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Trace metals in the water and margin sediments of the *Rio Doce* Basin in Linhares municipality, ES, Brazil

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Abstract

The Rio Doce Basin (DRB) is the largest freshwater source in Espírito Santo (ES) state, Brazil. In November 2015, the disruption of the iron tailings dam in the Mariana municipality, Minas Gerais state, Brazil, severely affected this river. In this study, we showed the trace metals concentrations in the water and margin sediments of the DRB during the dry and wet seasons. This new data was obtained in 2011, prior to the environmental disaster caused by disruption of the dams. We observed Cr, Ni and Pb contaminations in the sediments. The concentrations of these elements in the high river flow (wet season) were higher than the guideline values (GV) of level II and geoacumulation Index (I_{geo}). However, Fe and Mn concentrations were well above the GV in the wet season. The levels of these two elements were lower than the values found in the region's Haplic Cambisol. Furthermore, the comparison between our data and those of the technical reports released after the dams rupture shows that iron ore mine tailings greatly alter the trace metals concentration in water and sediments. However, we have observed a trend of resilience that requires more systematic and careful studies in DRB.

1. Introduction

The Rio Doce Basin (DRB) comprises 202 municipalities of Minas Gerais (MG) state and 28 of Espírito Santo (ES) state, Brazil. The pollution of the waters and sediments of this river is mainly due to the activities of more than 3.5 million people. In this watershed is located the largest steel industry of the Latin America and the largest open pit mining company in the world. Furthermore, several industries, hydroelectric, and agricultural and livestock activities are observed along the 897 km of the river.
The Institutes and Monitoring Committee of the Brazilian governments have investigated the DRB pollution. In 2002, it was created *Comitê da Bacia Hidrográfica do Rio Doce* (*in Portuguese*). Furthermore, the Water Administration Institute of Minas Gerais (IGAM) has been monitoring the water quality of the DRB-MG since 1997.
There are several studies on the quality of water and sediments of the DRB/MG and its tributaries.
The DRB-MG in Vale do Aço municipalities has Cr, Cd, and Mn contamination in the sediments of the dry season and a higher Fe, Al, Mn, and Zn concentration in the waters than in BRD-MG in Belmiro Braga-MG. This municipality does not have the influence of the steel activities **(Jordão et al., 1996)**.
High concentrations of Zn and Pb in the suspended solids and dissolved Al concentration about 15 times greater than 100 $\mu g\ L^{-1}$, which is the concentration of this element allowed in the class II water by the Brazilian legislation, were detected in Turvo Limpo River in Viçosa/MG to the southwest of DRB-MG **(Jordão et al., 2007)**.
In Carmo River in Mariana and Ouro Preto/MG municipalities, where it has high mining activity, the As levels in the water were seven-fold higher than the maximum limit of the Brazilian legislation (10 $\mu g\ L^{-1}$). In the study of **Varejão at al. (2011)**, concentrations of Cr and Ni higher than the level 1 and contents of As and Cd higher than the level 2 were observed in the sediments (CONAMA 344/2004).
In the Alto Rio Doce in the Mariana/MG municipality, As concentrations in the sediments ranged from below the limit of quantification (LOQ < 2.04 $\mu g\ g^{-1}$) to eighteen fold higher than the reference concentration of the region. In this river, the Cd concentrations were higher than the quality reference values (QRV <0.5 μg g-1) and probable effect concentration (PEC = 4.98 $\mu g\ g^{-1}$) in the dry and wet seasons **(Silva et al., 2013)**.
More recent studies identified the concentrations of Cr, Cu, Hg, Pb, and Zn in 41% in the DRB-MG sediments higher than the sediment quality guidelines (SQG) using threshold effect level (TEL), probable effect level (PEL) and severe effect level (SEL) **(Santolin et al., 2015; Campanha et al., 2014)**. The Cr concentration in all samples was higher than the SQG-PEL limit (90 μg). The Cu level in ten samples was larger than the SQG TEL limit (35.7 μg). The Zn concentration in five samples was above

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the SQG TEL (123 µg). Furthermore, the geochemical indicators showed that eight points of the DRB-MG were more contaminated with these elements than other points.

These studies also show the influence of steel activities on the chemical characteristics of DRB waters and sediments.

The DRB-ES is the largest freshwater source of the Espírito Santo state. The mouth of this river is in the Regência region in the Linhares/ES municipality. This is a region rich in natural resources with lagoons, environmental reserves, and beaches. The Goitacazes, Companhia Vale do Rio Doce and Sooretama reserves are Atlantic Forest biome.

Linhares/ES municipality has a flat topography with many lagoons, like the *Juparanã* lagoon with 30 km of extension. The climate of the region is classified as tropical hot and dries with rainfall in summer and dry winter. Clay soils and cambisols are observed in the region **(EMBRAPA, 2006)**. Furthermore, this municipality has its economic based on the furniture, alcohol, cocoa, clothing, oil, and natural gas production.

On November 5, 2015, the disruption of the *Fundão* and *Santarém* dams in Mariana/MG municipality dumped about 50 million m^3 of tailings in the Rio Doce River. These tailings traveled 663.2 km arriving at the river mouth on November 21, 2015. The *Baixo Guandu*, *Colatina*, *Marilândia*, and *Linhares* municipalities were directly affected with 11 tons of dead fish, since 3 tons at the river mouth. The Linhares/ES municipality has about 30% coverage of Atlantic Forest and DRB-ES has about 80 species of native fish and 13 endemic species. After one year of the environmental disaster, 11 of these endemic species of fish had extinction risks. The Samarco mire affected the piracema and fishing activities were interrupted to 1,134 anglers from the ES state, according to data from March 2016 **(IPEA, 2016)**.

