

## Research Letters

## Long-term contamination of the Rio Doce estuary as a result of Brazil's largest environmental disaster



Fabrício Â. Gabriel<sup>a,\*</sup>, Amanda D. Ferreira<sup>b</sup>, Hermano M. Queiroz<sup>b</sup>, Ana Luisa S. Vasconcelos<sup>b</sup>,  
Tiago O. Ferreira<sup>b</sup>, Angelo F. Bernardino<sup>a</sup>

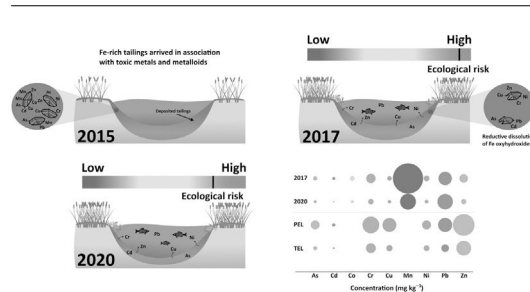
<sup>a</sup> Grupo de Ecologia Bentônica, Departamento de Oceanografia e Ecologia, Universidade Federal do Espírito Santo (UFES), Av. Fernando Ferrari, 514, Goiabeiras, Vitória, ES, CEP: 29075-910, Brazil

<sup>b</sup> Escola Superior de Agricultura Luiz Queiroz, Universidade de São Paulo (ESALQ/USP), Departamento de Ciência do Solo, Alameda das Palmeiras – Agronomia, Piracicaba, SP, CEP: 13418-900, Brazil

## HIGHLIGHTS

- Long-term (>4.2 years) contamination and ecological risks of the Rio Doce estuary.
- Sediment metal(loid)s concentrations support a continued potential adverse biological effect.
- Despite a decrease in metal(loid)s concentration, the chronic contamination is still above reference values.
- The Rio Doce estuary works as a sink for tailings and a source of toxic metal(loid)s.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The Rio Doce basin in SE Brazil was critically impacted in November 2015 by the spillage of millions of tons of mining waste. In the Rio Doce estuary, the tailings removed nearly 30% of estuarine benthic species and rapidly increased sediment contamination by metal(loid)s. Short-term impact assessments from 2015 to 2017 revealed severe ecological effects in the estuary linked to the deposited tailings, but the long-term patterns of contamination and their ecological risks are yet unclear. We analyzed the contamination and ecological risks of metal(loid) in the Rio Doce estuary up to 4.2 years after the short-term impacts in 2015. We found that 4.2 years after the impact, As, Cr, Cu, and Ni concentrations were still above the threshold effect levels of toxicity, while Cd and Pb exceeded probable effect levels. Although the concentrations of contaminants often show a stable temporal trend, sedimentary metal(loid) contents after the impact were continuously above the background values for the Rio Doce estuary. The ecological risk analysis suggested that sediment metal(loid) concentrations are high enough to cause adverse biological effects, supporting the hypothesis that there is chronic contamination of the estuarine ecosystem in the long-term. Our data suggests that without recovering actions, the Rio Doce estuary will likely be a sink of contaminants from the upper river basin. However, this capacity is limited due to the sensibility of Fe oxyhydroxides to reductive dissolution and metal(loid) release, leading to risks to the aquatic biota with potentially negative consequences to human health for decades to come.

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\* Corresponding author.

E-mail addresses: [fabricao.gabriel@outlook.com](mailto:fabricao.gabriel@outlook.com) (F.Â. Gabriel), [amandaduum@usp.br](mailto:amandaduum@usp.br) (A.D. Ferreira), [hermanomelo@usp.br](mailto:hermanomelo@usp.br) (H.M. Queiroz), [ana.vasconcelos@usp.br](mailto:ana.vasconcelos@usp.br) (A.L. Vasconcelos), [toferreira@usp.br](mailto:toferreira@usp.br) (T.O. Ferreira), [angelo.bernardino@ufes.br](mailto:angelo.bernardino@ufes.br) (A.F. Bernardino).

