Orbital: The Electronic Journal of Chemistry
journal homepage: www.orbital.ufms.br
e-ISSN 1984-6428

| Vol 10 | | No. 4 | | Special Issue June 2018 |

FULL PAPER

Metals and Arsenic in Water Supply for Riverine Communities Affected by the Largest Environmental Disaster in Brazil: The Dam Collapse on Doce River

Gabriel Oliveira de Carvalho*[a], André de Almeida Pinheiro[a], Dhoone Menezes de Sousa[a], Janeide de Assis Padilha[a], Juliana Silva Souza[a], Petrus Magnus Galvão[a], Thaís de Castro Paiva[a], Aline Soares Freire[b], Ricardo Erthal Santelli[b], Olaf Malm[a], and João Paulo Machado Torres[a]

[a]Laboratório de Radioisótopos Eduardo Penna Franca, Instituto de Biofísica Carlos Chagas Filho, Universidade Federal do Rio de Janeiro. Avenida Carlos Chagas Filho, 373, Bloco G, Sl. 061, Rio de Janeiro, 21941-902, Brazil.
[b]Departamento de Química Analítica, Instituto de Química, Universidade Federal do Rio de Janeiro. Avenida Athos da Silveira Ramos, 149, Cidade Universitária, Rio de Janeiro, 21941-909, Brazil

Article history: Received: 02 October 2017; revised: 21 February 2018; accepted: 27 February 2018. Available online: 20 June 2018. DOI: http://dx.doi.org/10.17807/orbital.v10i4.1081

Abstract:

Considered the worst environmental disaster in Brazilian history, the collapse of Samarco dam directly affected the Doce river. Inhabitants living along the river who relied mainly on Doce river's water supply for agriculture and human consumption faced risk from the mining residue exposure. This study aimed to investigate the disaster's impact on small family farmers living in Minas Gerais and Espírito Santo States by water elemental quantification and evaluate the potential pathways of contamination by survey. In July 2016, 48 water points - including well, river and public distributed water - of 3 cities (Belo Oriente, Governador Valadares and Colatina) were sampled for determination of As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sn and Zn elements. Ninety-eight percent of the inhabitants interviewed related Doce river water usage before the tragedy for diversified purposes, while only thirty-six per cent used it after the disaster, mainly for irrigation. Fe and Mn presented concentrations above the Brazilian legislation for drinking water and irrigation in all locations, but not in all samples. Pb concentration was above the drinking water legislation in one location. All the other elements concentrations were within safe limits. Colatina, the farthest city from the dam, presented the highest values, followed by Governador Valadares and Belo Oriente.

Keywords: contamination; Doce river; family farming; metals; dam collapse; water

1. Introduction

On 5th November of 2015, an iron-ore mining dam called Fundão collapsed in Mariana city, Minas Gerais State in Southeastern Brazil. More than 50 million cubic meters of toxic mud were leached [1, 2]. This event has been considered the worst Brazilian environmental disaster due to its large scale and social and environmental damages [3]. The dam belongs to the mining company Samarco, a joint venture of Vale S.A and BHP Billiton. The flood ran throughout more than 600 km of the Doce river, leading to a direct destruction of ecosystems, impacts on fauna and flora, as well as serious socioeconomic losses that caused problems regarding clean water supply for human consumption and agriculture [3, 4]. A multitude of social problems have risen after the dam rupture, mainly on water access for consumption and irrigation.

Mining activity in Minas Gerais State has been developed since the beginning of Portuguese colonization of Brazil. Due its rich mineral deposits, the region encompassing Mariana city is named "Iron Quadrangle". Formerly exploited targeting gold, nowadays, iron is the main metal

*Corresponding author. E-mail: gabriell.goc@biof.ufrj.br

of interest in this region [5]. Mining activity leads to the mobilization of trace elements to the environment. It has been identified an influence of iron-ore mining on the concentrations of the elements Fe, Mn, Cu, Hg, Cr, and Ni to the surrounding environment [6]. In that way, it can either add new sources of contamination, or mobilize the elements naturally occurring in the sediment.