Thus, the aim of this study was to compare trace metal concentrations before and after the disruption of the iron ore tailings dams in Marina/MG municipality. Our study shows unprecedented data on the environmental conditions of the DRB-ES in the Linhares/ES municipality four years before the disruption of these dams. In 2011, we determined the trace metals concentrations, pH and X-ray diffraction values in the margin sediments and water of three sampling points in the dry and wet seasons. The metals concentrations of the water were compared to the permissible values (PV) by the Brazilian legislation for water class II **(CONAMA nº 357/2005)**. The concentrations of these metals in the sediments were compared to the guideline values (GV) of **CONAMA Resolution No. 354/2004**, which has the classification levels of dredged material. In this resolution, freshwater of the level I and level II has, respectively, lower threshold than the low probability of adverse effects on biota and threshold greater than the probability of an adverse effect on biota **(CONAMA NO. 454/2012)**. The concentrations of Fe and Mn were compared with lowest effect level (LEL) and SEL **(Pereira et al., 2006)**. To verify the sediments contamination were determined the I_{geo} **(Asa et al., 2013)**.

Our results were compared with data from technical reports on the environmental conditions of DRB from 2010 to 2016. Thus, our results will remain as a historical reference on the environmental conditions of the DRB-ES, before the disruption of the iron ore tailings dams in Marina/MG municipality and may contribute to future environmental actions of preservation of this river.

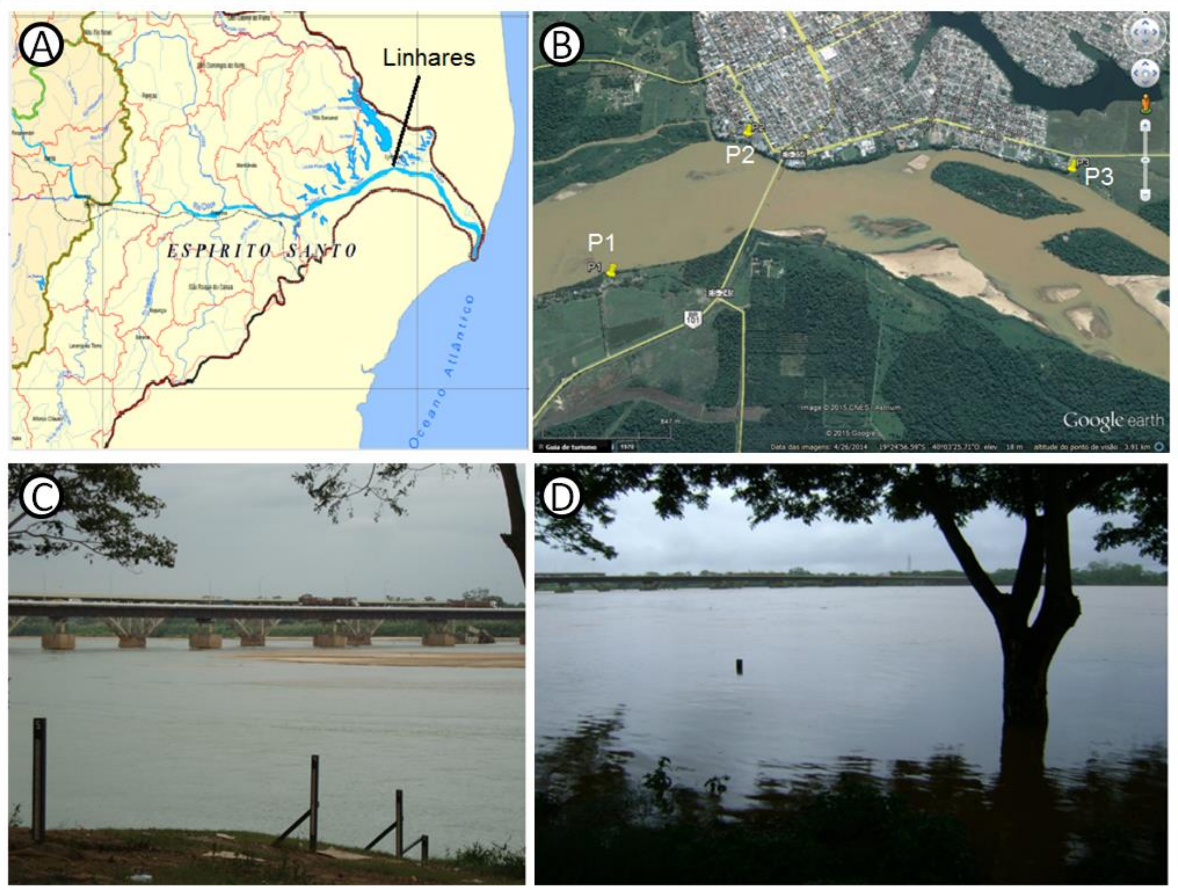

Figure 1. Fragment of a map of the Brazilian southeastern showing in the blue the Rio Doce watershed (A), Google Earth photograph of the sampling points (P1 to P3) in this river (B), and water levels in the dry (C, 12/10/2011) and wet (D, 11/30/2011) seasons.

