration versus sampling station)

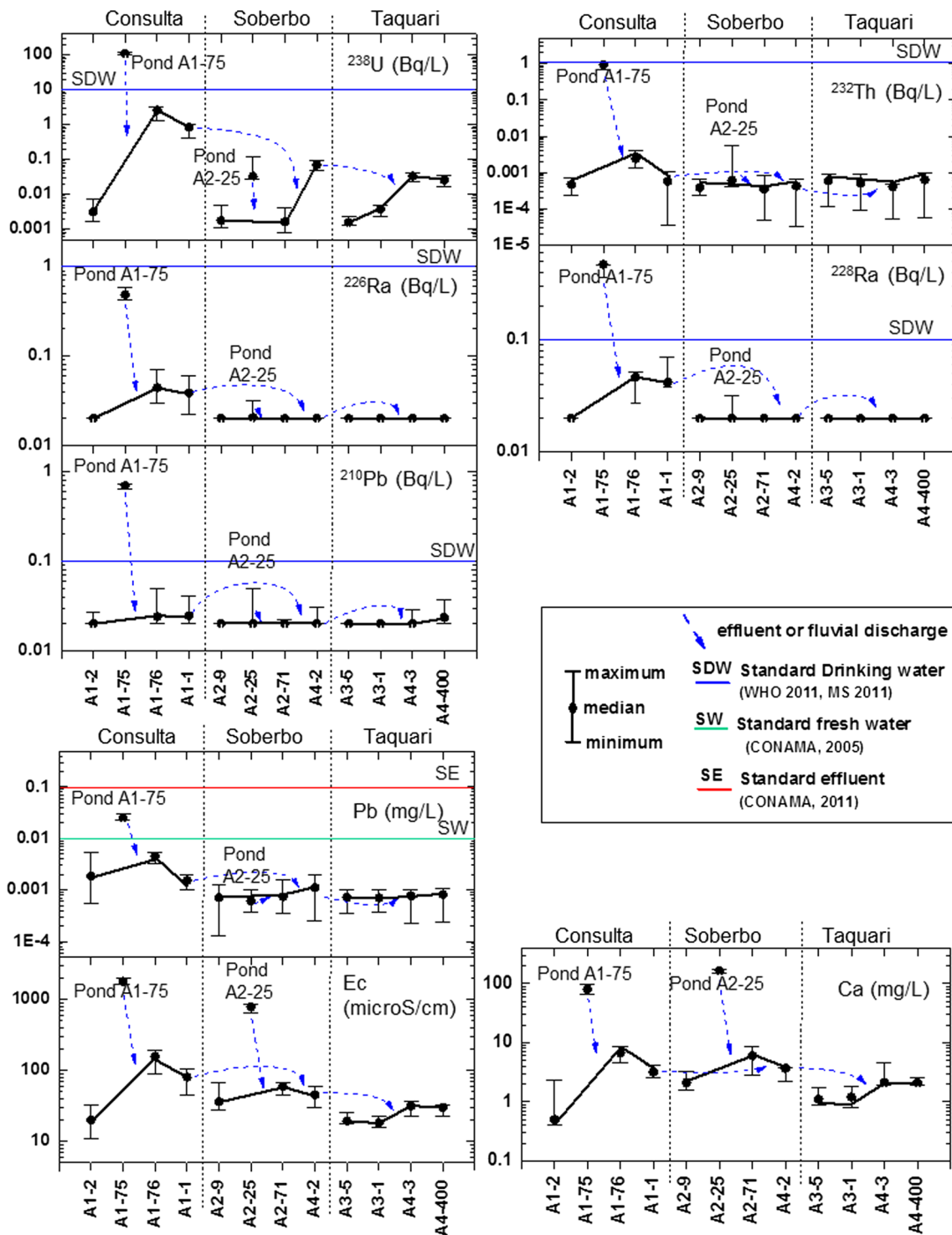
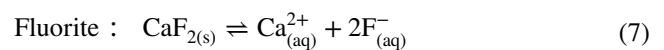
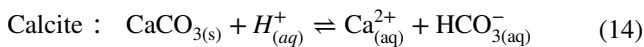
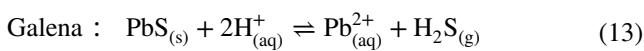
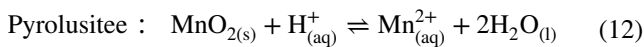
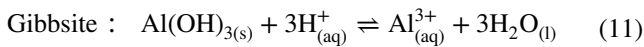
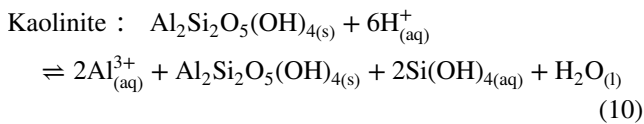
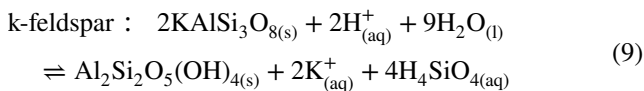
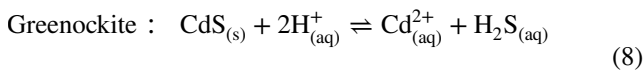


Fig. 3 Spatial variation of monitored parameters (concentration versus sampling station)

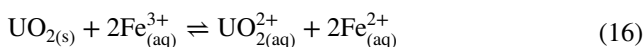
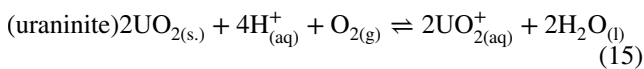
measured at the A1-75 pond is another indication of AMD influence, which greatly increases the concentration of the total dissolved solids due to the large concentrations of soluble salts produced by the reaction of sulfuric acid with minerals in the waste rock. Some mineral dissolution is probably occurring

inside the WRP#4, as described by the simplified equations from Eqs. 7 to 14 (Appelo and Postma 1999):

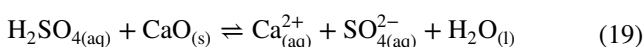
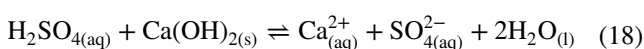
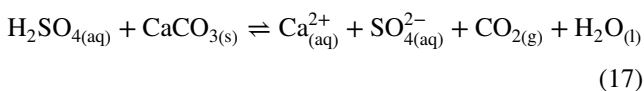




A simplified overall equation for the oxidative dissolution of uraninite is like Eq. 15 (Lottermoser 2010). According to Abdelouas (2006), the oxidation of uraninite can also be achieved by the oxidant  $\text{Fe}^{3+}$  (Eq. 16) produced in Eq. 3.



