

## Water Quality from Gualaxo do Norte and Carmo Rivers (Minas Gerais, Brazil) after the Fundão Dam Failure

*Qualidade da Água dos Rios Gualaxo do Norte e Carmo (Minas Gerais, Brasil) após o Rompimento da Barragem do Fundão*

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### Abstract

Mining waste is rich in trace elements, which present a high toxic potential and may represent a risk for aquatic ecosystems. The Fundão dam failure, considered the largest environmental disaster in the world, affected 663.2 km of watercourses, including Carmo and Gualaxo do Norte Rivers. The ore tail also affected the riverside communities, destroying villages, killing people and affecting the subsistence farming. To evaluate the influence of the mine tailing wave on the water quality of the Carmo and Gualaxo do Norte Rivers water samples were collected at nine points located in Barra Longa during the rainy season. Physicochemical parameters (conductivity, resistivity, Eh, total dissolved solids, pH and temperature) and major, minor and trace elements concentrations (Ba, Co, Cr, Cu, Ni, Sc, Sr, V, Zn, As, Pb, Al, Fe, Mn, Ca, K, Mg and P) were evaluated and compared with previous studies and conformity limits established by a national resolution (CONAMA Resolution N°357/2005). Only conductivity, Fe and Mn presented non-conformity values according to CONAMA Resolution N°357/2005. These results may be related not only to the dam burst but also to the rainy season and non-detectable pollution sources. Furthermore, the decreased levels in the toxic elements in the rivers over time, may be related to its association with sediments in addition to their flux to the Atlantic Ocean. Thus, after nearly six years, the environmental and social impacts are still alive and the minerals dragged to the riverbed could bring cumulative effects for the entire environment what means an uncertain future to the Rio Doce Basin and adjacent coastal zone.

**Keywords:** Hydrogeochemistry; Dam; Environmental contamination

### Resumo

Os resíduos da mineração são ricos em elementos-traço que apresentam alto potencial tóxico e podem representar riscos aos ecossistemas aquáticos. O rompimento da barragem do Fundão impactou um total de 663,2 km de corpos hídricos, dentre eles os rios do Carmo e Gualaxo do Norte. A lama também afetou as comunidades ribeirinhas, destruindo vilas, matando pessoas e afetando a agricultura de subsistência. Para avaliar a influência da onda de rejeitos na qualidade da água dos rios do Carmo e Gualaxo do Norte, amostras de água foram coletadas em nove pontos, próximos ao município de Barra Longa, durante a estação chuvosa. Os parâmetros físico-químicos (condutividade, resistividade, Eh, sólidos totais dissolvidos, pH e temperatura) e a concentração de elementos maiores, menores e traço (Ba, Co, Cr, Cu, Ni, Sc, Sr, V, Zn, As, Pb, Al, Fe, Mn, Ca, K, Mg e P) foram avaliados e comparados com estudos anteriores e com os limites de conformidade estabelecidos pela resolução nacional (Resolução CONAMA N°357/2005). Apenas a condutividade, Fe e Mn apresentaram valores em não conformidade com a Resolução CONAMA N°357/2005. Estes resultados podem estar relacionados não somente ao rompimento da barragem, mas também à estação chuvosa e a fontes poluidoras não detectáveis. Além disso, a diminuição da concentração de elementos tóxicos nos rios ao longo desse período, pode estar relacionada à associação dos mesmos aos sedimentos, além do carreamento até o oceano Atlântico. Assim, passados quase seis anos, os impactos ambientais e sociais continuam vivos e os minerais possivelmente arrastados para os leitos dos rios podem trazer efeitos cumulativos para todo o meio ambiente, o que significa um futuro incerto para a Bacia do Rio Doce e a zona costeira adjacente.

**Palavras-chave:** Hidrogeoquímica; Barragem; Contaminação ambiental

## 1 Introduction

Mining was the most important economic activity in Brazil in the 17<sup>th</sup> century. The Minas Gerais state has been historically known for gold exploration during this period, mainly in the region of the Vale do Rio Doce and the cities of Ouro Preto, Mariana and the municipality of Barra Longa (Ofosu-Mensah 2017). Currently, mining and metallurgy are still the main socio-economic activities in the region of Mariana and Ouro Preto due to great mineral deposits of iron, bauxite, gold and manganese.

Despite the economic importance, the mining activity results in residues rich in trace elements, such as lead, cadmium, arsenic and aluminum, which present high toxic potential, and may change physicochemical parameters of the watercourses (Dudka & Adriano 1997; Borba, Figueiredo & Cavalcanti 2004). These elements do not degrade when incorporated in aquatic ecosystems, remaining soluble or as precipitated on the sediments, which may cause risks throughout the food chain, even in low concentrations (Thornton 1996; Aires et al. 2018; Baalousha et al. 2018; Burritt & Christ 2018).

Founded in 1977, Samarco is a private mining company whose main product is iron, which is commercialized for the steel industries in the Americas, the Middle East, Asia and Europe (Samarco 2018). On November 5<sup>th</sup>, 2015, the Fundão dam, which belonged to the Germano mining complex located at the Mariana city, ruptured. Over 50 million m<sup>3</sup> of iron ore tailings were released into the environment and were gradually carried away until reach the sea, resulting in 663.2 km of impacted watercourses (Fernandes et al. 2016; Carmo et al. 2017).