2. Material and methods

We collected samples of water and margin sediment at three points of DRB in Linhares/ES municipality in the Brazilian southeastern (Figure 1CD). These samples were collected on October 12 and 30, 2011, respectively, in the dry and wet seasons to compare the metals concentrations between them.
The sampling points were:
P1 (INCAPER): 19°24'58.29"S and 40°4'33.17"W. This point was located in a farm that the Capixaba Institute of Research, Technical Assistance and Rural Extension (INCAPER) works with agricultural and livestock activities (Figure 1B).
P2 (PORTO RIO DOCE): 19°24'23.23"S and 40°4'1.56" W. This point was in the Pequeno River that connects the DRB to the *Juparanã* lagoon (Figure 1B).
P3 (IFES): 19°24'32.56"S and 40°2'37.66" W. P3 was the farthest point of the urban center of the Linhares/ES municipality. The campus of the *Federal Institute of Education*, Science and Technology of *Espírito Santo state* (IFES) and the ES-248 highway were the reference points (Figure 1B).

2.1 Metals determination in the water samples

The water samples were added in glass flasks previously washed with distilled water and nitric acid (HNO_3, 10% v/v) for 48 h and deionized water (mili-Q ELGA, 18 S cm^{-1}). In each flask with 500 mL of samples was added 2.5 mL of concentrated HNO_3. After, these flasks were kept in an icebox during transport for the laboratory. The samples (200 mL) were vacuum-filtered on cellulose ester membrane (Millipore, 0.45 µm and 47 mm of diameter). These procedures were performed in triplicate.
We determined the elemental concentration in the permeate (Tables 1-3). The negative control of these measurements was obtained with deionized water following the same procedure of the samples. The limit of detection (LOD) was based on the US EPA 200.8 **(USEPA, 1994)**.
These measurements were performed in the Inductively coupled plasma mass spectrometer (ICP-MS, ELAN DRC model) of the *Mass Spectrometry Laboratory/*Center of Nuclear Technology Development (CDTN) with the standard 3 (solution of 10 µg mL^{-1}, Perkin Elmer). The plasma energy was 1 400 W and gas flows were 16 (plasma), 1.2 (auxiliary), and 0.72 (nebulizer) L min^{-1}, respectively.

2.2 Metals determination in the margin sediments

Three samples of surface sediments per sampling point (Figure 1AB) were collected on the river margin from 0 to 30 cm depth using a plastic spoon. These samples were added to plastic bags. In the laboratory, the samples were oven dried and separated in a 1 mm mesh plastic sieve. We also removed the leaves and gravel of the samples.
For the trace metals determination in the sediments, 500 mg of these samples were added to Teflon crucibles containing 10 mL of concentrated HNO_3. These crucibles were kept for 45 min on an electric plate with sand. After the addition of 3 mL of hydrogen peroxide (30% H_2O_2, v/v) in the samples, the plate was heated for 5 min. Then, 3 mL of concentrated hydrochloric acid (HCl) and 10 mL of water were added to the wet residue. After filtration, the solution was transferred to a flask of 100 mL **(USEPA, 1986)**.
The analyzes were performed at the Atomic Spectrometry Laboratory of the Department of Chemistry of the Federal University of Espírito Santo in an inductively coupled argon plasma optical emission spectrometer (ICP-OES, Perkin Elmer, optima model 7000 DV). The gas flow of 15 (plasma), 1.0 (auxiliary) and 0.8 (nebulizer) L min^{-1}; radial view (λ /nm) for the Al (396.2), Cu (327.4), Fe (238.2), Li (670.8), Mn (257.6), Ni (231.6), and Zn (206.2); and axial view (λ/nm) for the Cd (228.8), Cr (267.7), Pb (220.4), V (292.5), and As (193.7) were used in the ICP-OES.
In the analytical curves, a multi-element standard (Spec Sol containing 23 elements: Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Ti, and Zn) of 100 µg mL^{-1} containing 30 elements at concentrations of 0.05, 0.10, 0.40, and 0.80 µg mL^{-1} of each was used. The LOD was determined with 3 standard deviations of 10 measurements of the negative control of this analytical curve **(Long, 1983)**.
The geoaccumulation index (Igeo) and Igeo classes (Table 1) determined the levels of contamination of the DRB sediments **(Asa et al. 2013)**. The I_{geo} is a parameter used to define the metal contamination in the sediment by the comparison between the metal concentration (CM) and the geochemical background concentration (Cbg) according to equation 1.

$$I_{geo} = log_2 \frac{CM}{1{,}5.Cbg} \text{ (equation 1)}$$

Samples for X-ray diffraction were also oven dried and separated in a 1 mm plastic sieve. After, they were crushed in a mortar. The X-ray equipment (Bruker, model D2 PHASER) of the *Programa de Pós-Graduação em Engenharia Metalúrgica e de Materiais* (*in Portuguese*) of the IFES campus in Vitória/ES/Brazil city in was used in this analysis. The Cu-K(alpha) radiation at 30 kV, 10 mA, and two thetas of 10 to 100º with continuous acquisition of 0.02º s^{-1} were the operating conditions of the equipment. Furthermore, this X-ray equipment has Diffrac. Suite (AXS 2009-2011, v. 0.27, Diffract-EVA) software that allowed automatic searches for spikes and probable minerals, smoothing curve and qualitative analysis.