Doce river is the second largest river of the southeast region of Brazil. Its draining basin encompasses an area of approximately 83,400 km^2. With a population superior to 3.5 million, there are diverse economic activities along this river, such as agriculture, mining, energy production, human and animal supply, and irrigation [7]. Family farming is practiced along the Doce river and, consequently, the riverine communities relied on the river water, mainly for irrigation, animal supply and fishery. In a broader definition, the Food and Agriculture Organization (FAO) considers that family farming is "a means of organizing agricultural, forestry, fisheries, pastoral and aquaculture production which is managed and operated by a family and predominantly reliant on family labor, including both women's and men's" [8]. Brazilian legislation has a stricter definition of family farmers which specify the maximum area, amongst other considerations [9]. Because of the usual small properties and low income, it depends strongly on the local availability of water and mineral resources of the soils.

The mud from the collapsed dam presented high proportion of sand and silt and it was mainly composed of SiO, Fe, Mn, Cu, Ca and Cr [10, 11]. The waste that leaked from the dam caused damages to human health, fishery resources, water quality, riparian vegetation and compacted the soil along the margins of the river [3, 4, 12]. Brazilian "Mineral Resources Research Company" (CPRM) reported higher Fe concentrations in the leaked mud (>15%) when compared to the region background values, while the other elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn) were in a comparable level [13]. Nonetheless, Mn and Fe concentrations in the Doce river have been reported to be respectively four times and one and half times higher than the water from an uncontaminated river nearby. In the same study, it was also observed potential risks of cytotoxicity, DNA damages and high potential of mobilization from mud to water for Pb, As, Sr, Fe, Mn and Al [11].

This study aimed to evaluate the potential toxic risk posed by the use of water by riverine farmers affected by the dam collapsed in Doce river, regarding chemical elements concentration (Mn, Fe, As, Cd, Sn, Pb, Ni, Cr, Zn, Cu, Hg), and identify the critical pathways for the arsenic and metal human exposure through the water uses.

2. Results and Discussion

All interviewed people between 18 and 82 years old were owner or in charge of small rural properties. Amongst them 32 were males, while 12 were females. The majority only had up to the middle school (65%), while few reached the high school (21%) and some of them did not study or were illiterate (14%). Twenty of them reported being farmers; the rest defined themselves by retired, fisherman, unemployed or housewives.

Some of the participants lived in remote areas or under very simple conditions without access to technology and media of information. Because of that, 20% of them reported only discovering about the dam collapse after the mud wave arrived at their properties, despite living far from the accident, at least 200 km downstream from Mariana town. As a consequence, 88% of the participants related changes and losses in their agricultural production. The majority, however, followed the news by television and anticipated the consequences of the disaster. For the author's information, there was no system or attempt to notify these vulnerable residents about the danger coming.

Concerning the Doce river water usage, 98% related using it before the tragedy for different purposes, such as irrigation animal supply, cooking, swimming, showering and fishing. On the other hand, only 36% used it after the disaster. And within this group, about 80% of them were only using it for irrigation, with different plants cultivation being reported. There was a concern about the health consequences of this water, as 60% of them considered the water not suitable for usage even after treatment. Because of the general concern about the public water, the majority of them stated buying mineral water for drinking and cooking, consequently increasing their expenses. Nonetheless, only 48% declared receiving public or private support regarding water supply, which means half of them had to rely on buying or donations.

Concentrations of elements in well water samples had a high coefficient of variation within locations and a wide range of values (min and max) (Table 1). This could be result of the large heterogeneity of element composition in the soil of Minas Gerais State [14] or even the heterogeneity of the mud from the dam [11]. Fe and Mn presented concentrations above the legislation for irrigation and drinking water [15, 16], while Pb had one concentration above the limit for drinking water in Belo Oriente. All other elements presented values below their maximum values permitted. In well water samples from Colatina, the maximum value for Mn was 10 times higher than the limit, and the maximum Fe found was almost 50 times higher than stipulated as safe. Belo Oriente presented the lowest values for the majority of elements analyzed. Moreover, Colatina city also had one well water sample with Arsenic concentration reaching the maximum permitted by legislation (Table 1; Table IS-supplementary material).