The disruption of the Fundão tailings dam was considered the largest environmental disaster in the world (Magliano & Angelo 2020). After nearly six years, the environmental and social impacts are still alive. Mining, together with family and subsistence farming around its main river, Gualaxo do Norte were the main economic activities of the communities affected by the ore tail. The community of Bento Rodrigues, in Mariana (MG), was the first to be flooded and also completely destroyed by the mud (Renova Foundation 2021). Moreover, the disaster made by the tailings wave affected the terrestrial and aquatic ecosystems, especially because of the water pollution with a large amount of mud and minerals (Magliano & Angelo 2020). Thus, the minerals dragged to the riverbed could bring cumulative effects for the entire environment not only of the past, but also of the present and future in the Rio Doce Basin and adjacent coastal zone. Recovery and compensation programmes have been implemented by organizations in charge. In the social context, it is important to highlight that Renova Foundation has been focusing on environmental recovery projects and community

resettlement of the villages destroyed by the mud. Currently, Renova is working in the construction of 30 houses that have been destroyed. So far, according to the Renova website only 7 houses have been finished, which seems not to be enough to mitigate the damage in all its aspects.

One of the main municipalities affected by the tailings originated from Fundão dam failure (Almeida et al. 2018) was Barra Longa, which is located near the confluence of the Carmo and Gualaxo do Norte Rivers. Therefore, it is pertinent to analyze water samples from both rivers, with the main objective to evaluate the concentrations of major, minor and trace elements, as well as changes in physicochemical parameters of the rivers. These analyses could help to observe the ecosystem health and also as an indicator for local population health that consumes fish and uses the water from the affected rivers (Meche et al. 2010; Bottino et al. 2017). Thus, this study aims to evaluate physicochemical parameters and trace element concentrations in Carmo and Gualaxo do Norte Rivers to monitor the problems related to the Fundão dam three years after its rupture.

## 2 Materials and Methods

### 2.1 Study Area

The Gualaxo do Norte River is one of the tributaries of the Carmo River and was impacted by the Fundão dam collapse in an estimated area of 27.9 km<sup>2</sup>, where 6.3 km<sup>2</sup> belong to a permanent preservation area. The Carmo River basin, comprises a drainage area of 2279 km<sup>2</sup>, covers up 14 municipalities and approximately 278,000 inhabitants (Instituto Brasileiro de Geografia e Estatística 2016, 2017). The river extends 134 km until its confluence with the Piranga River as they form the Doce River (Rodrigues et al. 2012).

The local geology consists predominantly of rocks such is orthogneisses with amphibolite, meta-ultramafic intercalations in the Mantiqueira Complex (Brandalise 1991). Further downstream, the Dom Silvério Group is predominantly composed for metasedimentary rocks (mica-shales and quartzites) (Jordth-Evangelista 1992). The sample collection area, the Rio do Carmo basin and the Gualaxo do Norte sub-basin cross a diversity of rocks, often mineralized in gold (enriched in elements such as As and Sb) and in iron (banded iron formations), showing great effect on the geochemistry of its waters. Both rivers cross practically all the most important units of the Quadrilátero Ferrífero, an important Brazilian mineral province, located northeast of the studied area (Costa 2001).

According to Radambrasil project (Projeto Radambrasil 1983), the natural vegetation of the Carmo River basin is characterized by semi-deciduous seasonal forest.

However, the anthropic activities have transformed the landscape over the years. Nowadays, the basin presents combined areas of pasture and capoeira, which are secondary vegetation, composed of sparse grasses and shrubs. In addition, the native vegetation has been replaced by eucalyptus reforestation in several places. Eucalyptus is a raw material for the production of coal, used extensively in the blast furnaces of the metallurgical industries in the region. The Carmo River basin is inserted mainly in climatic zones Cwa and Cwb according to Köppen classifications. Cwa predominates in lower regions and is characterized by

warm and humid summers with an average annual rainfall of 1100-1500 mm. On the other hand, Cwb dominates the highest levels and is characterized by milder summers with a mean temperature below 22 °C in the hottest months (Costa 2001).

Water samples were collected in the municipality of Barra Longa at nine different sampling points, on February 23<sup>rd</sup>, 2018, whose date, corresponds to the local rainy season. Three sampling points were located at the Carmo River, three at the Gualaxo do Norte River and three at the confluence of both rivers (Figure 1).