Table 1. Levels of contamination in the sediments by the geoaccumulation index (Igeo) **(Asa et al., 2013)**

Class	Values	Feature
0	$I_{geo} < 0$	Pollution-free environment
1	$0 \leq I_{geo} < 1$	Pollution free to moderately polluted
2	$1 \leq I_{geo} < 2$	Moderately polluted environment
3	$2 \leq I_{geo} < 3$	Moderately to heavily polluted
4	$3 \leq I_{geo} < 4$	Heavily polluted environment
5	$4 \leq I_{geo} < 5$	Heavily polluted environment to extremely polluted
6	$I_{geo} < 5$	extremely polluted environment

2.3 Statistical analyzes

The analyte concentrations were organized into X and Y matrices with I lines (samples) and J columns (variables). In the lines, each replicate was one sample. The J variables were the analyte concentrations in the water (µg mL^{-1}) and margin sediments (µg g^{-1}). These matrices were performed in the Mathlab 7.0 (The Math Works, Co., Natick MA, USA) and PLS-Toolbox (Eigenvector Research, Inc. PLS-Toolbox, version 3.02) software **(Wise, 2004)**. Principal Component Analysis (PCA) was used as an exploratory method **(Ferreira, 1999)**.

3. Results and discussion

We observed a variation in the rainfall amount between the sampling times in the low-flow of the dry season and high-flow of the wet season of the DRB-ES. A negative rainfall anomaly index (-25 to -50 mm) from 01 to 15 October 2011 was observed in the first sampling. While in the wet season, sampling this index from 16 to 31 November 2011 was positive (25 to 50 mm) **(CPTEC, 2011)**.

The water pH of the DRB-ES was between 6.8 and 7.4 with higher acidity in the wet season than in the dry season. According to the *Companhia de Pesquisa de Recursos Minerais* (CPRM), the water pH ranged from 6.6 to 8.0 at different sampling points between 2010 and 2015. In 2010, the water pH in Baixo Guandu/ES municipality was 6.6. In 2013, the pH in Colatine/ES city was of 6.2 to 8.0. In 2015, the pH was of 6.5 and 7.15 in the municipalities of Colatine and Linhares/ES, respectively **(CPRM, 2015)**.

The comparison of our data with other articles and official reports was important for a better evaluation of the environmental conditions of the DRB-ES in Linhares/ES before and after the disruption of the Mariana-MG dams.

3.1 Distribution of trace metals in water

Most of the metals analyzed in the water had concentrations below the permissible values (PV) for water class II (Table 1, **CONAMA 357/2005**). However, Al and Pb concentrations in the DRB-ES water were higher than the PV. The Al concentration decreases among the seasons (Table 1). In the low and high flows of the river, the concentration of this element was respectively 6.5 and 2.0 folds higher than the PV. The high Al concentration of the Linhares/ES Haplic Cambisol may have influenced this result (Table 1). In a study in water source under the influence in the hydromorphic soils in the coastal region of Linhares/ES, it was also observed a decrease of the Al concentration between the beginning and 39 days after of wet season **(Soares and Mendonça, 2001)**. The contents of this metal were from 480 to 330 at the beginning and 330 to 230 μg L^{-1} after the rains at two adjacent points of the Rio Doce River. Furthermore, the Al concentrations in the DRB in the red-yellow cambisol region were about 2.7 (Dias et al, 2005) fold higher than the dry season values in Linhares /ES (Table 1).

The Pb concentrations in P3 in the dry season and in P1 in the wet season were higher than PV and values found red-yellow cambisol region (2.55 to 4.10 μg L^{-1}). The geographic location of these sampling points may have influenced this result. P3 is located downstream from the city center and about 200 m from the highway ES-248 and P1 have traffic of agricultural machines. In these sampling points the Pb from gasoline additives can contaminate the waters and sediments of the river **(Parra et al, 2007)**.

The concentration of As was low in both seasons. The Cd and Cu concentrations in the wet season at P3 and P2 were also above the PV (Table 1).

The ten metals analyzed in PCA had 37.72% of the variance in the first component (Figure 2A). The dry season samples with high concentrations of Al, Cr, and Zn were grouped in the second and third quadrants (Figure 2A, table 1). Meanwhile, wet season samples with high levels of As, Cd, Co, Cu, Mn, and Ni were grouped in the positive quadrants (Figure 2A, table 1). Thus, these metals were important in separating the samples as a function of river flow and sampling points.

The Al, Cr, and Zn had a dilution effect from low to high river flow because their concentrations decreased from dry to wet seasons (Figure 2A, Table 1). While, the other metals (As, Cd, Co, Cu, Mn, and Ni) were leached during the wet season, increasing their concentrations in the water.

We have observed the dilution and leaching effects of metals in other studies, but there is no standard trend in these processes. The dilution effect of Cr between dry and wet seasons was also observed in only one sampling point in the Conceição River in the Santa Bárbara/MG municipality **(Parra et al, 2007)**. In this point, the Cr concentration was of 153 μg L^{-1} in the dry season (winter) to smaller than LOQ in the wet season (summer). In the other eight sampling points, the concentration of this element was below the LOQ. In this study, the leaching effect was also observed for the Ni with concentrations ranging from 15.75 to 115 μg L^{-1} in the dry season to below LOQ in the wet season. In New South Wales state, Australia it was observed dilution and leaching effects of metals between dry and wet seasons in the urban regions of the river **(Shah et al, 2007)**. In this study, Cr, Zn, As, Cu, Mn and Ni had a dilution effect, while the Cd showed a leaching effect. Furthermore, depending on the sampling points, the Mn, Zn, and Cu had changes in the behavior of the leaching and dilution effects between dry and wet seasons in the flow of fluvial waters in Vancouver city, Canada **(Li et al, 2009)**.

In 2010, the DRB waters Baixo Guandu/ES municipality had concentrations (μg L^{-1}) of As (1.0), Cd (0.5), Cr (1.5), Cu (4), Mn (3.5), Ni (3.5), Pb (1.0) and Zn (20) smaller than PV (CPRM, 2015). We observed that concentrations of As and Ni were not changed between 2010 and 2011 in the DRB water (Table 1). In this period, the concentration of Cd and Cu decreases, while the concentration of Mn, Pb, and Zn increased (Table 1).