## Introduction

Environmental disasters associated with mining activities are a global concern due to the risks of contamination (Bowker and Chambers, 2015; Garcia et al., 2017; Gil-Jiménez et al., 2017). As an example, tailings traditionally stored in dams offer a great risk to multiple ecosystems that may be located thousands of kilometers away from the mining operations (Magris et al., 2019). Tailing spills can significantly affect ecosystems downstream, impacting vast landscapes, rivers, cities, forests, crops, and lead to economic, social and ecological losses, in most cases with permanent effects (Bowker and Chambers, 2015).

In Brazil, the Samarco mine tailing disaster that occurred in November 2015 is an emblematic case of environmental disaster involving a dam failure, which caused significant impacts on terrestrial and aquatic systems (Gabriel et al., 2020a, 2020b; Gomes et al., 2017; Queiroz et al., 2018). Within days, the mine tailings spill silted up the watercourses downstream, buried houses, vegetation, and animals, and caused 19 human casualties (Carmo et al., 2017). In addition, the tailings traveled 600 km downriver and reached the Rio Doce estuary, permanently increasing sediment metal(loid) concentrations, burying, and killing benthic organisms and generating a tailing layer approximately 5 cm deep (Bernardino et al., 2019; Gomes et al., 2017; Queiroz et al., 2018).

The long-term effects of these impacts are yet largely unclear, even though there are multiple efforts in monitoring the aquatic ecosystems of the Rio Doce basin. In the Rio Doce estuary, the tailings arrived in association with toxic metals and metalloids (Queiroz et al., 2018; Sá et al., 2021), which increased the ecological risks to many aquatic species (Bernardino et al., 2019; Gabriel et al., 2020b). Moreover, biogeochemical processes in the estuary likely favor the long-term release of contaminants to the aquatic biota (Queiroz et al., 2018, 2021a), which suggests that this ecosystem will be a long-term hotspot for contaminants from the remaining tailings deposited over the Rio Doce upper basin, and a potential source of toxic compounds to the aquatic biota (Queiroz et al., 2018, 2021a, 2021b; Riba et al., 2002). These hypotheses have been partially supported by evidence showing that sediment metal concentrations (e.g., Al, Cr, Fe, and Mn) are not only associated to spatial changes in benthic assemblages within the estuary, but also that metals bound to Fe oxyhydroxides are being gradually released and bioaccumulating in fish, due to the reductive dissolution of Fe oxyhydroxides (Bernardino et al., 2019; Gabriel et al., 2020b; Queiroz et al., 2021a, 2021b).

In this sense, consolidating environmental quality indices from the Rio Doce estuary over multiple years is fundamental to assess the status of metal(loid)s pollution and its potential ecological risks (Liu et al., 2016). Sediment quality guidelines (SQGs) have been recognized as suitable tools to access the effects of toxic metals for both aquatic and human life. Methods of risk assessment can also assist in the proposal of measures for remediation, management strategies, and ecosystem monitoring. In fact, the integration and summarization of complex scientific data into single-values easily interpretable make these indices useful and applicable tools in communication with risk managers and decision-makers (Protano et al., 2014; Wilson and Jeffrey, 1994).

Several naturally occurring biogeochemical processes in estuarine sediments and soils can control the stability of metal-colloid interactions and, thus, the bioavailability of metals in estuarine ecosystems (Machado et al., 2016; Pejman et al., 2015; Segura et al., 2016; Wang and Chen, 2000). Hence, following the initial deposition of the Fe mine tailings in the Rio Doce estuary and their continued transport along the river basin, a long-term increase in metal(loid) concentrations in the estuary was registered (Queiroz et al., 2018, 2021a,b,c). Thus, there is a pressing need to understand the ecological risks in the Rio Doce estuary.

In this study, we monitored the Rio Doce estuarine sediments from August 2017 to January 2020 (1.9–4.2 years after the short-term impact) and pre-impact data were integrated from a previously published dataset (December 2015). Our objectives were to (1) determine the concentrations of the metal(loid)s (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in the sediments along the Rio Doce estuary; (2) to explore the degree of metal(loid) contamination using contamination indices; (3) to assess environmental risks of these metal(loid)s by comparison with sediment quality guidelines (SQGs) and the potential ecological risk of metal(loid)s for the ecosystem; (4) to determine the main metal(loid)s that contribute to the ecological risk in the estuary.

