

 <sup>a</sup> Universidade Federal de Ouro Preto, Departamento de Química,
 CEP 35400-000, Ouro Preto-MG, Brazil
 <sup>b</sup> Observatório Nacional, CEP 27700-000,
 Rio de Janeiro-RJ, Brazil

\*E-mail: angelaleao@ufop.edu.br

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# Evaluating the Water Quality of Springs in Paracatu de Baixo after the Fundão Dam Collapse

Avaliação da Qualidade da Água de Nascentes em Paracatu de Baixo, após Rompimento da Barragem de Fundão

André Vicente Alves,<sup>a®</sup> Louise Aparecida Mendes,<sup>a®</sup> Jonatã Barbosa Teixeira,<sup>b®</sup> Viviane Martins Rebello dos Santos,<sup>a®</sup> Vera Lúcia Miranda de Guarda,<sup>c</sup> Ângela Leão Andrade<sup>a</sup>.\*<sup>®</sup>

The collapse of the Fundão Dam in Mariana municipality (MG, Brazil), in 2015, resulted in approximately 60 million cubic meters of iron ore tailings being directly released into the Doce River watershed. Although it is presumed that the dam sludge is primarily composed of Si, Fe, and Mn, the accident occurred in an area with a geochemical source of arsenic, an anthropogenic source of mercury, and contaminated by other potentially toxic metals and metalloids (also with geochemical and anthropogenic sources); their mobilization along the river course is therefore highly probable. Therefore, this study aimed to analyze the water of Paracatu de Baixo, a sub-district of Mariana that was devastated by the Fundão Dam sludge, to evaluate the influence of sludge dust on the spring waters used by the few remaining residents who use this water for consumption and for irrigating vegetables they consume and sell. In this study, samples of rainwater and spring water were collected during both the rainy and sunny seasons in different locations in Paracatu de Baixo. On both dates, the physicochemical parameters studied (pH, turbidity, conductivity, hardness, nitrate, nitrite, total solids, and dissolved oxygen) were within the limits allowed by Resolution 357/05 of CONAMA and Portaria 1469. Ba, Cu, Zn, Al, Fe, and Mn metals were determined in the samples, but only the Al and Fe elements exceed the value recommended by the Brazilian legislation. Several of the metals found showed higher concentrations during the rainy season, which indicates that they are becoming available due to lithological issues rather than being caused by sludge dust.

Keywords: Fundão Dam; environmental damage; potentially toxic metals.

## 1. Introduction

In recent decades, contamination by potentially toxic metals has become an extremely important issue for the scientific community due to the damage they cause to the environment and living organisms. Anthropogenic contamination sources are usually related to the inadequate management of domestic waste, chemical, petrochemical, metallurgical, and mining industries, as well as the application of agrochemicals.<sup>1</sup>

Contamination by potentially toxic metals and metalloids near mining regions is of concern in Brazil, given that mining activity in Brazil has been, and still is, essential for economic development. Thus, since the artisanal mining of diamonds and gold, millions of tonnes of potentially toxic metals have been released, leading to the translocation of these elements into sediments, soils, surface, and groundwater as a consequence of mineral processing and the inadequate disposal of mining waste over centuries.<sup>2-5</sup> The hypothesis that old mines located in the Quadrilátero Ferrífero region could produce a serious environmental contamination impact was tested and confirmed. The breach of the Fundão dam in Mariana municipality (MG, Brazil) in 2015 caused around 60 million cubic meters of iron ore waste sediment to be released into the Doce River hydrographic basin. During its journey, an incalculable amount of solid materials was drained into the river plume, and the water quality parameters were completely altered.<sup>6</sup>

Along the channel of the Gualaxo do Norte river, the wave of tailings reached the rural community of Paracatu de Baixo. This sub-district of Mariana, Minas Gerais, Brazil, was heavily impacted by the mud, leaving many residents homeless, without water and work. However, part of the community, which was not directly impacted by the tragedy, remained in place, making use of water from springs for their survival. Some studies have been carried out to assess the water quality of the affected rivers,<sup>7-10</sup> but there is no record in the literature that presents data on water from springs close to the affected areas. Many questions have not yet been properly answered, which could lead, for example, to compromising the resident's health of Paracatu de Baixo.



Although the mud waste is classified as "non-hazardous," chemical analyzes of water, mud, soil, sediment, and dust collected in the affected area evidenced the presence of potentially toxic elements, such as Al, As, Mn, Ag, and Pb, detected at high levels.<sup>11-13</sup> Apparently, the energy of the mud flood was intense enough to cause the suspension, resuspension, and resolubilisation of compounds existing in old gold mines, as well as waste and sediments historically deposited in the Gualaxo do Norte and Carmo Rivers over the last centuries. Water, mud, and sediment samples collected hours,<sup>14</sup> days,<sup>15,16</sup> and months after this event showed the presence of several potentially toxic elements. Silva et al.<sup>17</sup> observed an increase in the quantities of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn after the dam breach, comparing the results obtained with those collected about six months before the accident. Even seven years after the Fundão dam breach, the extent of the environmental damage caused by the released mud is still not sufficiently clear. Have potentially toxic metals and metalloids been transported and accumulated in the soils of the margins, and can they be transferred to plants, animals, and humans? Could potentially toxic elements from the waste penetrate the soil and infiltrate the groundwater, making it impossible to plant and use spring water in the region? Is it possible that the spring water has been contaminated by the suspension of mud dust? Is the population exposed to a risk of contamination since they use spring water for drinking and irrigating vegetables they consume and sell the excess?