Belo Oriente, Governador Valadares and Colatina had respectively 4, 9 and 5 well samples with concentrations of Fe and 2, 3 and 2 well samples with concentrations of Mn above the stipulated as safe for human consumption (Figure 1). To the best of authors' knowledge, there are no previous studies for well water in this region for these elements before the dam collapse to compare with; nonetheless, it was observed an enrichment of Fe and Mn in sediments affected by the mud in the Doce river margins [12]. Moreover, in a study performed on well water sampled five months later than the accident, the authors reported Mn and Fe concentrations higher (Mn=520 µg L^{-1}; Fe=34130 µg L^{-1}) in the sampling point closer to the Doce river (Espírito Santo state), when compared to the farther sampling station (Mn=26 µg L^{-1}; Fe=3830 µg L^{-1}) [17]. Considering the high background concentrations for Fe and Mn in the sediments of "Iron Quadrangle" region - Fe=21.7 g L^{-1}, Mn=6.3 g L^{-1} [14], it could be expected a natural enrichment of these elements in well water along the area.

Fe concentrations in two samples of the supplemental water supply offered by the dam owner Samarco at the farthest city from the dam collapse (Colatina city) were not in accordance with to the Brazilian legislation regarding the human consumption. The values were two to three times higher than the threat value. The samples of supplemental water supply at the closest sampling point (Belo Oriente city) were in accordance with the legislation for all analyzed elements (Table 1).

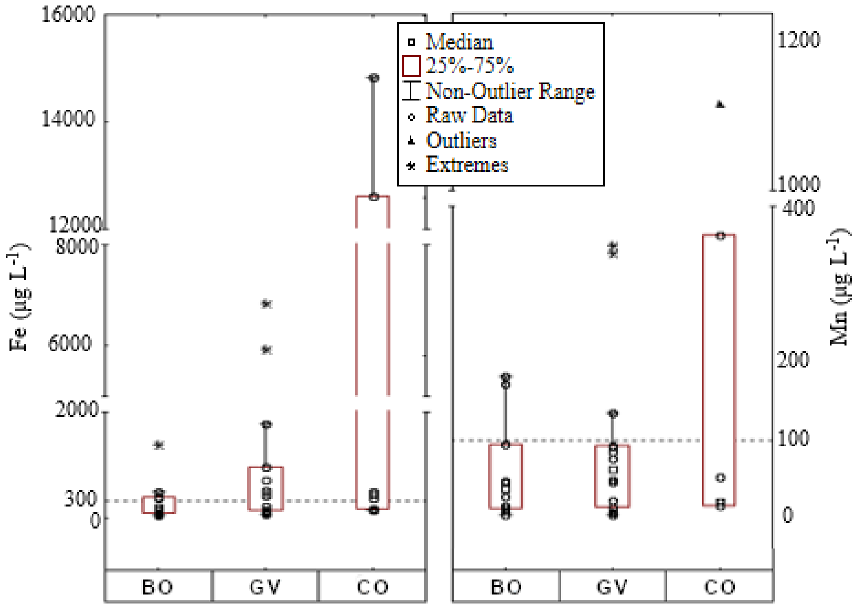

Figure 1. Boxplot representing data for Fe and Mn from well points for Belo Oriente (BO) - 200Km, Governador Valadares (GV) - 280Km - and Colatina (CO) - 400Km.

Considering Doce river water samples, the highest values were found for the farthest sampling station from the collapsed dam (Colatina city - 400 km), with critical values for Mn and Fe, above stipulated as safe for a class 2 river [18] - this legislation categorizes the water bodies in classes, being class-2 suitable for drinking and irrigation after conventional treatment, as well as recreational and fishing. Samples from Colatina presented maximum value for Fe and Mn concentration one order of magnitude higher than the threat limit (Table 1). In contrast, the closest city from the collapsed dam - Belo Oriente city (200 km) - presented the lowest values for the majority of elements analyzed. Because there is only 1 river sample for this city, the values cannot be conclusive. In addition, one river sample from Governador Valadares had Zn concentration above the class-2 threshold. Considering that CONAMA 357/2005 river regulation sets values for dissolved Fe and Cu and our study reports total Fe e Cu, direct comparisons are not possible. However, when comparing the concentrations with the other legislations, Colatina and Governador Valadares had river points with values of Fe above the stipulated for drinking.

Table 1. Elements concentration in river, well water and supplemental water supply for Belo Oriente, Governador Valadares and Colatina. Values are in µg L^{-1}. Bold values are above maximum values stipulated by Brazilian legislation. Drinking water: Portaria MS Nº 2914 - 12/12/2011. Irrigation: CONAMA 396/2008. Class 2 river: CONAMA-357/2005. * Values for dissolved metals.