## Materials and methods

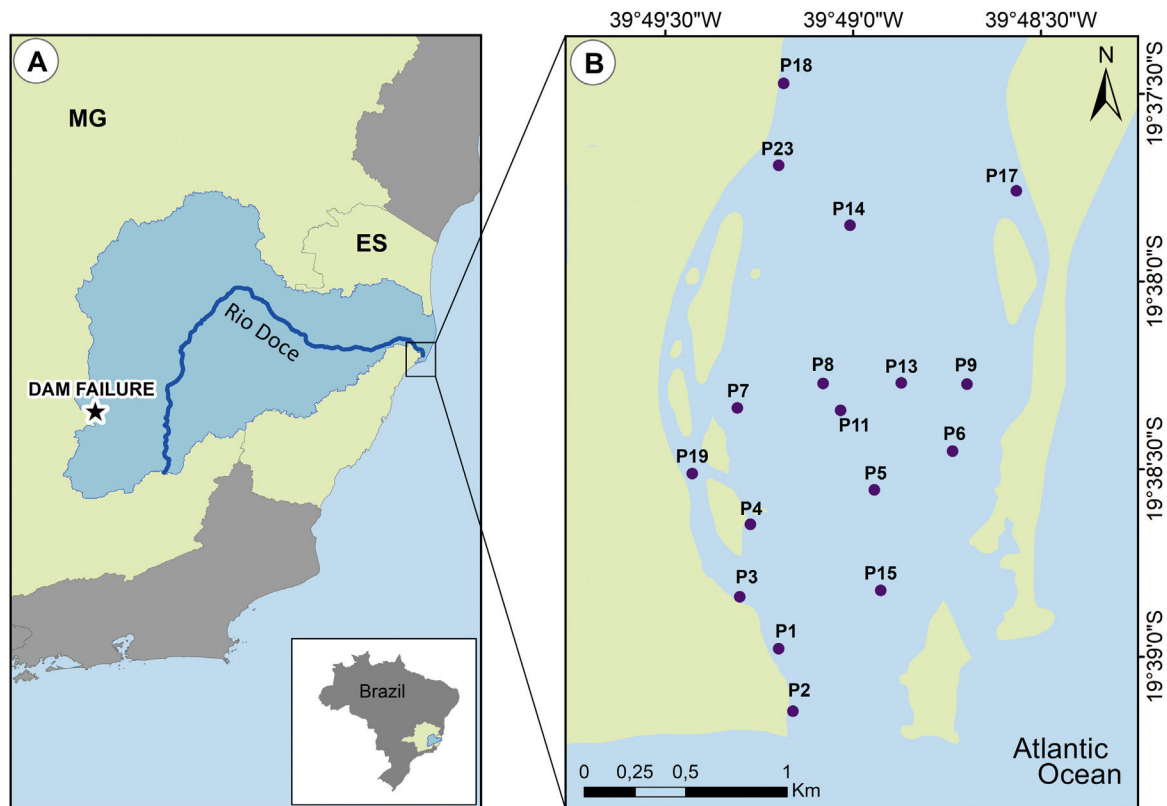
### Study area and sediments sampling

The Rio Doce estuary (19°38' to 19°45'S, 39°45' to 39°55'W) is in the Eastern Marine Ecoregion of Brazil, 600 km downstream of the tailing dam. The region has two well-defined seasons: a dry winter (April to September) and a rainy summer (October to March; Bernardino et al., 2015; Bissoli and Bernardino, 2018). The Rio Doce estuary receives an influx of continental nutrients that makes it highly productive and supports a diverse composition of fish and megafauna, and fishing is an important activity for the local population (Gabriel et al., 2020b; Pinheiro and Joyeux, 2007). It is noteworthy that fishing has been banned in the region since the dam collapse in 2015 and continues prohibited for over 5 years since the disaster due to the uncertainties of contamination risks in the region.