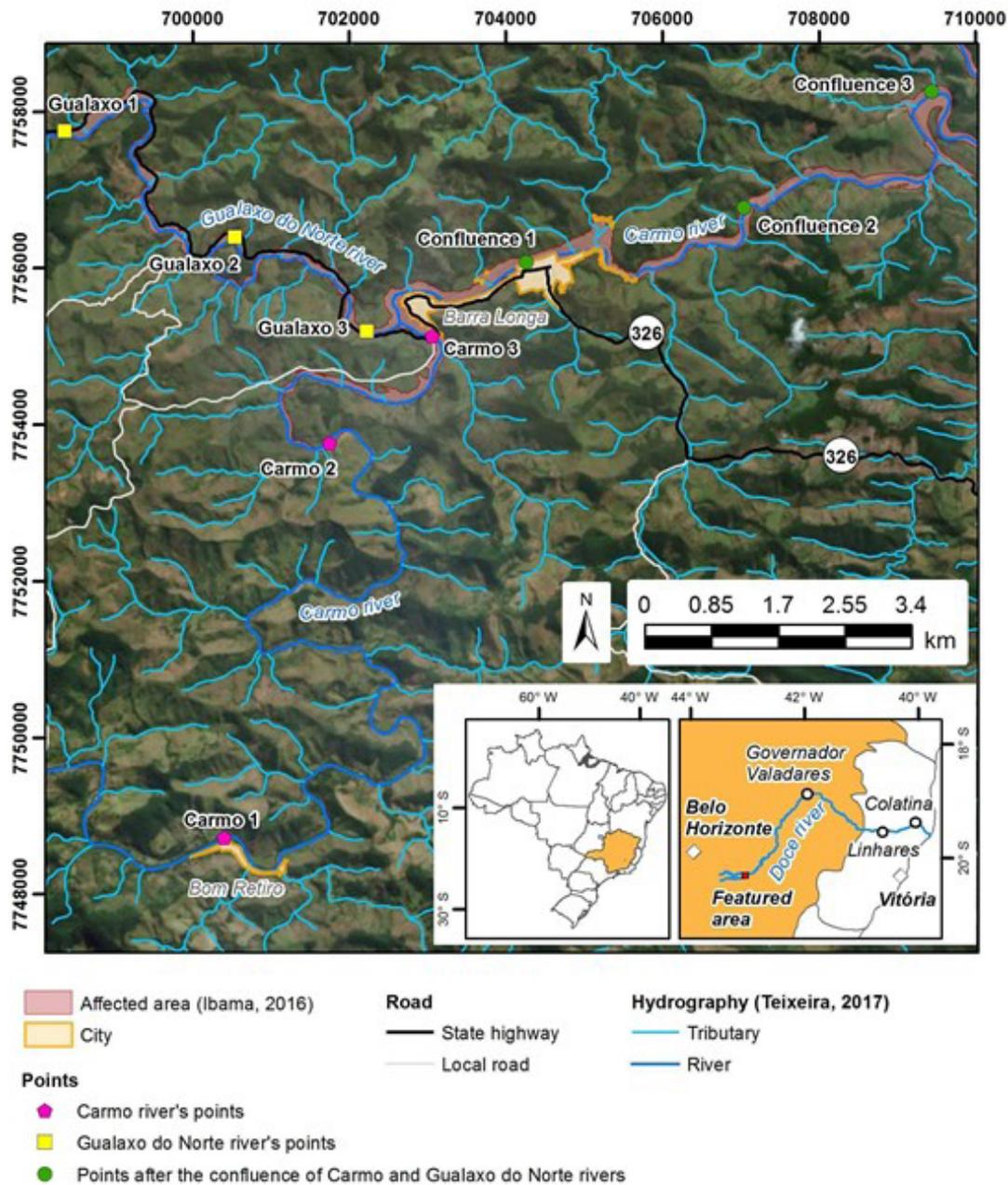


Figure 1 Map showing water-sampling points along Carmo and Gualaxo do Norte Rivers.

## 2.2 Sample Collection and Preparation

The bucket was rinsed with water from the sampling sites three times prior to collecting each sample. For each sampling point, 200 mL of the surface water was used to characterize the physicochemical properties of the water samples. On the other hand, 60 mL of the surface water was transferred to a high-density polyethylene (HDPE) for laboratory analysis. Water samples were collected by a 20 mL syringe and 0.45 µm membrane filter. Afterwards, the samples were acidified with 0.2 ml of the ultrapure nitric acid (HNO<sub>3</sub> - Merck - 65%) in order to keep metals in solution. The bottles were also rinsed prior to the sampling and then filled to the top. Samples were refrigerated and kept without light until laboratory analysis. The results were compared to limits established by the Brazilian National Council for the Environment (with the Portuguese acronym CONAMA) in the Resolution N°357/2005.

## 2.3 Physicochemical Parameters

Physicochemical parameters were analyzed using the multiparameter Ultrameter II 6 Psi, Serial # 6201163 for *in situ* measurements of electrical conductivity (µS), resistivity (kΩ), Eh (mV), total dissolved solids (mg.L<sup>-1</sup>), pH and temperature (°C) parameters.