Water intended for human use or consumption must meet strict quality criteria so as not to cause harm to consumers' health. Several parameters have been studied to indicate water quality, which is dependent on the intended use. When these values are higher than the established limits for a particular use, the water is deemed unfit. To verify the water quality in this study, the parameters obtained were compared to the definitions of CONAMA Resolution 357.18 The CONAMA Resolution 357/2005, enacted by the Brazilian National Environment Council in 2005, is an additional tool used to assess water quality. This resolution serves as a framework for classifying Brazil's water bodies, offering environmental guidelines for their use. Freshwater bodies are classified into five distinct categories based on their intended usage, ranging from "highly valuable" purposes such as drinking water, to lower-end uses like navigation and landscaping. Accordingly, each category of water usage has specific physical, chemical, and microbiological maximum values that must be met.

The issues raised in this work are relevant, persistent, and harm small farmers regarding the certification of organic products, which consequently reduces their clientele by not ensuring food safety. Therefore, the objective of this work was to analyze the water in Paracatu de Baixo, a sub-district of Mariana (MG) that was impacted by the Fundão dam mud, to evaluate the influence of mud dust on the spring water used by the few remaining residents who use this water for consumption and to irrigate vegetables that they consume and sell. This concern is due to the fact that it is known that mining wastes, such as dust, when exposed to weathering, are susceptible to leaching and erosion. Leaching of metals can cause contamination of surface water, groundwater, and soils in surrounding areas, endangering human health and ecology.<sup>19,20</sup>

## 2. Experimental

#### 2.1. Field of study

The community of Paracatu de Baixo (20°18'23.493" S and 43°13'48.769") is located in the Monsenhor Horta district in the rural area of Mariana, Minas Gerais, Brazil. Approximately 300 residents lived in the area, near the Gualaxo do Norte River. Family farming is a fundamental activity, as well as pig, chicken, and cattle raising. On November 5, 2015, iron ore tailings from the Fundão dam destroyed most of the occupied territory, leaving only the Church of Santo Antônio and a few houses on the slopes. According to the residents, the homes that still exist are supplied by wells or springs that are not chlorinated or filtered.

#### 2.2. Collection and analyzes

Water samples were collected during the rainy season at five different locations in Paracatu de Baixo (Table 1), on February 23 and April 2, 2022. On both dates, the day was sunny, but there had been atmospheric precipitation the day before collection. The collected water was cloudy and had suspended solids. Rainwater samples were also collected near P01.

 Table 1. Geographic coordinates of the locations where water sampling was performed

Code	Latitude	Altitude	
P01	20°18'24.106"	43°13'24.640"	
P02	20°18'24.235"	43°13'47.698"	
P03	20°18'23.202"	43°13'51.269"	
P04	20°18'29.365"	43°13'57.353"	
P05	20°18'27.068"	43°13'54.311"	

The collections during the dry season were carried out on June 22 and July 19, 2022, at the same locations where the collections were made during the rainy season.

The samples were collected in two polyethylene bottles for physicochemical analyzes at each collection point. About 1000 mL of water was collected in one bottle for the analyzes of different physicochemical parameters, and about 20 mL was collected in the other bottle for metal analyzes. Before being stored, the samples for metal analyzes were filtered through a 0.45  $\mu$ m filter and acidified with 3 drops of concentrated nitric acid to preserve the sample. The containers were properly labeled. Before collection, the taps at the collection sites were sterilized. This sterilization was carried out with a 70% ethyl alcohol solution, sprayed inside and outside, and then the water was allowed to run for a few minutes.

### 2.3. Analyzes

After water collection, all samples were placed in a thermal box (at 4 °C) and taken to the laboratory at Universidade Federal de Ouro Preto (UFOP) for analyzes of the following variables: pH, turbidity, electrical conductivity, hardness, nitrate, nitrite, total solids, and dissolved oxygen (DO).

To determine turbidity, a portable digital turbidimeter from Hach, model 2100P, was used, while a HACH 40 D HQ probe and LDO101 electrode were used to measure the DO. The turbidity was measured to evaluate the aesthetic quality of the water. Conductivity is the ability of a solution to conduct electric current, which is conditioned by the presence of ions in the medium. This parameter can help in understanding the leaching of rocks and minerals, being of great importance for water studies, since the pH has an influence on the dissolution and leaching of rocks and soils. The electrical conductivity and pH were measured with the HACH 40 D HQ probe and Intellical PHC101 electrode. Total solids were determined using the gravimetric method.<sup>21</sup>

The quantitative determination of nitrite  $(NO_2^{-})$  was performed by the diazotization reaction of the nitrite ion with sulphanilic acid and coupling with alpha-naphthylamine hydrochloride in an acidic medium. In this reaction, pinkcolored alpha-naphthylamine-*p*-azobenzenesulphonic acid is formed. The resulting product was spectrophotometrically determined at 540 nm.<sup>22</sup> For the determination of nitrate  $(NO_3^{-})$ , the salicylate method was used. In this method, nitronium ions  $(NO_2^{+})$  are formed in an acidic medium and with heating. When produced, these ions react with salicylate in a basic medium, forming mainly a yellow nitrobenzoic compound. Heating to dryness is necessary because water needs to be removed for  $NO_3^-$  conversion to  $NO_2^+$ .<sup>23</sup> The spectrophotometer used was the Genesys 10S, Thermo Scientific, USA model.

To determine the hardness, the complexometric volumetry technique was used. For this, 100.0 mL of each water sample was transferred to an Erlenmeyer flask, 2 mL of buffer solution was added, and approximately 0.05 g of the indicator eriochrome T black was added. The solution turned reddish. The burette was conditioned with the titrant ethylenediaminetetraacetic acid (EDTA) 0.01 mol L<sup>-1</sup> and titrated until a color change to blue was observed. The volume used in each sample was recorded and correlated with calcium carbonate (CaCO<sub>3</sub>). The analyzes was performed in triplicate.