The sediment sampling in the Rio Doce estuary was performed on five different campaigns from 2017 to 2020, covering both the rainy and dry seasons: August 2017 (21 months after the tailing arrival in the estuary), January 2018 (26 months), August 2018 (33 months), February 2019 (39 months), and January 2020 (50 months). Due to the high spatial heterogeneity found within the estuary (Gomes et al., 2017), here we used a random sampling design to study spatial and temporal changes on the Rio Doce estuarine region (salinities typically from 0.1 to 8). Bottom sediment samples (top 0–5 cm) were collected with a stainless steel Van Veen grab at 17 stations along the estuary in each campaign (Fig. 1). The samples were stored in containers previously decontaminated with HNO<sub>3</sub> 10% (v/v) and immediately preserved on ice and frozen (−20 °C) until analysis. Environmental conditions (water temperature, pH, salinity, and total dissolved solids-TDS) were measured at the sampling sites using a portable HANNA multi-parameter (HI9829).

### Laboratory procedures

The organic content was determined by loss-on-ignition through burning dry sediment sample in a muffle furnace at 550 °C for at least 4 h (Goldin, 1987). The particle size distribution in sediments was performed using the pipette method with previous treatment for oxidation of the organic matter with H<sub>2</sub>O<sub>2</sub> and dispersion using a combination of physical (overnight shaking) and chemical [0.015 mol L<sup>−1</sup> (NaPO<sub>3</sub>)<sub>6</sub> + 1.0 mol L<sup>−1</sup> NaOH] (Gee and Bauder, 1986). Dried samples were tri-acid digested (HNO<sub>3</sub>, HCl, and HF) on a microwave oven (CEM, Charlotte, NC USA) according to the United States Environmental Protection Agency (USEPA) 3052 protocol (USEPA, 1997). Total metal(loid) contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Fisher Scientific, Waltham, MA, USA) according to USEPA 6010C protocol (USEPA, 1997). Briefly, 0.5 g of the sediment sample was put in a Teflon vessel with mix-



**Fig. 1.** A) Location of the Rio Doce basin and of the Fundão tailings dam collapse, including the Rio Doce; B) Emphasis on the Rio Doce estuary on the SE Brazilian coast.

ture of 2 ml of  $\text{HNO}_3$  (65%) + 6 ml of  $\text{HCl}$  (37%) and 2 ml of  $\text{HF}$  (40%) and then digested for 40 min. After digestion, the solution was filtered through a  $0.8\ \mu\text{m}$  Millipore membrane, taken into 100 ml flask, and diluted 10 times with Milli-Q water. A blank (without sediment) was carried out equally. The analysis was performed in triplicate, standard solutions were prepared from dilution of certified standard solutions, and certified reference materials (NIST SRM 2709a) were used for comparison to measured and certified values to guarantee the quality control procedures (Supplemental data Table S1).

#### Contamination and ecological risks assessment

The metal(loid)s (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) were quantified in the sediment samples and compared to the baseline values obtained by our research group before and after the mine tailings arrival (Gomes et al., 2017). The contamination factor ( $\text{CF}_i$ ) for each metal(loid) at each site and the Nemerow multi-factor index ( $\text{P}_i$ ) was determined according to Table 1. The  $\text{CF}_i$  was calculated as the ratio of the metal(loid) concentration in the sample ( $C_i$ ) and the background concentration of the metal(loid) ( $B_i$ ). There is a scarcity of sediment geochemistry background values for the Rio Doce basin and, as a result, sediment quality guidelines are also unavailable. Therefore, we used the unique baseline from the estuary published by Gomes et al. (2017) as the background concentrations. In this study, sediment metal(loid) baseline concentrations from the Rio Doce estuary were obtained from samples collected 11, 9, and 2 days before the arrival of mine tailings in the estuarine ecosystem (Gomes et al., 2017).

The evaluation of ecological risks was made through the nominal ecological risk factor ( $\text{ER}_i$ ) and ecological risk index ( $\text{R}_i$ ), proposed by Hakanson (1980), determined according to Table 1. Ecological risk assessments integrate the concentrations of metal(loid)s with respect to their ecological effect, environmental effect, and toxicity

and serve as proxies for sediment safety. In addition, it represents the sensitivity of different biological communities to toxic elements and illustrates the potential eco-risks caused by metal(loid)s (Barkett and Akün, 2018). These factors have been widely used to determine ecological risks in locations impacted by mining (Barkett and Akün, 2018; Klubi et al., 2018; Liu et al., 2020; Marrugo-Negrete et al., 2021; Ngole-Jeme and Fantke, 2017).