	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sn	Zn
Reference values- Brazilian Legislation											
a-Drinking	10	5	50	2000	300	1	100	70	10	-	5000
b-Irrigation	-	10	100	200	5000	2	200	200	5000	-	2000
c-Class 2 river	10	1	50	9*	300*	0.2	100	25	10	-	180
Well water (ab)											
Belo Oriente (n=10)											
Min	0.1	0.1	0.5	3.3	47		3.7	1.3	0.26	0.6	8.4
Max	0.5	0.2	6.3	12.9	**1369**	<0.1	**183**	2.5	11	0.8	21.0
Median	0.2	0.1	2.4	4.5	190		37.5	1.9	0.5	0.7	14.2
Gov. Valadares (n=14)											
Min	0.1	0.1	0.2	2.3	63		4.2	1.1	0.3	0.6	5.9
Max	0.6	0.2	9.6	28.4	**6826**	<0.1	351	5.0	1.4	0.8	710.0
Median	0.2	0.1	1.1	3.4	**460**		62.5	1.7	0.5	0.7	27.3
Colatina (n=7)											
Min	0.2	0.1	1.5	2.7	145		16	0.7	0.5	0.7	3.7
Max	10	0.3	3.1	4.6	**14849**	<0.1	1115	13	1.6	0.9	14.8
Median	0.3	0.1	1.8	3.8	**426**		21	1.9	0.6	0.7	7.8
Supplemental water supply (a)											
Belo Oriente	0.2	0.2	0.4	2.7	114	<0.1	35	2.9	1.2	0.8	166.6
Colatina	0.4	0.1	1.7	3.7	169	<0.1	11	2.0	0.5	0.7	4.9
Colatina	0.4	0.1	1.9	6.0	**675**	<0.1	62	2.2	1.0	1.4	12.2
Colatina	0.3	0.1	1.4	10.9	**837**	<0.1	35	2.7	0.4	0.6	5.0
River Water (c)											
Belo Oriente	0.2	0.1	0.5	7.3	220	<0.1	**116**	1.1	0.4	0.6	11.12
Gov. Valadares	0.2	0.2	4.1	3.4	**1025**	<0.1	**522**	2.9	0.8	0.6	167.2
Gov. Valadares	0.1	0.2	1.6	3.1	71	<0.1	3	1.7	1	0.7	504.8
Colatina (n=5)											
Min.	0.2	0.1	2.0	3.2	132		9.7	1.9	0.3	0.7	4.7
Max.	3	0.2	4.0	49.8	**1841**	<0.1	**1455**	4.4	1.0	1.3	30.6
Median	0.5	0.1	2.7	4.4	**1437**		23	2.3	0.5	1.1	10.2

An independent group of research recorded higher concentrations for the elements As, Cd, Cr, Fe, Mn, Ni and Pb one month after the accident in the 3 river locations analyzed by our study. However, there was no increasing pattern of elemental concentration with the distance from the collapsed dam in April 2016 [17]. This different pattern could be related with the contamination movement leaching down the river. Moreover, a similar range of concentration for the elements analyzed in the Doce river has been found (samples collected at Bento Rodrigues, close to the dam rupture, on 28th November 2015), except Mn and Zn concentrations, which were higher in our study [11]. Because it reported a specific place different of our study, comparisons are limited. The Governmental Environmental Agency of the State of Minas Gerais (IGAM), which has a historical monitoring for the river, found an increase in concentrations of at least one order of magnitude for the elements As, Cd, Pb, Cr, Ni for some points of the Doce river, while Mn and dissolved Fe presented a steep increase after the collapse, followed by a reduction after 1 month [19]. It is important to note that similar levels of elements concentrations on Doce river have been related before the accident however the historical mean is lower than the values reported in our study. These results, also presented in the Table 2, underlie the need to continue monitoring the river contaminations to identify fluctuations and possible leaching of contaminants to underground water.

A previous study on Doce river after the dam collapse reported elements concentration in the particulate fraction as high as 48143 μg L^{-1} for Fe and 15514 μg L^{-1} for Mn, while their dissolved concentration were at least 2 orders of magnitude lower - 102 and 273 μg L^{-1}, respectively [20]. This result suggests that the larger amount of these elements is bounded to the suspended particles in the water. This could explain the high values found in our study since there was a high sediment input observed after the dam collapse. It is also important to observe the potential risk of remobilization from the particulate fraction, which can make them bioavailable.

