TECHNICAL COMMUNICATION



A Note on the Influence of the Mine Tailings Released in the Córrego do Feijão Mine Disaster on the Water Bodies of Brumadinho, Minas Gerais, Brazil

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Abstract

The rupture of the Córrego do Feijão iron mine Tailings Dam I killed at least 260 people and had major environmental and social impacts. We analyzed the chemical compounds dissolved in the surface water and the bottom sediments of Ferro-Carvão Creek, the watercourse directly affected by the disaster, and at points upstream and downstream of its confluence with Paraobeba River, the main watercourse of the region. We also analyzed samples of the released tailings and groundwater near the area directly affected. From an environmental geochemistry standpoint, the water analyses suggest that the water quality degradation was not as catastrophic as the human and material losses and damage to biota. The groundwater samples did not present disconformities according to the Brazilian Environmental Council (CONAMA). In fact, most of the surface water samples that exceeded the maximum allowed concentrations were upstream of the affected basin. This suggests that mining industry sources other than those associated with the disaster had damaged its water quality before the event. Thus, previous knowledge must be used to evaluate the real anthropic impact in events of this nature. It can also be an excellent tool to guide remediation in situations such as in the Córrego do Feijão Iron Mine disaster.

Keywords Córrego do Feijão iron mine · Tailings dams · Environmental geochemistry · Surface and groundwater pollution

Introduction

On January 25th, 2019, Tailings Dam I ruptured at the Córrego do Feijão Iron Mine, in the city of Brumadinho, Minas Gerais State, Brazil. It was the worst disaster involving tailings dams in the country, with 260 deaths and 10 missing people, and had severe socioeconomic and environmental

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impacts (Souza et al. 2021). It released 12 million m³ of mining tailings into the Ferro-Carvão Creek and Paraopeba River, the main watercourse of the region.

After the rupture, the tailings occupied an area of about 3.2 km² and were restricted to the Ferro-Carvão creek basin, the industrial facilities, and the dam itself. The breakup was a unique event with a shallow initial rupture, followed by a series of quick and shallow slips progressing backward to the tailings. The rupture was the result of the static liquefaction of the dam materials. Possible triggers were: (a) poor drainage in the dam structure since its construction; (b) the steep dam slope due to successive heightening during the mine's lifetime; and (c) the nature and form of deposition of the tailings, which generated significant tension within the dam, culminating in its rupture (Robertson et al. 2019).

The Brumadinho dam failure happened only three years after the SAMARCO mine disaster, which was also provoked by the rupture of a tailings dam in the State of Minas Gerais, a little more than 100 km away from the Brumadinho site. The environmental, financial, and social damage of the SAMARCO disaster was comparable to the Brumadinho dam failure. In that case, about 35 million m³ of mining



residues flowed down to the sea after the Fundão tailings dam failed, leaving 19 people dead, and transforming more than 650 km of rivers, especially the Doce river, into a mudflow (Hatje et al. 2017). Two disasters of similar nature in a short time notice led to widespread public consternation, and authorities and stakeholders have been keen to prevent it from ever happening again. The Brazilian Geological Survey, mining companies, and research centers have thus been involved in systematic studies on the subject.

The 206 km² study area is part of the Paraopeba River basin and located in the municipalities of Brumadinho and Mário Campos (Fig. 1). Two sampling stations are located upstream of the Ferro-Carvão Creek mouth (CC-020 and CC-017), two downstream (CC-015 and CC-016), and the remaining six correspond to the area affected by the tailings (JM-001 to JM-006), within the limits of Ferro-Carvão Creek, a small watershed contributing to Paraopeba River (Fig. 1).

In the region, a subtropical highland climate prevails (Cfb, according to the Köppen classification – Köppen 1936), with a remarkable seasonal variation in temperature and rainfall. In winter, the average minimum temperature is

 \approx 12—13 °C. During summer, the average maximum temperatures reach \approx 27 °C. The lowest average monthly precipitation is in July (\approx 9 mm), and the highest in December (\approx 320 mm), according to a 30-year historical average (Climatempo 2020).

The Ferro-Carvão Creek is part of the Paraopeba River basin, and both are part of the São Francisco River basin. The Paraopeba River basin has an area of 12,054 km², while the Ferro-Carvão Creek sub-basin is ≈3.2 km² in size. The Ferro-Carvão Creek, from its headwaters to its confluence with the Paraopeba River, is a Class 2 watercourse, as is the Paraopeba River, according to Brazilian legislation for watercourses (COPAM 1995). Class 2 means water with a fair quality, suitable for human consumption after conventional treatment, primary contact recreation, irrigation, and fishing. The main water uses in the Paraopeba River basin downstream of the Brumadinho region are agriculture, public supply, power generation, and industry (IGAM 2019).

The study area is located in the Quadrilátero Ferrífero (Iron Quadrangle), the most mineralogically relevant province in southeastern Brazil. It is a metallogenic province (Au, Fe, Mn), where supracrustal units are composed of

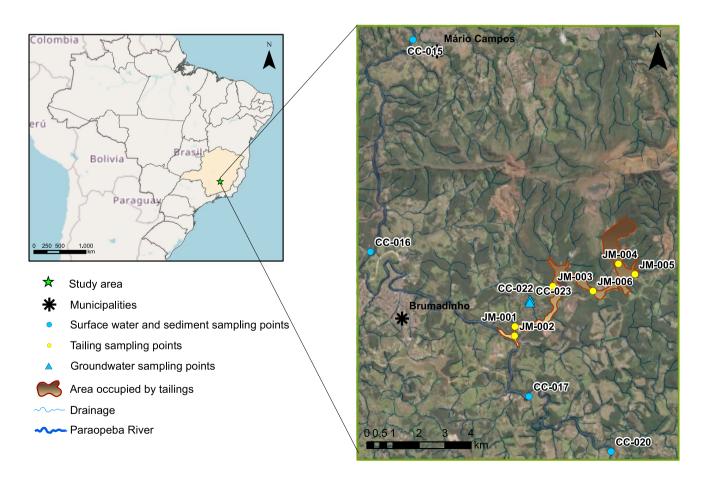


Fig. 1 Location of the study area in Minas Gerais State (MG), Brazil, with the delimitation of the area occupied by the tailings (brown area) and the sampling points