#### Quality criteria comparison

Metal(loid)s concentrations were compared to specific sediment quality guidelines for coastal and marine sediments and the protection of aquatic life, as determined by the National Oceanic and Atmospheric Administration (NOAA). These guidelines are based on the Threshold Effect Level – TEL, which represents the upper limit under which no adverse effects on the biological community are observed; and the Probable Effect Level – PEL, representing probable levels where adverse effects in the biological community would occur (Buchman, 2008).

#### Statistical analysis

Temporal changes of metal(loid) concentrations were tested using a centered and standardized matrix containing concentration values for each sample. Temporal variations in metal(loid) concentrations were tested by one-way analysis of variance (ANOVA) followed by Tukey's post hoc test to assess the differences among the different sampling dates after data homoscedasticity (Bartlett test) and normality (Shapiro Wilk test) assumptions were confirmed. Temporal changes in the metal(loid) concentrations, contamination indices, and ecological risk indices from pre-impact conditions (–11, –9, and –2 days; Gomes et al., 2017) and up to 4.2 years after the impact (21, 26, 33, 39, and 50 months) were com-

**Table 1**  
Metal(loid) contamination and ecological risk assessment indices applied to the sediments collected in the Rio Doce estuary after the mine tailing spill.

Index	Calculation	Criteria
Contamination factor (CF <sub>i</sub> ) (Hakanson, 1980)	$CF_i = \frac{C_i}{B_i}$ C <sub>i</sub> : concentration of examined metal in the sediment B <sub>i</sub> : background concentration of metal	CF <sub>i</sub> < 1 low 1 ≤ CF <sub>i</sub> < 3 moderate 3 ≤ CF <sub>i</sub> < 6 considerable CF <sub>i</sub> ≥ 6 very high contamination factor
Nemerow multi-factor index (P <sub>i</sub> ) (Ogunkunle and Fatoba, 2013)	$P_i = \sqrt{\frac{(CF_{i_{max}}^2 + CF_{i_{ave}}^2)}{2}}$ CF <sub>i<sub>ave</sub></sub> <sup>2</sup> : average value of the single-factor index CF <sub>i<sub>max</sub></sub> <sup>2</sup> : maximum value of the single-factor index	P <sub>i</sub> < 1 unpolluted 1 ≤ P <sub>i</sub> < 2.5 low 2.5 ≤ P <sub>i</sub> < 7 moderate 7 ≥ P <sub>i</sub> high polluted
Ecological risk factor (ER <sub>i</sub> ) (Hakanson, 1980)	ER <sub>i</sub> = TR <sub>f</sub> × CF <sub>i</sub> TR <sub>f</sub> : Toxic-response factor <sup>a</sup> CF <sub>i</sub> : Contamination factor	ER <sub>i</sub> < 40 low 40 ≤ ER <sub>i</sub> < 80 moderate 80 ≤ ER <sub>i</sub> < 160 considerable 160 ≤ ER <sub>i</sub> < 320 high ER <sub>i</sub> ≥ 320 very high potential ecological risk
Ecological risk index (R <sub>i</sub> ) (Hakanson, 1980)	$R_i = \sum_{i=1}^n ER_i$ ER <sub>i</sub> : Ecological risk factor	R <sub>i</sub> < 150 low 150 ≤ R <sub>i</sub> < 300 moderate 300 ≤ R <sub>i</sub> < 600 considerable R <sub>i</sub> ≥ 600 very high ecological risk

<sup>a</sup> TR<sub>f</sub> is the metal toxicity factor (Cd 30, As 10, Co = Cu = Ni = Pb 5, Cr 2, and Mn = Zn 1).

pared. All analyses were carried out using the Prism 8 software, version 8.0.2. Differences were considered significant at  $p < 0.05$ .

Pearson's correlation coefficient was calculated to determine the relationship between the metal(loid)s concentrations and Fe contents. Additionally, relationships among sediments variables (OM, TSD, temperature, pH, granulometry, salinity, metal(loid)s content) and ecological indices were assessed using principal component analysis (PCA) after the varimax orthogonal rotation so that the variables loaded predominantly into two components, making it possible to interpret the data structure. The PCA analysis was performed using the software XLSTAT version 2014.5.03.