In addition to the impact caused by the mud, other human activities can also influence the elements contamination profile. Considering a human population of more than three million residing along its basin [7], there are multiple potential agents which could impact the mobilization of contaminants to the river and underground water, such as: agricultural and industrial activities, domiciliary and industrial sewage, as well as historical mining in the region.

We found significant Pearson correlations ($p < 0.05$) between the elements Mn-As ($r = 0.89$), Mn-Fe ($r = 0.79$), Mn-Sn ($r = 0.53$), Fe-Ni ($r = 0.70$), As-Sn ($r = 0.56$), Cr-Cu ($r = 0.57$) and Fe-As ($r = 0.57$) for well waters ($n = 30$). The correlation between the concentrations of Fe and Mn may be related to the ore itabirita, which is abundant in the region. The co-occurrence of these elements is therefore natural in this geographical area [21, 22]. The soil composition could be also responsible for other correlations found in this investigation. However, more studies are needed to confirm this hypothesis, since our data are not enough to explain these findings. Additionally, groundwater is not affected by the exact same effects that influence river water, such as oxidation of Fe and Mn by atmospheric oxygen. There is also the adsorption of As in sedimentary particles enriched with Fe and Mn, which could explain the correlation between these elements [5].

These values are also higher than considered safe for drinking water by U.S. Environmental Protection Agency and European Environment Agency, which estimated the maximum contaminant levels for iron and manganese at 200 - 300 μg L^{-1} and 50 μg L^{-1}, respectively. Thus, considering the best and worst scenery the Doce river population are ingesting approximately 228 and 1674 μg/day of Fe and 22 and 124 μg/day exclusively by drinking water, assuming a daily water intake of 2 liters [23, 24].

Daily intake of these elements, above a safe concentration, can lead to health problems. Some diseases are associated with high levels of these elements in drinking water, for example, excess iron can cause genetic disorder (haemochromatosis), while manganese overload can cause neurologic disorder, such as the syndrome known as "manganism" which resemble Parkinson's disease and includes symptoms like neurobehavioral manifestations, weakness and rapid postural tremor and others [25-27]. In children, undesired effects include lower cognitive performance, impaired verbal function, and full-scale IQ scores [28].

Table 2. Elements concentration in the Doce river reported by other studies. Values are in μg L^{-1}. On the table A = river points not reached by the mud, B = river points reached by the mud, <LOD are values bellow the limit of detection (LOD), Naque is a city close to Belo Oriente. IGAM data refers to a data series (1997-2015) with multiple points along the river before and after the disaster. * Values for dissolved metals

	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
River water – Segura et al [11]									
A	0.04 ± 0.03	0.009 ± 0.005	0.09 ± 0.06	<LOD	61 ± 44	1.73 ± 1.04	0.3 ± 0.28	0.09 ± 0.07	19 ± 25
B	0.44 ± 0.35	0.027 ± 0.040	0.26 ± 0.41	<LOD	1166 ± 2583	135 ± 254	0.59 ± 0.50	<LOD	6.6 ± 6.2
River water – GIAIA [19]									
Naque 12/2015	<2	4	<40	-	25490	1210	50	<10	-
Naque 04/2016	<2	<1	<40	-	6690	142	<10	<10	-
Gov. Val. 12/2015	40	3	40	-	15865	1260	50	15	-
Gov. Val. 04/2016	<2	<1	<40	-	6360	104	<10	<10	-
Colatina 12/2015	14	5	40	-	3770	100	70	<10	-
Colatina 04/2016	4	<1	<40	-	1280	15	<10	<10	-
River water – IGAM [21]				Cu*	Fe*				
Before	28	1.5	70	411	2070	1654	28	67	-
After	108	15.8	2873	675	32260	936000	2280	1650	-

3. Material and Methods

In July 2016, eight months after the dam has collapsed, the water used for human and animal consumption and also for irrigation were sampled at 48 points, along 3 cities affected by the rupture of the dam. Water samples were collected from inhabitants' wells, from the Doce river and also from inhabitants' supplemental water supply - provided to them either by Samarco or government. The sampling sites were cities along the Doce River: Belo Oriente (n=16) and Governador Valadares (n=16) at Minas Gerais state and Colatina (n=16) at Espírito Santo state (Figure 2). These cities represent a distance gradient from the initial point of the disaster. Additionally, field blanks (n=3) for each city were collected.

