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BIOREMEDIATION AND BIODEGRADATION

Understanding the Environmental Impact of a Mine Dam Rupture in Brazil: Prospects for Remediation

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Abstract

The rupture of the Fundão mine dam in Mariana municipality, Minas Gerais State, Brazil, spilled the tailings across the Doce River basin. These tailings, composed of residues discarded from the beneficiation of iron ore, are rich in SiO_2 and Al_2O_3, as well as some ether amine compounds and NaOH. The aim of this study was to assess the distribution of these sediments, as well as their effect on the riparian zones reached, as compared with preserved sites. Sediment deposition in the river resulted in a morphological change from a meandering profile to a braided aspect. The nutrient and mineral content (P, K, Ca, Mg, Cu, Fe, Mn, Zn, and NO_3^-) and soil organic matter of the sediments were depleted, whereas NH_4^+, Na, and pH increased. A random presence of ether amines in the sediments was confirmed by quantitative and chromatographic analyses, with concentrations ranging from 0 to 57.8 mg kg^{-1}; Na reached values as high as 150 mg kg^{-1}. The impact of the dam tailings on biota was assessed by estimating total microbial biomass (phospholipid fatty acids), which were depleted in sediments relative to soils from preserved sites. Overall plant mortality, as well as a low resilience capacity, were also observed. Ether amines and Na present in the sediments had a strong toxic effect in the environment. Identification of these substances as the main impact factors will help guide future remediation efforts.

Core Ideas

- Dam disruption caused changes in the fluvial profile and nutrient depletion in the sediment.
- Depletion of microbial biomass in the sediment and plant mortality occurred.
- Despite the low organic matter and NO_3^- in the sediment, NH_4^+, Na, and pH increased.
- The environmental impact was attributed to the increase in NH_4^+, pH, and Na.
- Ether amine and Na from the dam are the main toxic factors.

In November 2015, the Fundão dam in Mariana municipality, Minas Gerais State, Brazil, ruptured. Around 43 million m^3 of dam tailings, originating from iron ore mining beneficiation, spread downslope across the Doce River basin (Silva et al., 2015). The strongest impact of the mine tailings extended over 17 km^2 of the Doce River basin (Carmo et al., 2017) and across the Gualaxo do Norte and Carmo Rivers (Fig. 1A and 1B), which hosted preserved fragments of Atlantic riparian forest (IBAMA, 2016). The wave of dam tailings directly affected 36 municipalities across the Doce basin and reached the Atlantic Ocean.

The rupture of the Fundão dam quickly changed the river's shape due to the rapid displacement of a large volume of material in a short period of time and over a vast area (Vervloet, 2016). The extent, degree, and consequences of this impact are still unknown, as a precise assessment of the nature of the tailings found in the dam and their physical, chemical, and biological effects on the environment is needed. Once the causative factors of this environmental impact are properly diagnosed, it will be possible to propose rehabilitation or remediation strategies.

The Fundão dam is located in the Quadrilátero Ferrífero region of Minas Gerais State, Brazil, where there are considerable iron ore deposits composed of metamorphosed iron formations (so-called banded iron formations). These formations contain iron-rich hematite, goethite, and siderite-magnetite. Beneficiation of the iron requires pellet feed fines with limited content of SiO_2, Al_2O_3, and other impurities and is achieved via the flotation technique (Filippov et al., 2014). The flotation technology allows the production of "superconcentrates" and highly purified hematite products and has been widely used by the Brazilian mining sector (Iwasaki, 1983; Peres and Mapa, 2008).

Reverse cationic flotation is the most widely used flotation technique in the iron ore industry worldwide (Ma et al., 2011),

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Abbreviations: FAPEMIG, Fundação de Amparo à Pesquisa do Estado de Minas Gerais; GC–MS, gas chromatography–mass spectroscopy; PLFA, phospholipid fatty acid; UHE Candonga, Hydroelectric Plant Unit in Candonga.