## Results

### Environmental conditions and ancillary variables

The Rio Doce estuarine sediments are predominantly composed of sand particles with occasional areas dominated by clay and silt (Supplemental Data Table S2). The sand content ranged from 79.7 to 95.6% on average from 2017 to 2020, with higher sand contents in 2020 (One-way ANOVA,  $p = 0.039$ ). On another hand, the content of fine particles (i.e., clay + silt) decreased significantly over time with the lowest values in 2020 (4.4%; One-way ANOVA,  $p = 0.038$ ). The sediment organic matter content ranged from 4 to 5.3% with a mean of 4.6%, showing no difference between the studied periods (One-way ANOVA,  $F = 0.32$ ,  $p = 0.86$ ).

The mean salinity during sampling campaigns ranged from 0.05 to 0.65, remaining stable during the study (One-way ANOVA,  $F = 1.33$ ,  $p = 0.27$ ). Differently, the concentration of total suspended solids (TSD) ranged from 53 to 561 and were highest during the sampling in August 2017 (One-way ANOVA,  $F = 5.27$ ,  $p = 0.0008$ ). Water temperatures ranged from 23.1 to 30.5 °C (Supplemental data Table S2).

### Metal(loid) concentration and temporal variations

There was a temporal decrease of all metal(loid)s concentration in the estuarine sediments from a peak in August 2017 (2 years after the impact), and the years of 2018, 2019 and 2020 (Fig. 2). The highest concentrations were detected in August 2017, when concentrations were significantly above pre-impact values. Sediment metal concentrations in Aug 2017 were up to 360 (Cd), 23.9 (Zn), 21.2 (Pb), and 20.3 (Co) times their respective

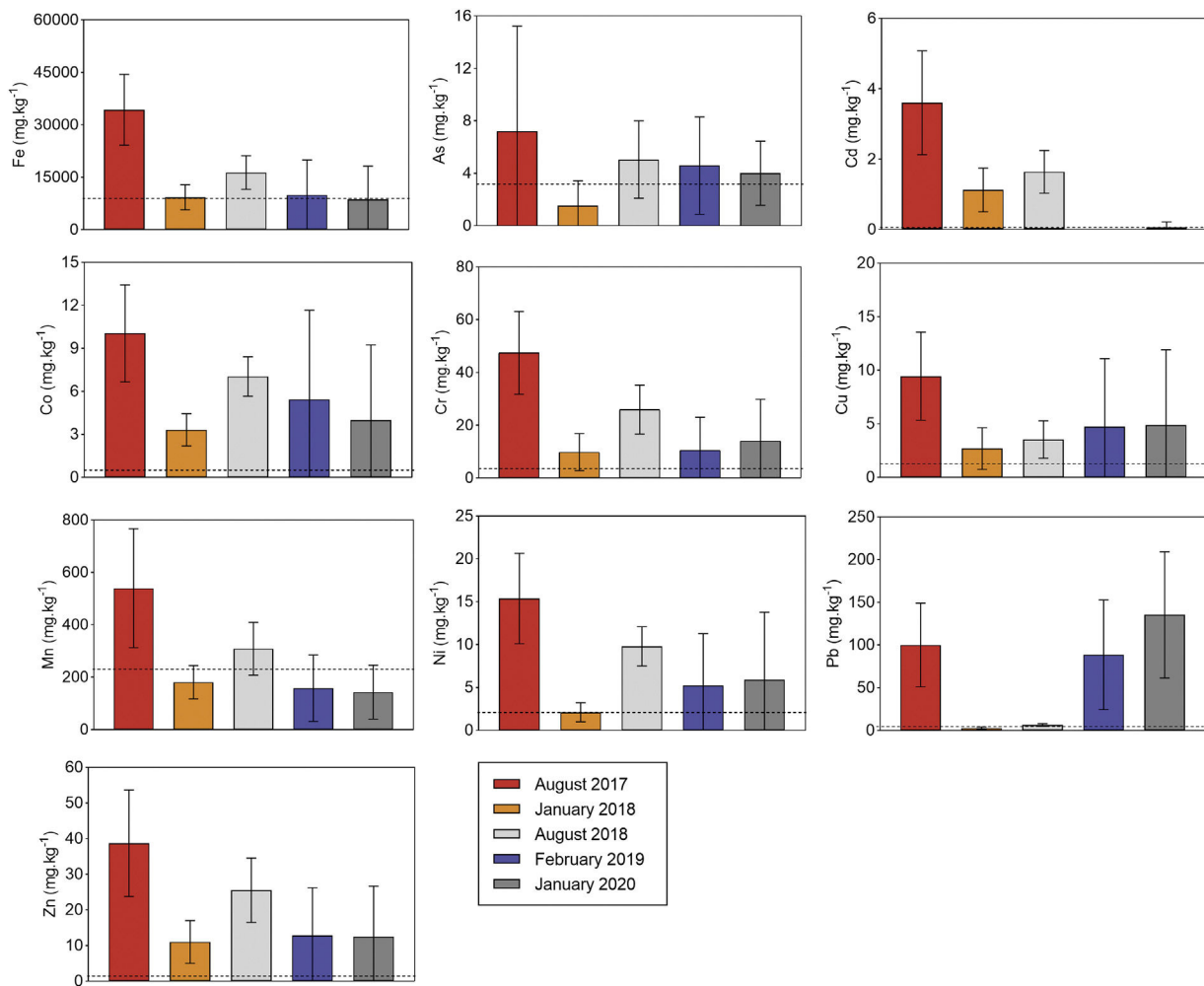
reference values. After Aug 2017, sediment metal concentrations decreased in 2018, but the concentration of metals remained stable in the following years (2018–2020). For example, Pb concentrations peaked in February 2019 (One-way ANOVA,  $p = 0.0229$ ) and January 2020 (One-way ANOVA,  $p < 0.0001$ ), and Mn peaked in several years during this study (One-way ANOVA,  $p < 0.0001$ ). Among the elements investigated and the periods sampled, in 2017 (August) Mn presented the highest absolute concentration ( $540.8 \pm 220 \text{ mg kg}^{-1}$ ), while Cd exceeded the reference value level to a greater degree (360-fold). Although the values were stable in 2018 (January and August), 2019 (February), and 2020 (January), they always remained above the reference values during our study (Fig. 2).

