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# Post-catastrophe Analysis of the Fundão Tailings Dam Failure in the Doce River System, Southeast Brazil: Potentially Toxic Elements in Affected Soils

**Marcelo Braga Bueno Guerra · Brian T. Teaney · Brianna J. Mount · Daniel J. Asunskis · Brennan T. Jordan · Ryan J. Barker · Eliana E. Santos · Carlos Ernesto G. R. Schaefer**

**Abstract** On November 5, 2015, after the collapse of the Fundão tailings dam, a massive amount of iron mine waste was released into the Doce River system in southeast Brazil. The aim of our study was to determine the mass fractions of potentially toxic elements in soil affected by the deposition of material by the waste wave. A preliminary screening was performed with portable X-ray fluorescence spectrometry (PXRF) and principal component analysis (PCA). The EPA 3050B method was further applied to digest the samples for quantitative determination of As, Ba, Cr, Cu, Mn, Ni, Pb, V, and Zn by inductively coupled plasma mass spectrometry. PCA was useful to classify the mine waste samples based on the Fe signal from the PXRF spectra, in spite of the heterogeneous nature of the material discharged into the Doce River system. The anomalous levels of As (up to 164 mg kg$^{-1}$) and Mn (as high as 2410 mg kg$^{-1}$) found in some mine waste and affected soil samples are within the background ranges typically observed in the soils of the Iron Quadrangle region. The toxicity characteristic leaching procedure shows no evidence of hazards regarding As, but a high natural background level of Mn was found in the mobile fraction. This preliminary environmental assessment highlights the importance of evaluation of long-term effects on soil directly impacted, as well as on the aquatic biota of the Doce River system and adjacent coastal environment given the large affected area, which includes regions with varying background levels of toxic elements.

**Keywords** Soil contamination · Mariana · Iron mine waste · ICP-MS · Arsenic · Manganese

## 1 Introduction

The safe land disposal of wastes in this everincreasingly populated world is a problem of major concern to the environmental protection authorities (ICOLD 2001). Mine wastes are of particular concern, given the large amount generated, and by the presence of potentially toxic elements (Lottermoser 2010). Mine wastes can be defined as unwanted by-products resulted from mining, mineral processing, and metallurgical extraction operations (Lottermoser 2010). Typically, these solid mine wastes are hydraulically moved to tailings dams close to the mine site (ICOLD 2001). Past estimates suggested that there were thousands of tailings dams around the world holding billions of tons of mine wastes (Rico et al. 2008a). These large waste

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impoundments are prone to failure due in part to maintenance costs, which remain high even after the mine closure, the lack of strict regulation, and engineering misconceptions in their design (Azam and Li 2010; Rico et al. 2008b). As a direct consequence of this recognized vulnerability, the number of reported tailings dam failures is dramatically increasing worldwide with the occurrence of at least one major accident annually in the last 20 years (WISE 2017).

The discharge of mine wastes into river systems caused by tailings dam failures is a severe threat to the quality of water and sediments and to the aquatic organisms and people living downstream (Kossoff et al. 2014). Several studies have assessed the environmental impacts of mine waste spills worldwide (Bird et al. 2008; Ciszewski and Grygar 2016; Liu et al. 2005; Ordóñez Fernandez et al. 2007; Wadige et al. 2016) with a focus on the determination of toxic element contents in soil and sediment samples. For example, the Aznalcóllar region in southwestern Spain was severely affected by a tailing mine spill in 1998 and is one of the most studied sites in the world regarding the evaluation of the adverse effects of toxic elements deposition from mine wastes (Grimalt et al. 1999; Hudson-Edwards et al. 2003; Kraus and Wiegand 2006; López-Pamo et al. 1999; Simón et al. 1999). Millions of cubic meters of mud containing high levels of As, Cu, Pb, and Zn were released to the environment into the area of the Doñana nature reserve, a World Heritage Site in recognition of the exceptional diversity of bird species (Grimalt et al. 1999).

On November 5, 2015, after the collapse of the Fundão tailings dam at a Samarco iron mine in the district of Mariana, southeast Brazil, a massive amount of waste was released into the Doce River system (Meira et al. 2016; Miranda and Marques 2016; Porto 2016; Schaefer et al. 2016). This unprecedented tragedy dumped more than 50 million cubic meters of mud that completely destroyed a small village and traveled more than 600 km to the Atlantic Ocean. This "tsunami" of mine waste caused 19 fatalities, produced a massive fish kill along the river, and affected the quality of potable water of hundreds of thousands of people living downstream (Miranda and Marques 2016). The long-term environmental impact to the floodplain soils, freshwater and marine biota in one of the most biologically diverse areas of the world is still unknown. Garcia et al. (2017) conservatively estimated that the regional loss of environmental services derived from the dam burst would be higher than US$500

million yearly. They also stated that at least 126 Brazilian mining dams are vulnerable to failure in the coming years.

Segura et al. (2016) provided preliminary data on the chemical and cytotoxicity profile of the waste from the Samarco iron mine by leaching, extraction, and toxicological bioassays. They collected soil, river water, and mud samples around Bento Rodrigues, the village destroyed by the mudslide, located within the neighborhood of the dam burst site. The most worrisome findings of this study were the potential cytotoxicity and DNA-damage exhibited in mud and soils and the high mobilizable fraction of Al, As, Ba, Fe, Mn, Pb, and Sr in the mud samples. Anomalous levels of Ag (up to 1087 $\mu$g L$^{-1}$) in surface water were also reported. The authors point out the importance of complementary studies aiming at the environmental assessment of the whole affected area as a way to provide more information for planning the remediation strategies.

The present study is focused on the evaluation of potentially toxic elements in the soil environment directly affected by the waste deposition in a site located ca. 50–90 km downstream to the dam failure. Sixty samples (encompassing mine wastes and soils) were collected along the floodplain, upstream to the Candonga hydroelectric dam, a site that still holds a huge amount of mud from the dam failure and is under intense dredging operation.