The *Grupo Independente para Impacto Ambiental* **(GIAIA, 2016)** showed an increase in contamination in the DRB in Linhares/ES after the rupture of the Samarco dams, but of December 2015 to April 2016 there was a reduction of this contamination. The concentrations (μg L^{-1}) of As (72 to 5), Cd (5 to 1), Mn (240 to 480), Ni (60 to 10) and Si (120 to 10) were reduced in water. The Pb levels (<10 μg L^{-1}) did not change in this period. However, levels of As (7 fold), Cd (5 fold), Mn (2 fold), Ni (2 fold), and Se (12 fold) were above the PV. These levels were also higher than our data (Table 1). Furthermore, only Al total increased between 2015 and 2016 ranging from 350 to 810 μg L^{-1}. In 2016, Al concentration was between 1.2 and 4.8 fold higher than our values in the dry and wet seasons (Table 1).

The data from November 2015 of the DRB environmental conditions in Linhares/ES city provided by the company responsible for the Mariana/MG dams and contained in the report of the *Coordenação Geral de Emergências Ambientais* **(CGEMA, 2016)** showed, respectively, Al and Pb concentrations 300 and 3.6 fold above the PV and 140 and 176 fold greater than the our data (Table 1).

The concentrations (mg L^{-1}) of Al (0.095), As (<0.002), Cd (<0.002), Cu (<0.005) and Pb (0.002 and 0.005) of the report with data November 11 and December 9/2015 of the CPRM (station ED-A0013-A) were lower than VP. Thus, there are no indications of contamination of the DRB with these elements with the inclusion of atypical metals in the river water after the rupture of the Mariana-MG dams **(CPRM, 2015)**.

The As concentrations in Linhares/ES (Table 1) were much lower than the levels of this element in the Carmo River (36.7 - 68.3 μg L^{-1}) in the Mariana and Ouro Preto/MG municipalities, which has an intense mining activity (Varejão et al., 2011). However, the As determination in DRB-ES indicates a probable transfer of elements from mining activity of the Minas Gerais state to environmental reserves at the river mouth. This transfer was also observed in 2010 by the **CPRM (2015)**.

Thus, the concentrations of Al and Pb in the DRB-ES are of concern due to agricultural, livestock and fishery activities of the region. The Al is toxic to humans with evidence of Alzheimer's disease and Pb accumulation of in the human and animal has adverse health effects **(WHO, 1998)**.

3.2. Distribution of trace metals in margin sediments

We did not find the geochemical background of DRB-ES sediment in none article. Thus, we determined the Igeo using the geochemical background of Al, Cr, Pb, Ni, and Mn of the Gualaxo River that is to the north of the DRB-MG **(Costa et al., 2003)**.

The metal contamination increased from the dry season to the wet season with changes in Igeo classes in all analyzed metals (Tables 2 and 3).