## 2.4 Major, Minor and Trace Elements

Major and minor elements were analyzed using the Agilent 725 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES - axial plasma) (see the system operating parameters and conditions on Table 1) and trace elements using an Agilent 770 Inductively Coupled Plasma Mass Spectrometer (ICP-MS - radial plasma) (see the system operating parameters and conditions on Table 2) at the Geochemistry Laboratory of the Federal University of Ouro Preto, Brazil. The limit of quantification (LOQ) was calculated by using the following equation (Shrivastava & Gupta 2011):  $LOQ = X + 10s$ , where X means values of the blanks and s means the standard deviation of the blanks. The ICP-OES was used for the quantification of Al, Fe, Mn, Ca, K, Mg, Ba e P (Table 3). The ICP-MS was used for the quantification of Co, Cr, Cu, Ni, Sc, Sr, V, Zn, As and Pb (Table 4). The ICP multi-element standard solution (Merck) and multi-element calibration standard 1 (Agilent Technologies) were analyzed to monitor instrumental performance. A blank and five points calibration curve were generated to each element using their respective standards (SpecSol and High-Purity Standards). All solutions were acidified with 1% nitric acid, suprapur - Merck (Fernandez-

Turiel et al. 2000). The Table 5 and 6 shows the limits of quantification (LOQ) of the analyzed elements.

Waters from Doce River does not have an approved framework proposal. However, according to Article 42 in CONAMA Resolution N°357/2005 (Conselho Nacional do Meio Ambiente 2005) and Brazil's State Council of Environmental Politics (with the Portuguese acronym COPAM, Conselho Estadual de Política Ambiental 2008), "Freshwater will be considered as Class 2 until their respective frameworks have been approved". Therefore, the Doce River watershed and its tributaries are considered as Class 2, which means this water may be destined to: (1) supply for human consumption, after conventional treatment; (2) primary contact recreation; (3) irrigation for vegetables, fruits, parks, gardens, sports and leisure fields; (4) agriculture, fisheries and aquaculture.

## 3 Results

### 3.1 Physicochemical Parameters

#### 3.1.1. Temperature

The measured temperature is adequate to the period and its variations during the day (February 23<sup>rd</sup>, 2018), where the values were between 24 ° C to 27 ° C (Table 7).

#### 3.1.2. Conductivity and Resistivity

According to COPAM resolution (Conselho Estadual de Política Ambiental 2008), there are no limits established for electrical conductivity. However, values above 100 µS currently indicate impacted environments (Von Sperling 2007). Resistivity parameter also does not present established limits, although, it is known that such parameter is inversely correlated with conductivity values, since it represents the electrical resistance capacity of material. Although the historical conductivity average of studied rivers was lower before the dam rupture (Instituto Mineiro de Gestão das Águas 2016) the conductivity and resistivity values found at present study did not indicate an impacted environment.

In the last three years since the Fundão Dam rupture the conductivity values decreased, mainly in Gualaxo do Norte River, which used to present a relatively high conductivity value above the indicative limit for impacted environments. The conductivity is influenced by temperature, decreasing with the increasing in temperature and vice-versa, due thermal agitation (Mandal 2014). This phenomenon could be observed at Carmo River sampling point 1, where the peak in conductivity is probably due to the low temperature (Table 7).

**Table 1** The system operating parameters and conditions – ICP–OES.

ICP–OES	
Power (Kw)	1350
Plasma gas flow (L/min)	15.0
Nebulizer flow (L/min)	1.0
Nebulizer pressure (kPa)	200
Nebulizer system	Cross flow
Replicates	5

**Table 2** The system operating parameters and conditions - ICP-MS.

Quadrupole ICP–MS	
Power (W)	1550 W
Plasma gas flow (L/min)	15 L/min
Auxiliary flow (L/min)	1.2 L/min
Nebulizer flow (L/min)	1.05 L/min
Integration time	300 (ms)
Replicates	3
Internal standard	<sup>185</sup> Re
Minimal conditions	<sup>140</sup> Ce <sup>16</sup> O <sup>+</sup> / <sup>140</sup> Ce < 1.5% and <sup>140</sup> Ce <sup>2+</sup> / <sup>140</sup> Ce+ < 3.0%
Standard mode	
Stabilization time	5 s
Isotopes	<sup>209</sup> Bi, <sup>140</sup> Ce, <sup>162</sup> Dy, <sup>152</sup> Eu, <sup>167</sup> Er, <sup>157</sup> Gd, <sup>165</sup> Ho, <sup>115</sup> In, <sup>139</sup> La, <sup>175</sup> Lu, <sup>144</sup> Nd, <sup>208</sup> Pb, <sup>141</sup> Pr, <sup>79</sup> Se, <sup>150</sup> Sm, <sup>169</sup> Tm, <sup>173</sup> Yb
Sensitivity	<sup>7</sup> Li > 10000 cps, <sup>89</sup> Y > 22000 cps, <sup>205</sup> Tl > 9000 cps
Collision cell mode (ms)	
Stabilization time	30 s
Isotopes	<sup>75</sup> As, <sup>111</sup> Cd, <sup>45</sup> Sc, <sup>89</sup> Y
Sensitivity	<sup>59</sup> Co > 5000cps, <sup>89</sup> Y > 5000 cps, <sup>205</sup> Tl > 6000 cps e <sup>78</sup> Ar <sub>2</sub> < 30 cps
He gas flow	3.0 mL/min

**Table 3** The main concentration of major elements in the waters of studied area collected during the rainy season. Concentrations (in µg.L-1) were analyzed by ICP-OES.