Archean greenstone and overlying Neoarchean—Paleoproterozoic sedimentary rocks, and border domes of Archean gneisses and granites. The main geological units are the granite-gneissic complex (Belo Horizonte Complex and Bonfim Complex – including the Sousa Noschese gneiss), ancient basement rocks; and the Minas Supergroup (supracrustal metamorphic rocks with sedimentary origin), in particular the Itabira Group, which includes the Cauê Formation, the host rock for the iron ore in the region, the itabirite (Farina et al. 2016). The Córrego do Feijão Iron Mine is an open-pit mine, and the ore is composed of brittle and compact hematite with subordinate siliceous itabirite rocks (Gomes 2009). Built with upstream elevation, tailings dam I had a crest height of 86 m and 720 m in length (VALE 2019). Originally occupying an area of 249,500 m² and a volume of 11,700,000 m² (Girodo 2005), it was mainly constituted of hematite, martite, goethite, magnetite (Fe-oxides and hydroxides), and quartz (Gomes 2009).

The area has two main aquifer units, one with a secondary porosity and permeability provided by discontinuities (the fractured central-south System of the granite-gneissic complex) and one with a dominant primary porosity (the Cauê Aquifer, composed of the granular materials of the Cauê Formation). Despite containing a high-degree metamorphic unit, the Cauê formation is part of a granular porous system since its interstitial porosity dominates rather than fractures (Cardoso et al. 2012).

There are quite a few studies in the area regarding the environmental consequences of the dam failure and subsequent disaster. In the Brumadinho collapse, some authors focused on the geotechnical causes and effects of the dam rupture. Rotta et al. (2020) used a satellite-driven soil moisture index, and InSAR radar products to assess pre-disaster scenarios and the direct causes of the tailings dam collapse. Vergilio et al. (2020) evaluated the concentrations of metals and the biological effects on water and sediments of the Paraopeba River after the dam rupture. These authors concluded that the tailings were formed by fine particulate material with large amounts of Fe, Al, Mn, Ti, rare earth metals, and toxic metals. In the water, the levels of Fe, Al, Mn, Zn, Cu, Pb, Cd, and U were higher than the maximum values allowed by Brazilian legislation. Cr, Ni, Cu, and Cd sediment concentrations were higher than the established sediment quality guidelines. Teramoto et al. (2021) addressed the possible effects of metal contamination caused by the disaster, with the speciation of metals in the river water and desorption of metals from sediments to support a risk assessment. They concluded that the labile concentrations of metals were low based on the respective total and dissolved concentrations, with relatively higher concentrations of Fe and Mn indicating a possible association with the mine tailings. They also showed that the total metal concentrations in the rainy season were higher than in the dry season and emphasized the centuries-old mining activities in the area, and the consequent high background levels of metals. Souza et al. (2021) evaluated the potential genotoxic effects in water and sediment samples coming from affected streams five days after the rupture. They reported that water samples collected at the sites closest to the dam caused more genotoxic effects, due to the higher bioavailability of metals, in comparison to the sediments. However, the authors observed this genotoxicity in sites not yet reached by the tailings, indicating previous contamination by sewage, agriculture, and mining waste. Few other studies have focused on the environmental and geochemical consequences of the Brumadinho disaster, and even fewer on its hydrogeological effects.

The present work aims to evaluate the interaction of the tailings with the surface water and groundwater of the Brumadinho region, from an environmental and hydrogeochemical standpoint. Additional objectives comprise:

- obtaining local geochemical background values for comparative purposes;
- emphasizing the importance of previous knowledge of the water, sediment, and soil chemical compositions in the Brazilian territory (background values), an aspect frequently neglected in the country literature (vital for the management of these accidents and prevention and remediation of problems caused by anthropic or natural agents);
- simplified preliminary analysis of the water and hydrogeological characteristics of the Ferro-Carvão Creek basin.

Methods

The work presents data from two field surveys representing the wet (Feb/2019) and dry seasons (Jul/2019) in the study area. Sediment (4 samples) and tailings (6 samples) sampling occurred in Feb/2019, and surface water samples were collected in both surveys (5 samples each). Two groundwater samples obtained near the collapsed dam in Feb/2019 complemented the field work. The sample locations are shown in Fig. 1.

The surface water samples were collected through disposable syringes, filtered with a 0.45 µm nitrocellulose syringe filter, and packed in two 50 mL polyethylene centrifuge tubes, one for cations and the other for anions. To preserve soluble cations in the samples, 2 mL of HNO3 1:1 v/v were added in the cation analysis tube. The water samples were kept refrigerated until the moment of analysis. Additionally, four physical–chemical parameters were measured with an OAKTON PCD650 multi-probe device: pH, dissolved oxygen, electrical conductivity, and temperature. Groundwater samples were collected in two COPASA (Minas Gerais sanitation company) monitoring wells and



followed the same procedures. The chemical analyses for cations and anions were performed by ICP-OES (inductively coupled plasma optical emission spectrometry) model 7300 from Perkin Elmer and ion chromatography model ICS 5000 from Thermo, respectively, at the Laboratory of Mineral Analysis (LAMIN) of the SGB/CPRM branches in Rio de Janeiro and Manaus, with the exception of mercury, which was analysed with an DMA-80 mercury analyzer Milestone model, at LAMIN/Manaus. The alkalinity was measured by the potentiometric method.