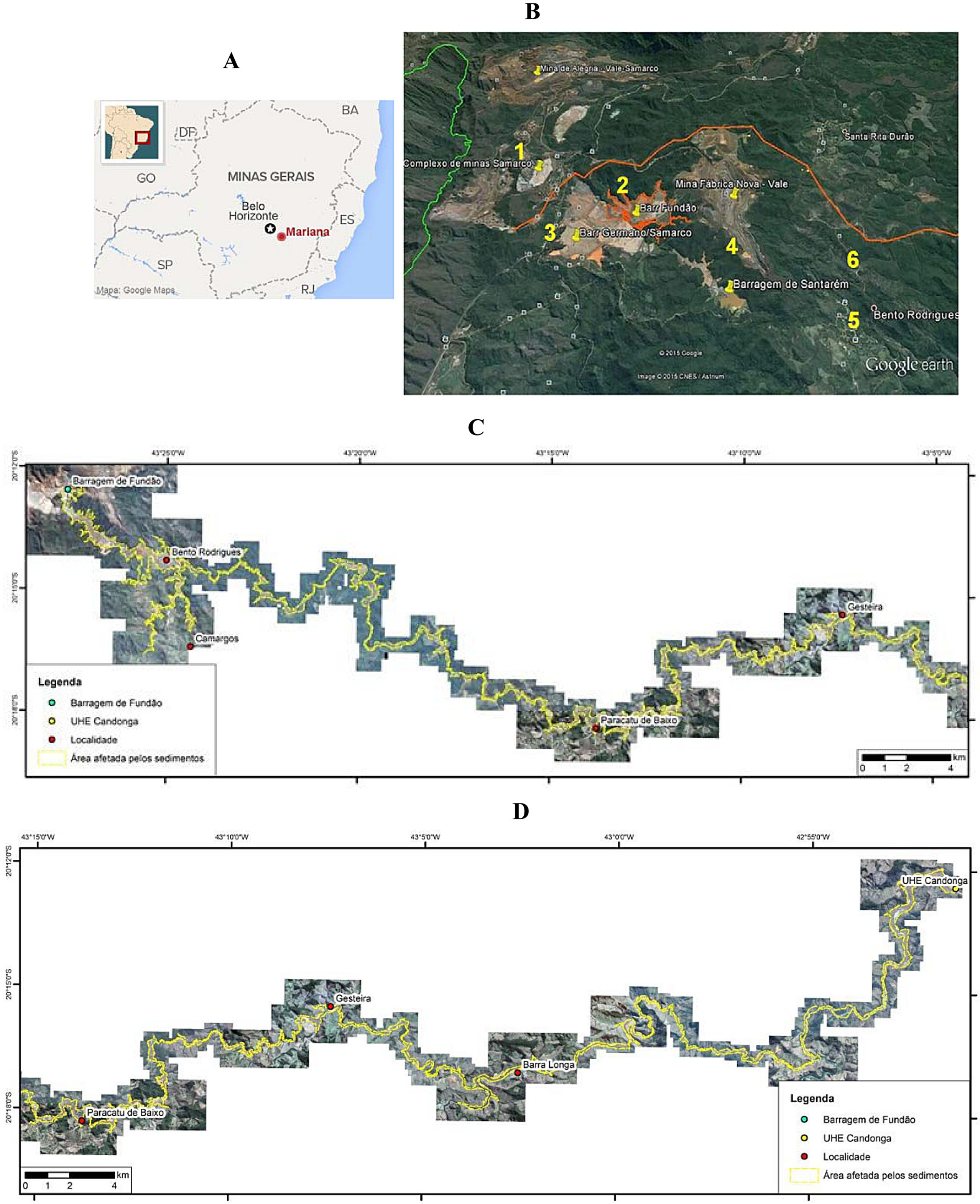

Fig. 1. (A) Location of Mariana town in Minas Gerais State, Brazil. (B) Photo showing (1) the mine complex, (2) Fundão dam, (3) Germano dam, (4) Santarém dam and stream, (5) the Bento Rodrigues district, and (6) Gualaxo do Norte River. (C, D) Morphology of the basin between Fundão dam (blue) and the Hydroelectric Plant Unit in Candonga (Candonga, yellow) showing changes in the river morphology across the affected municipalities (red) caused by the dam tailings.

including Brazilian mining companies (Reis, 2004; Araujo et al., 2005; Batisteli, 2007; Peres and Mapa, 2008). The process commonly starts with desliming, which is performed using dispersants with the addition of flocculants such as gelatinised cornstarch (used as an iron oxide depressant or precipitator) (Araujo et al., 2005; Filippov et al., 2014). Desliming efficiency is achieved by increasing the pH with NaOH, which favors electrostatic repulsion among the particles to separate the hematite. The main mechanism of the reverse flotation of quartz from iron ore is based on the electrostatic theory of flotation, which depends on the zeta potential of the mineral on silicate particles at a pH ∼8.0 (Fouchee et al., 2016).

Different amines are used as cationic collectors during the reverse flotation of iron ores. Quaternary NH_4^+ salts are the most effective cationic collectors (Yuhua and Jianwei, 2005); they present both ionic and molecular species in the aqueous phase, depending on the pH. The collectors of primary fatty amines, which have the polar group $(O–CH_2)_3$ inserted between the radical and the polar head NH_2 and are known as ether amines, are highly efficient. Flotation is performed in an alkaline pH (NaOH), which stabilizes both the cationic and the molecular species of the amine, allowing for the cationic species to work as collectors and the molecular species to act as a frother (Araujo et al., 2005; Filippov et al., 2014). Among several cationic collectors tested (Papini et al., 2001), a mixture of mono- and diamines is the preferred option in the iron ore mining sector in Brazil.

During the flotation process, the hematite is adsorbed by starch molecules in the lower part of the flotation machine and follows the water flux as concentrated pellets, while the amine is adsorbed onto the quartz surface, forming the frother. The latter is then collected at the top of flotation machine and spilled as tailings into a dam (da Luz and Lin, 2002; Araújo et al., 2008). Given this process, it may be inferred that the tailings released by the disruption of the Fundão dam could be rich in both sediments (quartz) and the toxic chemicals used in reverse cationic flotation, such as ether amine and Na. The aim of this study was to assess the physical, chemical, and biological nature of the environmental impact caused by the dam disruption over the riparian zones to inform management decisions for remediation and rehabilitation procedures.

Materials and Methods

Study Site

The Fundão dam belongs to a mine complex located in the Mariana municipality (Minas Gerais, southeastern Brazil) in the Doce River basin (Fig. 1A), which holds the tributary Carmo and Gualaxo do Norte Rivers. This mine complex includes mine-waste piles, pipelines, and two other dams (Germano and Santarem dams) besides the Fundão dam (Fig. 1B). The collapse of the Fundão and Santarém dams spilled >43 million m^3 of tailings over the Santarém stream and the Gualaxo do Norte, Carmo, and Doce Rivers. Among the 36 towns reached by the dam tailings, the Bento Rodrigues and Paracatu de Baixo districts were entirely destroyed. We chose the area between Bento Rodrigues and Barra Longa, which includes Paracatu de Baixo, for our sample collection (Fig. 1C and 1D) because it is nearest to the disrupted dam.

Hydrosedimentological and Morphological Analyses

For the delimitation, characterization, and analysis of the affected region between Bento Rodrigues and the Hydroelectric Plant Unit in Candonga(UHE Candonga), satellite images were obtained from the Google Earth Pro software (https://www.google.com/earth/, spatial resolution = 3.0 m) from July to August 2016. Using the software Terra Incognita (https://sourceforge.net/p/terraincognita2/wiki/Home), 263 images were captured and used to construct a mosaic. The delimitation of the site affected by the sediments was performed using ArcGIS software (https://www.esri.com/pt-br/arcgis/products/arcgis-pro/overview, version 10.2.2), and its dimension was calculated using the Geocentric Reference system for the Americas (SIRGAS 2000) and Albers equal-area conic projection following the criteria of the Brazilian Institute of Geography and Statistics (IBGE, 2017). These data were confirmed in the field.

Experimental Design

Soils from two preserved sites (unreached by sediments) and sediment samples from five impacted sites were collected (Table 1, Supplemental Fig. S1) at 20-cm depth along 3 km of each study site. Preserved Site 1 is a fragment of riparian forest located at the margin of the Carmo River (20.209841° S, 43.186671° W), which receives sewage discharge from the town Mariana. Preserved Site 2 is a preserved fragment of riparian forest along the very well preserved Lavras Velhas River (20.203134° S, 43.171361° W), a tributary of the Carmo River.