The analyzes of the metals was performed using an inductively coupled plasma optical emission spectrometer (ICP OES, Agilent 725) of the Environmental Geochemistry Laboratory of the Department of Geology of the Universidade Federal de Ouro Preto. The analytical curve was prepared from multielement solution 10 mg L<sup>-1</sup>, Merck. A multielement solution of 100 ppb, Merck, containing the elements analyzed, was used to evaluate the accuracy of the method, resulting in recoveries between 90 and 101%.

## 3. Results and Discussion

Tables 2 and 3 display the statistical calculation summary of the mean concentrations of 8 water quality parameters at the sampling points in Paracatu de Baixo in samples collected during the dry and wet seasons.

**Table 2.** Physicochemical parameters (average  $\pm$  standard deviation) found at the sampling points in Paracatu de Baixo in samples collected during thedry and wet seasons and maximum allowed values according to CONAMA Resolution 357<sup>18</sup> and Portaria 1469<sup>24</sup>

						Samı	oles					
Parameters	MAX/*	P01C**	Р	01	Р	02	Р	03	Р	04	Р	05
	MAV*	Wet	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
pН	6,0-9,51***	$6.6\pm0.2$	$6.6\pm0.1$	$7.1\pm0.6$	$6.8\pm0.0$	$7.2\pm0.5$	$6.6\pm0.0$	$7.0\pm0.7$	$6.7\pm0.0$	$7.3 \pm 0.3$	$6.8\pm0.1$	$7.1 \pm 0.8$
Turbidity (NTU)	100*	$1.4 \pm 0.1$	$10.9\pm0.1$	4.4 ± 1.3	$7.8\pm0.0$	$2.3\pm0.6$	8.3 ± 0.0	$2.6\pm0.1$	5.1 ± 0.1	1.9 ± 0.3	16.3 ± 0.2	4.7 ± 0.8
Conductivity (µS cm <sup>-1</sup> )	110*	3.5 ± 0.4	27.2 ± 1.2	39.4 ± 0.1	27.0 ± 1.7	$26.4\pm0.1$	24.6 ± 0.7	27.3 ± 0.1	30.9 ±0.6	33.7 ± 0.1	$14 \pm 1$	18.6 ± 0.1
Hardness (mg CaCO <sub>3</sub> L <sup>-1</sup> )	500***	4.3 ± 0.1	$4.6\pm0.0$	9.0 ± 0.0	$4.9\pm0.0$	$5.2\pm0.0$	$4.9\pm0.0$	$4.4\pm0.0$	3.4 ± 0.0	$2.7\pm0.1$	$1.2\pm0.0$	$4.4 \pm 0.1$
Nitrate (mg L <sup>-1</sup> )	10*	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.09 ± 0.00	0.06 ± 0.00	0.03 ± 0.00	0.05 ± 0,00	0.06 ± 0.00	$0.05 \pm 0.00$	$0.05 \pm 0.00$	0.06 ± 0.00
Nitrite (mg L <sup>-1</sup> )	1*	0.01 ± 0.00	0.18 ± 0.00	0.34 ± 0.00	$0.22 \pm 0.00$	$0.32 \pm 0.00$	$0.25 \pm 0.00$	0.33 ± 0,00	$0.28 \pm 0.00$	0.31 ± 0,00	0.19 ± 0.00	$0.32 \pm 0.00$
Total solids (mg L <sup>-1</sup> )	500*	0.01 ± 0.01	$0.01 \pm 0.00$	0.01 ± 0.00	$0.01 \pm 0.00$	$0.02 \pm 0.01$	$0.01 \pm 0.00$	0,01 ± 0,01	$0.01 \pm 0.00$	0.01 ± 0,00	0,01 ± 0,00	$0.01 \pm 0.00$
DO (mg L <sup>-1</sup> )	> 5*	$7.4 \pm 0.1$	$7.3 \pm 0.3$	$7.8\pm0.1$	$7.5\pm0.2$	$7.8 \pm 0.2$	$7.6 \pm 0.1$	$7.8 \pm 0.1$	$7.4\pm0.2$	$7.9\pm0.1$	$7.3\pm0.3$	$7.9\pm0,0$

\*MAV = Maximum allowed value according to CONAMA Resolution 357/2005.<sup>18</sup> \*\*Rainwater. \*\*\*Portaria 1469.<sup>24</sup> Mean ± standard deviation of three analyzes in samples collected on two days.