The A2-25 pond samples show relative high values of sulfate concentration and EC (Table 1). Although not as high as in the A1-75 pond, these values point out the presence of AMD. The AMD in the TD could be generated by pyrite oxidation at two places (Cipriani 2002; Golder 2012): (i) in the tailings—the pyrite might have been only partially oxidized during the chemical processing and would end up its oxidation inside the TD and (ii) in the pyrite-rich rocks used to build the dam. The A2-25 pond pH was not so acidic due to the procedures adopted to increase the pH of the waste deposited in the TD, using calcium-rich neutralization agents mainly  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{CaO}$  (Eqs. 17–19).



Compared to the furthest upstream station A2-9 (near the source of the Sobebo Creek), the samples from the A2-25 pond exhibited higher concentrations of F, U, Cd, Mo, and  $\text{Ca}^{2+}$ , and a moderate to high concentration of Al, Zn, As,  $^{238}\text{U}$ , and Mn as shown in Table 1 and Figs. 2 and 3. The presence of these high values can be explained by the nature of the ore chemical processing (OCP) at the yellow cake plant.

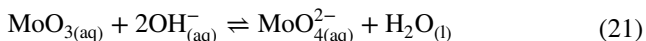
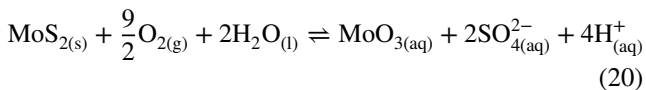
The OCP generated a large quantity of tailings that were mainly treated with calcium-rich material (limestone, lime, and calcium hydroxide) in order to neutralize their acidity (Eqs. 17–19). The treated effluents, containing significant concentrations of  $\text{CaSO}_4$  and cations (Al, Mn, Zn, U, among others) in the form of oxides, were transferred to the TD. With respect to uranium inside the TD, the chemical processing recovered on average 60% of the total U. The remaining 40% was deposited inside the TD, half of which consisted of soluble uranium (Golder 2012).

The other source of the high metal concentrations in A2-25 pond is deemed to be the sludge formed by the neutralization of the acid mine drainage with lime that was pumped to the TD from 1983 to 1998 (De Carvalho Filho 2014, 2016) and since then has been stored temporarily in the open pit. According to Gomes et al. (2012), the main crystalline phases in the sludge are ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and calcite ( $\text{CaCO}_3$ ), with minor amounts of fluorite ( $\text{CaF}_2$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ ). These authors found high contents of U, Ca,  $\text{SO}_4^{2-}$ , and Zn in the water-soluble (exchangeable) and carbonate fractions. They concluded that the sludge mineral assembly could be sources of dissolved  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , Fe, Zn, Mn, U, and Al under various environmental conditions. The solubility of these minerals was benefited by the acidity and high ionic strength of the medium (Skoog et al. 2013). In addition, the high content of Ca and bicarbonate in the neutralized wastes can greatly increase the solubility of U through the formation of highly stable and soluble ternary Ca-U- $\text{CO}_3$  complexes (Cumberland et al. 2016).

The concentration of molybdenum is higher in the A2-25 pond than in the A1-75 pond (Table 1, Figs. 2 and 3). A probable reason for this is the difference in pH values between the ponds, which affects the oxidation of jordisite ( $\text{MoS}_2$ ), the main molybdenum sulfide mineral found in the Caldas U-ore. In an oxidizing medium, jordisite generates  $\text{H}_2\text{MoO}_4$  as one of their products, an insoluble chemical species in acidic medium (pH up to 4) (Montero-Serrano et al. 2009), which is the predominant situation at the A1-75 pond (pH 4). As the pH raises, this chemical species deprotonates, making it more soluble:  $\text{HMoO}_4^-$  predominates in the range pH 4 to 5, and the quite soluble species  $\text{MoO}_4^{2-}$  predominates at pH > 5. The pH in the A2-25 pond was about 6 (Figs. 2, 3), which benefited the molybdate species.



This being the case, the high concentration of Mo in A2-25 pond could be explained by Eqs. 20 and 21. Joridite oxidation can be expressed by Eq. 20, where this mineral in the presence of oxygen and water oxidizes, forming molybdenum trioxide (MoO<sub>3</sub>). Upon contact with a less-acidic medium at the A2-25 pond, MoO<sub>3</sub> solubilizes producing molybdate ions (Eq. 21), probably the predominate species in this pond.

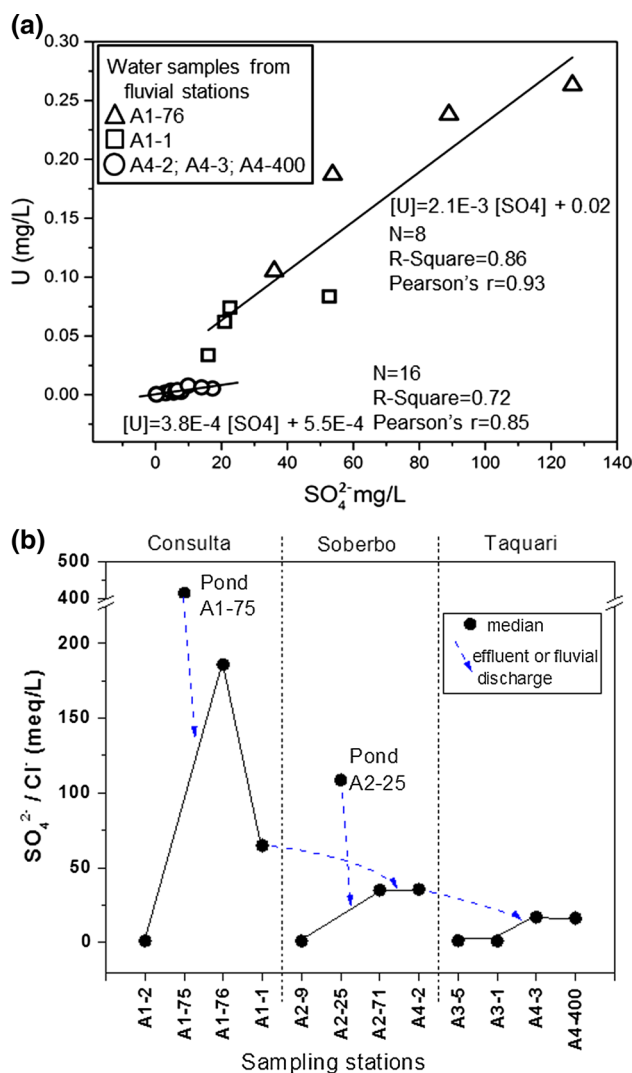


### Fluvial hydrochemistry

The values measured at station A1-2, located upstream the CUM (Figs. 2, 3), show that effluent discharges from A1-75 pond caused a significant effect on the chemical composition of water in Consulta Brook (i.e., at sampling stations A1-76 and A1-1). The discharge of mine effluents has contributed to the decrease in pH and increases in all other analyzed parameters (except Fe and Mo) that were measured at these sampling stations. Considering the results from station A2-9 on Soberbo Creek, it is observed that effluents from A2-25 pond caused an increase in the values of EC, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, as well as in Mo and Ca at station A2-71. In comparison to station A2-71, station A4-2 exhibited an increase in F<sup>-</sup>, U, Mn, Cd, Zn, As, acidity (pH), and <sup>238</sup>U probably due to the discharge from the Consulta Brook. Further downstream in the Taquari River, it is observed that in relation to stations A3-5 and A3-1, the waters from stations A4-3 and A4-400 were enriched in F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, U, Mn, Cd, Zn, As, Mo <sup>238</sup>U, and Ca, as well as in dissolved solids or EC.