The sedimentary quality guidelines (SQG) indicated that baseline Cr, Cu, Zn, As and Pb concentrations in the Rio Doce estuary were below the SQG values, suggesting acceptable overall ecosystem health prior to the disaster. After the disaster in August 2017, total Cd and Pb concentrations were 1.7 and 6.4 times the PEL value, respectively (Table 2). Similarly, sediment Pb was 2.3–2.4-fold higher than the PEL limits in 2019 and 2020, respectively. Arsenic, Cd, Cr, Cu, Ni, and Pb were also above the TEL values, being over 10-fold for Cd in 2017, 9-fold for Pb in 2020, and 4-fold for As in 2017 (Table 2). Thus, TEL and PEL values indicate that contamination by As, Cd, Cr, Cu, Ni, and Pb was frequently observed at the Rio Doce estuary, suggesting a nearly continuous risk to the biota since the disaster in 2015.

### Contamination assessment

The metal(loid) contamination factor suggested a large variety of contamination conditions in the Rio Doce estuary. In general, the results indicated that the estuarine surface sediments were categorized as “very high” regarding the contamination by Cr, Ni, Cd, Cu, Pb, Co, and Zn in August 2017 (Fig. 3). In contrast, in 2019 (February) and 2020 (January), the metals Cr, Ni, Cd, and Cu exhibited low to considerable contamination. The elements Pb, Co, and Zn persisted in the classification of “very high” until January 2020, with Pb ranging from low to moderate contamination in 2018 (August) and in 2019 (February). Therefore, Cd was the element that most contributed to the contamination of the estuarine sediment over time (CF  $128.4 \pm 152.3$ ), followed by the values of CF<sub>i</sub> for Pb ( $13.5 \pm 15.1$ ), Zn ( $12.4 \pm 9.8$ ), and Co ( $12.0 \pm 9.3$ ).