## 2 Materials and Methods

### 2.1 Sampling Protocol

On November 24, 2015, soil and mine waste samples were collected from riverbank sites in the study area (Fig. 1). Table 1 provides a detailed description of the sampling sites, number of collected samples per site, maximum depth of the sample collected, and soil classification according to USDA Soil Taxonomy ( 1999). Sixty samples, weighing ca. 200 g each, were collected and stored in clean Ziplock® bags and kept refrigerated until laboratory processing. Three classes of samples were collected: 1—control soil samples ($n = 12$), 2—affected soil samples ($n = 23$), and 3—mine wastes ($n = 25$). A schematic overview highlighting the contaminant pathway along the Doce River system and the sampling sites in the riverbank is shown in Fig. 1.

**Fig. 1** Map of the Doce River basin highlighting the contaminant pathway from the dam failure site and the sampling locations along the riverbank (corresponding to sites in Table 1, coordinates UTM) together with a diagram showing a typical sampling site
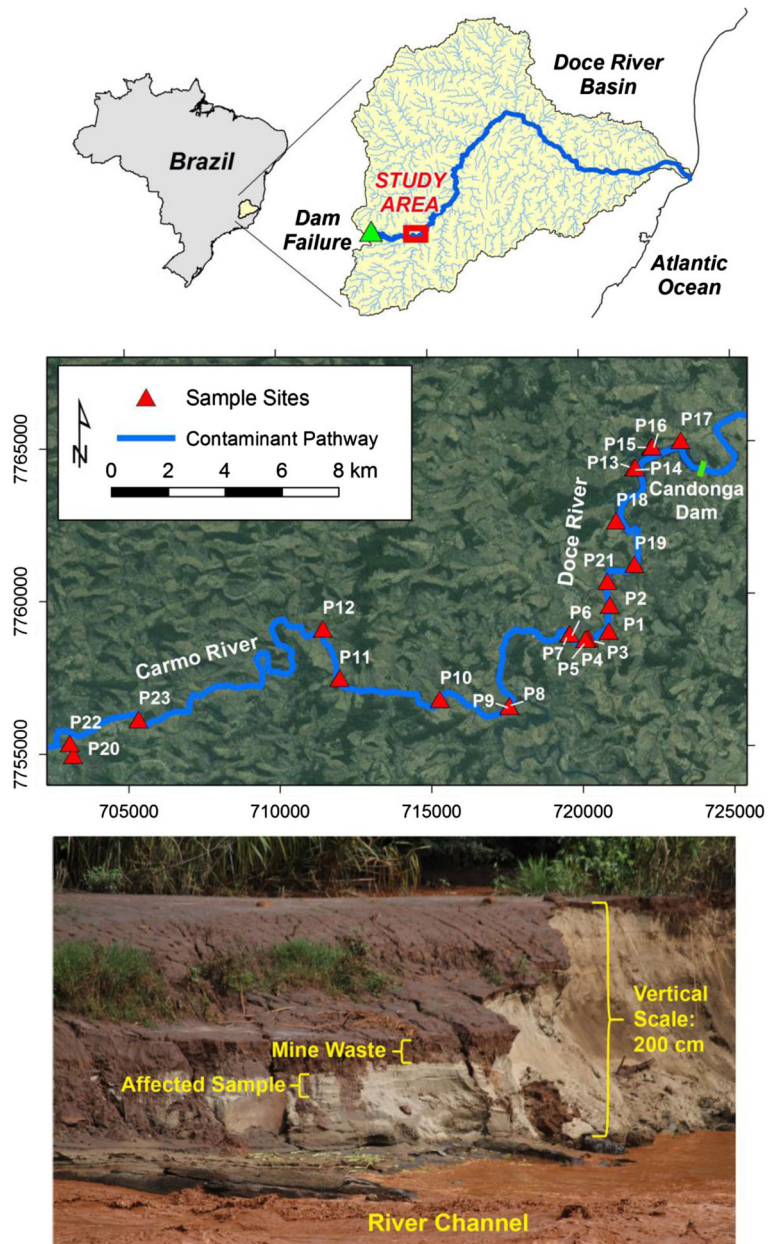


## 2.2 Sample Pre-treatment

Once in the laboratory, the samples were placed inside previously decontaminated polyethylene containers and oven-dried at 60 °C. Afterwards, a representative portion was selected (ca. 50 g), stored in double-layer plastic bags, and sent to Black Hills State University for chemical analysis. Prior to chemical analysis, ca. 3 g of the dried material was ground in a Mixer/mill (8000 M model, Spex SamplePrep LLC, Metuchen,

USA) furnished with tungsten carbide balls. Samples were ground for 45 min (3 cycles of 15 min grinding). Between each cycle, the grinding apparatus was left to cool for 15 min. In order to avoid cross-contamination, all grinding balls and end-caps were thoroughly cleaned, initially with soap and deionized water, and then left in contact with 20% $m/v$ NaOH solution for 15 min. The grinding pieces were scrubbed with sponge, rinsed with deionized water, and left to dry in a laminar flow hood located inside a class 1000 clean room. Before grinding

**Table 1** Description of the collected samples

| Sampling site[a] | Number of collected samples | Maximum depth (cm) | Sample ID[b] | Remarks (site details and soil classification[c]) |
|---|---|---|---|---|
| P1 | 1 | 30 | 1 | – |
| P2 | 1 | 40 | 2 | Soil from a riparian forest. Fluvent |
| P3 | 2 | 100 | 3, 4 | Margin of the Doce River. Fluvent |
| P4 | 3 | 60 | 5–7 | Fluvent |
| P5 | 6 | 120 | 8–13 | – |
| P6 | 2 | 35 | 14, 15 | Fluvial plain with incipient erosion |
| P7 | 4 | 110 | 16–19 | Fluvent |
| P8 | 2 | 60 | 20, 21 | Fluvent |
| P9 | 2 | 100 | 22, 23 | Fluvent |
| P10 | 2 | 120 | 24, 25 | – |
| P11 | 3 | 180 | 26–28 | Soil sample from a fluvial plain |
| P12 | 4 | 100 | 29–32 | Fluvent |
| P13 | 2 | 70 | 33, 34 | Fluvent |
| P14 | 2 | 60 | 35, 36 | Inceptisol |
| P15 | 3 | 50 | 37–39 | Fluvent |
| P16 | 1 | 100 | 40 | Saprolite of gneiss |
| P17 | 3 | 60 | 41–43 | Fluvent |
| P18 | 3 | 80 | 44–46 | Fluvent |
| P19 | 4 | 100 | 47–50 | Ultisol |
| P20 | 2 | 70 | 51, 52 | Sampling site far 2 m from the Carmo River |
| P21 | 2 | 50 | 53, 56 | – |
| P22 | 3 | 80 | 54, 55, 58 | – |
| P23 | 3 | 45 | 57, 59, 60 | – |