These concentration increases identified in the Soberbo Creek (station A4-2) and in the Taquari River (stations A4-3 and A4-400) are mainly related to the effluent discharges from the A1-75 pond, but with contributions from the A2-25 pond effluents as indicated by certain chemical elements (e.g., Mo and Ca). Thus, it is possible to characterize the AMD migration pathway in the fluvial system at the study area, from the ponds to the most downstream station (A4-400) about 15 km away. The results have also shown high concentrations of Fe, Al, and Mn (Figs. 2, 3) in river water at places upstream of the CUM, in which geogenic conditions prevail and which are free of any contribution from the mine effluents. Iron was the parameter whose behavior best described the geogenic influence in the study area; insofar as its concentration was ubiquitously higher than those in the effluents and consistently higher than those in the stations immediately downstream the ponds.

In Fig. 4a, two groups with distinct trend lines were identified. One of them consists of samples collected at stations A1-76 and A1-1, more affected by the AMD. The other group defines a distinct U/SO<sub>4</sub> ratio and is constituted by stations (A4-2, A4-3 and A4-400) farthest from the CUM and less influenced by the AMD. However, the U/SO<sub>4</sub> ratio is not so adequate to track AMD. This is due to the ability of U to form a wide range of soluble complexes under different chemical conditions (Langmuir 1997; Bourdon et al. 2003), so that shifts in the U/SO<sub>4</sub> ratio could induce erroneous conclusions. The SO<sub>4</sub>/Cl mass ratio is likely to be more sensitive indicators of the presence or absence of AMD effects, and it is usually applied for this purpose (Chandra and Gerson 2010; Dogramaci et al. 2017). According to Dogramaci et al.



**Fig. 4** Plots showing the relationship between: **a** uranium and sulfate concentration in surface water near the mine site from selected fluvial stations; **b** sulfate and chloride concentration (meq L<sup>-1</sup>) in the ponds and in the surface water near the mine site

(2017),  $\text{SO}_4/\text{Cl}$  ratio  $> 3$  indicates that sulfide oxidation is the main source of sulfate in water.

Medians of the values  $\text{SO}_4/\text{Cl}$  calculated for the water samples from the ponds and streams in the vicinity of the CUM (Table 1) are shown in Fig. 4b. By comparing these medians, it can be observed that the stations located upstream of the CUM present the lowest values of the ratio  $\text{SO}_4/\text{Cl}$  ( $< 1.5$ ), indicating a smaller intensity of the pyrite oxidation (AMD). On the other hand, the ponds A1-75 and A2-25 present high values for that ratio, 416 and 109, respectively, which is a sound indication of the strong existence of AMD. Therefore, the graph (Fig. 4b) clearly depicts the migration of the AMD from the ponds to the downstream sampling stations.

Radionuclides from the uranium series in uranium ore should be in secular radioactive equilibrium. However, once the radionuclides are exposed to oxidizing conditions, the equilibrium may be somewhat disturbed, due to the distinct chemical behavior of each radionuclide undergoing geochemical processes (Abdelouas 2006; Carvalho et al. 2015). Figure 5a plots the pattern of  $^{226}\text{Ra}/^{238}\text{U}$  alteration versus sulfate concentration in the waters from stations A1-75 (pond), A1-76, and A1-1. It can be observed in this figure that the higher the sulfate concentration, the lower the  $^{226}\text{Ra}/^{238}\text{U}$  ratio in the water phase. Higher sulfate concentration should promote precipitation of radium sulfate ( $\text{RaSO}_4$ ), a quite insoluble compound, leading to lower  $^{226}\text{Ra}/^{238}\text{U}$  ratios. In Fig. 5b, it is seen that  $^{226}\text{Ra}/^{238}\text{U}$  actually varies with pH; the higher the AMD intensity (i.e., lower pH and higher sulfate) the larger the radioactive  $^{226}\text{Ra}/^{238}\text{U}$  disequilibrium in the water phase. This disequilibrium, previously mentioned by Fernandes and Franklin (2001), can be used to trace AMD.

## Assessment of compliance with water quality guidelines

As shown in Figs. 2 and 3, only the samples from pond A1-75 exceeded the Brazilian legal standards for effluent discharge into watercourses (CONAMA 2005, 2011) for pH, F, Mn, and Zn. Fluvial waters downstream of pond A1-75, particularly in Consulta Brook, were non-compliant with respect to fresh water quality standards (CONAMA 2005, 2011) for  $\text{F}^-$ , Cd, U, Zn, Al, Mn, Fe, and pH (Figs. 2, 3). These parameters violated their quality limits as a consequence of effluent discharges from pond A1-75 (with the exception of iron). No radionuclide concentration exceeded the activity concentration limits established by the Brazilian Ministry of Health (MS 2011) and by the World Health Organization (WHO 2011).

There was non-compliance to standard values for Al, Mn, and Fe in water samples collected at stations upstream the CUM (Figs. 2, 3), in an environment where geogenic influences should prevail. Among these three elements, the iron concentrations were those which most exceeded the water quality standards. This is relevant because it questions the validity of applying legal quality limits for these parameters in the study area. Thus, the regulators should take into account such natural high concentrations.

## Environmental isotopes

The  $\delta$  values of the stable isotopes  $^2\text{H}$  and  $^{18}\text{O}$ , measured in 12 samples from streams and ponds in the study area, are plotted in Fig. 6a, together with the Global Meteoric Waterline (GMWL) and the regional Belo Horizonte Meteoric Waterline (BHMWL) (IAEA 2015).