Sediments from the ruptured dam formed a layer 0.5 cm to 2 m thick over the natural soils of affected riparian zones. We collected samples at five different sites reached by the dam tailings, which were called "groups of samples." Soil samples from the preserved sites and sediment samples from affected sites were collected at two points, 2.5 km apart, along a 3-km transect at each site (Supplemental Fig. S1). At each collection point, we collected three composite samples, each formed by a mixture of three subsamples from points 500 m apart (Supplemental Fig. S1). The experimental design of sample collection was: two samples per site × three replicates × seven sites = 42 samples. Samples from Group 1 were collected in the Carmo River basin at Barra Longa (20.231609° S, 43.015010° W). Samples from Group 2 were collected at the margin of the Gualaxo do Norte River in Paracatu de Baixo (20.175579° S 43.140731° W). Samples from Group 3 were collected at the Gualaxo do Norte river margin in Bento Rodrigues (20.140705° S, 43.252341° W). These three group samples were collected in 2016. Samples from Group 4 were collected at the margin of the Gualaxo do Norte River in Bento Rodrigues, and the Group 5 samples were collected on the Gualaxo do Norte margin at Paracatu de Baixo and Barra Longa in 2017.

The soil samples were kept at 4°C until they were analyzed. All these samples were used for physical, chemical, and biological analyses.

Mineralogical Analysis

For mineralogical characterization, a mixed sediment sample for each collected group was analyzed by X-ray diffraction. These samples were dried in an oven at 105 ± 5°C and sprayed on agate gravel. The analysis was performed in Rigaku equipment

(Geigerflex model) using a copper tube. Identification of the phases and deconvolution of the diffractograms were performed using Crystallographica Search-Match (CSM) software (Oxford Cryosystems, Oxford, UK; https://www.oxcryo.com).

Chemical Analyses

Chemical analysis of nutrients, exchangeable cations, and metals in the sediments or soils samples were performed according to the EMBRAPA protocols using the Mehlich method for P, K, Mg, Ca, OM, Mn, Zn, Cu, Na, Fe, B, and S (EMBRAPA, 1997). Total inorganic N was determined by semimicro-Kjeldahl digestion (Bremner, 1960) using KCl for soil extraction, and NH_3 and NO_3^- content were determined according to Bremner and Keeney (1965).

Ether Amine Analyses

The quantification of ether amines in soil samples and the ether amine standards (Flotigam EDA 3 and Fotigam 2835-2) was performed using the colorimetric bromocresol green methodology described by Araújo et al. (2009), and detection was performed using a spectrophotometer (Shimadzu UV-160A). To characterize and confirm the presence of ether amine in the samples, gas chromatography–mass spectroscopy (GC–MS) analysis of the sediment extract was performed (Araújo et al., 2009) using a GC–MS-QP2010 ULTRA (Shimadzu). The column was an Rxi-1MS 30-m × 0.25-mm × 0.25-μm (Restek) column, and the initial column temperature was 100°C for 5 min, after which it was raised to 250°C by 10°C min^{-1}. The split mode injector

Table 1. Chemical and physical analyses of sediments collected at different impacted sites or soil groups: Carmo River (G1), Gualaxo do Norte River in 2016 (G2 and G3), and Gualaxo Norte River in 2017 (G4 and G5) in comparison with Preserved Site 1 (Carmo River) and Preserved Site 2 (Lavras Velhas River).

Variable	Groups	Mean	SD	*p* value	Multiple comparisons	
					Preserved 1	Preserved 2
pH	Preserved 1	6.37	0.06	**0.049†**		
	Preserved 2	4.570	0.3			
	G1	8.30	0.15		**0.004**	**0.002**
	G2	8.40	0.2		**0.002**	**0.001**
	G3	7.95	0.27		**0.02**	**0.003**
	G4	7.48	0.05		**0.008**	**0.004**
	G5	8.33	0.1		**0.004**	**0.0025**
P (mg kg^{-1})	Preserved 1	11.00	1.00	**0.029**		
	Preserved 2	6.58	0.65			
	G1	5.83	1.5		**0.044**	0.18
	G2	6.00	1.0		**0.014**	0.47
	G3	8.83	1.29		0.23	0.085
	G4	5.67	1.26		0.167	0.068
	G5	5.17	0.79		**0.015**	0.35
K (mg kg^{-1})	Preserved 1	56.00	1.00	**0.004**		
	Preserved 2	74.0	3.0			
	G1	20.17	2.3		**0.015**	**0.0045**
	G2	11.33	0.79		**0.001**	**0.001**
	G3	10.83	0.75		**0.001**	**0.001**
	G4	4.83	1.33		**0.001**	**0.001**
	G5	14.50	1.05		**0.001**	**0.001**
Ca (mg kg^{-1})	Preserved 1	655.33	28.01	**0.001**		
	Preserved 2	275	9			
	G1	175.67	8.5		**0.002**	0.091
	G2	210.00	4.5		**0.001**	**0.004**
	G3	429.00	12.5		**0.005**	**0.004**
	G4	197.00	4.8		**0.002**	**0.001**
	G5	172.83	7.9		**0.001**	**0.001**
Mg (mg kg^{-1})	Preserved 1	157.00	9.54	**0.001**		
	Preserved 2	72.67	2.52			
	G1	22.33	3.1		0.02	0.005
	G2	11.00	1.79		0.001	**0.001**
	G3	15.33	1.76		0.001	**0.001**
	G4	12.50	1.5		0.001	**0.001**
	G5	20.83	2.58		0.001	**0.001**
S (mg kg^{-1})	Preserved 1	5.67	0.58	**0.006**		
	Preserved 2	11.67	1.53			
	G1	16.50	2		**0.033**	**0.047**
	G2	24.17	1.55		**0.003**	**0.012**
	G3	27.33	4.5		**0.014**	**0.031**
	G4	9.33	1.53		0.122	**0.035**
	G5	18.33	1.29		**0.001**	**0.001**

† Means in bold are significantly different from preserved sites according to Tukey's multiple range test at 5% confidence level ($p \leq 0.05$).

was at 250°C, and the GC–MS interface was at 250°C. A mass selective detector was used, and electron-impact ionization mass spectrometry was performed at 70 eV and 250°C. The carrier gas was He at 2.0 mL min^{-1}, and the injected volume was 2 μL. Data were recorded using the software GC–MS Solution (Shimadzu, https://www.ssi.shimadzu.com/products/gas-chromatography-mass-spectrometry/gcmssolution-software.html).