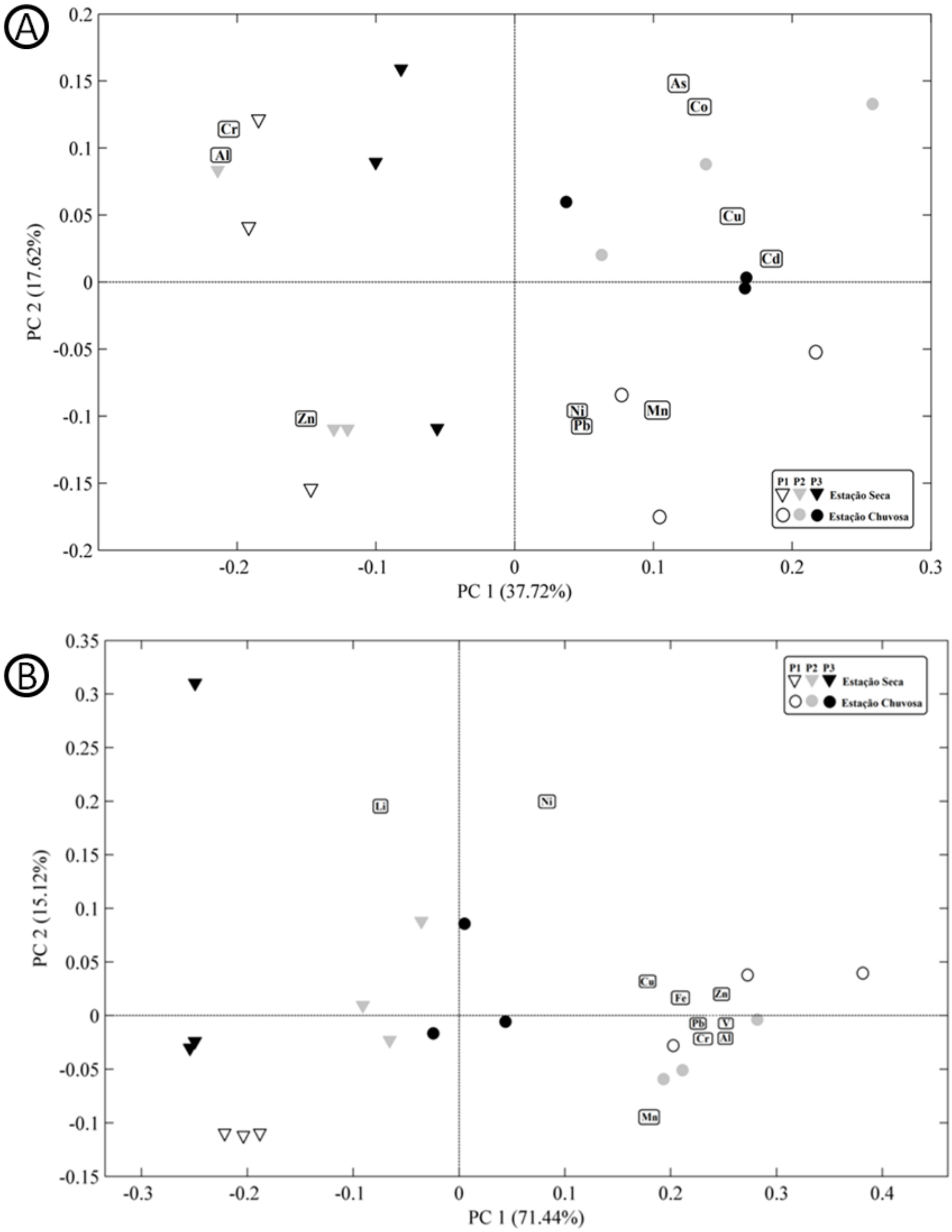

Figure 2. Principal Component Analysis of the distribution of metals in water samples (A) and margin sediments (B) obtained at three sampling points (P1 to P3) of the Rio Doce watershed in the Linhares/ES/Brazil municipality in the dry (▼) and wet (●) seasons of 2011.

Table 2 - Concentration of trace metals (μg L^{-1})[a] in water samples obtained at three sampling points (P1 to P3) of the Rio Doce watershed in the Linhares/ES/Brazil municipality in the dry and wet seasons of 2011

Metals	Dry season			PV (μg.L^{-1})[b]	Wet season		
	P1	P2	P3		P1	P2	P3
Al	650 ± 46	565 ± 28	564 ± 28	100	213 ± 11	170 ± 5	187 ± 17
As	0.70 ± 0.03	0.41 ± 0.04	0.59 ± 0.03	10	0.74 ± 0.04	0.96 ± 0.05	1.00 ± 0.04
Cd	< 0.14			1	0.72 ± 0,04	0.81 ± 0,07	1.33 ± 0.04
Co	0.57 ± 0.02	0.55 ± 0.02	0.80 ± 0,04	50	0.78 ± 0.03	0.87 ± 0.04	0.72 ± 0.04
Cr	8.0 ± 0.3	7.0 ± 0,4	7.5 ± 0,4	50	2.1 ± 0.10	2.9 ± 0.10	2.1 ± 0.10
Cu	2.5 ± 0.1	2.5 ± 0.1	1.4 ± 0.1	9	7.3 ± 0.20	16.1 ± 0.8	5.1 ± 0.2
Mn	33.5 ± 1.7	34.2 ± 1,7	31.4 ± 0,9	100	55.3 ± 2,2	33.1 ± 1,7	40.5 ± 2.8
Ni	3.0 ± 0.1	3.2 ± 0.1	3.0 ± 0.2	25	16.1 ± 0.5	3.9 ± 0.3	3.8 ± 0.3
Pb	7.5 ± 0.3	8.9 ± 0.3	15.4 ± 0.6	10	13.3 ± 0.3	7.6 ± 0.2	9.7 ± 0.4
Zn	85.7 ± 1.7	63.8 ± 2,6	8.4 ± 0,5	180	34 ± 1	16.9 ± 0.7	10.2 ± 0.4
Se	<1.3			10	<1.3		

[a]Mean of triplicates. [b]Permissible values (PV) by the Brazilian legislation for water class II (CONAMA 357/2005). Limit of detection = Al: 342; As: 0.25; Cd: < 0.14; Co: 0.14; Cr: 4.11; Cu: 0.60; Mn: 0.67; Ni: 0.45; Pb: 8.1; Zn: 5.0; Se: < 1.3 (μg L^{-1}).

Table 3. Geoaccumulation index of margin sediments samples obtained at three sampling points (P1 to P3) of the Rio Doce watershed in the Linhares/ES/Brazil municipality in the dry and wet seasons of 2011

Metals	Geoaccumulation index	Class
	Dry season	
Al	- 0.1	0
Cr	-0.1	0
Pb	3.5	4
Ni	0.7	1
Mn	-3.4	0
	Wet season	
Al	4.3	5
Cr	2.2	3
Pb	5.0	5
Ni	2.3	3
Mn	1.5	2