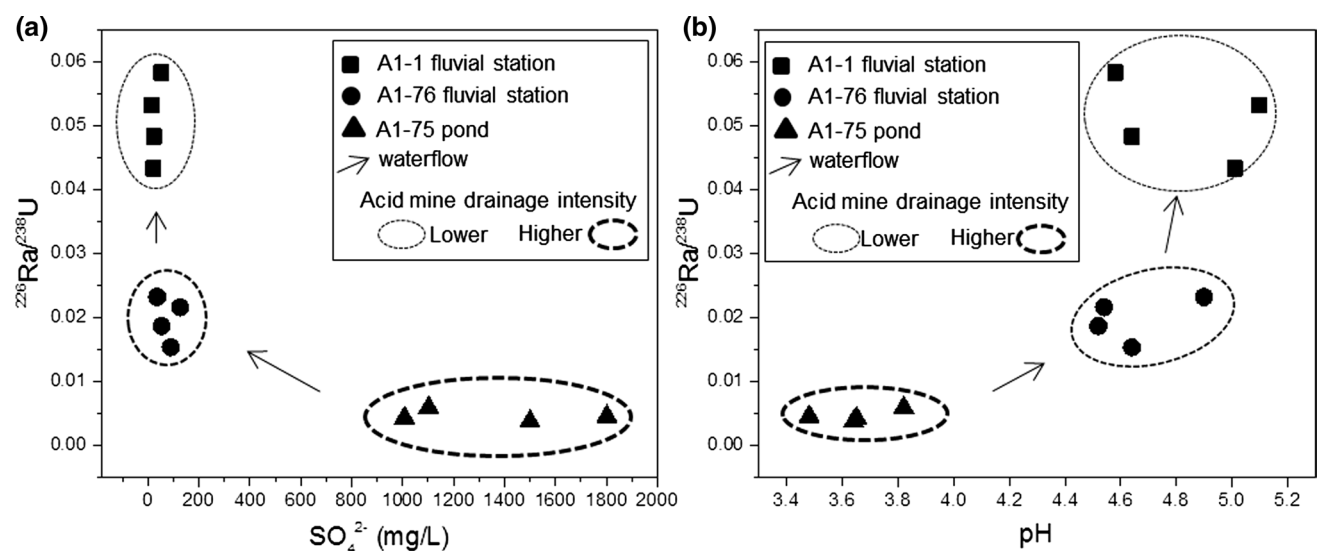


Fig. 5  $^{226}\text{Ra}/^{238}\text{U}$  versus sulfate (a) and pH (b)

Figure 6a shows that the isotopic signature of the collected samples scatters along and close to the BHMWL and above the GMWL. The isotope signature at pond A1-75 plots over the regional meteoric waterline. This is an indication that evaporation was not an important control on the water chemistry in this effluent pond. This likely reflects the short residence time for water in the pond, which is pumped continuously to the acid neutralization unit.

On the other hand, water from A2-25 pond displays a typical isotopic signature associated with evaporation, i.e., it plots below the meteoric waterline (Clark and Fritz 1997; Domenico and Schwartz 1997). As the tailings dam behaves as a lentic hydrological system, water in this

structure is exposed to a long period of evaporation before flowing into the A2-25 pond, in which further evaporation occurs. At station A1-2, the water also shows signs of having undergone some evaporation, because of the lentic conditions that also predominate there. This is consistent with the rather lentic characteristics prevailing at the upper stretch of the Consulta Brook.

The variation of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values along the watercourses plotted in Fig. 6b suggests that (1) discharges from pond A1-75 promote a depletion of  $^2\text{H}$  and  $^{18}\text{O}$  in the river water flowing past its discharge from A1-2 to A1-76; (2) the effluent from pond A2-25, which is highly enriched in  $^2\text{H}$  and  $^{18}\text{O}$ , causes an enrichment of these heavy isotopes of the waters downstream its discharge, as measured at station A2-71.

**Multivariate statistical analysis (first approach): considering fluvial and pond samples (all 48 samples)**

The dendrogram in Fig. 7a shows the application of the cluster technique, grouping all 48 samples into three groups. **Cluster 1** consists of the samples from the A1-75 pond, while the samples from the A2-25 pond constitute **Cluster 2**. **Cluster 3** includes the samples collected at the stations located in the watercourses. Thus, cluster analysis distinguished each one of the ponds from the fluvial sampling stations.

It is observed that water quality in the A2-25 pond is more similar to that in the fluvial sampling stations than to water from pond A1-75. This may be due to AMD in the A1-75 pond imposing a hydrochemical signature that is dissimilar from the other samples.

PCA/FA analysis was executed in 16 parameters for all 48 samples, and an eigenvalue greater than 1 was used as a criterion for extracting the factors required to explain data variance (Kaiser 1960). The eigenvalues ( $> 1$ ) of the three extracted factors, their loadings, their percentage of variance, and the cumulative percentage of the parameters variations are shown in Table 2. Factor loadings which had absolute values higher than 0.70 (Kaiser 1960) were considered to show a strong association and are marked in bold. The three factors explain 93.2% of the total variance, and the respective biplot graph is shown in Fig. 7b.

**Factor 1** explains 73.3% of the total variance and has strong loadings on EC, pH,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ , Al, As, Cd, Pb, Mn, U, Zn,  $^{238}\text{U}$ , and  $^{232}\text{Th}$ . These parameters are strongly related to the AMD, whose occurrence is well characterized in the A1-75 pond (Figs. 2, 3, 7b) that receives acidic effluents generated in WRP#4. Therefore, this factor was termed “**AMD-WRP#4 factor.**” Calcium in this factor had a low loading that should be reflecting only the dissolution of the Ca-rich