Samples of river bottom sediments were collected in a composite form (in more than one place around the water collection point) with a stainless-steel drag sampler or with plastic spoons and bowls. The samples were packed in plastic bags, subsequently sealed, and identified. The tailings samples of the Ferro-Carvão Creek basin were collected at six different points inside the affected area with auger drilling. In the present work, "tailings" is a term used to represent the materials resulting from the rupture of the dam. The original tailings is the material left over from ore processing and stored in the dam before the rupture, and the residues analyzed in this work are quite heterogeneous, due to the mixture with the different materials that were present in the mudslide path. We collected about 1 to 2 kg of the tailings material (the first 20 cm of tailings were discarded due to the intense movement of people in the rescue operations). The solid samples were prepared and analyzed in the SGS-Geosol laboratory (Vespasiano, MG-Brazil). The samples were dried at room temperature and sieved to 250 mesh. The chemical analyses of major and trace elements were performed through acid digestion with hot aqua regia (HCl:HNO3 3:1 v/v). Iron and manganese in tailings had to pass through lithium tetraborate fusion due to their high concentration, instead of acid digestion with hot aqua regia. The analytical techniques used were ICP-MS (mass spectrometry with inductively coupled plasma) for the aqua regia procedure and XRF (x-ray fluorescence) for the fusion procedure. To create the figures, graphs, and tables, we used ArcGis 10.6 and Excel, respectively. The principal component analysis (PCA) was done using Statistica 10.

Results

Material Resulting from the Rupture (Tailings)

The six samples collected from the material deposited in the Ferro-Carvão Creek basin were analyzed, and the results are presented in supplemental Table S-1. Of the 56 elements analyzed, seven were not detected (Ag, Au, B, Na, Re, Se, and Ta), and two exceeded the ICP-MS maximum limit of quantification (Fe and Mn). Therefore, two samples were

analyzed by x-ray fluorescence (XRF) to investigate Fe and Mn oxides.

River Bottom Sediment

The analytical results for the river bottom sediment sampling stations (CC-020, CC-017, CC-016, and CC-015) of the Paraopeba River, obtained in the first field campaign (Feb/2019), are shown in supplemental Table S-2. Of the 56 elements analyzed, five (Au, B, Na, Re, and Se) were undetected in the Feb/2019 samples, and Fe and Mn exceeded the maximum limit of quantification for the ICP-MS in two samples downstream of the Ferro-Carvão Creek (CC-015 and CC-016).

Surface Water

Tables 1 and 2 show the analytical results of surface water samples from the two field surveys (February and July 2019. Of the 35 elements analyzed, 16 (As, B, Be, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, Se, Sn, Ti, and Zn) were undetected in the samples from February/2019. The samples from July/2019 were analyzed for 11 elements (Al, Ba, Ca, Fe, K, Mg, Mn, Na, Si, Sr, and Zn), and all were above the methods' detection limit in all samples.

Regarding the physical-chemical parameters, Tables 1 and 2 show the results measured in loco from the samples of February and July 2019. The pH was generally neutral to slightly acidic. The electrical conductivity in the samples taken upstream and downstream of the Ferro-Carvão Creek increased from wet to dry season, whilst in the Ferro-Carvão Creek, it decreased from February to July 2019. The dissolved oxygen values, measured in February 2019, show an oxidizing environment.

Groundwater

Table 3 summarizes the results obtained for the chemical and physical—chemical analysis of groundwater from the Parque das Cachoeiras wells within the Ferro-Carvão Creek basin. No values exceeded the maximum allowed concentrations (MACs) specified by CONAMA Resolution N° 396 (CONAMA 2008) and few elements were effectively detected (Al, Ba, Li, Zn, Ca, Na, Mg, K).

The groundwater balance followed the Thornthwaite and Mather (1955) method to characterize the water regime of the Ferro-Carvão Creek basin. It comprehended the period between 2015 to 2019. We used the Rolim & Sentelhas (1999) spreadsheet with historical data from the Brazilian Meteorology & Climate Institute—INMET at the Ibirité Meteorological Station − Rola Moça (≈14 km from



Table 1 Analytical results of surface water of Field Survey 1 (Feb/2019). Data source: Geological Survey of Brazil (CPRM 2019a)