Belo Oriente is located approximately 200 km from the Fundão Dam at Minas Gerais state and samples were collected in the most impacted area of this city. Governador Valadares city, also at Minas Gerais State, is approximately 280 km distant from Mariana city. It is the largest city, compared to the other two. Samples were collected in the river margins, as well as in islands where farmers used to live and develop agriculture. Colatina is located at Espírito Santo State, at approximately 460 km away from Mariana.

Prior to sample collection, all sampling bottles were decontaminated with 5% neutral detergent (Extran®, Merck KGaA, Darmstadt, Germany) for 12h and then decontaminated with 10% (v/v) HNO_3 (J.T.Baker, NEUTRASORB®, México) solution for more 12h. Sampling was conducted accordingly to the 1669 protocol from U.S. Environmental Protection Agency (EPA) [29]. Water was collected in 1 L glass bottles and conditioned with HCl (v/v) (Loba chemie, Mumbai, India) 0.5% for mercury quantification and HNO_3 10% (v/v) for analysis of the other elements.

Total mercury concentrations were performed by cold vapor atomic fluorescence spectroscopy (CVAFS) with automatized system (Merx, Brooks Rand Labs®). Samples analyses were done accordingly to the standard protocol EPA 1631 [30]. In the process, 25g of the water samples were processed with 100 μL of Bromine chloride. Following, 100 μL of Hydroxylamine 30% and then 100 μL of Tin(II) chloride 20% were added to the samples. Quality assurance procedures included the analyses of analytical blanks and standard solutions (in concentration of the middle of the analytical curve) between each 16 vials, where the precision recovery was in a range of 70-130%.

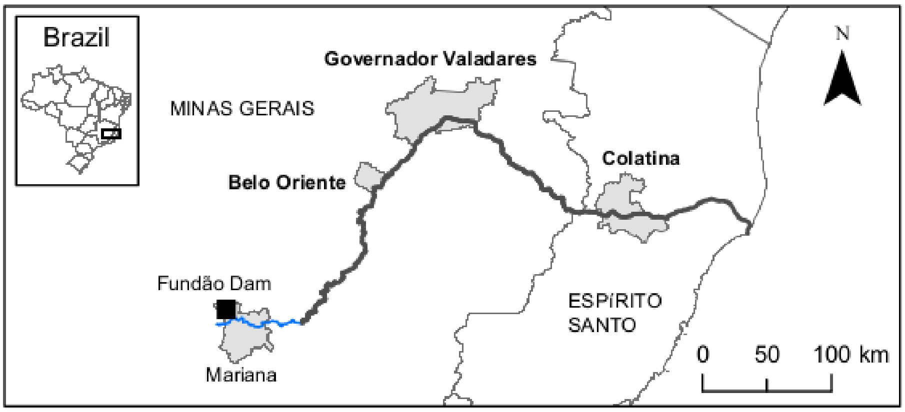

Figure 2. Map showing the three cities investigated at this study. Exact sampling points omitted to protect participants confidentiality.

The quantification of total Zn, Ni, Cr and Cu was performed in a flame atomization atomic absorption spectrometer (FAAS, model AA240FS, Varian). For the FAAS analysis, 1 L of each sample was previously reduced to 20 mL using hot plate, with periodic addition of HCl 37% at 1 hour intervals, until complete digestion and final volume of 50 ml. Concentrations of Fe, Mn, As, Cd, Sn e Pb were obtained in an Inductively coupled plasma mass spectrometer (ICP-MS, X Series II model, Thermo Fisher Scientific, Bremen, Germany) with operational software PlasmaLab at Laboratório de Desenvolvimento Analítico (LaDA) at Federal University of Rio de Janeiro, Brazil. Operational instrumental conditions are presented in Table 3. For ICP analysis, water samples were previously filtered on 0.45 µm cellulose acetate filters (Whatman). In such assay, the authors assumed that the applied sample acidification provided an appropriated extraction/digestion for the purpose of the present study, which is the acute toxicological risk for human health. Although it means that this is not the total element fraction in the sample, the authors consider that the elements that are strongly bound to the particles do not represent an important toxicological human health threat. An internal standardization was performed by monitoring the isotopes of ^{45}Sc, ^{72}Ge, ^{103}Rh and ^{205}Tl.

For both analysis, the quality control (QC) was carried out through the use of analytical and field blanks, which were processed in the same way as the samples. The mean field blanks concentrations were subtracted from the samples. Standard solutions of the elements analyzed were separately injected with known concentrations as quality control, and the recoveries were between 90% and 110%.