[a] See Fig. 1

[b] Sample class: mine waste (1, 5, 6, 8, 9, 10, 11, 12, 14, 20, 22, 24, 26, 28, 29, 35, 37, 41, 44, 45, 51, 52, 54, 56, 60), affected (4, 7, 13, 15, 17, 19, 21, 23, 25, 27, 30, 31, 33, 36, 38, 40, 42, 47, 48, 49, 53, 55, 57), and control samples (2, 3, 16, 18, 32, 34, 39, 43, 46, 50, 58, 59)

[c] According to the USDA Soil Taxonomy

another sample, ca. 2 g of silica gel, high-purity grade (Sigma-Aldrich, Steinheim, Germany) was ground by applying the same protocol of the soil samples in order

to remove any residual contaminants. Lastly, vessels, balls, and end-caps were cleaned with high-purity ethanol 50% *v/v*.

### 2.3 Preliminary Screening with Portable EDXRF and PCA

Preliminary energy dispersive X-ray fluorescence spectrometry (EDXRF) screening was performed with a portable handheld spectrometer (Tracer III-SD model, Bruker AXS, Madison, USA), equipped with a 2-W Rh target X-ray tube and a 10-mm$^2$ X-Flash® Peltier-cooled silicon drift detector (SDD). Sample presentation for analysis was in the form of loose powder, where 1 g of the ball-milled sample was transferred to a 31-mm double open-ended X-ray cell (Spex SamplePrep) sealed with a Prolene® thin film. This amount of ground material was chosen based on previous experiments using the NIST SRM 2710a aimed at finding enough mass to make up a sufficiently thick layer ensuring "infinite thickness" for the 10.55 keV X-ray emission line. The operating conditions were measurement time (120 s) in triplicate, monitored spectral region (1–40 keV), 40 kV X-ray tube voltage, and 7 μA current. The net counts per channel was calculated using the Bruker Spectra Artax software (Bruker Nano GmbH, Berlin, Germany), version 7.4.0.0. The principal component analysis (PCA) calculi were performed using the Pirouette 4.5 rev. 1 software (Infometrix, Bothell, USA) as described elsewhere (Guerra et al. 2013).

### 2.4 Pseudototal and Mobile Fractions

Acid leaching of the soil and mine waste samples was performed following the EPA 3050 B method (EPA 1996), slightly adapted. The toxicity characteristic leaching procedure (TCLP) was applied for extracting the readily mobilizable fraction of the elements following the US EPA Method 1311 (EPA 1992). For the application of the EPA 3050B method, 0.2500 g of ball-milled samples were accurately weighed into 50-mL polypropylene digestion vessels. Then, 2.5 mL of sub-boiling double-distilled $HNO_3$ at 50% *v/v* were added to all samples and analytical blanks. The material was left inside a fume hood overnight at room temperature as a pre-digestion step. Afterwards, heating was conducted at 95 °C under reflux for 15 min in a HotBlock digestion system (Environmental Express, Charleston, USA) composed by a PTFE-coated graphite

block in a Kydex® housing. A cooling step was conducted and followed by the addition of 1.25 mL of double sub-boiling distilled HNO$_3$ (Sigma-Aldrich) prepared in a PFA Acid Purification System (DST-1000, Savillex, Eden Prairie, USA). The vessels were heated at 95 °C under reflux for 2:30 h and after cooling, 0.5 mL of deionized water with a resistivity of 18.2 MΩ cm and 0.75 mL of H$_2$O$_2$ 30% *v/v* (OPTIMA Grade, Fisher Scientific, Fair Lawn, USA) were added. Finally, after 1 h of heating under reflux at 95 °C, the cool solutions were transferred to 50-mL centrifuge tubes and 10 mL of deionized water were added. The supernatant was separated by centrifugation at 8500 rpm for 30 min. The liquid phase was transferred to a volumetric flask and the volume was made up to 25 mL with deionized water. All obtained digests were further diluted (up to 50-fold) with deionized water and an appropriate amount of a double sub-boiling distilled HNO$_3$ was added for reaching 1% HNO$_3$ final concentration. An inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7900, Tokyo, Japan) operated in helium collision mode was used for the quantitative determination of the following elements in the resulting solutions from the EPA 3050B method: As, Ba, Cr, Cu, Mn, Ni, Pb, V, and Zn. The ICP-MS operating conditions are detailed in Table 2. Bi, Ge, In, and Sc were added as internal standards to all test samples, calibration standards and analytical blanks at 50 μg L$^{-1}$ final concentration. A certified reference material, Montana I Soil (NIST SRM 2710a), was also digested and analyzed to check the trueness of the method. For the TCLP protocol, 0.2500 g of the selected ball-milled samples ($n = 23$), in triplicate, was weighed into 15-mL centrifuge tubes. Afterwards, 5 mL of the extractant solution was added. This solution, fluid no. 1 of the EPA Method 1311, was chosen after applying the recommended protocol for pH measurement and it was prepared from glacial CH$_3$COOH (Trace Metals Basis, Sigma-Aldrich). The tubes were shaken for 18 h at 150 rpm in an end-over-end shaker. Finally, the supernatant was separated by centrifugation at 8500 rpm for 15 min. As and Mn were determined by ICP-MS after appropriate dilution. As part of the quality assurance/quality control (QA/QC) program, a sample was selected and spiked with known amounts of the target analytes as a way to verify