	CC-A-020	CC-A-017	JM-A-001	CC-A-016	CC-A-015	CONAMA Resolution N° 357—Class 2
Al (mg/L)	0.1408 ^a	0.1792	ND	0.0774	0.0832	0.1
As (mg/L)	ND^2	ND	ND	ND	ND	0.01
B (mg/L)	$<$ L Q^b	<lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td>0.5</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td><lq< td=""><td>0.5</td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td>0.5</td></lq<></td></lq<>	<lq< td=""><td>0.5</td></lq<>	0.5
Ba (mg/L)	0.0198	0.0219	<lq< td=""><td><lq< td=""><td><lq< td=""><td>0.7</td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td>0.7</td></lq<></td></lq<>	<lq< td=""><td>0.7</td></lq<>	0.7
Be (mg/L)	ND	ND	ND	ND	ND	0.04
Ca(mg/L)	4.2265	3.9164	11.167	3.0054	2.9499	
Cd (mg/L)	ND	ND	ND	ND	ND	0.001
Co (mg/L)	ND	ND	ND	ND	ND	0.05
Cr (mg/L)	ND	ND	ND	<lq< td=""><td><lq< td=""><td>0.05</td></lq<></td></lq<>	<lq< td=""><td>0.05</td></lq<>	0.05
Cu (mg/L)	<lq< td=""><td><lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td>0.009</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td>0.009</td></lq<></td></lq<></td></lq<>	ND	<lq< td=""><td><lq< td=""><td>0.009</td></lq<></td></lq<>	<lq< td=""><td>0.009</td></lq<>	0.009
Fe (mg/L)	0.4234	0.4528	<lq< td=""><td>0.1953</td><td>0.2151</td><td>0.3</td></lq<>	0.1953	0.2151	0.3
Hg (mg/kg) filtrate	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005	
Hg (mg/kg) raw	< 0.0005	< 0.0005	0.0014	< 0.0005	< 0.0005	0.0002
K (mg/L)	2.3204	2.323	2.2328	2.0451	1.9824	
Li (mg/L)	<lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td>2.5</td></lq<></td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td>2.5</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td><lq< td=""><td>2.5</td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td>2.5</td></lq<></td></lq<>	<lq< td=""><td>2.5</td></lq<>	2.5
Mg(mg/L)	1.4752	1.4903	3.7098	1.0851	1.0581	
Mn (mg/L)	0.0231	0.0558	0.4166	0.0802	0.0354	0.1
Mo (mg/L)	ND	ND	ND	ND	ND	
Na (mg/L)	4.7881	4.727	1.7625	3.6383	3.4657	
Ni (mg/L)	<lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td>0.025</td></lq<></td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td><lq< td=""><td><lq< td=""><td>0.025</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td><lq< td=""><td>0.025</td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td>0.025</td></lq<></td></lq<>	<lq< td=""><td>0.025</td></lq<>	0.025
Pb (mg/L)	<lq< td=""><td><lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td>0.01</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td>0.01</td></lq<></td></lq<></td></lq<>	ND	<lq< td=""><td><lq< td=""><td>0.01</td></lq<></td></lq<>	<lq< td=""><td>0.01</td></lq<>	0.01
Sb (mg/L)	ND	ND	<lq< td=""><td>ND</td><td>ND</td><td>0.005</td></lq<>	ND	ND	0.005
Se (mg/L)	ND	ND	ND	<lq< td=""><td>ND</td><td>0.01</td></lq<>	ND	0.01
Si (mg/L)	5.492	5.648	1.252	5.062	5.02	
Sn (mg/L)	<lq< td=""><td><lq< td=""><td>ND</td><td>ND</td><td><lq< td=""><td></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>ND</td><td>ND</td><td><lq< td=""><td></td></lq<></td></lq<>	ND	ND	<lq< td=""><td></td></lq<>	
Sr (mg/L)	0.0452	0.0433	0.0387	0.0312	0.0314	
Ti (mg/L)	<lq< td=""><td><lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td></td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td></td></lq<></td></lq<></td></lq<>	ND	<lq< td=""><td><lq< td=""><td></td></lq<></td></lq<>	<lq< td=""><td></td></lq<>	
V (mg/L)	<lq< td=""><td><lq< td=""><td>0.005</td><td><lq< td=""><td><lq< td=""><td>0.1</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>0.005</td><td><lq< td=""><td><lq< td=""><td>0.1</td></lq<></td></lq<></td></lq<>	0.005	<lq< td=""><td><lq< td=""><td>0.1</td></lq<></td></lq<>	<lq< td=""><td>0.1</td></lq<>	0.1
Zn (mg/L)	<lq< td=""><td><lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td>0.18</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>ND</td><td><lq< td=""><td><lq< td=""><td>0.18</td></lq<></td></lq<></td></lq<>	ND	<lq< td=""><td><lq< td=""><td>0.18</td></lq<></td></lq<>	<lq< td=""><td>0.18</td></lq<>	0.18
F- (mg/L)	0.0989	0.0874	<lq< td=""><td>0.0645</td><td>0.0613</td><td>1.4</td></lq<>	0.0645	0.0613	1.4
Cl- (mg/L)	2.8761	2.5922	1.4551	2.1827	2.0724	250
NO2- (mg/L)	0.0714	0.0336	0.0972	<lq< td=""><td><lq< td=""><td>1</td></lq<></td></lq<>	<lq< td=""><td>1</td></lq<>	1
Br- (mg/L)	0.0275	0.029	0.1076	0.0249	0.0222	
NO3- (mg/L)	2.6918	2.6853	0.9654	1.8353	2.0221	10
SO42- (mg/L)	4.0827	3.8602	ND	3.4041	2.9637	250
PO43- (mg/L)	0.0273	0.0243	0.0923	0.6409	ND	
рН	7.02	7.46	6.5	6.9	6.87	6 a 9
Electrical Conductivity (μS/cm)	75.19	75.7	140.4	58.3	59.1	
Dissolved Oxygen (mg/L)	10.21	10.26	8.06	9.15	9.73	>5
Temperature (°C)	23.1	22.8	27.3	26.9	25	

ND not detected



^aValues in red: analytical results above the maximum value allowed by CONAMA Resolution N° 357 for Class 2 rivers

^b < LQ = Bellow quantification limit

 Table 2
 Analytical results of surface water of the Field Survey 2 (July/2019)