Microbial Biomass Estimation

Phospholipid fatty acids (PLFAs) were extracted from lyophilized soil according to the Bligh and Dyer method (Bligh and Dyer, 1959), and the lipid fractionation was performed according to Gehron and White (1983) and White et al. (1979). The extracts were analyzed using a gas chromatograph with flame ionization detection (HP Model 5890 Series 2 chromatograph). Fatty acid chemical structures were verified by GC–MS (HP Model 5890 Series 2 gas chromatograph and HP Model 5971 mass selective detector), and PLFAs were expressed as equivalent peak responses to the internal standard. Peak areas were converted to PLFA per microgram of dry soil (absolute abundance). The estimation of total microbial biomass was performed as the sum of all PLFA signatures. Around 44 PLFA signatures from study soils were assessed (data not shown), and the effect of overlying sediment was estimated by the total C microbial biomass.

Floristic Inventory

A floristic inventory was performed from fertile specimens collected in preserved fragments in the Rio Doce State Park located in the Doce River basin. Species identification was done by comparing the material from BHCB Herbarium from the Federal University of Minas Gerais as described by França and Stehmann (2013). Another floristic survey was undertaken in an impacted riparian area of Gualaxo River located at Paracatú de Baixo (Fig. 1C and 1D) 1 yr after the disaster.

Statistical Analysis

The studied variables were compared among the sites (preserved and impacted sites) using an ANOVA test to normal variables and Kruskal–Wallis test to non-normal variables. The multiple comparison for normal variables were done with a Tukey test and for non-normal variables with a Nemenyi test using R statistical software (https://www.r-project.org/).

Results and Discussion

Hydrosedimentological and Morphological Impacts

An estimated 20 Mm^3 of sediment was deposited in the Gualaxo do Norte, Carmo, and Doce Rivers (study zones) in a segment extending 119.20 km between the collapsed dam and the UHE Candonga (Machado, 2017). Rapid deposition of this large sediment volume greatly altered fluvial morphology. Results of hydrosedimentological analysis (Fig. 1C and 1D) showed waterway silting of the Fundão and Santarém dams and intensification of tailing bar formation. Below the confluence of the Gualaxo do Norte and Carmo Rivers, there was a significant change in morphology, from a fluvial meandering morphological profile to a braided aspect with multiple channels formed with variable dimensions, particularly near the UHE Candonga.

The sediment was disaggregated with low cohesion, favoring erosion processes with a random distribution. (Fig. 2A). The sediment characterized in Fig. 2B had a lighter, drier surface layer, similar to a mixture of sand and salt, with an inner layer that was moist and gelatinous. These characteristics are not commonly observed in sediments, suggesting a different composition. Similarly, the waters in Gualaxo do Norte River (Bento Rodrigues) presented frothing, as shown in Fig. 2C, which was not observed in the preserved waters (Carmo and Lavras Velhas Rivers). Soil erosion and plant mortality of riparian vegetation is shown in Fig. 2D, 2E, and 2F; plant mortality did not affect all vegetation homogeneously along the river. These results suggest the presence of toxic elements in the sediments, such as those reported subsequent to other dam disruptions and/or mine tailings spills (e.g., during the Lagdo dam disaster in Cameroon; Tesi et al., 2016; in the Namoi River in Australia, Leonard et al., 2001; and during the Aznalcollar mine tailings spill in Spain, Gallart et al., 1999).

Physical and Chemical Analyses of Riparian Sediments

The mineralogical analysis using X-ray diffraction (Supplemental Fig. S2) showed that preserved-site soils followed the sequence quartz (sand) > mica and kaolinite (clays) > hematite, whereas at the impacted site, there was a predominance of quartz and hematite (Groups 1, 2, 3, and 4) in the sediments. The natural geological formation of the Quadrilátero Ferrífero contains quartz, several Fe-bearing silicates, micas, and pyroxene, as well as carbonates, feldspars, Fe-rich hematite, goethite, magnetite, and clays (Filippov et al., 2014). The natural soils from the Rio Doce Valley exhibit a coexistence of Latosols, Cambisols, and Argissols, with greater chemical fertility in the latter, and the dominant textural class is sandy clay loam. Therefore, clays are especially dominant in more fertile soils, such as those from the preserved sites (Albuquerque-Filho et al., 2008). Thus, the high sand content found in the riparian zone of study site is likely to come from the dam material.

Chemical analysis of the riparian sediments from the dam tailings showed a significant reduction in K, Ca, Mg (Table 1), Fe, and Zn (Supplemental Table S1) in relation to both control soils that were collected in the preserved sites (Carmo and Lavras Velhas Rivers), independently of the five collection points as shown for Groups 1, 2, 3, 4, and 5. Such lower levels of these elements in relation to soil from the preserved sites may be explained by the fact that the sediments originated from the dam tailings. In relation to P (Table 1) and Cu (Supplemental Table S1), there was a reduction in the sediment samples only in comparison with soils from Preserved Site 1 (Carmo River), but their levels were as low as those found at Lavras Velhas margins (Preserved Site 2). Manganese was also reduced compared with Preserved Site 1, but increased compared with Preserved Site 2 (Table 1). This may be explained by the fact that Preserved Site 1 receives urban sewage discharge, whereas the latter is an undisturbed site. However, while borium concentrations remained approximately constant across the collection points (Supplemental Table S1), S increased in relation to the preserved sites (Table 1). These results indicate that the analyzed metals (Cu, Fe, Mn, and Zn) do not show toxicity, as also observed by Guerra et al. (2017) in affected sediments. Furthermore, there was a significant difference in soil