SP	Al (µg.L <sup>-1</sup> )	Ba (µg.L <sup>-1</sup> )	Ca (mg.L <sup>-1</sup> )	Fe (µg.L <sup>-1</sup> )	K (mg.L <sup>-1</sup> )	Mg (mg.L <sup>-1</sup> )	Mn (mg.L <sup>-1</sup> )	P (mg.L <sup>-1</sup> )
G1	33.12	18.07	2.73	249.15	0.83	1.14	47.34	0.10
G2	24.63	16.74	2.73	207.67	0.85	1.14	28.40	0.09
G3	27.70	16.85	2.76	218.22	0.90	1.15	29.35	0.09
C1	73.68	15.92	3.95	275.65	1.11	1.45	175.95	0.10
C2	53.43	15.01	1.86	291.88	0.97	0.63	195.64	0.10
C3	62.07	7.67	1.88	217.28	0.86	0.66	27.64	0.10
C <sub>o</sub> 1	45.72	10.43	2.02	241.39	0.91	0.72	43.28	0.10

Table 3 Cont.

SP	Al ( $\mu\text{g.L}^{-1}$ )	Ba ( $\mu\text{g.L}^{-1}$ )	Ca ( $\text{mg.L}^{-1}$ )	Fe ( $\mu\text{g.L}^{-1}$ )	K ( $\text{mg.L}^{-1}$ )	Mg ( $\text{mg.L}^{-1}$ )	Mn ( $\text{mg.L}^{-1}$ )	P ( $\text{mg.L}^{-1}$ )
C <sub>2</sub>	53.98	11.01	2.02	239.60	0.86	0.75	41.71	0.10
C <sub>3</sub>	64.01	13.04	2.06	351.03	0.99	0.74	65.17	0.10
LOQ	<b>8.82</b>	<b>0.48</b>	<b>0.0217</b>	<b>7.04</b>	<b>0.0197</b>	<b>0.0197</b>	<b>2.28</b>	<b>0.065</b>

G1, G2 and G3 - sampling points of the Gualaxo do Norte River. C1, C2 and C3 - sampling points of the Carmo River. C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> - Sampling points located at the confluence of Carmo and Gualaxo do Norte Rivers. SP - sampling points. LOQ - Limit of quantification.

**Table 4** Concentration of the main trace elements in the waters of the study area collected during the rainy season. Concentrations (in  $\mu\text{g.L}^{-1}$ ) were analyzed by ICP-MS.

SP	As ( $\mu\text{g.L}^{-1}$ )	Cr ( $\mu\text{g.L}^{-1}$ )	Cu ( $\mu\text{g.L}^{-1}$ )	Co ( $\mu\text{g.L}^{-1}$ )	Ni ( $\mu\text{g.L}^{-1}$ )	Pb ( $\mu\text{g.L}^{-1}$ )	Sc ( $\mu\text{g.L}^{-1}$ )	Sr ( $\mu\text{g.L}^{-1}$ )	V ( $\mu\text{g.L}^{-1}$ )	Zn ( $\mu\text{g.L}^{-1}$ )
G1	0.25	0.17	1.36	0.15	0.35	0.19	0.90	16.01	0.23	1.72
G2	0.23	0.15	1.24	0.09	0.40	0.09	0.88	15.57	0.18	1.11
G3	0.26	0.13	1.34	0.09	0.41	0.10	0.89	15.98	0.18	0.93
C1	2.44	0.37	2.54	0.19	0.98	0.24	0.98	23.60	0.50	18.83
C2	2.93	0.36	2.48	0.53	0.91	0.39	0.91	12.88	0.64	9.89
C3	2.43	0.33	1.29	0.10	0.55	0.08	0.88	12.61	0.45	2.54
C <sub>1</sub>	1.85	0.30	1.59	0.12	0.47	0.13	0.86	13.08	0.45	1.96
C <sub>2</sub>	1.47	0.26	1.20	0.11	0.38	0.09	0.85	13.09	0.40	1.05
C <sub>3</sub>	1.52	0.35	1.82	0.25	0.56	0.28	0.87	13.42	0.57	3.79
LOQ	<b>0.015</b>	<b>0.014</b>	<b>0.021</b>	<b>0.004</b>	<b>0.021</b>	<b>0.032</b>	<b>0.010</b>	<b>0.010</b>	<b>0.010</b>	<b>0.257</b>

G1, G2 and G3 - sampling points of the Gualaxo do Norte River. C1, C2 and C3 - sampling points of the Carmo River. C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> - Sampling points located at the confluence of Carmo and Gualaxo do Norte Rivers. SP - sampling points. LOQ - Limit of quantification.