	CC-A-020	CC-A-017	JM-A-001	CC-A-016	CC-A-015	CONAMA Resolution N° 357—Class 2
Al (mg/L)	0.0704	0.0504	0.0427	0.0402	0.0412	0.1
As (mg/L)	NA^2	NA	NA	NA	NA	0.01
B (mg/L)	NA	NA	NA	NA	NA	0.5
Ba (mg/L)	0.0331	0.0358	< 0.010	0.0327	0.0526	0.7
Be (mg/L)	NA	NA	NA	NA	NA	0.04
Ca(mg/L)	16.475	17.0625	23.8176	16.3617	16.8052	
Cd (mg/L)	NA	NA	NA	NA	NA	0.001
Co (mg/L)	NA	NA	NA	NA	NA	0.05
Cr (mg/L)	NA	NA	NA	NA	NA	0.05
Cu (mg/L)	NA	NA	NA	NA	NA	0.009
Fe (mg/L)	0.3317^{a}	0.1718	0.0382	0.1005	0.1492	0.3
Hg (mg/kg) filtrate	NA	NA	NA	NA	NA	
Hg (mg/kg) raw	NA	NA	NA	NA	NA	0.0002
K (mg/L)	1.9958	1.9885	1.9653	1.9887	2.0625	
Li (mg/L)	NA	NA	NA	NA	NA	2.5
Mg(mg/L)	2.899	2.98	3.2005	2.9112	2.9972	
Mn (mg/L)	0.0154	0.0343	0.3628	0.0632	0.0687	0.1
Mo (mg/L)	NA	NA	NA	NA	NA	
Na (mg/L)	4.7881	4.727	1.7625	3.6383	3.4657	
Ni (mg/L)	NA	NA	NA	NA	NA	0.025
Pb (mg/L)	NA	NA	NA	NA	NA	0.01
Sb (mg/L)	NA	NA	NA	NA	NA	0.005
Se (mg/L)	NA	NA	NA	NA	NA	0.01
Si (mg/L)	12.0542	11.9878	7.9095	11.9103	10.9878	
Sn (mg/L)	NA	NA	NA	NA	NA	
Sr (mg/L)	0.0692	0.0722	0.0442	0.0694	0.0703	
Ti (mg/L)	NA	NA	NA	NA	NA	
V (mg/L)	NA	NA	NA	NA	NA	0.1
Zn (mg/L)	0.0748	0.0638	0.0665	0.0469	0.5272	0.18
F- (mg/L)	0.13	0.14	0.06	0.13	0.16	1.4
Cl- (mg/L)	5.04	5.53	1.45	5.42	6.37	250
NO2- (mg/L)	0.03	0.02	0.25	0.03	0.05	1
Br- (mg/L)	0.03	0.03	0.06	0.04	0.04	
NO3- (mg/L)	6.26	6.2	2.92	6.02	6.47	10
SO42- (mg/L)	6.4	8.11	9.89	8.19	8.55	250
PO43- (mg/L)	$<$ L Q^b	0.22	<lq< td=""><td><lq< td=""><td><lq< td=""><td></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td></td></lq<></td></lq<>	<lq< td=""><td></td></lq<>	
pH	7.2	7.12	6.58	6.94	7.39	6 a 9
Electrical Conductivity (µS/cm)	86.8	92.2	79.65	91.4	98.99	
Dissolved Oxygen (mg/L)	NA	NA	NA	NA	NA	>5
Temperature (°C)	16.4	17.8	25.7	19.5	20	

Data source: Geological Survey of Brazil (CPRM 2019a)

NA not analysed



^aValues in red: analytical results above the maximum value allowed by CONAMA Resolution N° 357 for Class 2 rivers

^b < LQ Lower than quantification limits

Table 3 Analytical results of groundwater collected during Field Survey 2 (Jul/2019)

	CC-022	CC-023	CONAMA Resolution N 396 (Human Consump- tion)
Al (mg/L)	0.0125	0.0101	0.2
As (mg/L)	<lq< td=""><td><lq< td=""><td>0.01</td></lq<></td></lq<>	<lq< td=""><td>0.01</td></lq<>	0.01
B (mg/L)	<lq< td=""><td><lq< td=""><td>0.5</td></lq<></td></lq<>	<lq< td=""><td>0.5</td></lq<>	0.5
Ba (mg/L)	0.0358	0.0575	0.7
Be (mg/L)	<lq< td=""><td><lq< td=""><td>0.004</td></lq<></td></lq<>	<lq< td=""><td>0.004</td></lq<>	0.004
Co (mg/L)	<lq< td=""><td><lq< td=""><td>_</td></lq<></td></lq<>	<lq< td=""><td>_</td></lq<>	_
Cd (mg/L)	<lq< td=""><td><lq< td=""><td>0.005</td></lq<></td></lq<>	<lq< td=""><td>0.005</td></lq<>	0.005
Cr (mg/L)	<lq< td=""><td><lq< td=""><td>0.05</td></lq<></td></lq<>	<lq< td=""><td>0.05</td></lq<>	0.05
Cu (mg/L)	<lq< td=""><td><lq< td=""><td>2</td></lq<></td></lq<>	<lq< td=""><td>2</td></lq<>	2
Fe (mg/L)	<lq< td=""><td><lq< td=""><td>0.3</td></lq<></td></lq<>	<lq< td=""><td>0.3</td></lq<>	0.3
K (mg/L)	1.7205	2.5488	_
Li (mg/L)	<lq< td=""><td>0.0061</td><td>2.5 (irrigation)</td></lq<>	0.0061	2.5 (irrigation)
Mg (mg/L)	0.5619	0.9288	_
Mn (mg/L)	<lq< td=""><td><lq< td=""><td>0.1</td></lq<></td></lq<>	<lq< td=""><td>0.1</td></lq<>	0.1
Mo (mg/L)	<lq< td=""><td><lq< td=""><td>0.07</td></lq<></td></lq<>	<lq< td=""><td>0.07</td></lq<>	0.07
Na (mg/L)	4.0959	5.4135	200
Ni (mg/L)	<lq< td=""><td><lq< td=""><td>0.02</td></lq<></td></lq<>	<lq< td=""><td>0.02</td></lq<>	0.02
Pb (mg/L)	<lq< td=""><td><lq< td=""><td>0.01</td></lq<></td></lq<>	<lq< td=""><td>0.01</td></lq<>	0.01
Sb (mg/L)	<lq< td=""><td><lq< td=""><td>0.005</td></lq<></td></lq<>	<lq< td=""><td>0.005</td></lq<>	0.005
Se (mg/L)	<lq< td=""><td><lq< td=""><td>0.01</td></lq<></td></lq<>	<lq< td=""><td>0.01</td></lq<>	0.01
Sn (mg/L)	<lq< td=""><td><lq< td=""><td>_</td></lq<></td></lq<>	<lq< td=""><td>_</td></lq<>	_
Si (mg/L)	12.6234	15.7882	_
Sr (mg/L)	0.0148	0.0308	-
Ti (mg/L)	<lq< td=""><td><lq< td=""><td>_</td></lq<></td></lq<>	<lq< td=""><td>_</td></lq<>	_
V (mg/L)	<lq< td=""><td><lq< td=""><td>0.05</td></lq<></td></lq<>	<lq< td=""><td>0.05</td></lq<>	0.05
Zn (mg/L)	0.2593	0.2654	50
F- (mg/L)	0.21	0.12	1.5
Cl- (mg/L)	0.98	0.79	250
NO2- (mg/L)	0.04	0.04	1
Br- (mg/L)	0.03	0.02	-
NO3- (mg/L)	3.94	3.66	10
SO42- (mg/L)	0.14	0.08	250
PO43- (mg/L)	<lq< td=""><td><lq< td=""><td>-</td></lq<></td></lq<>	<lq< td=""><td>-</td></lq<>	-
$CO_3^=$ (mg/L)	0	0	-
HCO_3^- (mg/L)	14.16	0	_
pH	6.4	6	_
Electrical Conductivity (μS/cm)	37.25	49.17	-