	Points											
Elements	MAV*	P01C **	<b>P01</b> (n	ng L <sup>.1</sup> )	<b>P02</b> (1	mg L <sup>-1</sup> )	<b>P03</b> (n	ng L <sup>.1</sup> )	<b>P04</b> (r	ng L <sup>.1</sup> )	<b>P05</b> (r	ng L <sup>.1</sup> )
	$(mg \ L^{\cdot 1})$	$(mg L^{\cdot 1})$	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Ba <sup>1</sup>	0.70	0.00355	0.0166	0.0183	0.0141	0.0109	0.0169	0.0108	0.0227	0.0124	0.0160	0.00899
$Cu^1$	0.09	< LQ	0.00767	<lq< td=""><td><lq< td=""><td><lq< td=""><td>&lt; LQ</td><td>0.0059</td><td><lq< td=""><td><lq< td=""><td>&lt; LQ</td><td><lq< td=""></lq<></td></lq<></td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td><lq< td=""><td>&lt; LQ</td><td>0.0059</td><td><lq< td=""><td><lq< td=""><td>&lt; LQ</td><td><lq< td=""></lq<></td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>&lt; LQ</td><td>0.0059</td><td><lq< td=""><td><lq< td=""><td>&lt; LQ</td><td><lq< td=""></lq<></td></lq<></td></lq<></td></lq<>	< LQ	0.0059	<lq< td=""><td><lq< td=""><td>&lt; LQ</td><td><lq< td=""></lq<></td></lq<></td></lq<>	<lq< td=""><td>&lt; LQ</td><td><lq< td=""></lq<></td></lq<>	< LQ	<lq< td=""></lq<>
$Zn^1$	0.18	0.00869	0.0224	<lq< td=""><td><lq< td=""><td>0.0210</td><td>0.00315</td><td>0.0140</td><td><lq< td=""><td><lq< td=""><td>0.00474</td><td>0.00380</td></lq<></td></lq<></td></lq<></td></lq<>	<lq< td=""><td>0.0210</td><td>0.00315</td><td>0.0140</td><td><lq< td=""><td><lq< td=""><td>0.00474</td><td>0.00380</td></lq<></td></lq<></td></lq<>	0.0210	0.00315	0.0140	<lq< td=""><td><lq< td=""><td>0.00474</td><td>0.00380</td></lq<></td></lq<>	<lq< td=""><td>0.00474</td><td>0.00380</td></lq<>	0.00474	0.00380
Al <sup>1</sup>	0.10	< LQ	0.135	<lq< td=""><td>0.0546</td><td>0.00770</td><td>0.0245</td><td><lq< td=""><td>0.0300</td><td><lq< td=""><td>0.160</td><td><lq< td=""></lq<></td></lq<></td></lq<></td></lq<>	0.0546	0.00770	0.0245	<lq< td=""><td>0.0300</td><td><lq< td=""><td>0.160</td><td><lq< td=""></lq<></td></lq<></td></lq<>	0.0300	<lq< td=""><td>0.160</td><td><lq< td=""></lq<></td></lq<>	0.160	<lq< td=""></lq<>
Fe <sup>1</sup>	0.30	0.0377	0.594	0.151	0.676	0.0947	1.02	0.0794	0.299	0.0544	0.543	0.114
$Mn^1$	0.10	0.00441	0.00946	<lq< td=""><td>0.0310</td><td>0.00680</td><td>0.0999</td><td><lq< td=""><td>0.0250</td><td><lq< td=""><td>0.0103</td><td><lq< td=""></lq<></td></lq<></td></lq<></td></lq<>	0.0310	0.00680	0.0999	<lq< td=""><td>0.0250</td><td><lq< td=""><td>0.0103</td><td><lq< td=""></lq<></td></lq<></td></lq<>	0.0250	<lq< td=""><td>0.0103</td><td><lq< td=""></lq<></td></lq<>	0.0103	<lq< td=""></lq<>

Table 3. Element concentrations obtained in the evaluated samples and maximum allowed values according to CONAMA Resolution 35718

\*MAV = Maximum allowed value according to CONAMA Resolution 357/2005.18 \*\* Rainwater. LQ = limit of quantification

The concentrations of the inorganic chemicals in the water were determined by ICP OES. For this, the samples were analyzed in triplicate for determination of Ba, Cd, Co, Cr, Li, Mo, Ni, Sc, Ti, V, Y, Cu, Zn, As, Pb, Al, Fe, Mn, Ca, K, Na, Mg, P, and S. The metals Cd, Co, Cr, Li, Mo, Ni, Sc, Ti, V, Y, As, and Pb were not detected. The results were expressed as mg L<sup>-1</sup> and compared to CONAMA Resolution 357/2005,<sup>18</sup> according to its respective class of water (for Doce River, Class I). Since the CONAMA 357 legislation does not establish limits for Ca, K, Na, Mg, P, and S, their concentrations were not included.

The pH result was satisfactory since they were within the established limits (Table 2). pH values close to neutral were also found by other authors who studied spring water.<sup>25</sup> In the study by Leite *et al.*,<sup>26</sup> they associated the higher content of Al in rivers from the Pico do Itacolomi region, Ouro Preto, MG, Brazil, with the rocks found in the region and the lower pH value. Similarly, it is interesting to note that, in our study, at all sampling points, the dry season showed higher pH values and lower concentrations of Al.

The analyzes carried out showed that the turbidity levels in the collected water were in accordance with the limits established by law, being below the permitted level of 100 Nephelometric Turbidity Units - NTU (Table 2). Primavesi *et al.*,<sup>27</sup> Mosca,<sup>28</sup> and Donadio *et al.*<sup>29</sup> evidenced the function of riparian vegetation in containing solids that could reach the water. In this work, despite the spring being located in a region without vegetation cover, turbidity presented an adequate value.

The analyzes results showed a low conductivity value (Table 2). This result is due to the low concentration of ions present, which is possibly due to the fact that the water comes from a spring and does not receive effluents from the main chemical waste generators.

In the present study, even though the water was contaminated with some ions, it had hardness values below the limit allowed.

The presence of nitrate in water is mainly due to domestic sewage. Nitrite, on the other hand, a compound composed essentially of protein, is primarily found in feces, sewage, and food residues.<sup>30</sup> The results demonstrate that in the studied water, nitrite, and nitrate levels are below

the maximum allowed (Table 2). Similarly, to what was explained for the conductivity values found, the low values of nitrate and nitrite may be due to the fact that we studied spring water, which has not come into contact with human waste and residues. This result is discordant with the values found by Castro and Mendonça<sup>31</sup> and Agioda *et al.*<sup>32</sup>, who observed that after the first rains, there was an increase in nitrate concentration. They explained this increase due to fertilization, mineralization of organic matter accumulated during the dry period, and pig excrement. In this study, the value found may be because the sample collection was done at the end of the rainy season.