Table 3. Experimental conditions used on ICP-MS equipment to element determination in water samples.

Parameter	Experimental Conditions
RF Power	1400 W
Nebulizing flow rate	0.90 L min^{-1}
Auxiliary gas flow rate	0.70 L min^{-1}
Aditional gas flow rate	0.14 L min^{-1}
Cold gas flow rate	13.0 L min^{-1}
Dwell time	10 ms
Resolution	300
Sample uptake rate	0.90 mL min^{-1}
Type of Nebulizer chamber	Conical
Nebulizer	Meinhard

A socio-environmental questionnaire was used to draw the profile of the inhabitants and evaluate the potential pathways of human contamination by the water affected by the collapsed dam. In order to be eligible to participate in this study, participants must have resided close to the Doce river, as to be impacted by the dam collapse either directly or indirectly. Within these requirements, the socio-environmental questionnaire was applied and rendered general information about its use and residents profile. It was accompanied by an informed consent form to explain the research purposes of the study. The questionnaire can be accessed on the supplementary material.

4. Conclusions

Our study revealed that water used by many riverine families along the Doce River is unsuitable for agriculture or consumption. There are no pre-disaster studies in the region, so we cannot affirm the disaster is responsible for the contamination profile observed. Nevertheless, it is very important to note that the disaster caused families shifting the source of water they rely on, from river to well or donation, due to the lack of public and private support. We can highlight that the use of this water in the long term could be associated with health risks.

Further studies and a long-term monitoring on the water quality along the Doce river are essential, since metals and other contaminants from the mud deposited in the sediment can be continually resuspended and released to the river and underground water. We also recommend an investigation of potential contaminations in the food produced in the region.

Supporting Information

Table IS. Elements concentration in river, well water and supplemental water supply for all Belo Oriente, Governador Valadares and Colatina sampling points. Values are in μg L^{-1}.

Acknowledgments

Funding for the fieldwork and analysis of trace elements was provided by Greenpeace through Rio de Gente project. Part of the fieldwork funds were provided by the Federal University of Rio de Janeiro (UFRJ) through the availability of official vehicles of the institution. The Brazilian National Council for Scientific and Technological Development (CNPq), the Coordination of Improvement of Higher Level Personnel (CAPES) and State of Rio de Janeiro Research Foundation (FAPERJ) supported the post-graduate students participating in the project through the scholarship awarded.

References and Notes

[1] Fernandes, G. W.; Goulart, F. F.; Ranieri, B. D.; Coelho, M. S.; Dales, K.; Boesche, N.; Bustamante, M.; Carvalho, F. A.; Carvalho, D. C.; Dirzo, R.; et al. *Natureza & Conservação* **2016**, *14*, 35.[Crossref]

[2] Porto, M. F. S. *Caderno de Saúde Pública* **2016**, *32*, 1. [Crossref]

[3] Felippe, M. F.; Costa, A.; Franco, R.; Matos, R. *Revista Geografias* **2016**, *0*, 63. [Link]

[4] Garcia, L. C.; Ribeiro, D. B.; Roque, F. O.; Ochoa-Quintero, J. M.; Laurance, W. F. *Ecological Applications* **2017**, *27*, 5. [Crossef]

[5] Cagnin, R. C.; Quaresma, V. S.; Chaillou, G.; Franco, T.; Bastos, A. C. *Sci. Total Environ.* **2017**, *607–608*, 304. [Crossref]

[6] Pereira, A. A.; Hattum, B. van; Brouwer, A.; Bodegom, P. M. van; Rezende, C. E.; Salomons, W. *J. Soils Sediments* **2008**, *8*, 239. [Crossref]

[7] Plano Integrado De Recursos Hídricos Da Bacia Hidrográfica Do Rio Doce. 2010. Available from: http://www.cbhdoce.org.br/pirh-parh-pap/pirh. Access August, 2017.

[8] International Year of Family Farming 2014: Master Plan. 2013. Available from: http://www.fao.org/fileadmin/user_upload/iyff/docs/Final_Master_Plan_IYFF_2014_30-05.pdf . Access August, 2017.

[9] Brazil. Law 11326, **2006**. Available from: http://www2.camara.leg.br/legin/fed/lei/2006/lei-11326-24-julho-2006-544830-normaatualizada-pl.html. Access August, 2017.