< LQ Lower than quantification limits

dam I) (INMET 2019). The soil parameters were based on the values suggested on the SISDAGRO website, the INMET Agricultural Decision Support System, considering that most of the basin soils are cambisols (CPRM 2010).

From the water budget values obtained in the balance (Fig. 2), we estimated the contribution from aquifers to the river flow. By multiplying the sum of the annual surplus by the basin area, the result is a flow rate in L/s.

The average flow rate calculated in the Ferro-Carvão Creek basin, based on annual surpluses and the basin area, gave an average value of 630 L/s, compatible with a value of 600 L/s obtained through the regionalization of the flow by the Geological Survey of Brazil hydrology team (CPRM 2019b).

Discussion

The elements Cd, Cu, Fe, Ge, Hg, Mn, P, Sr, U, W, and Zr, were found around 2 to 4 times higher concentrations in the tailings and sediments of the stations downstream of the confluence of the Ferro-Carvão Creek with the Paraopeba River (JM-Average, CC-016, and CC-015). Upstream stations (CC-020 and CC-017) of Paraopeba River have significantly lower concentrations. It could indicate that these elements have a stronger association with the tailings and signalize their influence in other means of sampling. Laureano et al. (2022) observed that the mineralogy of the tailings (after rupture) is composed of associations of hematite, hematite (high concentration) and kaolinite + hematite, which is reasonable due to the original composition and the nature of the mining.

From the Brazilian Environmental Legislation, 13 (6.02%) sediment/tailings analyses were above the maximum allowed values (MAVs) by CONAMA Resolution N° 454 (CONAMA 2012) for As (12–18 mg/kg, Cr (42–94 mg/kg), Ni (18.93–7.9 mg/kg), Hg (0.17 mg/kg), and Pb (37.6 mg/kg).

Arsenic was present in all of the sediment samples in similar amounts, and so it is difficult to confirm with our data if there is a close relationship with the tailings. These high levels may have other origins, perhaps natural or linked to previous gold mining, a centuries-old activity in the region (GONÇALVES et al. 2006; VICQ et al. 2015). The same reasoning applies to nickel. Chromium had much higher values in the stations upstream of the event. Laureano et al. (2002) point out that the presence of these metals and other potentially toxic elements (Fe, Mn, As, Cr, and Ni) was described before the tailings rupture in the river sediments of the Paraopeba basin and could have a partially natural contribution. Mercury and lead were detected in only one sample in the lower downstream station, just on the limit of CONAMA Resolution N° 454 – level 1 (CONAMA 2012).

The results of surface water samples for the February/2019 campaign (Table 1) showed only six analyses (3.33%) with values above the MAC established by CON-AMA Resolution N° 357 for surface waters of Class 2



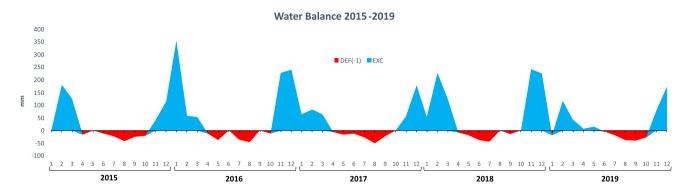


Fig. 2 Hydrograph obtained from the water balance representing the period of water surplus and water deficit in the Ferro-Carvão Creek basin. Blue portions are periods of recharge to aquifer

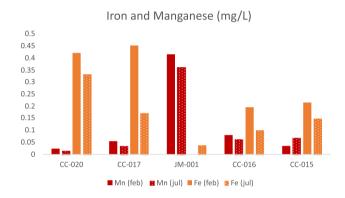


Fig. 3 Iron (Fe) and Manganese (Mn) concentrations in surface water samples taken in February and July 2019 at the sampling points

rivers (CONAMA 2005). Four out of the six samples were collected upstream of the event location, so they were not influenced by the tailings. The other two analyses that exceeded the MAC were from the Ferro-Carvão Creek itself (JM-001). In the results of July/2019 (Table 2), only three analyses (5.45%) exceeded the MACs (CONAMA 2005). In all of the performed analyses, except for mercury, the elements are in the dissolved form since the water sample was filtered in the field.

Among the elements highlighted as possible indicators of the influence of tailings, only Fe, Mn, Hg, and Sr showed detectable results in the surface water. Although strontium is in the list of the characteristic elements of iron mining tailings, it does not present significant concentrations in the samples of the area. Mercury was not detected in the filtered sample, i.e. it was not dissolved in the water. Cadmium and copper were not detected in the February 2019 sample and were not analyzed in the July 2019 samples. Ge, P, U, W, and Zr are not part of the routine analysis for surface water, and it was impossible to establish a relationship with them.