Total solids are the sum of total dissolved solids and total suspended solids. The analyzes result showed that the value for total solids was within the limits allowed by CONAMA Resolution No. 357/2005.<sup>18</sup> This result is consistent with the turbidity results. In this study, the low turbidity and total solids may be related to the fact that the spring is located in a pasture region. Fernandes *et al.*<sup>33</sup> also observed that well-managed pasture in the watershed provides soil protection benefits and does not increase the amount of total solids in the water.

According to Von Sperling<sup>34</sup> and Latuf,<sup>35</sup> low DO values are indicative of the increased decomposition of organic matter and pollution in the aquatic environment through organic waste disposal. In this study, despite the presence of a pasture near the spring, the DO value was within CONAMA Resolution 357.<sup>18</sup> According to Franco and Hernandez,<sup>36</sup> low DO values are observed where sewage is discharged into water sources, as found by Vanzela<sup>37</sup> in the Três Barras stream, which receives sewage from the city of Marinópolis, SP. In the area studied in this work, there was no sewage near the spring, which explains the adequate values found.

With regard to the metals quantified in the water samples, only Fe and Al exceeded the concentration stipulated by CONAMA Resolution 357,<sup>18</sup> at times (Table 3). Samples P01 and P05 exceeded the maximum allowed concentration for aluminum in the rainy season and samples P01, P02, P03 and P05 had an iron content higher than that allowed also in the rainy season. Generally, with precipitation, there is a dilution process of the components present in the water, meaning that the tendency is for the concentration to decrease, not to increase. However, for Al and Fe, the opposite behavior was observed, indicating the solubilization of the material near the spring, releasing these metals into the water. Although Fe is also present in the dry season, but with lower concentration, it is possible to say that this element is more prone to mobility in the two seasons in relation to the other metals. It is also observable that during the dry season, aluminum and manganese have low mobility. The metal iron violated the maximum allowed values according to CONAMA Resolution 357<sup>18</sup> in all seasons, having a behavior similar to that observed for aluminum and manganese, with higher concentrations in the rainy season. However, it is more prone to mobility in both seasons.

The high concentrations of these elements in the water cannot be explained by the suspension of mud dust in the study area. If this were the case during the dry season, there should be a high content of these elements. However, the opposite was observed with a decrease in concentration. Thus, it is possible that mud dust does not affect the spring water used to supply the residents of Paracatu. The most likely origin of these elements may be related to geogenic sources rather than anthropogenic sources. According to the lithostratigraphic map and the collection points, the results of Fe for periods with higher rainfall indices showed a significant increase. This is due to the high rate of weathering of the geological material in the upper course of the Gualaxo do Norte River and the consequent leaching of the altered biotite–gneiss rock<sup>38</sup> near the spring (Figure 1). This high concentration is related to the chemical weathering of biotite  $(K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2)$ , a mineral that has Fe in its structure, which appears weathered in the outcropping samples.<sup>38</sup> Manganese  $(Mn^{2+})$  was another ion that showed an increase in its concentration rate during periods of higher rainfall. Similar to Fe, mineral leaching is the main agent for the increase in these concentrations. According to Costa (2001),<sup>39</sup> the Gualaxo do Norte River has oxides that carry manganese in their crystalline structure along the stream.

Aluminum (Al) was another element that had its concentration increased during rainy periods, except for point P02, which only had its content quantified during rainy periods. Being one of the most abundant elements in the Earth's crust, this indicates the occurrence of the contribution of this element through the chemical weathering of geological material found in felsic banding (light-colored granite bands) of biotite–gneiss outcrops in the region. In these granite bands, plagioclase ((Na, Ca) AlSi<sub>3</sub>O<sub>8</sub>) can be found, which, when altered by hydrolysis, forms kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)). This may explain the Al content found in the region, which, despite its abundance in the crust, has low solubility, which explains its lower concentration compared to the Fe concentration.

The results found for Al and Fe cause a little concern, since there was a violation of the maximum allowed value established by CONAMA 357.<sup>18</sup> It is important to mention that Fe is essential for the proper functioning of



Figure 1. Lithostratigraphic map of the sample collection region. Black dots indicate the collection coordinates, red dots represent the geochemical sampling of the current sediments<sup>38</sup> from the Mariana sheet, and yellow dots represent the outcropped rocks described by the same sheet

Parameter	Present study	Silva <i>et al.</i> 2022 <sup>7</sup>	IGAM 201849
pН	6.60 - 7.30	7.00 - 7.10	5.80 - 8.20
Turbidity (NTU)	1.4 – 16.3	44 - 58	6.04 - 435,400
Conductivity (µS cm <sup>-1</sup> )	3.5 - 39.4	60 - 65	40.6 - 244.8
Total solids (mg L-1)	0.01 - 0.02	_	50 - 112,470
DO (mg L-1)	7.3 - 7.9	8.0	0.6 - 9.0
Cu (mg L <sup>-1</sup> )	0.00590 - 0.00767	0.002 - 0.0284	0.0284 - 0.04
Zn (mg L-1)	0.00315 - 0.0225	-	0.0226 - 0.539
Al (mg L <sup>-1</sup> )	0.00770 - 0.160	0.005 - 0.651	0.024 - 2.39
Fe (mg L <sup>-1</sup> )	0.0377 - 1.02	0.0646 - 0.645	0.0646 - 6.758
Mn (mg L <sup>-1</sup> )	0.00680 - 0.0999	0.0048 - 3.675	0.0048 - 103.8

Table 4. Comparison of results obtained in this study and other references

the human organism since this element is a constituent of haemoglobin.<sup>40</sup> However, the high exposure to this element due to consumption of water with concentrations that violate the norm results in health risks. Fe can cause hemochromatosis, which leads to cancer, irregular heartbeat, and liver cirrhosis, among other dysfunctions of the body.<sup>41-43</sup>

Some researchers have reported that Al accumulation is associated with various pathological effects, such as lung injuries,<sup>44</sup> bone abnormalities,<sup>45</sup> and neurological disorders.<sup>46,47</sup> Capriello *et al.*<sup>48</sup> stated that Al exposure can promote oxidative stress in nervous tissue, inducing neurodegeneration and neuronal necrosis, which constitute the basis of neurological diseases, such as Alzheimer's and Parkinson's diseases.