The PCA for 10 metals analyzed in the margin sediments had 71.44% of the variance in the first component (Figure 2B). This PCA, metals with a high concentration in the sediments had a correlation with the wet season (Figure 2B, Table 2).
The leaching effect of Al was confirmed by increasing kaolinite peaks, (Al_2 [SiO_5] $(OH)_4$) in the wet season (Figure 2B, Tables 4 and 5). This increase may be due to the soil type. According to Pacheco (2015), the yellow clay soil (PA2) and Haplic Cambisol (CX35) has a high concentration of this element (Al_2O_3 =319.60 g kg^{-1}, equivalent to Al = 169.4 g kg^{-1}).
The concentrations of the toxic metals (Cr and Pb) were higher than the GV level II in P2 in the dry season and all sampling points in the wet season (Table 2).
The Ni concentrations were above GV level I in all points in the two seasons and above GV level II in P2 in the dry season and P1 and P3 in the wet season (Table 2).
The concentrations of Mn and Fe that do not have GV in the Brazilian legislation were above the GV level II of the international reference in both seasons. However, the concentrations of these elements were respectively 5 and 3.5 times greater than GV in the wet season **(Pereira et al, 2006)**. These results were confirmed by the presence of goethite (FeO.OH), hematite (Fe_2O_3), and gotrelite (MnO_2) in the sediments at both seasons (Figure 3, table 5). Furthermore, the high concentrations of these elements in the wet season may be due to the sediment contamination by the Vitória/ES to Minas Gerais railway. The concentrations of Fe and Mn lower than to the Haplic Cambisol of Linhares/ES (Fe_2O_3 = 73.19 g kg^{-1}, equivalent to Fe = 2.56% and MnO_2 = 1.01 g kg^{-1}, equivalent to Mn = 640 mg kg^{-1}) was observed by **Pacheco (2015)**.
The concentrations of As, Cd, Cu, Fe, and Zn in Baixo Guandu /ES city **(CPRM, 2015)** were higher than our values for the dry season of 2011 (Tables 4 and 6). Thus, there was a reduction in the levels of these metals in the DRB-ES sediments from 2010 to 2011.
The Al concentrations of the metals in the margin sediments under river effects in Linhares / ES **(Pacheco, 2015)** were higther than our values in P1 and P3 in the dry season, but between 3.6 and 14 fold below the values of the wet season (Tables 3 and 4). Furthermore, we observed a decrease in Fe and Pb levels and an increase in As, Cd, Cr, Cu, Mn, Ni, Zn and V levels from 2011 (Table 4) to 2015 (Table 6) in this points. These results are important because it makes a comparison of the metal levels before and after the rupture of the Mariana/MG dams.
In 1996, the DRB-MG in the Vale do Aço municipalities had high concentrations of Cr, Ni, and Mn in margin sediments of the dry season which may be due to the low river flow or mining and metallurgy activities. In this study, Pb and Fe concentrations were well below of the background in Belmiro Braga/MG (Fe = 1.57 %) (Jordão et al., 1996). In addition, the maximum concentration (μg g^{-1}) of Ni (39.65), Mn (5802), and Fe (25.91 %) in the dry season samples were higher than the GV and our concentrations of the dry season (Table 2) **(Silva et al., 2013)**.
Another study in the most recent DRB-MG in points monitored by IGAM, the authors identified Cr, Cu, Hg, Pb, Zn in 41% of the sediment samples analyzed (Table 4) **(Santolin et al., 2015)**. The concentration of these elements was above the sediment quality guidelines (SQG) and the Igeo showed that eight of these sampling points were heavily contaminated. This study was carried out in a region near the Espírito Santo/Brazil state. However, our concentrations of metals in the margin sediments of the DRB-ES were different from the metals levels obtained in the DRB-MG (Tables 4 and 6).
The high concentrations of metals in the wet season may be due to the solids and sediments amount in the water (Figure 3, table 2). In the high river flow, these solids are in high quantity in the superficial layer due to its rapid speed of renovation by the sedimentation cycle and the fluvial sedimentation. These solids come from agricultural soils and roads adjacent to the river **(Baggio and Horn, 2008)**. This leaching occurs mainly at the high river flow and contributes to the increase of the metals concentration in the margin sediments **(Muggler et al., 2005)**, as observed in our study (Table 2). The lead of the margin sediments, for example, may be due to the influence of the urban area where the addition of this metal occurs in the soil **(Oliveira and Marins, 2011; Pusch et al., 2007)**.
In the dry season, it was observed a concentration great for Cu and Zn, good for Cr and Ni, and bad for Pb. While in the wet season, the concentration was good for Cu, regular for Zn, bad for Ni, and very bad for Cr and Pb. This classification was performed according to the **CETESB (2014)** criteria.
In the most recent conditions, according to the latest **CPRM (2015)** report (station ED-S-0013-A), the DRB-ES sediments after the environmental disaster of the Mariana-MG dams show increase in concentrations of As, Cr and Fe and decrease in Ni, Mn and Pb in Linhares/ES (Tables 3 and 4). Meanwhile, the **CGEMA (2016)** report showed increase in maximum concentrations (mg kg^{-1}) of As, Cd, Cr, Cu, Fe (%), Ni and Zn and decrease in Mn and Pb to our data in the wet season of 2011 (Tables 3 and 4). This report, As, Cr and Mn had concentrations above the level 1 of the GV, iron concentration was 3.6 fold above the international GV and Cd and Ni above level 2.
We observed more quartz (Qtz) in the dry season than in the wet season, while kaolinite (Ka) amount was the inverse. In both seasons, quantities of goethite (Gth), grotelite (Gr) and dolomite (Dol) were low (Figure 3, Table 5).
Our results had good reproducibility with standard deviations below 10%. Thus they can be used to verify the environmental conditions of the DRB before and after the rupture of the iron ore dams and to investigate the remediation processes.

Table 4 - Concentration of trace metals (μg L^{-1}) of margin sediments samples obtained at three sampling points (P1 to P3) of the Rio Doce watershed in the Linhares/ES/Brazil municipality in the dry and wet seasons of 2011