Dissolved Fe was present in higher concentrations in the samples upstream of the event (Fig. 3). The comparison of

February (wet season) with July (dry season) shows that the dissolved iron concentration was higher in the wet season for all samples. This is possibly due to the increased amount of material leached into the river during the rainy seasons.

Results of the July/2019 campaign shows a low concentration of dissolved iron (0.0387 mg/L), compared to the values previously measured by Cunha and Machado (2005). One possible explanation may be that the iron is predominantly suspended, since a large amount of iron was suddenly discharged into the river and may have exceeded the solubility coefficient, considering that the iron release occurred in an oxidizing environment. Another possible reason is that the tailings met an environment with an unsuitable pH to dissolve iron, since the river pH is near neutrality. Iron tends to be strongly adsorbed onto colloids and river sediments (Licht 1998), and in pH 5–8 conditions, it has very little mobility, remaining as particulate iron hydroxide (Fe(OH)₂).

Dissolved Mn occurs in much larger quantities in the samples collected in the Ferro-Carvão Creek than in the samples upstream and downstream of the river confluence. The downstream samples have concentrations slightly higher than the upstream samples in both months of the sampling campaign. It follows the same geochemical pattern as the Fe, with higher concentrations in the wet season (Fig. 3).

Figure 4 is a bi-plot graph of the principal components analyses (PCA), which correlated the variables Al, Fe, Mn, pH, and electrical conductivity for all of the samples. We added Al because it is a frequent element in oxides and hydroxides, like Fe and Mn. The variables are superposed to the cases (samples) in the graph.

The PCA explains the variance of these variables. In both analyses, the first two principal components (PC1 and PC2) explain 64.58% and 32.14% of the variance of the variables in February. In July, it represents 82.99% and 14.80%. There are two end members in the February analysis (upstream and the tailings points) and one well-defined intermediate member.



PCA analysis Superficial Water- February 2019

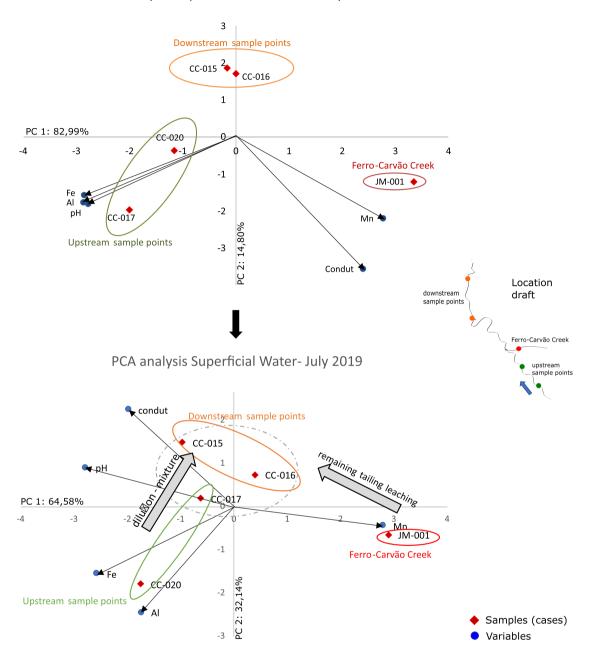


Fig. 4 Bi-plot graph with results of PCA before and after rupture. The horizontal axis corresponds to principal component 1 (PC1) and the vertical axis to principal component 2 (PC2). The diamonds represent the samples (cases) and circles represents the variables

In the February PCA, Fe, Al, and pH are statistically grouped and represent the upstream sample points, while Mn and electrical conductivity were the variables that better fit the tailings. In July, it is clear that there is a good mixture of those two end members and the main influence of the upstream points is probably due to dilution with the

non-affected waters. Being in the dry season certainly influenced this mixture because there was no large input from the remaining tailings through leaching. Another interesting point is that electrical conductivity was closer to that of the upstream point, showing that this parameter is reaching a new equilibrium.



Table 4 Reference data of analyses prior to the dam rupture and Paraopeba Basin background

Physics-chemical parameters and elements	Ferro-Carvão Creek (2005) ^a		Paraopeba Basin ^b	Ferro-Carvão Creek (2019) ^c	
	Wet season	Dry Season	Basin background	Wet season	Dry season
pH	7.5	7	6.73	6.5	6.58
DO (mg/L) ^c			5.86	8.06	NA
Condut. (µs/cm)		36	72.1	140.4	79.65
Al (mg/L)			0.034	ND^5	0.043
As (mg/L)			0.0001	ND	NA
B (mg/L)			0.0001	<LQ ⁶	NA
Ba (mg/L)			0.022	<lq< td=""><td>< 0.010</td></lq<>	< 0.010
Be (mg/L)			0.0001	ND	NA
Ca (mg/L)	3.56	3.57	7.568	11.167	23.818
Cd (mg/L)			0.0001	ND	NA
Co (mg/L)			0.0001	ND	NA
Cr (mg/L)			0.0001	ND	NA
Cu (mg/L)			0.0001	ND	NA
Fe (mg/L)	1.21	0.21	0.425		0.038
Hg (mg/L)			0	< 0.0005	NA
K (mg/L)			1.056	2.2328	1.965
Li (mg/L)			0.0001	<lq< td=""><td>NA</td></lq<>	NA
Mg (mg/L)			1.132	3.7098	3.201
Mn (mg/L)	0.79	0.23	0.055	0.4166	0.363
Mo (mg/L)			0.0001	ND	NA
Na (mg/L)			4.73	1.7625	3.252
Ni (mg/L)			0.0001	<lq< td=""><td>NA</td></lq<>	NA
Pb (mg/L)			0.0001	ND	NA
Sb (mg/L)			0.0001	<lq< td=""><td>NA</td></lq<>	NA
Se (mg/L)			0.0001	ND	NA
Si (mg/L)			13.9	1.2517	7.910
Sn (mg/L)			0.0001	ND	NA
Sr (mg/L)			0.03281	0.0387	0.044
Ti (mg/L)			0.0001	ND	NA
V (mg/L)			0.0001	0.005	NA
Zn (mg/L)			0.0001	ND	0.067
Bromide (mg/L)			0.0001	0.1076	NA
Chloride (mg/L)			0.99	1.4551	NA
Fluoride (mg/L)			0.044	<lq< td=""><td>NA</td></lq<>	NA
Phosphate (mg/L)			0.0001	0.0923	NA
Nitrate (mg/L)			0.68	0.9654	NA
Nitrite (mg/L)			0.01	0.0972	NA
Sulphate (mg/L)			0.28	ND	NA