[10] Silva, A. C.; Cavalcante, L. C. D.; Fabris, J. D.; Júnior, R. F.; Barral, U. M.; Farnezi, M. M. de M.; Viana, A. J. S.; Ardisson, J. D.; Fernandez-Outon, L. E.; Lara, L. R. S.; et al. *Revista Espinhaço UFVJM* **2017**, *9*, 44. [Crossref]

[11] Segura, F. R.; Nunes, E. A.; Paniz, F. P.; Paulelli, A. C. C.; Rodrigues, G. B.; Braga, G. Ú. L.; Pedreira Filho, W. R.; Barbosa, F.; Cerchiaro, G.; Silva, F. F.; et al. *Environ. Pollut.* **2016**, *218*, 813. [Crossref]

[12] 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. *Water. Air. Soil Pollut.* **2017**, *228*, 252. [Crossref]

[13] Monitoramento Especial da Bacia do Rio Doce - CPRM. 2015. Available from: http://www.cprm.gov.br/publique/media/hidrologia/eventos_criticos/riodoce_relatorio2.pdf . Access August, 2017.

[14] de Souza, J. J. L. L.; Abrahão, W. A. P.; de Mello, J. W. V.; da Silva, J.; da Costa, L. M.; de Oliveira, T. S. *Sci. Total Environ.* **2015**, *505*, 338. [Crossref]

[15] Brazil. Legislation CONAMA 396. 2008. Available from: http://portalpnqa.ana.gov.br/Publicacao/RESOLU%C

3%87%C3%83O%20CONAMA%20n%C2%BA%20396.pdf. Access August, 2017.

[16] Brazil. Ministério da Saúde PORTARIA 2914. 2011. Available from: http://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914_12_12_2011.html . Access August, 2017.

[17] GIAIA. Relatório-Técnico Determinação De Metais Na Bacia Do Rio Doce (Período: Dezembro-2015 a Abril-2016) 2016. Available from: http://giaia.eco.br/wp-content/uploads/2016/06/Relatorio-GIAIA_Metais_Vivian_revisto5.pdf . Access August, 2017.

[18] Brazil. Legislation CONAMA 357. 2005. Available from: http://www.mma.gov.br/port/conama/res/res05/res35705.pdf . Access August, 2017.

[19] IGAM. Acompanhamento da Qualidade das Águas do Rio Doce Após o Rompimento da Barragem da Samarco no distrito de Bento Rodrigues – Mariana/MG. 2016. Available from: http://www.igam.mg.gov.br/images/stories/2016/QUALIDADE/3Relatorio_Tecnico_Monitoramento_Rio_Doce_Rev01_02_2016.pdf . Access August, 2017.

[20] Hatje, V.; Pedreira, R. M. A.; de Rezende, C. E.; Schettini, C. A. F.; de Souza, G. C.; Marin, D. C.; Hackspacher, P. C. *Scientific Reports* **2017,** *7*, 10706. [Crossref]

[21] Chemale, Jr. F.; Rosière, C. A.; Endo, I. *Precambrian Research* **1994**, *65*, 25. [Crossref]

[22] Roeser, H. M. P.; Roeser, P. A. *Revista Geonomos* **2013**, 18. [Crossref]

[23] US Environmental Protection Agency. Drinking Water Standards and Health Advisories. 2012 Available from: https://www.epa.gov/sites/production/files/2015-09/documents/dwstandards2012.pdf . Access August, 2017

[24] European Union. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. **1998**. Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31998L0083 . Access August, 2017.

[25] WHO. Manganese in Drinking-water. 2011. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/manganese.pdf . Access August, 2017.

[26] WHO. Iron in Drinking-water. 2003. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/iron.pdf . Access August, 2017.

[27] Racette, B. A. *NeuroToxicology* **2014**, *45*, 201. [Crossref]

[28] Bjørklund, G.; Chartrand, M. S.; Aaseth, J. *Environ. Res.* **2017**, *155*, 380. [Crossref]

[29] US Environmental Protection Agency. Method 1669: Sampling ambient water for trace metals at EPA water quality criteria levels. 1996. Available from: https://www.epa.gov/sites/production/files/2015-10/documents/method_1669_1996.pdf . Access August, 2017.

[30] US Environmental Protection Agency. Method 1631 Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry 1996. Available from: https://www.epa.gov/sites/production/files/2015-08/documents/method_1631e_2002.pdf. Access August, 2017.