Metals (μg g^{-1})[a]	Dry season			GV (μg g^{-1})[b]	Wet season		
	P1	P2	P3		P1	P2	P3
Al	3916 ± 794	15950 ± 1661	2535 ± 588	-	53623 ± 12656	43252 ± 8535	21687 ± 5462
As	< LD	< LD	< LD	5.9 - 17[b]	< LD	< LD	< LD
Cd	< LD	< LD	< LD	0.6 - 3.5[b]	< LD	< LD	< LD
Cr	43.8 ± 0.7	96 ± 5	39.5 ± 0.1	37.3 - 90[b]	195 ± 11	179 ± 5	111 ± 5
Cu	< LD	36 ± 4	< LD	35.7 – 197.0[b]	82 ± 7	75.2 ± 4.6	48 ± 4
Fe (%)	2.0 ± 0.4	5.7 ± 0.3	1.4 ± 0.4	2 - 4[c]	14 ± 3	12 ± 2	8 ± 2
Li	3.3 ± 0.4	13.7 ± 2.6	2.5 ± 0.4	-	37 ± 4	29 ± 7	16 ± 6
Mn	3558 ± 130	1710 ± 51	178 ± 9	460 - 1100[c]	4833 ± 215	5519 ± 123	2792 ± 301
Ni	< LD	45 ± 5	19.0 ± 0.8	18.0 – 35.9[b]	59 ± 4	25 ± 3	38 ± 5
Pb	88 ± 8	124 ± 10	118 ± 5	35.0 - 91.3[b]	220 ± 11	254 ± 24	150 ± 6
V	< LD	< LD	< LD	-	227± 14	218 ± 17	125 ± 6
Zn	< LD	125 ± 4	< LD	123.0 – 315.0[b]	223 ± 6	221 ± 6	174 ± 11

[a]Mean of triplicates. [b]Guideline values (GV) by the Brazilian legislation (CONAMA 454, 2012). [c]GV of international reference (Pereira et al., 2006). Limit of detection (LD) = Al: 19.28; As: 90.7; Cd: 7.8; Cr: 18.6; Cu: 10.83; Fe: 7.85; Li: 2.58; Mn: 0.93; Ni: 18.72; Pb: 73.5; V: 124.5; and Zn: 27.90 (μg g^{-1})

Table 5. Distribution of minerals identified by X-rays in margin sediments samples obtained at three sampling points (P1 to P3) of the Rio Doce watershed in the Linhares/ES/Brazil municipality in the dry and wet seasons of 2011.

Minerals	Dry season			Wet season		
	P1	P2	P3	P1	P2	P3
Kaolinite	+	++	++	+++	+++	+++
Dolomite	+				+	+
Goethe	+	++	+	++	++	++
Grotelite	++	+	+	++	+	++
Hematite	+	+	+	+	+	+
Quartz	+++	+++	+++	++	++	++

*Subtitles: (+): traces; +: present; ++: dominant; +++: predominant. Sampling points (P1 to P3)

Table 6 - Concentration of trace metals (μg g $^{-1}$) of margin sediments of the Rio Doce watershed obtained in other studies

Metals (ppm)	Studies of					
	1996	2010	2015*	2015**	2015***	2016
Al			2400	3740 – 6106	8.5 %	
As		12	34	3.10 – 4.90		7
Cd		0.06	0.02	2.90 – 2.40	< LD	42.5
Cr	789	52	27	33.20 – 63.80	96	45.7
Cu		24.4	16	6.10 – 11.70	22	35.2
Fe (%)	0.14	5.49	10.17	0.40 – 0.89	6.9	14.38
Mn	2540	651	235	352.8 – 598.5	1009	692
Ni	142	20.9	5.6	23.80 – 40.30		42.4
Pb	105	17.7	5.6	22.90 – 21.80	25.3	21.6
V				23.60 – 37.00		
Zn		55	18	23.90 - 44.90	82.8	62.8

Source: Jordão (1996), CPRM (2010 and 2015*). Pacheco (2015**), Santolin (2015***), CGEMA (2016)

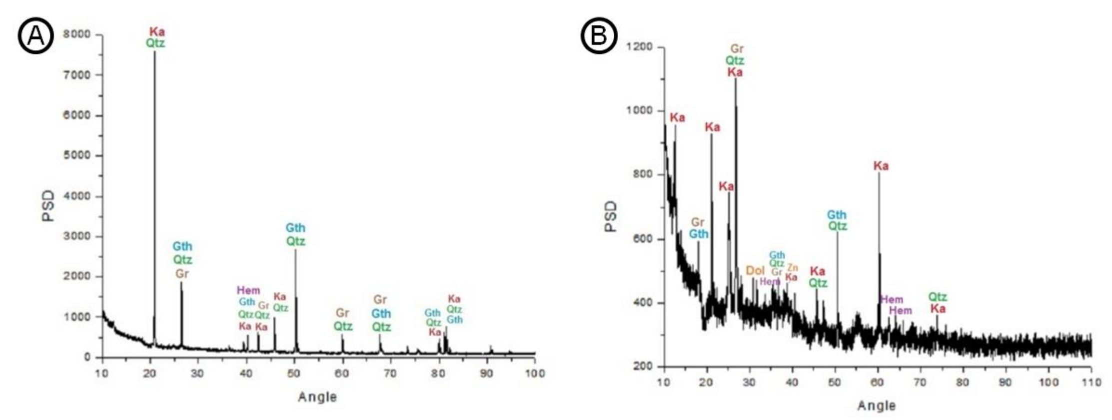

Figure 3. Diffractograms of margin sediments of the sampling point 2 of the Rio Doce watershed in the Linhares/ES/Brazil municipality in the dry (A) and wet (B) seasons of 2011

4. Conclusion

This study is an important record on the metals concentrations in the waters and margin sediments of the Rio Doce watershed in Linhares/ES/Brazil, which is the main city before the mouth of this river. We observed that there is no consensus in the technical reports on the contamination of metals in the DRB. They show an anomaly in the metals concentrations in the water and in the margin sediments after the dams break, indicating that atypical metals were included in the DRB-ES water in the Linhares/ES region. However, there is a trend of reducing metal concentrations over time that requires further systematic and careful studies, including rainfall impacts.

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Declaration of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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