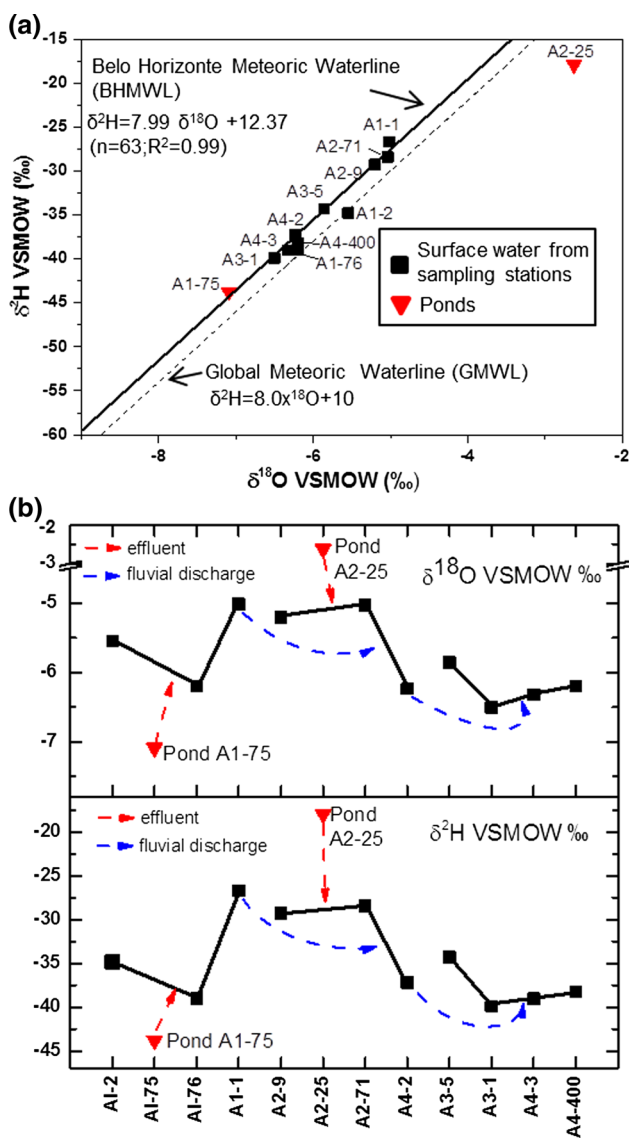
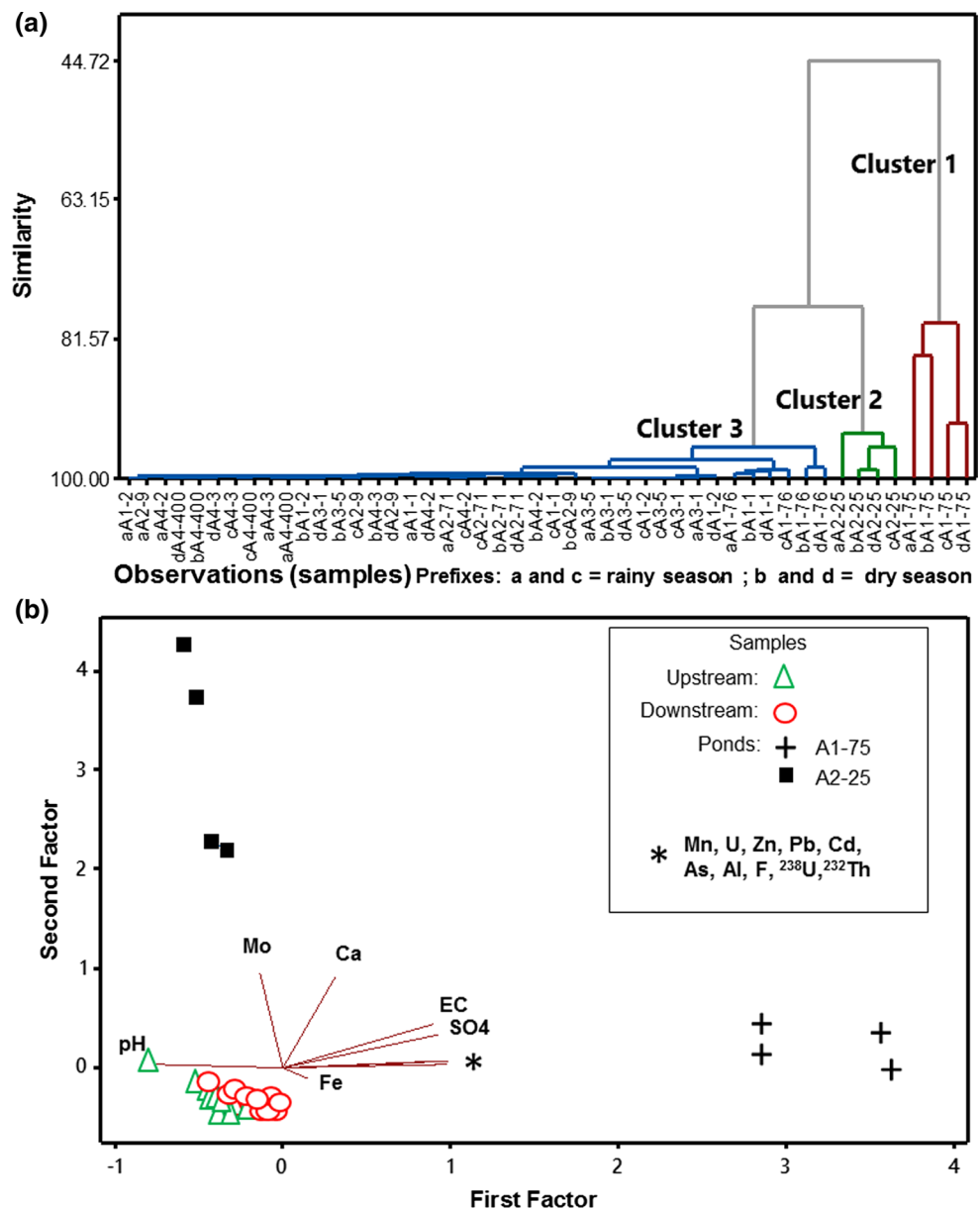


Fig. 6 a  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  water composition from fluvial and pond stations; b  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  variation along the sampling stations

**Fig. 7** Dendrogram (a) and biplot (b) for all 48 samples



minerals, as calcite and fluorite (Eqs. 7 and 14), and not the addition of calcium-rich neutralizing agents.

**Factor 2** explains 13.2% of the total variance and has strong loadings only for Ca and Mo. This is well characterized in the A2-25 pond (Figs. 2, 3, 7b). Due to the high loading for calcium, Factor 2 is interpreted as being associated with the calcium-rich neutralizing agents applied in the effluents deposited in the TD, and secondarily with the dissolution of Ca-mineral as calcite and fluorite. It also reflects Mo, whose solubility increases with the medium's alkalinity (Takeno 2005; Montero-Serrano et al. 2009). Thus, the Factor 2 was named “**Ca-Mo-TD factor.**”

**Factor 3** explains 6.7% of the total variance and has a strong loading only for Fe. As previously discussed, Fe is the analyzed parameter whose spatial distribution best reflects the geogenic influence on water quality in the study area. Thus, this factor was termed as “**Fe-geogenic factor.**” Due to the scale of Fig. 7b and to the huge reflection of Factors 1 and 2 in A1-75 and A2-25 ponds, respectively, it is not possible to identify a clear segregation between the samples from the other stations.

#### Multivariate statistical analysis (second approach): considering only fluvial samples (40 samples)

Three groups were individualized by the dendrogram shown in Fig. 8a. **Cluster 1** includes chemical parameters

**Table 2** Factor loadings of the varimax-rotated factors, eigenvalues (> 1), percentage of variance and cumulative percentage of the three extracted factors

Parameter	Factor 1	Factor 2	Factor 3
EC	<b>0.890</b>	0.444	- 0.040
pH	- <b>0.757</b>	0.036	0.004
SO <sub>4</sub> <sup>2-</sup>	<b>0.929</b>	0.332	- 0.088
F <sup>-</sup>	<b>0.845</b>	0.044	0.013
Al	<b>0.962</b>	0.075	- 0.138
As	<b>0.969</b>	0.041	- 0.085
Cd	<b>0.987</b>	0.078	- 0.107
Pb	<b>0.978</b>	0.040	- 0.136
Fe	0.146	- 0.114	- <b>0.979</b>
Mn	<b>0.992</b>	0.064	- 0.087
Mo	- 0.138	<b>0.951</b>	0.088
U	<b>0.990</b>	0.065	- 0.083
Zn	<b>0.987</b>	0.065	- 0.087
Ca	0.313	<b>0.918</b>	0.042
U-238	<b>0.990</b>	0.065	- 0.083
Th-232	<b>0.964</b>	0.078	- 0.114
Eigenvalue	11.724	2.109	1.076
% of Variance	73.3	13.2	6.7
Cumulative %	73.3	86.5	93.2

that are characteristic of AMD, such as those present at high concentrations in pond A1-75. **Cluster 2** consists of Ca and Mo, at high concentrations predominantly in the A2-25 pond. Iron, the only constituent of **Cluster 3**, has a relatively low similarity with the other groups, suggesting that it does not have a significant relation to the ponds' waters.