**Table 5** Limits of quantification (LOQ) and wavelengths from major and minor elements measured by ICP-OES.

Element	LOQ	Wavelength (nm)
Al	8.82 $\mu\text{g/L}$	396.152
Ba	0.48 $\mu\text{g/L}$	455.403
Ca	0.0217 $\text{mg/L}$	422.673
Fe	7.04 $\mu\text{g/L}$	259.940
K	0.0197 $\text{mg/L}$	766.491
Mg	0.0197 $\text{mg/L}$	279.553
Mn	2.28 $\mu\text{g/L}$	257.610
P	0.065 $\text{mg/L}$	213.618

**Table 6** Limits of quantification (LOQ) and the mass from trace elements measured by ICP-MS.

Element	LOQ	Mass
As	0.015 $\mu\text{g/L}$	75
Cr	0.014 $\mu\text{g/L}$	52
Cu	0.021 $\mu\text{g/L}$	63
Co	0.004 $\mu\text{g/L}$	59
Ni	0.021 $\mu\text{g/L}$	60
Pb	0.032 $\mu\text{g/L}$	208
Sc	0.010 $\mu\text{g/L}$	45
Sr	0.010 $\mu\text{g/L}$	88
V	0.010 $\mu\text{g/L}$	51
Zn	0.257 $\mu\text{g/L}$	66

**Table 7** Physicochemical parameters measured *in situ*.

Sampling points	Temperature (°C)	Conductivity (µS)	Resistivity (kΩ)	TDS (mg.L <sup>-1</sup> )	pH	Eh (mV)
G1	27.6	44.95	21.63	28.95	7.13	147
G2	26.7	45.28	21.48	29.07	6.72	147
G3	26.6	46.85	20.76	30.12	6.82	142
C1	24.0	65.72	14.78	42.26	6.67	110
C2	24.7	44.92	21.64	28.83	6.94	105
C3	26.7	50.96	18.35	34.05	6.74	137
C <sub>o</sub> 1	25.6	47.53	20.43	30.60	6.96	131
C <sub>o</sub> 2	26.6	43.40	22.41	27.83	6.95	170
C <sub>o</sub> 3	26.1	45.34	21.47	29.07	6.67	138

G – Gualaxo do Norte River, C – Carmo River, C<sub>o</sub> – sampling points located at the confluence between Carmo and Gualaxo do Norte Rivers.

### 3.1.3. Total Dissolved Solids (TDS)

According to CONAMA Resolution N°357/2005 (Conselho Nacional do Meio Ambiente 2005), the maximum allowed value for total dissolved solids (TDS) is 500 mg.L<sup>-1</sup>. Hence, it is observed at present study that such values are below the allowed limit. According with the Instituto Mineiro de Gestão das Águas (2016) data, the total dissolved solids decrease over time since the Fundão dam failure, demonstrating a reduction in the number of dissolved solids in the water. Consequently, a year after the dam failure, these values were already below the limit established by the CONAMA Resolution (Conselho Nacional do Meio Ambiente 2005). After that, the TDS results were below the rainy season historical average in 2018, except at Carmo River sampling point 1 which may be related to tributaries contribution near the sampling point (Table 7).

### 3.1.4. pH e Redox Potential (Eh)

The pH values are slightly between acidic and basic (6.6 to 7.1), while Eh values are around 140 mV, with a small variation along the rivers sampling points (Table 7). These results are below to the values found by Hatje et al. (2017), indicating a variation over the years. However, both parameters are within acceptable river limits, since the ideal pH for aquatic life maintenance ranges from 6 to 9, according to CONAMA Resolution (Conselho Nacional do Meio Ambiente 2005) and Eh values demonstrate normal river oxygenation. It is also noticeable that even though the pH values are above the historical average, they are still within the minimum and maximum limits established by CONAMA Resolution (Conselho Nacional do Meio Ambiente 2005).

## 3.2 Major, Minor and Trace Elements

The values for major, minor and trace elements (Ba, Co, Cr, Cu, Ni, Sc, Sr, V, Zn, As, Pb, Al, Ca, K, Mg and P) concentration demonstrate conformity for Class 2 waters, as set out in CONAMA Resolution (Conselho Nacional do Meio Ambiente 2005), except for Fe and Mn, which presented non-conformity values at confluence sampling point 3 for Fe, and at Carmo sampling points 1 and 2 for Mn (Figures 2 and 3).

Previously the present work, Segura et al. (2016) and the Governmental Environmental Agency of the State of Minas Gerais (Instituto Mineiro de Gestão das Águas 2016), reported the evaluation of some environmental parameters in water samples collected just before the confluence of Gualaxo do Norte and Carmo Rivers. In our study, all the water samples analyzed shown metals concentrations lower than the values founded by Segura et al. (2016) for residual water, excepted in the sampling points C1 and C2 to Mn. Although most of our values are lower than those recorded in 2016, they are exceeding the reference values established by CONAMA Resolution and the historical maximum average for Fe at point M3 and exceeding the reference values established by CONAMA Resolution at points C1 and C2 for Mn (CONAMA 357/2005) (Figures 2 and 3). However, even in non-conformity, Mn concentration values founded in the present work are below the historical maximum average in the region.