**Table 2** Operating conditions for ICP-MS measurements

| | |
|---|---|
| Nebulizer | MicroMist |
| Spray chamber | Scott type |
| Plasma mode | Low matrix |
| Radio frequency—power | 1550 W |
| Sampling depth (mm) | 8.0 |
| Plasma gas flow rate (L/min) | 15 |
| Carrier gas flow rate (L/min) | 1.05 |
| Peristaltic pump speed (rps) | 0.1 |
| Internal diameter of the sample inlet tube (mm) | 1.02 |
| Spray chamber temperature (°C) | 2 |
| Sampling cone | Nickel |
| Skimmer cone | Nickel |
| Lens tune | Autotune |
| Extract 1 lens | 0 V |
| Extract 2 lens | −185 V |
| Omega Bias | −100 V |
| Omega lens | 10.8 V |
| Deflect | 0.0 V |
| He flow rate (mL/min) | 4.3 |
| Energy discrimination | 5.0 V |
| Isotopes monitored | $^{45}$Sc, $^{51}$V, $^{52}$Cr, $^{55}$Mn, $^{60}$Ni, $^{63}$Cu, $^{66}$Zn, $^{72}$Ge, $^{75}$As, $^{115}$In, $^{137}$Ba, $^{208}$Pb, $^{209}$Bi |
| Integration time/mass | 100 ms |
| Replicates | 3 |
| Sweeps/replicate | 10 |

possible matrix effects in the elemental analysis of the extracts obtained from the TCLP protocol. In addition, ca. one third of the extracts obtained through the EPA 3050B method were sent to another ICP-MS facility for assessing interlaboratory reproducibility.

## 3 Results and Discussion

### 3.1 Preliminary Screening with Portable EDXRF and PCA

The preliminary assessment of toxic metals contamination was performed by using a non-destructive portable analytical technique (handheld EDXRF) combined with a chemometric tool (PCA) in order to treat the large

amount of data (2048 variables from each X-ray spectrum) obtained from the screening of the 60 samples. The first principal component explained 99.1% of the variance in the data and allowed an appropriate classification of the samples regarding the iron content as 83% of the control samples presented negative values in the PC1 and ca. 70% of the mine waste samples presented positive values for the same parameter (Fig. 2a, b). However, after a variable selection, i.e., selecting the spectral region between 1 and 11 keV and excluding the X-ray peaks from the major soil constituents (Al, Si, K, Ca, Ti, and Fe), no clear trend of grouping was observed (Fig. 2c–e). This finding corroborates with the heterogeneous nature of the material discharged into the Doce
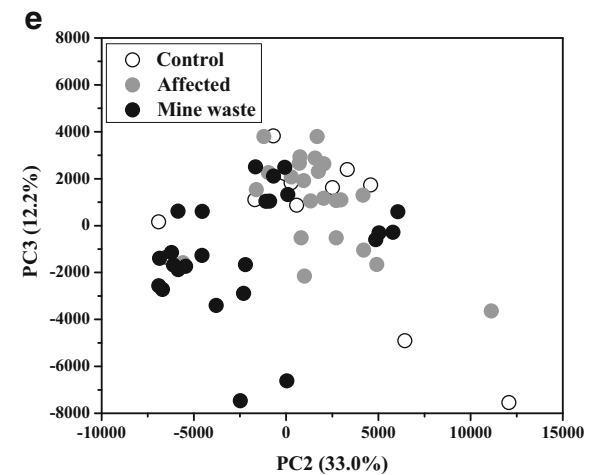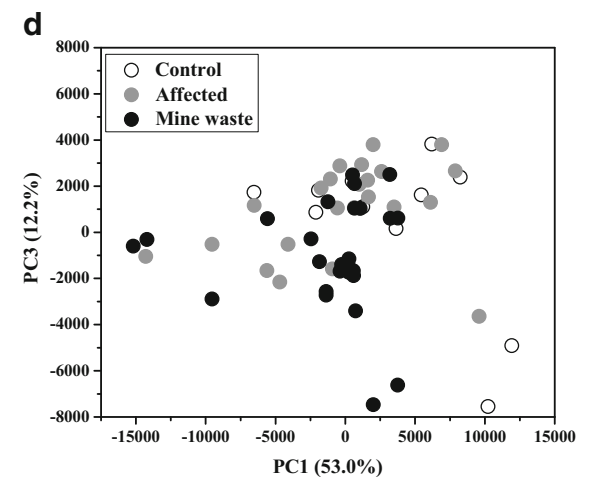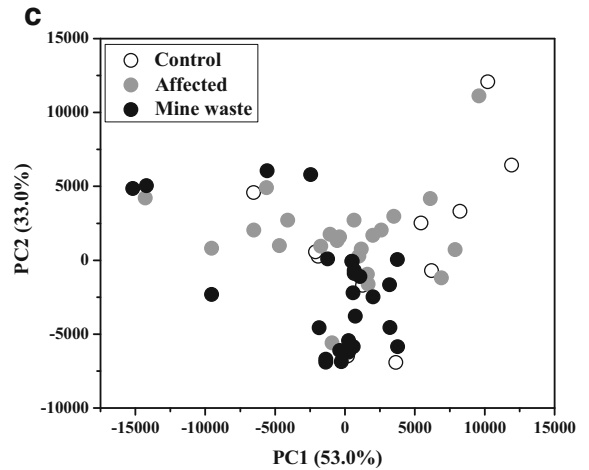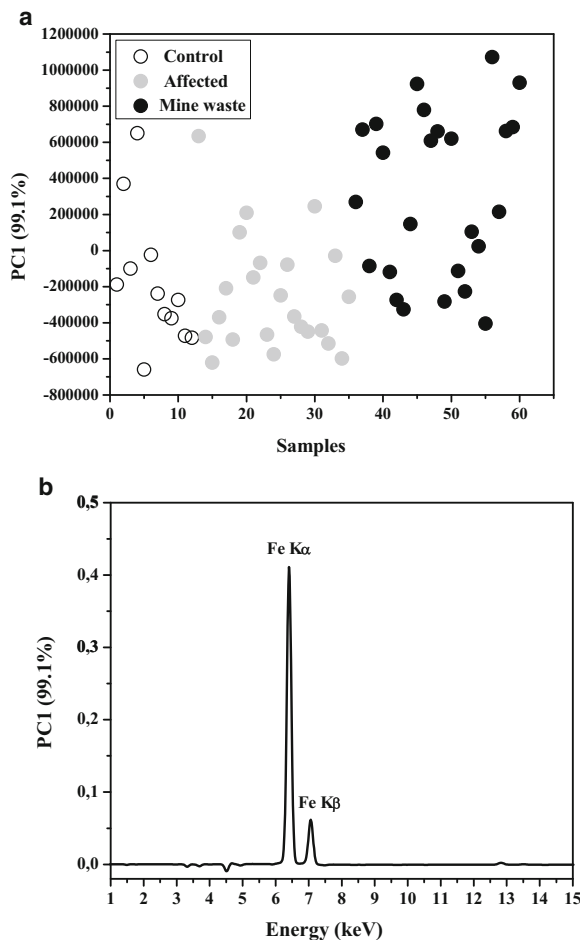