For eigenvalue > 1, the same three factors identified by first approach were extracted. They explain 91.4% of the total variance (Table 3; Fig. 8b): **AMD-WRP#4 factor** explains 72.6%; **Ca-Mo-TD factor** explains 11.2%; and **Fe-geogenic factor** explains 7.6%.

The biplot graph of Fig. 8b suggests that the fluvial samples can be segregated into four groups. **Groups (1)** and **(2)** are composed, respectively, of the samples collected at stations A1-76 and A1-1, located immediately downstream of the A1-75 pond in Consulta Brook. These two groups reflect the changes in water quality associated with AMD impacts (**AMD-WRP#4 factor**) in these two fluvial stations due to effluent discharges from the A1-75 pond. **Group (3)** is composed mostly of samples collected at station A2-71, located immediately downstream of the A2-25 pond, in the Soberbo Creek. This group depicts the **Ca-Mo-TD factor** influence in the waters of station A2-71 due to the A2-25 pond discharges.

**Group (4)** consists predominantly of samples collected at station A4-2, located in the Soberbo Creek and downstream the Consulta Brook mouth. These samples mainly reflect the influence of the **AMD-WRP#4 and Ca-Mo-TD factors**, as well as the samples that makeup **Group (5)** located further downstream in the Taquari River. **Group (6)** consists of almost 90% of samples collected at the stations located upstream of the CUM facilities. This group does not have any influence from the previous factors, i.e., it should be representing the geogenic conditions in the study area.

## Conclusions

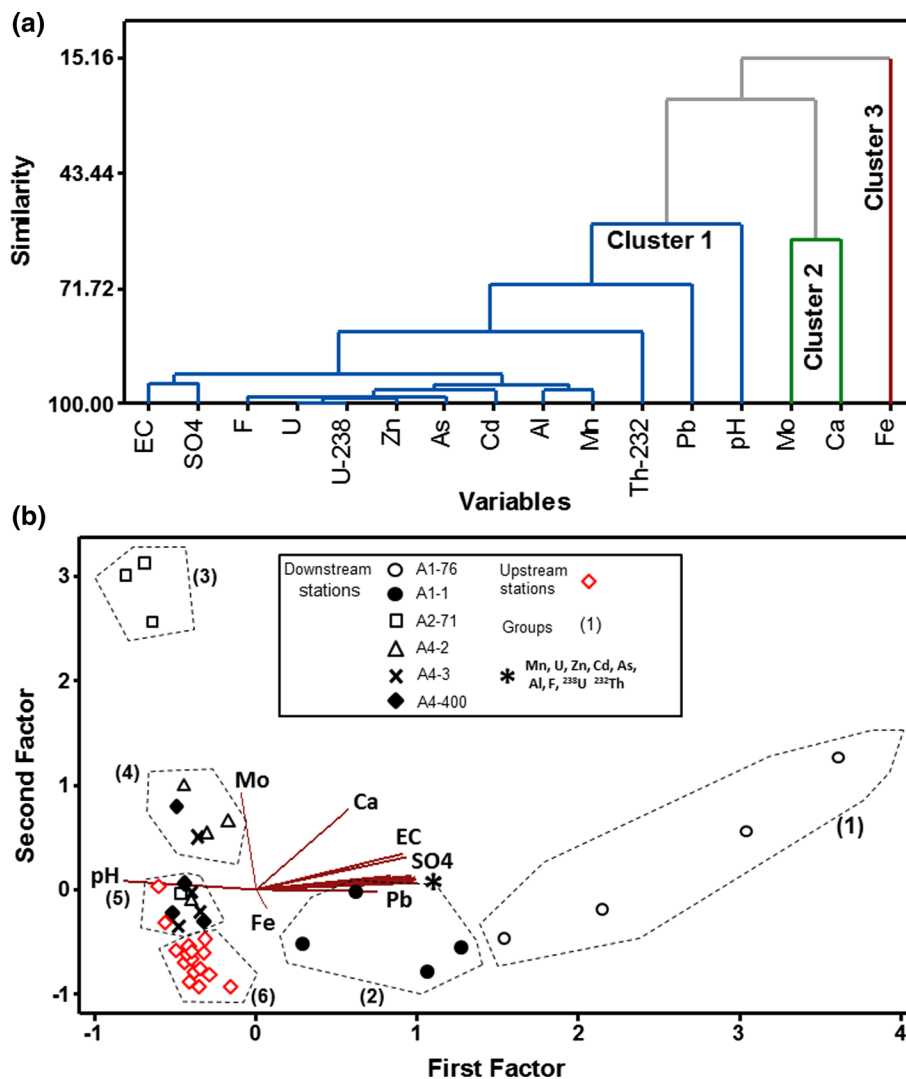
The research has shown that CUM effluents, particularly from the WRP#4 and the TD, are having significant influences in downstream water quality. This conclusion is based on the results obtained by means of all the considered techniques. In particular, the measured variations in <sup>18</sup>O and <sup>2</sup>H provide evidence for the migration of effluents from these two parts of the mine to nearby streams. The hydrochemical evaluation has shown that effluents from the WRP#4 caused in the downstream watercourses, an increase of **up to 10 times** for EC, <sup>232</sup>Th, Pb, <sup>226</sup>Ra, and <sup>228</sup>Ra; **from 10 to 100 times** for Cd, Zn, Al, Mn, Ca, and As; **from 100 to 500 times** for SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>; and **about 800 times** for U and <sup>238</sup>U. The increases caused by discharges from the tailings dam are **up to 10 times** for EC, Zn, Al, Ca, F, and Mo; and **about 50 times** for SO<sub>4</sub><sup>2-</sup>.

The changes in SO<sub>4</sub>/Cl ratio clearly depicted the AMD pathway from the ponds to downstream watercourses. It was demonstrated that the extent of disequilibrium between <sup>226</sup>Ra and <sup>238</sup>U is directly associated with the extent to which water in the area has been affected by AMD discharges and can be a natural tracer to monitoring the extent of AMD contamination in the area.

The multivariate analysis yielded a three-factor model which could be used to distinguish between mine-related and natural geogenic sources of chemical constituents in water. The **AMD-WRP#4 factor** represents the acid mine drainage generated by the WRP#4 and is associated with low pH values and high concentrations of sulfate and dissolved metals downstream. The **Ca-Mo-TD factor** depicts the chemical characteristics of the effluents from the TD. It mainly reflects the impact of the addition of neutralizing Ca-rich agents and also the Mo high concentrations. The **Fe-geogenic factor** involves only Fe and represents the natural characteristics of the study area waters.