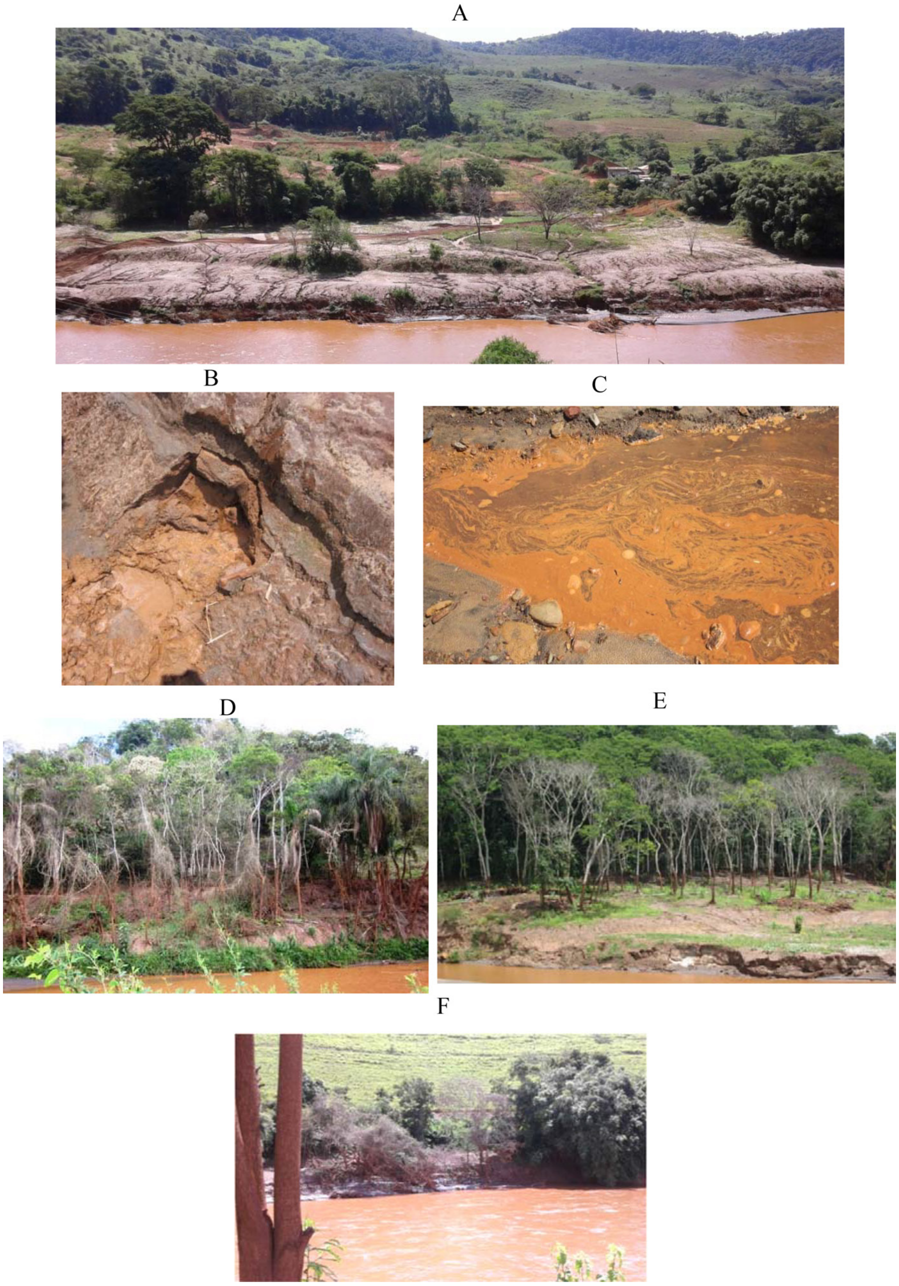

Fig. 2. (A) Sediments deposited at the margins of Carmo River in Barra Longa municipality. (B) Aspect of superficial and inner layer of the sediment at the margins of Gualaxo do Norte River. (C) Water aspect of the Gualaxo do Norte River. (D, E, F) Random mortality of woody species at riparian forest reached by the dam sediments.

pH, which was 5.2 in soil from the preserved site and 8.1 in the sediment (Table 1).

A significant loss of organic matter is shown in Fig. 3A, accompanied by a strong reduction in NO_3^- (Fig. 3B) in the sediments of riparian zones relative to both the preserved sites. In contrast, the N-NH_4^+ content in the sediments of all impacted sites did not differ from the preserved sites, especially Preserved Site 1 (Fig. 3C). Only Group 2 and Group 5 samples had a lower NH_4^+ content than Preserved Site 2 (Fig. 3C). In most soils worldwide, the NH_4^+/NO_3^- ratio is commonly very low; the NO_3^- concentration is much higher than NH_4^+ because NH_4^+ in natural soils is commonly nitrified in 1 or 2 wk, resulting in NO_3^- accumulation (Crawford and Glass, 1998; Ju et al., 2004). Our results do not agree with the literature; Fig. 3D shows a high NH_4^+/NO_3^- ratio at all the impacted sites, contrasting with the preserved sites. Considering that the natural soil of riparian zones was covered by the tailings and there was no previous management of these sites, as well as the low N-NO_3^- and soil organic matter contents found, such high NH_4^+/NO_3^- ratio would not be expected. These results suggest both an additional N-NH_4^+ source and its accumulation, since NO_3^- was not formed.

The elements Mg, K and Zn, as well as NO_3^- and NH_4^+, are commonly found in soil bound to organic matter or clay by ionic forces (Brady and Weil, 2007). Whereas Mg, K, and Zn in common soil come from both the weathering of rocks and organic matter decomposition, the origin of N depends exclusively on soil organic matter decomposition (Brady and Weil, 2007). Thus, in this study, it could be expected that the loss of organic matter and clay in the sediments from the tailings would also result in the depletion of these elements. Therefore, the