The variation in iron and manganese concentrations may be related not only to the Fundão dam rupture, but also because of the rainy season and pH among other physicochemical variables (Segura et al. 2016). The temperature of weather increases during the rainy season, which directly affect the temperature of flowing water. As expected, a significant positive correlation was observed with the

electrical conductivity and the temperature. The slightly acidic pH values could be related with the metals variation since the metal solubility increases with decreasing pH value (increasing acidity). At the pH range reported, Fe oxides are stable and Fe may exist in the water-column as suspended particles. The majority of the cations can be adsorbed onto the negative-surface of Fe-oxides particles (Hill 2010; Manahan 2000), which could result in levels of chemical elements

lower than the expected. The results obtained in this work also show that the concentration of Fe was three to five times lower than values obtained by Quadra et al. (2019) and lower than the maximum concentration of dissolved Fe ( $0.57 \text{ m.L}^{-1}$ ) before the dam rupture (Agência Nacional das Águas 2015). The concentration of dissolved Mn is consistent with other works conducted in the Doce River after the Fundão dam rupture (Segura et al. 2016; Quadra et al. 2019).

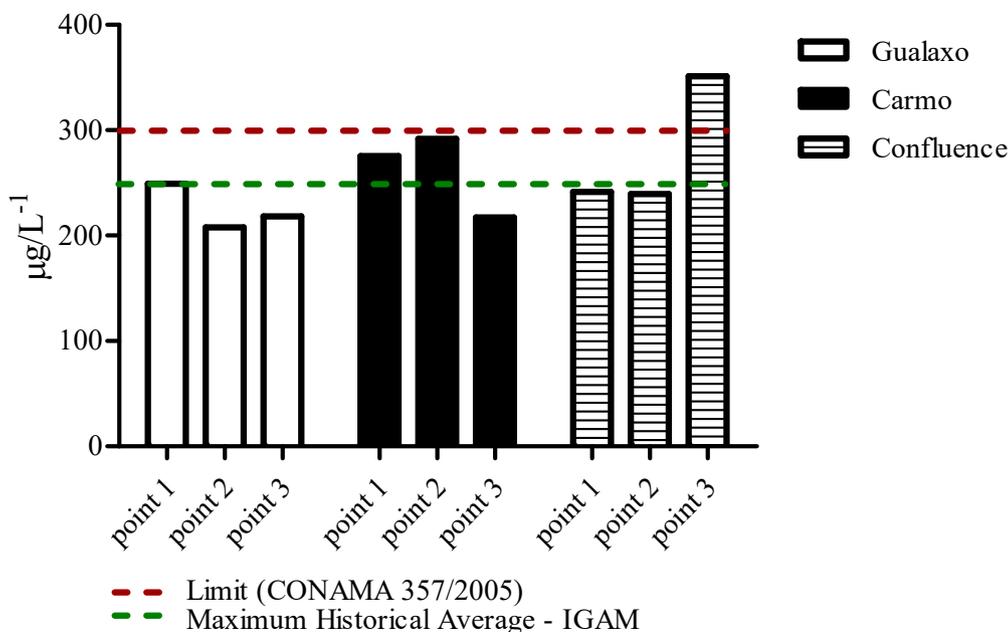


Figure 2 Graph showing Fe concentration along the sampling points during the rainy season on February 23<sup>rd</sup>, 2018.