It is strongly recommended that measures be taken to mitigate the generation of acid mine drainage as well as to

**Fig. 8** Dendrogram (a) and biplot (b) for fluvial stations samples



avoid its flow to the water bodies. It is also recommended that the neutralization process be constantly monitored and optimized in order to reduce the application of calcium-based neutralizing agents. In addition, it is suggested that procedures such as adsorption and/or precipitation be adopted in order to decrease the concentration of Ca

and Mo in the waters that pour from TD. It should be highlighted that a chance exists that the excess of calcium in the water may considerably increase the mobility of the uranium due to the formation of soluble complexes of Ca-U-CO<sub>3</sub>. The operator has already begun to implement some necessary measures.

**Table 3** Factor loadings of the varimax-rotated

Parameter	Factor 1	Factor 2	Factor 3
EC	<b>0.908</b>	0.333	-0.073
pH	- <b>0.821</b>	0.081	-0.248
SO <sub>4</sub>	<b>0.928</b>	0.312	-0.040
F	<b>0.977</b>	0.115	-0.050
Al	<b>0.960</b>	0.130	-0.163
As	<b>0.989</b>	0.058	-0.027
Cd	<b>0.976</b>	0.080	0.002
Pb	<b>0.746</b>	-0.020	-0.259
Fe	0.059	-0.177	- <b>0.926</b>
Mn	<b>0.971</b>	0.089	-0.066
Mo	-0.092	<b>0.933</b>	0.187
U	<b>0.985</b>	0.107	-0.065
Zn	<b>0.989</b>	0.091	-0.044
Ca	0.575	<b>0.767</b>	-0.006
U-238	<b>0.985</b>	0.107	-0.065
Th-232	<b>0.830</b>	0.121	-0.376
Eigenvalue	1.618	1.799	1.213
% of Variance	72.6	11.2	7.6
Cumulative %	72.6	83.8	91.4

**Acknowledgements** This work was financially supported by the Brazilian Scientific and Technological Development Council (CNPq) and by the Minas Gerais Foundation for Research Support (FAPEMIG). The authors are thankful to the Brazilian Institute for Mineral, Water, and Biodiversity Resources (INCT-Acqua), and to the Brazilian Nuclear Industries (INB) for operational and technical cooperation. We also would like to thank Mr. Nivaldo Carlos da Silva (Poços de Caldas Laboratory-LAPOC/CNEN), for radiochemistry analyses, and Mr. Massimo Gasparon (University of Queensland), for the isotopic analyses.

## References

- Abdelouas A (2006) Uranium mill tailings: geochemistry mineralogy, and environmental impact. *Elements* 2:335–341
- Abreu CB, Fleming PM, Ciminelli VST, Lopez DL, Horta PCR, Branco OEA (2011) Soil gas compositions as a tool for understanding acid mine drainage formation and air flow in a uranium waste rock pile. In: 11th International mine water association congress, Aachen. *Mine Water Managing the Challenges*, pp 247–252
- Adamu CI, Njanje T, Edet A (2014) Hydrochemical assessment of pond and stream water near abandoned barite mine sites in parts of Oban massif and Mamfe Embayment, Southeastern Nigeria. *Environ Earth Sci* 71:3793–3811. <https://doi.org/10.1007/s12665-013-2757-5>
- Appelo CAJ, Postma D (1999) *Geochemistry, groundwater and pollution*. A.A. Balkema, Rotterdam
- Bahar MM, Reza MS (2010) Hydrochemical characteristics and quality assessment of shallow groundwater in a coastal area of southwest Bangladesh. *Environ Earth Sci* 61:1065–1073
- Bourdon B, Henderson GM, Lundstrom CC, Turner SP (2003) Uranium-series geochemistry: reviews in mineralogy & geochemistry, vol 52. *Geochemical Society, Mineralogical Society of America*, Washington DC, USA
- Campos MB, Azevedo H, Nascimento MRL, Roque CV, Rodgher S (2011) Environmental assessment of water from a uranium mine (Caldas, Minas Gerais State, Brazil) in a decommissioning operation. *Environ Earth Sci* 62:857–863
- Canovas CR, Olias M, Nieto JM, Sarmiento AM, Ceron JC (2007) Hydrogeochemical characteristics of the Tinto and Odriel Rivers (SW Spain). Factors controlling metal contents. *Sci Total Environ* 373:363–382
- Carvalho FP, Oliveira JM, Malta M (2015) Natural radioactive isotopes and water quality in a uranium mining region. In: *International symposium on isotope hydrology—revisiting foundations and exploring frontiers*, 11–15 May 2015. IAEA-Water resources programs, Vienna, Austria, pp 144–147
- Chandra AP, Gerson AR (2010) The mechanisms of pyrite oxidation and leaching: a fundamental perspective. *Surf Sci Rep* 65:293–315
- Cipriani M (2002) *Mitigation of social and Environmental Impacts Caused by the Definitive Closure of Uranium Mines*, Ph.D. Thesis (in portuguese), State University of Campinas
- Clark ID, Fritz P (1997) *Environmental isotopes in hydrogeology*. CRC Press, Boca Raton
- CONAMA Conselho Nacional de Meio Ambiente (2005) Resolução nº 357, de 18 de março de 2005. Brasília
- CONAMA Conselho Nacional de Meio Ambiente (2011) Resolução nº 430, de 13 de maio de 2011. Brasília
- Cumberland SA, Douglas G, Grice K, Moreau JW (2016) Uranium mobility in organic matter-rich sediments: a review of geological and geochemical processes. *Earth Sci Rev* 159:160–185
- De Carvalho Filho CA (2014) *Quality assessment of surface waters in vicinity of the caldas uranium mining and industrial facilities, Minas Gerais (Brazil)*. (In Portuguese). Ph.D. Thesis. Nuclear Technology Development Center (Brazil)
- De Carvalho Filho CA, Moreira RM, Guimarães BF, Ferreira VVM, Auler LMLA, Palmieri HEL, Oliveira AFG, Dutra PH (2016) Hydrochemical assessment of surface water in watersheds near the Uranium Mining and Milling Facilities of Caldas. Brazil. *Environ Earth Sci* 75:187. <https://doi.org/10.1007/s12665-015-5070-7>
- Dogramaci S, McLean L, Skrzypek G (2017) Hydrochemical and stable isotope indicators of pyrite oxidation in carbonate-rich environment; the Hamersley Basin, Western Australia. *J Hydrol* 545:288–298
- Domenico PA, Schwartz FW (1997) *Physical and chemical hydrogeology*, 2nd edn. Wiley, New York
- Drever JI (1997) *The geochemistry of natural waters, surface and groundwater environments*, 3rd edn. Prentice Hall, New Jersey
- Fernandes HM, Franklin MR (2001) Assessment of acid rock drainage pollutants released at the uranium mining site of Poços de Caldas – Brazil. *J Environ Radioact* 54:5–25
- Fernandes HM, Veiga LHS, Franklin MR, Prado VCS, Taddei JF (1995) Environmental impact assessment of uranium and milling facilities: a study case at the Poços de Caldas uranium mining and milling site, Brazil. *J Geochem Explor* 52:161–173
- Fernandes HM, Franklin MR, Veiga LHS, Freitas P, Gomiero LA (1996) Management of uranium mill tailing: geochemical process and radiological risk assessment. *J Environ Radioact* 30:69–95
- Fernandes HM, Franklin MR, Veiga LHS (1998) Acid rock drainage and radiological environmental impacts: a study case of the Uranium mining and milling facilities at Poços de Caldas. *Waste Manag* 18:169–181
- Fernandes HM, Franklin MR, Gomiero MR (2008) Critical analysis of the waste management performance of two uranium production units in Brazil-part I: Poços de Caldas production centre. *J Environ Manag* 87:59–72
- Ferreira VVM, Filho CAC, Rodrigues PCH, Fleming PM, Meira-Belo LC (2012) Radiometric evaluation in a uranium mine under a decommissioning process. *Energy Environ Res* 2:13–27