Table 4 shows the comparison of the results obtained in this work (with spring water) with other studies carried out in the rivers affected by the mud, adjacent to Paracatu de Baixo. For the results of IGAM 2018,<sup>49</sup> the Gualaxo do Norte, Carmo, and Doce rivers were considered, obtained in the emergency monitoring between November 7, 2015 and December 7, 2017. The studies by Silva *et al.*<sup>7</sup> were carried out in Doce River.

The physical-chemical data, such as pH, turbidity, conductivity, total solids, and dissolved oxygen, are inferior to the studies carried out by Silva *et al.*<sup>7</sup> and IGAM 2018.<sup>49</sup> It is also observed that the concentrations of metals evaluated in this work are lower than those found by IGAM 2018,<sup>49</sup> except for the element Mn, which exceeds the lowest content found. When comparing with the study by Silva *et al.*,<sup>7</sup> there is a similarity in the concentrations, highlighting again the Mn with the highest value found, about 40 times higher than that found in the present work. In view of these comparisons, it is reasonable to say that the spring water captured in Paracatu de Baixo is more suitable for domestic use in relation to the aforementioned works, although other parameters must be evaluated in order to conclude on the potability of the water.

Even though mud did not affect the water resources of the sub-district of Paracatu, it is always important to conduct research aimed at assessing environmental and human health. Any results related to the well-being of the population should be developed and disseminated to ensure and improve the quality of life. This study presents results that could contribute to future studies in the field of public health.

## 4. Conclusion

This study aimed to investigate the water used by residents of Paracatu de Baixo, a sub-district of Mariana, which was heavily impacted by mud from the Fundão Dam. Although the physicochemical parameters studied were in accordance with CONAMA Resolution 357/05, the concentration of Al and Fe metals is above the permitted level, causing concern. However, mud dust did not influence the high levels of these elements in the water, as it was a lithological issue.

### References

- Solomons, W.; Förstner, U.; *Metals in the hydrocycle*. Springer-Verlag: Berlim, 1984. [Crossref]
- Borba, R. P.; Figueiredo, B. R.; Rawlins, B.; Matschullat, J.; Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil. *Environmental Geology* 2003, 44, 39. [Crossref]
- Bundschuh, J.; Litter, M. I.; Parvez, F.; Román-Ross, G.; Nicolli, H. B.; Jean, J.-S.; Liu, C.-W.; López, D.; Armienta, M. A.; Guilherme, L. R. G.; Cuevas, A. G.; Cornejo, L.; Cumbal, L.; Toujaguez, R.; One century of arsenic exposure in Latin America: a review of history and occurrence from 14 countries. *Science* of The Total Environment 2012, 429, 2. [Crossref] [PubMed].
- Ono, F. B.; Guilherme, L. R. G.; Mendes, L. A.; Carvalho, G. S.; Replication of an ivg protocol to estimate bioaccessible arsenic in materials from a gold mining area in Brazil. *Revista Brasileira de Ciência do Solo* 2012, *36*, 1355. [Crossref]
- Ono, F. B.; Guilherme, L. R. G.; Penido, E. S.; Carvalho, G. S.; Hale, B.; Toujaguez, R.; Bundschuh, J.; Arsenic bioaccessibility in a gold mining area: a health risk assessment for children. *Environmental Geochemistry and Health* 2012 34, 457. [Crossref]