Fig. 2  Graphics obtained from the principal component analysis of the EDXRF data from the 60 analyzed samples: **a** scores plot with all variables, **b** loadings plot with all variables, **c** scores plot (PC1 versus PC2) after variables selection, **d** scores plot (PC1 versus PC3) after variables selection, and **e** scores plot (PC2 versus PC3) after variables selection







Fig. 2  (continued)

River system after the dam failure. According to an official report (Morgenstern et al. 2016), which aimed at evaluating the causes of the accident, two dikes

containing materials exhibiting different chemical and physical properties were the basis of the whole system that collapsed. The dikes stored sand and slimes (clay-like material) and during the fast flowslide, these materials were mixed in different proportions along the river channel and banks downstream.

### 3.2 Pseudototal and Mobile Fractions of Potentially Toxic Elements

The pseudototal levels of the potentially toxic elements investigated herein (As, Ba, Cr, Cu, Mn, Ni, Pb, V, and Zn) were accessed by the acid digestion of the soil and mine waste samples following the EPA 3050B method. This digestion method can put in solution the elemental fraction that may become environmentally available. The analytical figures of merit for ICP-MS measurements are shown in Table 3. The found elemental mass fractions for the NIST SRM 2710a (Montana I Soil) are shown in Table 4. For all elements, the found levels were in the expected ranges according to the leachable data provided by the certificate of analysis. The pseudototal levels of the determined elements in the three classes of samples can be seen in the Fig. 3a–i. There was observed a noteworthy enrichment for As (Fig. 3a) and Mn (Fig. 3e) in some mine waste and affected samples. For Mn, the following data were found: control soil samples (from 78 to 1568 mg kg$^{-1}$; average = 579 mg kg$^{-1}$), affected soil samples (from 123 to 2410 mg kg$^{-1}$; average = 904 mg kg$^{-1}$), and mine waste samples (from 203 to 2298 mg kg$^{-1}$; average = 824 mg kg$^{-1}$). For As, the found data were as follows: control soil samples (from 0.7 to 24.8 mg kg$^{-1}$; average = 5.2 mg kg$^{-1}$ As), affected soil samples (from

0.8 to 55 mg kg$^{-1}$; average = 17.6 mg kg$^{-1}$ As), and mine waste samples (from 0.8 to 164 mg kg$^{-1}$; average = 12.5 mg kg$^{-1}$ As).

Table 5 shows the pseudototal and mobile fractions for Mn and As in the selected samples ($n$ = 23). Several affected soil and mine waste samples analyzed herein surpassed the prevention value (15 mg kg$^{-1}$ As) established by the National Environment Council of Brazil (CONAMA 2009). One mine waste sample presented pseudototal As levels more than ten times higher than the threshold value (Table 5, sample 28). The Geological Survey of Brazil (Companhia de Pesquisa de Recursos Minerais, CPRM 2016) together with the National Water Agency (ANA, Agência Nacional das Águas) conducted an extensive monitoring program of the impacted area within the Doce River basin. They reported higher As levels in suspended river sediments in comparison with stream sediments, indicating that

**Table 4** Certified and found mass fractions for the NIST SRM 2710a—Montana I Soil

| Element | Certified mass fraction[a] | Found mass fraction[b] |
|---|---|---|
| Arsenic | 1300–1600 | 1480 ± 120 |
| Barium | 490–540 | 488 ± 28 |
| Chromium | 9.2–11 | 9.6 ± 0.8 |
| Copper | 3100–3500 | 3400 ± 268 |
| Lead | 4700–5800 | 4550 ± 320 |
| Manganese | 1500–1800 | 1670 ± 114 |
| Nickel | 4.8–6.1 | 6.1 ± 0.6 |
| Vanadium | 35–43 | 37 ± 3 |
| Zinc | 3300–4400 | 4270 ± 320 |

[a] Leachable data from NIST 2710a

[b] Average ± 2SD

**Table 3** Analytical figures of merit for the quantitative determination of As, Ba, Cr, Cu, Mn, Ni, Pb, V, and Zn by ICP-MS

| Parameters | Isotopes | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $^{75}$As | $^{137}$Ba | $^{52}$Cr | $^{63}$Cu | $^{55}$Mn | $^{60}$Ni | $^{208}$Pb | $^{51}$V | $^{66}$Zn |
| Limit of detection[a] (μg L$^{-1}$) | 0.01 | 0.03 | 0.01 | 0.02 | 0.02 | 0.04 | 0.02 | 0.002 | 0.07 |
| Limit of quantification[b] (μg L$^{-1}$) | 0.03 | 0.09 | 0.03 | 0.06 | 0.06 | 0.1 | 0.06 | 0.006 | 0.21 |
| Linear correlation coefficient ($r$) | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Calibration range (μg L$^{-1}$) | 0.1–1000 | 0.1–1000 | 0.1–1000 | 0.1–1000 | 0.1–1000 | 0.1–100 | 0.1–1000 | 0.01–1000 | 1–1000 |
| Measurement precision[c] (%) | 0.9 | 1.6 | 1.5 | 1.4 | 1.7 | 1.4 | 0.9 | 1.2 | 1.1 |