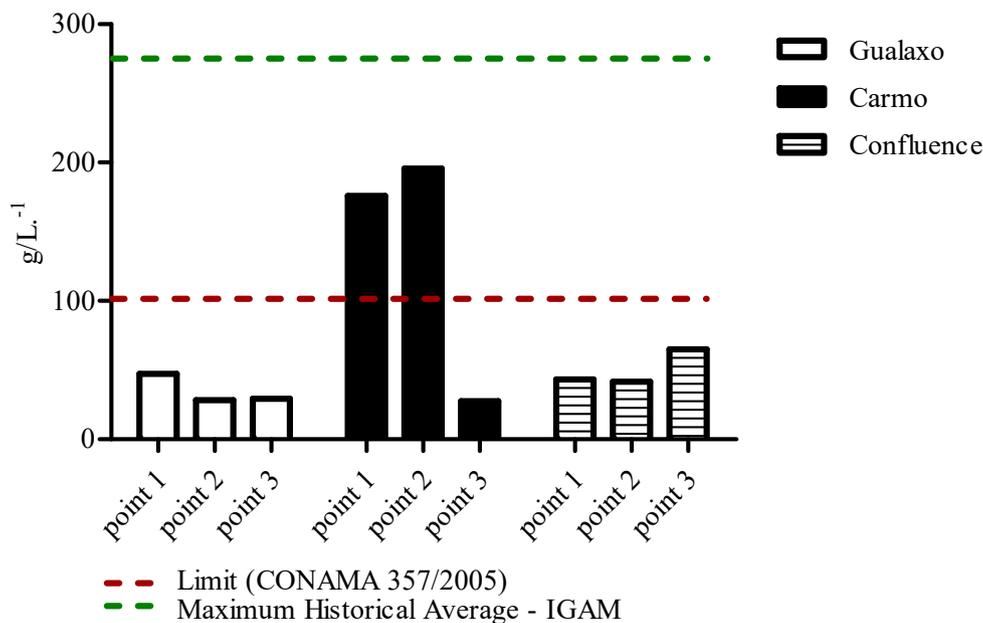


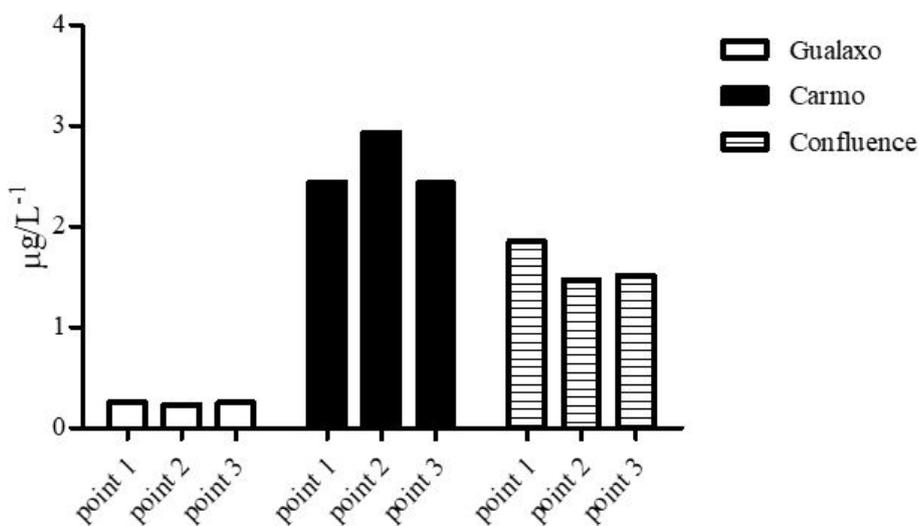
Figure 3 Graph showing Mn concentration along the sampling points during the rainy season, on February 23<sup>rd</sup>, 2018.

Although the metal concentrations decreased after the dam failure, large amounts of sediments of the initial slurry flood wave could be trapped in the riverbanks (Hatje et al. 2017) or associated with Mn and Fe oxides, which may occur as concretions or particle coatings (Baker 1968). These oxides are excellent scavengers of trace metals, but they are unstable under conditions of restriction or oxygen absence (Tessier, Campbell & Bisson 1979). Besides the values founded are still no conformant for some sampling points indicating that Fe and Mn could be mobilized and becoming more bioavailable along its transport along the river. According to Hatje et al. (2017) positive anomalies of trace elements in the regions are expected to result from both the lithology, naturally enriched in metals, and mining. Furthermore, iron and manganese are considered toxic elements and their accumulation in the body occur mainly by water ingestion and contaminated air inhalation, which depending on concentrations may lead to serious illnesses (Alahabadi & Malvandi 2018). Manganese intoxication is also known as manganism, affecting the respiratory tract, which can cause pulmonary embolism and bronchitis, and also affects the central nervous system (CNS), leading to muscle problems, Parkinson’s disease and hallucinations

(Dobson, Erikson & Aschner 2004). Iron poisoning mainly affect internal organs such as the heart, pancreas and liver, causing severe liver disease (Jagobs, Greene & Gendel 1965; Guimarães 1967; Moosavi 2015). Therefore, the increase of Fe and Mn at some sampling points could be a problem for public water supply, as well as for the population health that makes use of the water in daily life (Zaw & Chiswell 1999).

**3.2.1. Aluminum, Arsenic and Zinc**

Some chemical elements, such as Al, As and Zn, even showing overall conformity, presented discrepant values at some sampling points. The As presents high concentrations at Carmo River sampling points 1, 2 and 3 (Figure 4). The high concentrations for this element are characteristics of anthropic activities, such as gold exploration in the middle of the 17<sup>th</sup> century, and also in consequence of its geogenic origin (Bidone et al. 2018). Besides, the elements Al and Zn also demonstrate high concentrations for the Carmo River. However, these values might be due to non-detectable pollution sources, or to a greater load of these elements in the river from natural sources.



**Figure 4** The graph demonstrating As concentration along the sampling points during the rainy season, on February 23<sup>rd</sup>, 2018.

**4 Conclusions**

It is undeniable that mining has contributed for decades to the economic development of the municipalities of Minas Gerais located near to the mineral exploration areas. However, the economic development generated has been achieved at the expense of anthropogenic activities contrary to the preservation of the natural conditions of

the river resources of the region. In order to monitor the problems related to the dam failure on aquatic environments, it is necessary to follow the standards established by CONAMA Resolution N°357/2005. This Brazilian Resolution establishes maximum allowable values for physical, chemical and biological parameters as limiting for water quality. Our findings showed that only the conductivity and the elements Fe and Mn presented non-

conformity to the standards established by CONAMA resolution. Three years after the Fundão dam burst, it is noticeable that the concentrations of most major, minor and trace elements have decreased. However, the decrease trend in toxic elements levels on the aquatic ecosystems may be possibly related to different sources and including its association with sediments in addition to their flux to the Atlantic Ocean. These possibilities show us that is necessary to keep an eye on all aspects of the impact and continue monitoring the affected areas.

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