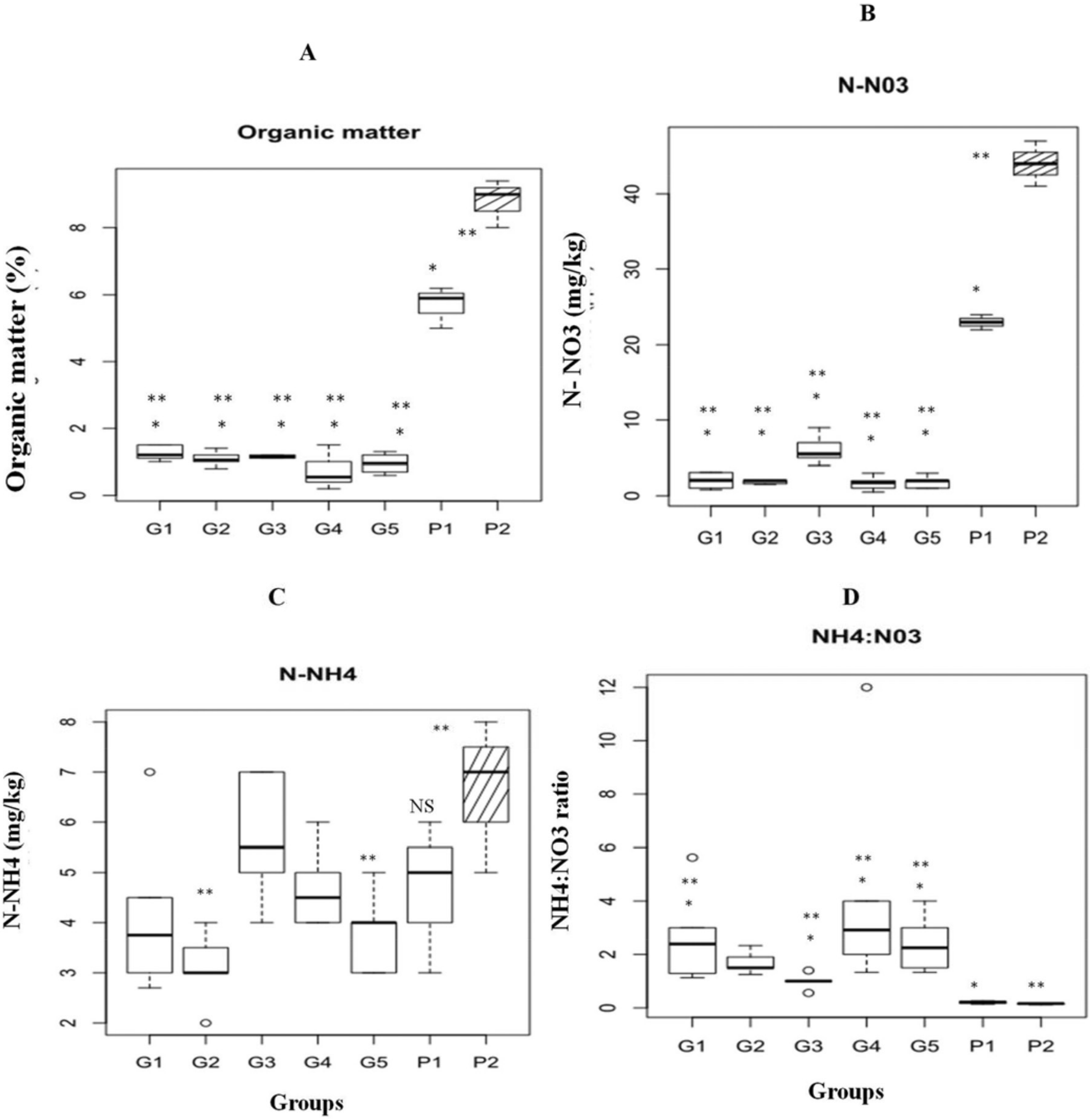

Fig. 3. (A) Organic matter, (B) N-NO$_3$, and (C) N-NH$_4$ contents and (D) the NH$_4$/NO$_3$ ratio of different impacted sites or soil groups ([G1] Carmo River, [G2, G3] Gualaxo do Norte River in 2016, and [G4, G5] Gualaxo Norte River in 2017) in comparison with Preserved Site 1 (Carmo river, *) and Preserved Site 2 (Lavras Velhas River, **). Mean values ± SEM are shown. Means denoted with * (comparison with Preserved Site 1) and ** (comparison with Preserved Site 2) are significantly different according to Tukey's multiple range test at 5% confidence level ($p \leq 0.05$). NS means not significant.

increase of the N-NH$_4^+$ in the sediments may likely be explained by an additional NH$_4^+$ source not present in preserved soils.

The relevant increase in soil pH from 5.2 in preserved soil to 8.1 in sediment can be understood based on the iron ore beneficiation process, particularly the reverse flotation which takes place at an optimum pH ~9 (Araujo et al., 2005; Filippov et al., 2014; Fouchee et al., 2016). It would be expected that the increase in soil pH might be followed by an elevation not only in NH$_4^+$ concentration but also in Na. Indeed, Na is used in the iron ore flotation process to stabilize the ether amines by increasing the pH to 10 (Araujo et al., 2005; Filippov et al., 2014). A significant increase of Na was observed (Fig. 4A) in the impacted sediments in relation to the preserved sites. Therefore, the triad pH, Na, and N-NH$_4^+$ that were found to be markedly high in the sediment is likely to have come from the dam material. Similarly, Klebercz et al. (2012) reported elevated pH values varying from 8.14 to 9.88 in bauxite-processing residue sediments (red mud) spilled by the failure of the Ajka aluminum plant in Hungary, which positively correlated with a high exchangeable Na.

Ether Amine and Sodium Distribution in the Riparian Sediments

Ether amine was registered in all the sediment samples, but not in soils from the preserved sites (Fig. 4B). However, varied concentrations of ether amines were found across the basin, ranging from 5 to 57.8 mg kg^{-1} in samples from Bento Rodrigues (nearest to the dam) and from 3 to 45.6 mg kg^{-1} in Barra Longa, which is the most distant collection point from the dam. Thus, ether amine was found randomly distributed along the channel, which may justify the high NH$_4^+$ content in the sediment. In the same way, a high and varied concentration of Na was found in the sediments across the basin. The average Na concentration found in preserved soil was 4 mg kg^{-1}, contrasting with those found in the sediments, which ranged from 18 to 150 mg kg^{-1} (Fig. 4A), suggesting toxicity.