[a] LOD = {[(3.3 × BEC × RSD$_{blank}$) / 100)], $n$ = 10 independent procedural blanks}

[b] LOQ = 3 × LOD

[c] Coefficient of variation obtained from $n$ = 10 measurements of a standard solution containing 10 μg L$^{-1}$ of each element
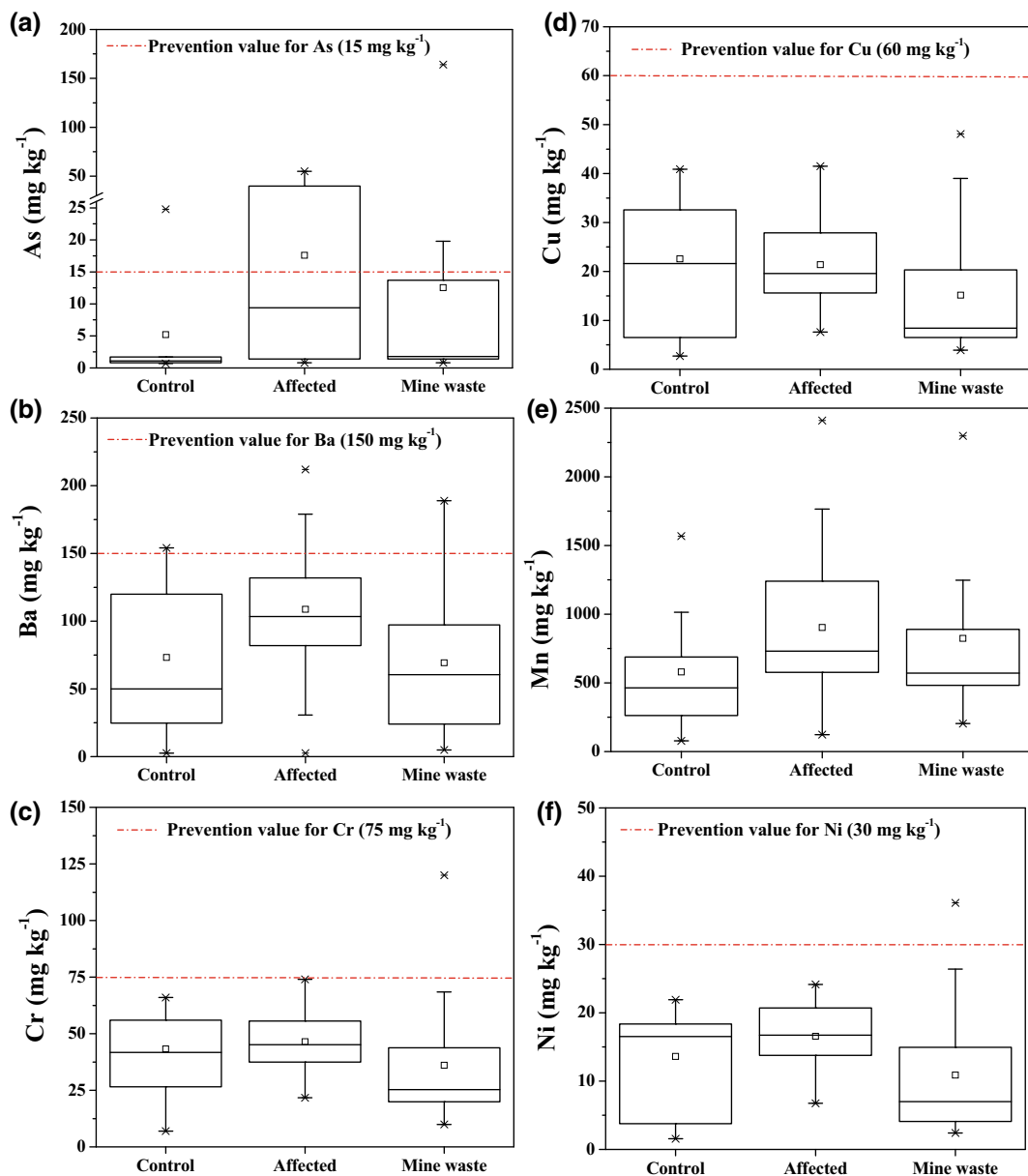
**Fig. 3** Box and whisker plots showing the elemental mass fractions obtained from the EPA 3050B digestion method (pseudototal fraction) and ICP-MS measurements for all analyzed samples ($n = 60$) together with the prevention values preconized by CONAMA: **a** As, **b** Ba, **c** Cr, **d** Cu, **e** Mn, **f** Ni, **g** Pb, **h** V, and **i** Zn. The boxes consist of the 25th and 75th percentiles. The whiskers represent the 5th and 95th percentiles. Minimum (−), maximum (−), median (−), and mean (*white square*) values, as well as the 1st (×) and 99th (×) percentiles are presented

this element may be associated with fine particles of arsenopyrite from the Iron Quadrangle region.