- Fraenkel MO, Santos RC, Lourenço FEVL, Muniz WS (1985) Jazida de urânio no planalto de Poços de Caldas, Minas Gerais. In: Departamento Nacional da Produção Mineral DNPM. Principais Depósitos Minerais do Brasil, v. 1, Cap. 5, pp 89–103
- Franklin MR (2007) Numerical modeling of water flow and Geochemical Processes Applied to the Prediction of Acid Drainage at a Waste Rock Pile in the Uranium Mine of Poços de Caldas – MG (in Portuguese). Ph.D. Thesis, Federal University of Rio de Janeiro
- Godoy JM, Godoy ML, Carvalho ZL (1994) Development of a sequential method for the determination of U-238, U-234, Th-232, Th-230, Ra-228, Ra-226 and Pb-210 in environmental samples. *J Radioanal Nucl Chem* 182:165–169
- Golder Associates Brazil Consulting and Projects Ltd (2012) Plan for de Recovery of Degraded areas – INB UTM Caldas. Technical Report No. RT-006\_099-515-3023\_01-j
- Gomes AFS, Lopez DL, Ladeira ACQ (2012) Characterization and assessment of chemical modifications of metal-bearing sludges arising from unsuitable disposal. *J Hazard Mater* 199–200:418–425
- IAEA International Atomic Energy Agency (2015, May) GNIP-Global Network of Isotopes in Precipitation. Retrieved March 10, 2017. [http://www-naweb.iaea.org/napc/ih/IHS\\_resources\\_gnip.html](http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html)
- Kaiser HF (1960) The application of electronic computers to factor analysis. *Educ Psychol Meas* 20:141–151
- Krishna AK, Satyanarayanan M, Govil PK (2009) Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India. *J Hazard Mater* 167:366–373
- Langmuir D (1997) Aqueous environmental geochemistry. Prentice-Hall, USA
- Lapido Loureiro FEV, Dos Santos RC (1988) The intra-intrusive uranium deposits of Pocos de Caldas, Brazil. *Ore Geol Rev* 3:227–240
- Lottermoser B (2010) Mine wastes: characterization, Treatment and Environmental Impacts. Springer, Berlin, Heidelberg
- Lottermoser B (2017) Environmental indicators in metal mining. Springer, Cham
- Montero-Serrano JC, Martinez-Rodrigues M, Tribouillard N, Riboulleau A, Garbán G (2009) Comportamiento geoquímico del molibdeno y sus isótopos em el ambiente sedimentário – Um resumen bibliográfico. *Rev Biol Mar Oceanogr* 44(2):263–275
- Najar IA, Khan AB (2012) Assessment of water quality and identification of pollution sources of three lakes in Kashmir, India, using multivariate analysis. *Environ Earth Sci* 66:2367–2378. <https://doi.org/10.1007/s12665-011-1458-1>
- Obeidat MM, Awawdeh M, Al-Rub FA (2013) Multivariate statistical analysis and environmental isotopes of Amman/Wadi Sir (B2/A7) groundwater, Yarmouk River Basin, Jordan. *Hydrol Process* 27:2449–2461. <https://doi.org/10.1002/hyp.9245>
- Rebello M, da Silva EF, Rocha F (2015) Characterization of Portuguese thermo-mineral waters to be applied in peloids maturation. *Environ Earth Sci* 73:2843–2862
- Rodgher S, Azevedo H, Ferrari CR, Roque CV, Ronqui LB, Campos MB, Nascimento MRL (2013) Evaluation of surface water quality in aquatic bodies under the influence of uranium mining (MG, Brazil). *Environ Monit Assess* 185:2395–2406
- MS Ministério da Saúde (2011) Portaria N° 2914, de 12 e dezembro de 2011. Brasília
- Schorscher HD, Shea ME (1992) The regional geology of the Poços de Caldas alkaline complex: mineralogy and geochemistry of selected nepheline syenites and phonolites. *J Geochem Explor* 45:25–51
- Silva NC, Chagas EGL, Abreu CB, Dias DCS, Lopez D, Guerreiro ETZ, Alberti HLC, Braz ML, Branco O, Fleming P (2014) Radon as a natural tracer for gas transport within uranium waste rock piles. *Radiat Prot Dosimetry* 160:74–77
- Skoog DA, West DM, Holle FJ, Crouch SR (2013) Fundamentals of analytical chemistry, 9th edn. Brooks/Cole, USA
- Takeno N (2005) Atlas of Eh-pH diagrams—intercomparison of thermodynamic databases. Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST), Open File Report No. 419, Japan
- U. S. Environmental Protection Agency-USEPA (1994) Acid mine drainage prediction. Office of Solid Waste, Washington, DC
- Waber N, Schorscher HD, Peters T (1992) Hydrothermal and supergene uranium mineralization at the Osamu Utsumi mine, Poços de Caldas, Minas Gerais, Brazil. *J Geochem Explor* 45:53–112
- WHO World Health Organization (2011) Guidelines for drinking-water quality, 4th edn. WHO Library Cataloguing-in-Publication Data, Vienna
- Williams RE (1975) Waste production and disposal in mining, milling, and metallurgical industries. Miller-Freeman Publishing Company, San Francisco
- Wu ML, Wang YS (2007) Using chemometrics to evaluate anthropogenic effects in Daya Bay, China. *Estuar Coastl Shelf Sci* 72:732–742. <https://doi.org/10.1016/j.ecss.2006.11.032>
- Yu FC, Fang GH, Ru XW (2010) Eutrophication, health risk assessment and spatial analysis of water quality in Gucheng Lake, China. *Environ Earth Sci* 59:1741–1748. <https://doi.org/10.1007/s12665-009-0156-8>