- IGAM (2019). INSTITUTO MINEIRO DE GESTÃO DAS ÁGUAS – IGAM. Séries Históricas de Monitoramento da Qualidade das Águas Superficiais do Estado de Minas Gerais. Available in: <a href="http://200.198.57.118">http://200.198.57.118</a>:8080/ handle/123456789/405>. Available at: April 28th 2023.
- Silva, G. J.; Borges, A. C.; Moreira, M. C.; Rosa, A. P.; Statistical process control in assessing water quality in the Doce river basin after the collapse of the Fundão dam (Mariana, Brazil). *Journal* of Environmental Management 2022, 317, 115402. [Crossref] [PubMed]
- 8. SEMAD-IGAM Sistema Estadual de Meio Ambiente Instituto Mineiro de Gestão das Águas Governo do Estado de Minas Gerais. MONITORAMENTO DA QUALIDADE DAS ÁGUAS SUPERFICIAIS DO RIO DOCE NO ESTADO DE MINAS GERAIS, RELATORIO TECNICO Acompanhamento da Qualidade das Aguas do Rio Doce Após o Rompimento da Barragem da Samarco no distrito de Bento Rodrigues - Mariana/ MG. 01 DE FEVEREIRO DE 2016, p. 75. Available at: <a href="http://www.igam.mg.gov.br/component/content/article/16/1632-monitoramento-da-qualidade-das-aguas-superficiaisdo-rio-doce-no-estadode minas-gerais">http://www.igam.mg.gov.br/component/content/article/16/1632-monitoramento-da-qualidade-das-aguas-superficiaisdo-riodoce-no-estadode minas-gerais, 2015></a>
- Segura, F. R.; Nunes, E. A.; Paniz, F. P.; Paulelli, A. C. C.; Rodrigues, G. B.; Braga, G. U. L.; Pedreira Filho, W. R.; Barbosa Jr, F.; Cerchiaro, G.; Silva, F. F.; Batista, B. L.; Potential risks of the residue from Samarco's mine dam burst (Bento Rodrigues, Brazil). *Environmental Pollution* **2016**, *218*, 813. [Crossref] [PubMed]
- IGAM. Monitoramento da Qualidade das Águas Superficiais do Rio Doce no Estado de Minas Gerais. Instituto Mineiro de Gestão das Águas, 2015. [Link]
- Carmo, F. F. do; Kamino, L. H. Y.; Junior, R. T.; Campos, I. C. de; Carmo, F. F. do; Silvino, G.; Castro, K. J. da S. X. de; Mauro, M. L.; Rodrigues, N. U. A.; Miranda, M. P. de S.; Pinto, C. E. F.; Fundão tailings dam failures: the environment tragedy of the largest technological disaster of Brazilian mining in global context. *Perspectives in Ecology and Conservation* 2017, *15*, 145. [Crossref]
- Guerra, M. B. B.; Teaney, B. T.; Mount, B. J.; Asunskis, D. J.; Jordan, B. T.; Barker, R. J.; Santos, E. E.; Schaefer, C. E. G. R.; Post-catastrophe analysis of the Fundão tailings dam failure in the Doce River system, Southeast Brazil: potentially toxic elements in affected soils. *Water, Air, & Soil Pollution* 2017, 228, 252. [Crossref]
- 13. IBAMA Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis, Ministério do Meio Ambiente. Diretoria de Proteção Ambiental - DIPRO e Coordenação Geral de Emergências Ambientais - CGEMA. Laudo Técnico Preliminar: Impactos ambientais decorrentes do desastre envolvendo o rompimento da barragem de Fundão, em Mariana, Minas Gerais, Novembro de 2015, p. 38. [Link]
- Quadra, G. R.; Roland, F.; Barros, N.; Malm, O.; Lino, A. S.; Azevedo, G. M.; Thomaz, J. R.; Andrade-Vieira, L. F.; Praça-Fontes, M. M.; Almeida, R. M.; Mendonça, R. F.; Cardoso, S. J.; Guida, Y. S.; Campos, J. M. S.; Far-reaching cytogenotoxic effects of mine waste from the Fundão dam disaster in Brazil. *Chemosphere* 2019, *215*, 753. [Crossref] [PubMed]

- Alves, R. I. S.; Machado, C. S.; Beda, C. F.; Fregonesi, B. M.; Nadal, M.; Sierra, J.; Domingo, J. L.; Segura-Muñoz, S. I.; Water quality assessment of the Pardo River Basin, Brazil: a multivariate approach using limnological parameters, metal concentrations and indicator bacteria. *Archives of Environmental Contamination and Toxicology* **2018**, *75*, 199. [Crossref] [PubMed]
- 16. IBAMA Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis, Ministério do Meio Ambiente. Diretoria de Proteção Ambiental - DIPRO e Coordenação Geral de Emergências Ambientais - CGEMA. Parecer técnico sobre os resultados obtidos nas coletas de amostras de água e sedimento no rio Doce e na região da foz, no estado do Espirito Santo, 2016. [Link]
- Silva, D. de C.; Bellato, C. R.; Neto, Marques, J. de O.; Fontes, M. P. F.; Trace elements in river waters and sediments before and after a mining dam breach (Bento Rodrigues, Brazil). *Química Nova* 2018, *41*, 857. [Crossref]
- CONAMA. Resolução CONAMA No 357/2005 Conselho Nacional do Meio Ambiente-Ministério do Meio Ambiente, 2005. [Link]
- Verma, A.; Kumar, R.; Yadav, S.; Distribution, pollution levels, toxicity, and health risk assessment of metals in surface dust from Bhiwadi industrial area in North India. *Human and Ecological Risk Assessment: An International Journal* 2020, 26, 2091. [Link]
- Khan, S.; Shahnaz, M.; Jehan, N.; Rehman, S.; Shah, M.T.; Drinking water quality and human health risk in Charsadda district, Pakistan. *Journal of Cleaner Production* 2013, 60, 93. [Crossref]
- ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS NBR 10644. Águas - Determinação de resíduos (sólidos) – Método Gravimétrico Rio de Janeiro:, 1989. 7 p. [Link]
- 22. Lara, W. H.; Takahashi, M. Y.; Silveira, N; Determinação de nitritos e nitratos em conservas de carne. *Revista do Instituto Adolfo Lutz* **1978**, *38*, 161.
- Yang, J. E.; Kim, J. J.; Skogley, E. O.; Schaff, B. E.; A simple spectrophotometric determination of nitrate in water, resin and soil extracts. *Soil Science Society and America Journal* 1998, 62, 1108. [Link]
- BRASIL. Portaria N° 1469/2000, do Ministério da Saúde. Estabelece os procedimentos e responsabilidades relativos ao controle e vigilância da qualidade da água para consumo humano e seu padrão de potabilidade. Diário Oficial da União, Brasília, 01 de janeiro de 2001. [Link]
- Marmontel, C. V. F.; Rodrigues, V. A.; Parâmetros indicativos para qualidade da água em nascentes com diferentes coberturas de terra e conservação da vegetação ciliar. *Floresta e Ambiente* 2015, 22, 171. [Crossref]
- Leite, M. G. P.; Fujaco, M. A. G.; Nalini Jr, H. A.; Castro, P. T. A.; Influence of geology in the geochemistry signature of Itacolomi State Park waters, Minas Gerais-Brazil. *Environmental Earth Sciences* 2010, *60*, 1726. [Crossref]
- Primavesi, O.; Freitas, A. R. de; Primavesi, A. C.; Oliveira, H. T. de; Water quality of the Canchim's Creek watershed in São Carlos, SP, Brasil, occupied by beef and dairy cattle activities.