The systematic enrichment observed for As and Mn in some soil samples directly affected by the dam spill might not be alarming, given the naturally high background of the Iron Quadrangle region (mean and coefficient of variation: 168 mg kg$^{-1}$ As (174%) and

6301 mg kg$^{-1}$ Mn (197%), according to Souza et al. 2015). However, considering the large impacted area along the Doce River system, care must be taken when predicting possible threats to the whole ecosystem. In this regard, the state of Espírito Santo, which was severely affected by the dam burst, presents much lower As and Mn background levels in the soil (from 6.4 to
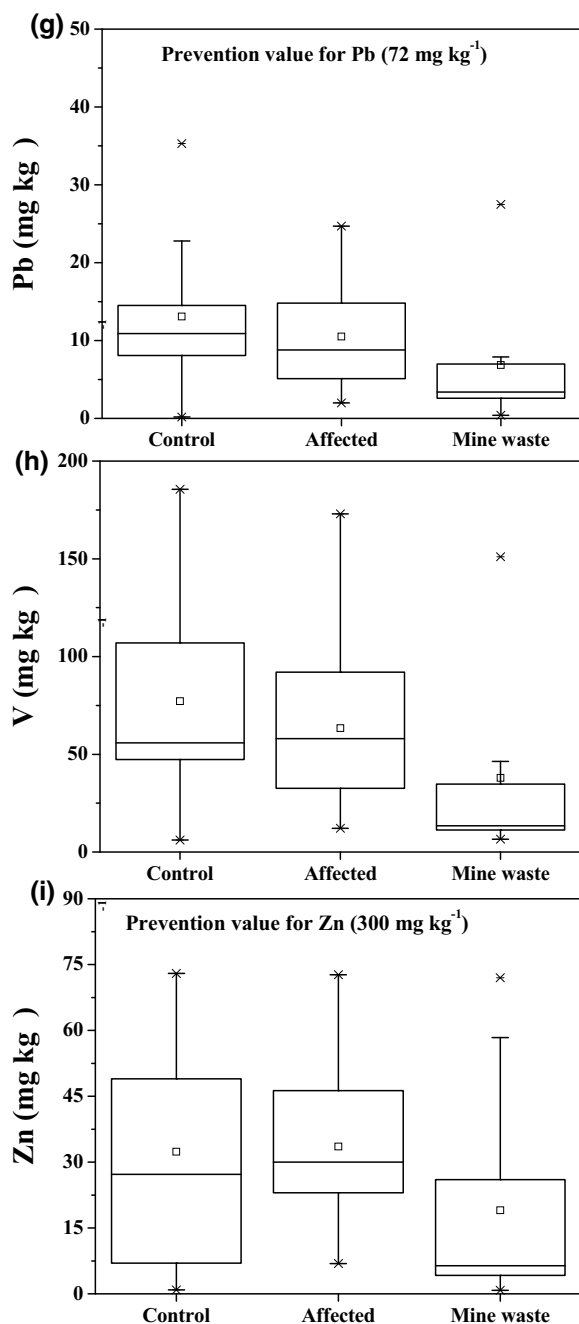
**(g)** Prevention value for Pb (72 mg kg⁻¹)

**(h)**

**(i)** Prevention value for Zn (300 mg kg⁻¹)

**Fig. 3** (continued)

28 mg kg$^{-1}$ As and from 5.6 to 602 mg kg$^{-1}$ Mn, according to Paye et al. 2010). In addition, the high surface area of small particle sizes of the deposited mud (ranging from 1 to 200 μm, as reported by Segura et al. 2016), can boost the bioavailability of such elements to the food chain.

The Brazilian Institute of Environment and Renewable Natural Resources (IBAMA) released a report that presents the data obtained from the physicochemical and biological analysis of water and sediment samples collected between November 2015 to February 2016 in several sites along the Doce River system (IBAMA 2016). Anomalous As levels (as high as 47 mg kg$^{-1}$) were observed in sediment samples collected from the delta of the Doce River in the state of Espírito Santo.

The EDXRF data (Fig. 4) obtained from the screening step corroborates the As and Mn contamination pattern evidenced by the pseudototal contents. Furthermore, a Pearson correlation matrix was generated to investigate the relationship between the As and Mn pseudototal levels in the affected soil samples. A high correlation coefficient was found ($r = 0.83$) indicating the same source of these elements in the disturbed environment. Once As and Mn enrichment was systematically observed in the soil samples directly affected by the mine waste spill, those samples presenting the highest levels of these elements were selected for further evaluation of the mobile fraction by applying the TCLP protocol.

In order to evaluate the data obtained from the TCLP protocol, it is useful to apply the "100-times rule" prescribed by the United States Environmental Protection Agency (USEPA 1994). This approach recommends that a waste can be considered hazardous if the mobile fraction of the elements is higher than 100-times the drinking water guideline values. Based on these considerations, the As mobile levels cannot be regarded of environmental concern (Table 5). In the case of Mn, some samples presented mobile fraction higher than 10 mg L$^{-1}$, but even a control soil sample exceeded this limit (Table 5), indicating a high natural background level.

## 4 Conclusions and Outlook

The high levels of As and Mn documented in some mine waste and affected samples may not be regarded as an environmental concern because of the natural anomalous background levels of these elements in the soils of the Iron Quadrangle region. However, given the large area impacted by the mudslide, local studies must be conducted to evaluate the real menace to these ecosystems.