Data sources: Geological Survey of Brazil. ^aCunha and Machado 2005, ^bViglio and Cunha 2018, ^cthis work *DO* dissolved oxygen, *ND* not detected, <LQ=lower than quantification limits, *NA* not analyzed, hollow=not specified in the source data

The concentration of trace elements in surface water systems is generally due to the geochemistry of rocks and soils of the hydrographic basin. Pollution and chemical reactions,

such as adsorption on particles or other surfaces and sediment deposition also play a role (Guilherme et al. 2005). In the present study, the three factors positively influence the



presence of these elements, as they are already naturally present due to the basin's rocks and soil's geochemistry and augmented by the subsequent dissolution of the tailings.

Regarding the groundwater, no elements of concern related to the tailings were detected. This is a significant result because these samples were collected six months after the event and were located near the tailings deposition site. This indicates that up to the field campaign time, no significant influence due to the disaster on the groundwater. The groundwater in the area is bicarbonate-sodium (CC-022) and chloride-sodium types (CC-023). This classification, together with the electrical conductivity and pH of these samples, is in line with what was described by Mourão (2007) for the hydrochemistry of aquifers in granite-gneissic rocks of the fractured central-south unit (ANA 2013). In that study, the wells presented poorly mineralized waters, with low electrical conductivity (on average 13.2 μ S/cm) and a pH of about 6.

Data from 2009, obtained by Viglio and Cunha (2018), shows the background value for the Paraopeba River basin surface water (median values). In addition, Cunha and Machado (2005) collected surface water samples in the Ferro-Carvão Creek and highlighted three elements that appeared with high values: Ca, Fe, and Mn. The other elements were not mentioned in the study, since they presented values below the limit of detection and below the environmental legislation threshold (Cunha and Machado 2005). Table 4 displays all this information with the analytical results of the JM-001 sampling point of the present work.

Figure 5 shows that the Ferro-Carvão Creek already presented high values of Fe and Mn before the rupture of the tailings dam. These values vary according to the season because a large amount of dissolved material leaches into the drainages during the wet season (Cunha and Machado 2005).

Some concentrations exceeded the MAC criteria (0.3 mg/L for Fe and 0.1 mg/L for Mn). These high Fe and Mn values may be a natural characteristic of the region's water, associated with the mining history in the area, or both.

Concluding Remarks

Most of the water samples that exceed Brazilian federal regulations (CONAMA Resolution N° 357) are upstream of the Ferro-Carvão Creek's confluence with the Paraopeba River, indicative of a river system previously subjected to contamination sources rather than the disaster. This is particularly evident with the analyzed groundwater samples.

This would probably not be the case if the dynamics of the affected water bodies or the chemical nature of the tailings were different (Laureano et al. 2022). Although mainly impacted by the presence of Fe and Mn, the water samples do not present the high levels of the trace elements that are commonly toxic to human health and to the environment as a whole. According to Guilherme et al. (2005), in rivers relatively unpolluted with high turbidities, such as the Paraopeba River, a higher proportion of trace elements occur in a particulate form (chemical precipitates, colloids), rather than dissolved. The analysis of both the river bottom sediments and the tailings clearly show trace element levels that exceed those dissolved in the surface water. Regarding the groundwater, even with scarce data to support any conclusion, the effect of the disaster is probably small due to the characteristics of the material and the basin hydrogeology.

Finally, the analytical results obtained in the present work indicate that there probably was no major environmental damage from a hydrogeochemical standpoint, although this is perhaps a minor factor given the huge human and material

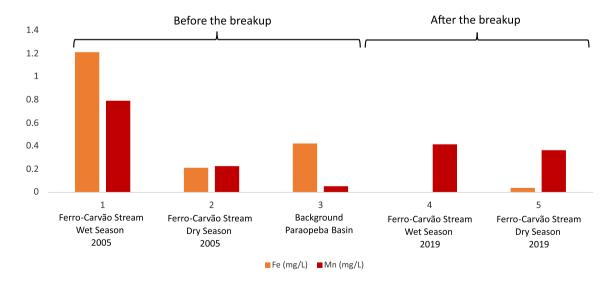


Fig. 5 Comparative graph of iron (Fe) and manganese (Mn) concentration in surface water before (A) and after (B) the dam rupture



losses that resulted from the event. The work also documents the extreme importance of monitoring the geochemical background of a site, as a reference that allows for measuring the effect of such events on the environment. However, more studies are necessary to evaluate the scenario, such as studies of the interactions in the solid-solution interface, adsorption/desorption of metals, and speciation of the metals present in high concentrations in the sediments and tailings.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10230-023-00916-8.

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Data Availability All data used to elaborate the article from surface water, groundwater, sediment and tailings were obtained with the participation of the Geological Survey of Brazil in the context of the 'Special Monitoring Program of the Paraopeba River', and are available in this document and the supplementary material.

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