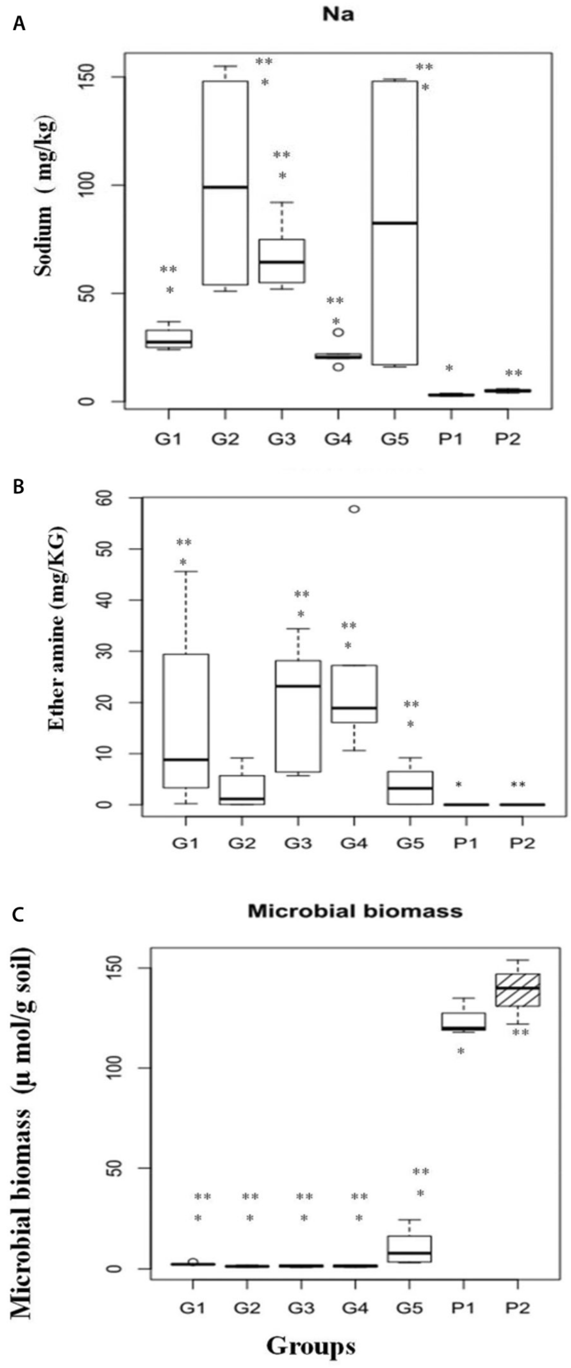

Fig. 4. (A) Sodium and (B) ether amine contents and (C) microbial biomass (%) of different impacted sites or soil groups ([G1] Carmo River, [G2, G3] Gualaxo do Norte River in 2016, and [G4, G5] Gualaxo Norte River in 2017) in comparison with Preserved Site 1 (Carmo river, *) and Preserved Site 2 (Lavras Velhas River, **). Mean values ± SEM are shown. Means denoted with * (comparison with Preserved Site 1) and ** (comparison with Preserved Site 2) are significantly different according to Tukey's multiple range test at 5% confidence level ($p \leq 0.05$).

Similar to the ether amines, different levels of Na were found at the same collection point (e.g., 20–150 mg kg^{-1} in Bento Rodrigues), also suggesting a nonhomogeneous distribution of this element. Therefore, the higher-than-expected concentration and irregular distribution of both substances (N-NH_4^+ and Na) reinforces their exogenous source from dam tailing. After the flotation process of iron ore beneficiation, ether amines and Na are released to the dam tailings, where they are expected to remain (Araujo et al., 2010). However, when dam failure exposes the environment to these substances, the consequences are unknown. Amines and Na have been documented to be harmful to several aquatic organisms (Newsome et al., 1991; Schultz et al., 1991; Shi et al., 2018), including microbial communities (Rietz and Haynes, 2003; García et al., 2007; Shi et al., 2018), crustacea (García et al., 2007), fish (Saube, 1986), and plants (Gigon and Rorison, 1972; Roosta and Schjoerring, 2007).

To confirm the presence of ether amines in these sediments, gas chromatography–mass spectrometry (GC–MS) analysis of sediment samples was performed in comparison with an ether amine standard (Flotigam EDA3). Figure 5 shows three different regions in the chromatogram based on retention time: Region I (10–12.5 min), Region II (12.5–16 min), and Region III (17.5–22.5 min). All three regions showed a similar peak pattern in relation to the ether amine standard, but at a lower intensity. Table 2 presents the relative percentage of compounds found in the sediment samples and the ether amine standard. The relative proportion of the monoamine $CH_3(CH_2)_9O(CH_2)_3NH_2$ (Fragment 1) found dominant in the standard was 13%, whereas in the sediment samples, it ranged from 0.03 to 5.1%. The proportion of the diamine $NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$ (Fragment 2) was found to be similar in some sediment samples and the standard, but markedly high in one of the sediment samples (Group 1), as shown in Table 2. The proportion of Fragment 3, the monoamine $CH_3(CH_2)_3CH(CH_2CH_3)CH_2O(CH_2)_3NH_2$, was higher in the sediment samples than in the standard. These results can be understood by the fact that Fragment 1 is a fatty monoamine with low ionic degree and is less reactive, whereas the others show a higher ionic degree, favoring their binding with other sediment compounds. Thus, Fragments 2 and 3 become more stable and able to be accumulated in the sediments. The greater proportion of monoamine Fragment 1 was found in samples collected closer to the dam, reinforcing that this is the source of ether amines and that the less reactive fragments seem to be washed out along the channel, as shown by the frothing aspect of water (Fig. 2C).

Effect of Dam Sediments on Microbial Biomass

There was a strong inhibition of total microbial biomass as assessed by the profiling of PLFA, which has been widely used to assess changes in microbial communities in soil in response to environmental stresses (Frostegåard and Bååth, 1996; Grayston and Prescott, 2005; Card and Quideau, 2010). Figure 4C highlights the strong inhibition of the microbial biomass in the sediments from the impacted area compared with preserved sites. Similarly, Segura et al. (2016) observed a decline in microbial diversity and an increase in cytotoxicity and DNA damage in soils collected in Bento Rodrigues after this disaster. Thus, such a strong depletion of the total microbial biomass in the sediment samples may be attributed not only to the loss of soil organic matter, but mainly to the toxic effect of Na and ether amines, which were found in high concentrations in comparison with control soils at the preserved sites. Furthermore, the inhibition of total microbial community may explain the low levels of NO_3^- found in the sediments, as the nitrification process may be impaired by NH_4^+, but especially by Na toxicity (Rietz and Haynes, 2003).