*Brazilian Archives of Biology and Technology* **2002**, *45*, 209. [Crossref]

- Mosca, A. A. O.; *Dissertação de Mestrado*, Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo, 2003. [Crossref]
- Donadio, N. M. M.; Galbiatti, J. A.; Paula, R. C. de; Qualidade da água de nascentes com diferentes usos do solo na bacia hidrográfica do córrego Rico, São Paulo, Brasil. *Engenharia Agrícola* 2005, 25, 115. [Crossref]
- Braga, E. de A. S.; *Dissertação de Mestrado*, Universidade Federal do Ceará, 2006. [Link]
- Castro, C. B. de; Mendonça, A. S. F.; Impactos de ações antrópicas em bacias de mananciais rurais de montanha sobre parâmetros de qualidade de água. *Revista Brasileira de Recursos Hídricos* 2004, 9, 17. [Crossref]
- Agioda, A.; Merlo, C.; Carmantrand, B.; Simon, J. C.; JAMET, P.; *Resumos da Conferência sobre agricultura e meio ambiente*, Viçosa, Brasil, 1992.
- Fernandes, M. M.; IOST, C.; Gomes, S. D.; Boas, M. A. V.; Influência do uso do solo na qualidade de água da microbacia Glória, Macaé - RJ. *Engenharia Ambiental* 2011, 8, 105.
- 34. Von Sperling, M.; *Princípios do tratamento biológico de águas residuárias*, 3a ed., UFMG: Belo Horizonte, 2005.
- Latuf, M. de O. Diagnóstico das águas superficiais do Córrego São Pedro, Juiz de Fora - MG. *Geografia* 2004, 13, 21. [Link]
- Franco, R. A. M.; Hernandez, F. B. T.; Qualidade da água para irrigação na microbacia do Coqueiro, Estado de São Paulo. *Revista Brasileira de Engenharia Agrícola e Ambiental* 2009, 13, 772. [Crossref]
- Vanzela, L. S.; Dissertação de Mestrado, Universidade Estadual Paulista, 2004.
- CPRM. Servico Geologico do Brasil, 1993. LEVANTAMENTOS GEOLÓGICOS BÁSICOS DO BRASIL, MARIANA - Folha SF.23-XB-1. Brasília – DF, Brasil, 1993. [Link]
- Costa, A. T.; *Dissertação de Mestrado*, Universidade Federal de Ouro Preto, 2001. [Link]
- 40. Sharma, G. K.; Jena, R. K.; Ray, P.; Yadav, K. K.; Moharana, P. C.; Cabral-Pinto, M. M. S.; Bordoloi, G.; Evaluating the geochemistry of groundwater contamination with iron and manganese and probabilistic human health risk assessment in endemic areas of the world's largest River Island, India.

*Environmental Toxicology and Pharmacology* **2021**, 87,103690. [Crossref] [PubMed]

- Yadav, K. K.; Kumar, S.; Pham, Q. B.; Gupta, N.; Rezania, S.; Kamyab, H.; Yadav, S.; Vymazal, J.; Kumar, V.; Tri, D. Q.; Talaiekhozani, A.; Prasad, S.; Reece, L. M.; Singh, N.; Maurya, P. K.; Cho, J.; Fluoride contamination, health problems and remediation methods in Asian groundwater: comprehensive review. *Ecotoxicology and Environmental Safety* 2019, *182*, 109362. [Crossref]
- 42. Rostern, N. T.; The effects of some metals in acidified waters on aquatic organisms. *Oceanography & Fisheries* **2017**, *4*, 555. [Crossref]
- Chaturvedi, R.; Banerjee, S.; Chattopadhya, P.; Bhattacharjee, C. R.; Raul, P.; Borah, K.; High iron accumulation in hair and nail of people living in iron affected areas of Assam, India. *Ecotoxicology and Environmental Safety* 2014 110, 216. [Crossref] [PubMed]
- 44. Kongerud, J.; Soyseth, V.; Respiratory disorders in aluminum smelter workers. *Journal of Occupational and Environmental Medicine* **2014**, *56*, S60. [Crossref] [PubMed]
- 45. Klein, G. L. Aluminum toxicity to bone: a multisystem effect? Osteoporosis and Sarcopenia 2019 5, 2. [Crossref] [PubMed]
- Colomina, M. T.; Peris-Sampedro, F.; Aluminum and Alzheimer's disease. *Advances in Neurobiology* 2017 18, 183. [Crossref] [PubMed]
- Morris, G.; Puri, B. K.; Frye, R. E.; The putative role of environmental aluminium in the development of chronic neuropathology in adults and children. How strong is the evidence and what could be the mechanisms involved? *Metabolic Brain Disease* 2017 32, 1335. [Crossref] [PubMed]
- Capriello, T.; Meglio, G.; Maio, A.; Scudiero, R.; Bianchi, A. R.; Trifuoggi, M.; Toscanesi, M.; Giarra, A.; Ferrandino, I.; Aluminium exposure leads to neurodegeneration and alters the expression of marker genes involved to parkinsonism in zebrafish brain. *Chemosphere* 2022 307, 135752. [Crossref]
- IGAM. Acompanhamento da Qualidade das Águas da Rio Doce após Rompimento da Barragem da Samarco no Distrito de Bento Rodrigues - Mariana/MG: tabelas de resultados, 2018b. Available ar: <a href="http://repositorioigam.meioambiente.mg.gov.br/">http://repositorioigam.meioambiente.mg.gov.br/</a> handle/123456789/462>. Accessed on May 13th 2023.