**Table 5**  Pseudototal and mobile fractions for manganese and arsenic in selected samples

| Sampling site | Sample ID | Sample class | Mn pseudototal (mg kg$^{-1}$) | Mn mobile (mg L$^{-1}$)[a] | As pseudototal (mg kg$^{-1}$)[b] | As mobile (μg L$^{-1}$)[c] |
|---|---|---|---|---|---|---|
| P2  | 2  | Control  | 940 ± 12   | 4.69 ± 0.05 | 24.3 ± 0.1  | 1.8 ± 0.4     |
| P7  | 16 |          | 1014 ± 10  | 8.1 ± 0.3   | 24.8 ± 0.9  | 3.1 ± 0.5     |
| P17 | 43 |          | 1568 ± 6   | 30.0 ± 0.4  | 1.5 ± 0.2   | 2.4 ± 0.5     |
| P4  | 7  | Affected | 938 ± 79   | 2.2 ± 0.3   | 24 ± 1      | 2.3 ± 0.4     |
| P5  | 13 |          | 622 ± 10   | 6.4 ± 0.2   | 17.8 ± 0.5  | 3.7 ± 0.4     |
| P6  | 15 |          | 946 ± 21   | 3.95 ± 0.03 | 18 ± 2      | 1.27 ± 0.09   |
| P7  | 17 |          | 935 ± 12   | 3.3 ± 0.1   | 46.9 ± 0.5  | 1.9 ± 0.6     |
| P8  | 21 |          | 2410 ± 33  | 7.38 ± 0.09 | 55 ± 4      | 2.6 ± 0.6     |
| P9  | 23 |          | 1765 ± 32  | 4.57 ± 0.07 | 46.4 ± 0.4  | 2.1 ± 0.3     |
| P10 | 25 |          | 1240 ± 52  | 2.75 ± 0.07 | 39.8 ± 0.7  | 1.9 ± 0.5     |
| P11 | 27 |          | 1619 ± 7   | 16.3 ± 0.5  | 45.4 ± 0.8  | 1.9 ± 0.3     |
| P19 | 47 |          | 1318 ± 4   | 28.5 ± 0.6  | 9.2 ± 0.4   | 4.9 ± 0.2     |
| P21 | 53 |          | 1400 ± 21  | 8.9 ± 0.3   | 47.3 ± 0.1  | 3.33 ± 0.07   |
| P23 | 57 |          | 993 ± 82   | 3.08 ± 0.05 | 15.5 ± 0.9  | 0.65 ± 0.01   |
| P4  | 6  | Waste    | 736 ± 15   | 4.3 ± 0.2   | 18 ± 1      | 1.7 ± 0.2     |
| P5  | 9  |          | 889 ± 25   | 4.86 ± 0.02 | 7.8 ± 0.3   | 0.38 ± 0.06   |
| P5  | 12 |          | 703 ± 4    | 8.4 ± 0.1   | 17.3 ± 0.2  | 2.6 ± 0.2     |
| P9  | 22 |          | 1955 ± 46  | 6.9 ± 0.1   | 19.8 ± 0.1  | 1.15 ± 0.03   |
| P11 | 28 |          | 1531 ± 46  | 9.8 ± 0.2   | 164 ± 3     | 6.2 ± 0.5     |
| P14 | 35 |          | 918 ± 90   | 7.55 ± 0.01 | 2.7 ± 0.1   | 1.15 ± 0.15   |
| P17 | 41 |          | 2298 ± 52  | 22.6 ± 0.3  | 17 ± 1      | 5.4 ± 0.6     |
| P18 | 44 |          | 2168 ± 29  | 27.7 ± 0.7  | 14.6 ± 0.4  | 4.9 ± 0.3     |
| P18 | 45 |          | 1247 ± 25  | 22.2 ± 0.2  | 1.4 ± 0.1   | 1.5 ± 0.2     |

Mobile fraction data assessed by the extraction of 0.2500 g of ball-milled sample with 5 mL of extracting fluid

[a] Guideline for water quality (class 1) preconized by the Brazilian Legislation (CONAMA 2005): 0.1 mg L$^{-1}$ Mn

[b] Prevention value preconized by CONAMA: 15 mg kg$^{-1}$ As

[c] Guideline for water quality (class 1) preconized by CONAMA: 10 μg L$^{-1}$ As



**Fig. 4**  Fragment of EDXRF spectrum highlighting the main X-ray peaks (from 1 to 11 keV) obtained from the analysis of the following samples: a mine waste (sample 28), an affected (sample 27), and a control soil (sample 32) by the portable handheld XRF spectrometer. As and Mn mass fractions data obtained from the EPA 3050B digestion method followed by ICP-MS measurements: mine waste: (164 ± 3) mg kg$^{-1}$ As and (1531 ± 46) mg kg$^{-1}$ Mn, affected soil sample: (45.4 ± 0.8) mg kg$^{-1}$ As and (1619 ± 7) mg kg$^{-1}$ Mn, and control soil sample: (1.60 ± 0.01) mg kg$^{-1}$ As and (325 ± 4) mg kg$^{-1}$ Mn
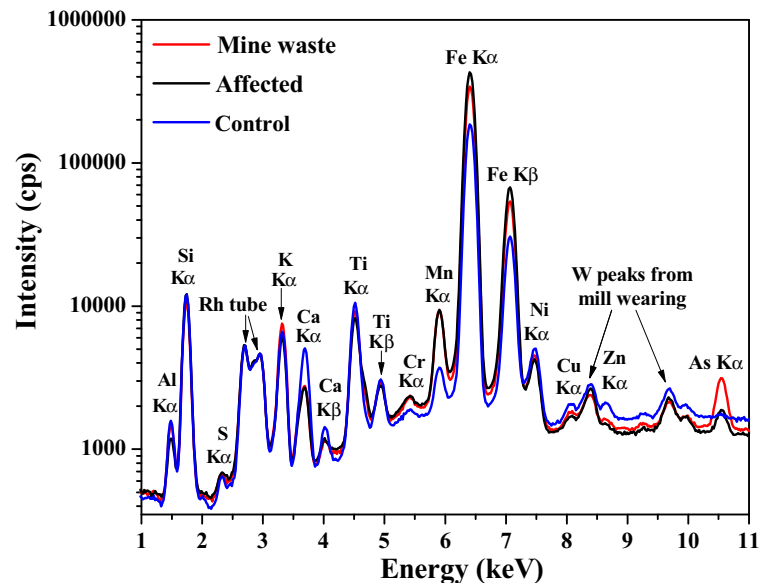
This preliminary environmental assessment highlights the importance of evaluation of long-term effects on soil directly impacted, as well as on the aquatic biota of the Doce River system and adjacent coastal environment. The reported data can also assist in the establishment of appropriate environmental impact mitigation strategies.

Other parts of the world are facing similar problems resulting from tailings dam failures, with the inherent drastic consequences from both environmental and economic point of views. In this regard, strict protocols should be universally adopted for the prevention of such tragic events and the implementation of efficient emergency measures to protect the ecosystem and to save the lives of the people in the impacted areas.

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