Several toxic elements may be found in the material from mine dams, depending on the type of mine. Carcinogenic

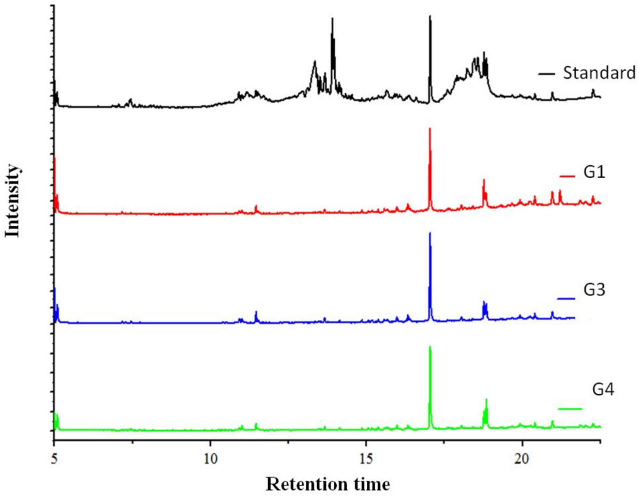

Fig. 5. Gas chromatography–mass spectrometry chromatogram of mixed samples extracted from sediments of the Carmo River (G1), Gualaxo do Norte River in 2016 (G3), and Gualaxo Norte River in 2017 (G4) collected at different sites in comparison with standard Flotigan EDA 3.

USEPA 16 polycyclic aromatic was reported after the Lagdo dam flood disaster in Cameroon in 2012 (Tesi et al., 2016). The Aznalcollar mine disaster spilled tailing contaminated with sulfide from pyritic sludge in Spain in 1988 (Gallart et al., 1999), and in Romania in 2000, the disaster of the Baia Mare and Baia Borsa released environmental contaminants identified ascyanide and heavy minerals (Soldan et al., 2001; Rico et al., 2008). Ether amine and Na are the main toxic compounds found in the tailings spilled from the Fundão dam in Mariana.

Effect of Dam Sediments on Vegetation

The dam tailing wave destroyed riparian forests along the Gualaxo do Norte and Carmo Rivers. A significant portion of the vegetation that was reached by the sediments could not withstand the impact and gradually perished in the year after the disaster (Fig. 2D–2F). Plant mortality might have resulted from soil nutrient deficiency and the toxic effect of Na and NH_4^+. However, not all adult plant individuals of the same species that were reached by the tailings died, suggesting a random effect of toxic compounds along the channel (Fig. 2E and 2F). A list of dominant plant species native to the Brazilian Atlantic Forest found in preserved fragments of riparian forests along the Doce River basin and a list of plant species recorded in the affected area 1 yr after the disaster are shown in Supplemental Table S2. Most native species did not regenerate, and some leguminous species, as well as the pioneer species *Ricinus communis* L., were dominant. Interestingly, the latter dominant species has a high demand for N-NH_4^+ (Albuquerque et al., 2006). Thus, some native leguminous and/or pioneer native species seem to be more resilient to the impact, likely related to their N metabolism.

These results show a toxic effect of the sediments on vegetation, likely caused by NH_4^+ (ether amines) and/or Na. It is well known that NH_3–NH_4^+ toxicity in higher plants has been associated with plant growth suppression, evident as leaf chlorosis and curling (Kirkby, 1968; Britto and Kronzucker, 2002; Roosta and Schjoerring, 2007), leading to plant mortality, which is extensively described in the literature (Kirkby, 1968; Gigon and Rorison, 1972; Britto and Kronzucker, 2002; Britto et al., 2014). Additionally, Na stress can also contribute to plant growth inhibition, senescence, and death in the field. The effects of salinization on soil and plants caused by excess Na are due to an increase in the osmotic pressure caused by an increase of retention forces of water and salts. This, in turn, increases soil density, reduces water infiltration, and favors soil disruption, making the soil more erodible and infertile (Halliwell et al., 2001). Increasing soil osmotic pressure due to salinity may prevent plants from absorbing water, because they will not be able to overcome this osmotic force even when the soil is moist. The plants stop growing and show symptoms of burns and necrosis. (Zhu, 2001). Elevated pH and Na were also implicated in the ecotoxicity of fluvial sediments derived from an accidental spill of bauxite-processing residue (red mud) in Ajka, Hungary (Klebercz et al., 2012).

Our results strongly suggest that NH_3 associated with ether amine, as well as Na toxicity, may explain the plant symptoms and mortality observed in the field, contributing to low resilience capacity and loss of biodiversity.

Conclusions

This study is the first comprehensive assessment of the environment impact of the failure of the Fundão dam and subsequent widespread release of tailings. The dam rupture resulted in a change in river morphology, from a fluvial meandering profile to the formation of a braided aspect with multiple channels. We did not detect metal toxicity related to Fe, Cu, Mn, and Zn. The main candidates responsible for environmental toxicity were ether amine and Na, which were known to be present in the dam and were detected at high levels in the sediments but not in control soils from preserved sites. Sediments that reached riparian zones showed a reduction of fertility, especially soil organic matter and NO_3^-, with a concomitant increase in NH_4^+, Na, and pH. These increases may explain the depletion of microbial biomass and overall plant mortality in the impacted zone. Identification of soil ether amines and Na as the main impact factors will help guide future remediation efforts.

Table 2. Relative percentage of chemical fragments described from gas chromatography–mass spectrometry for sediments samples collected in Carmo River (G1), Gualaxo do Norte River in 2016 (G3), and Gualaxo Norte River in 2017 (G4) in comparison with standard Flotigan EDA 3

m/z†	Fragments	Relative percentage			
		Standard	G1	G3	G4
		%			
215	$CH_3(CH_2)_9O(CH_2)_3NH_2$	12.9	5.21	0.03	1.23
188	$NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$	2.82	53.0	2.92	1.18
187	$CH_3(CH_2)_3CH(CH_2CH_3)CH_2O(CH_2)_3NH_2$	0.76	38.7	1.79	4.45

† *m/z*, mass/charge ratio.

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