**Fig. 2.** Mean (SD) of metal(loid)s concentrations ( $\text{mg kg}^{-1}$ ) in the sediment from the Rio Doce estuary. The black dashed line represents the metal(loid)s contents at the sediment (0–5 cm) 11 days before the disaster (Gomes et al., 2017).

**Table 2**

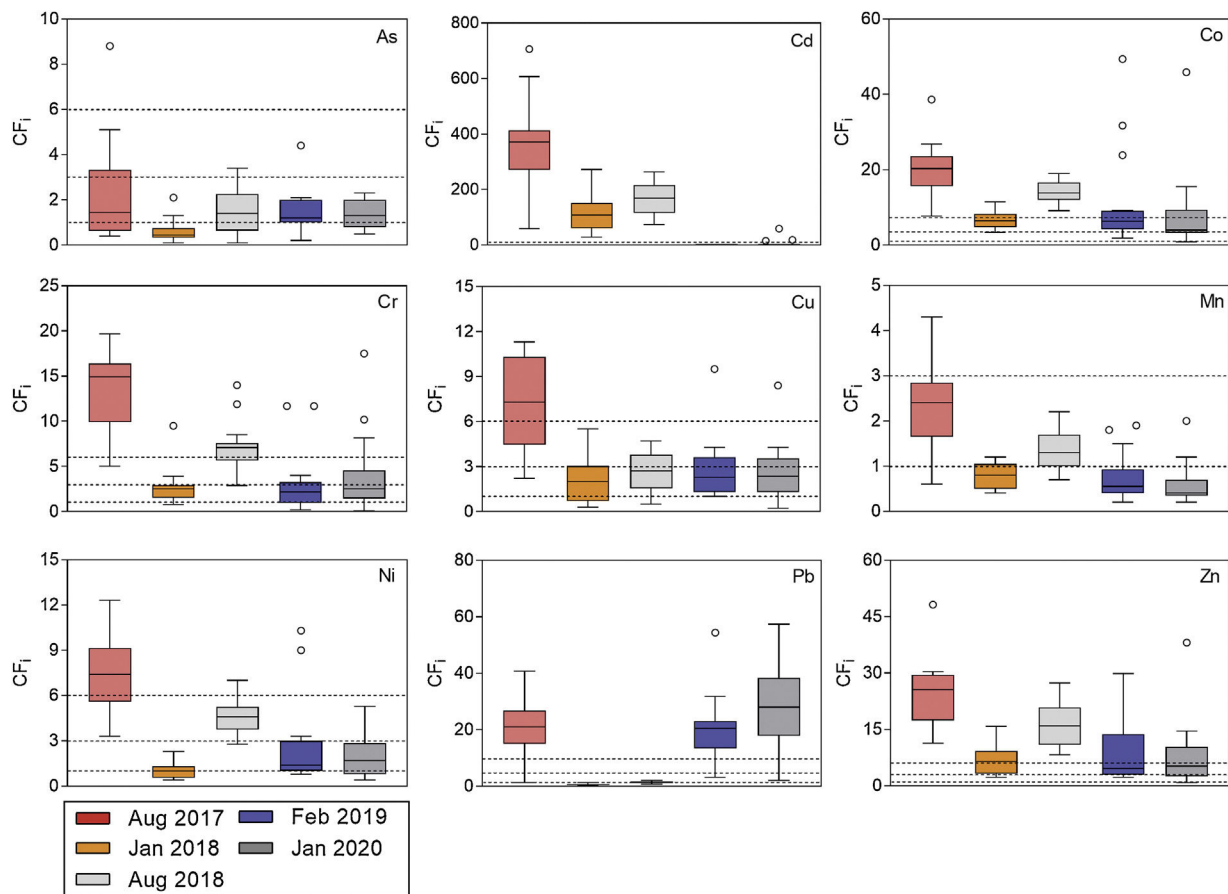
Mean  $\pm$  SD (min-max) of metal(loid)s concentrations and thresholds for sediment quality classification according to National Oceanic and Atmospheric Administration – NOAA, Threshold Effect Level – TEL and Probable Effect Level – PEL. Values in  $\text{mg kg}^{-1}$ .

Month/Year	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
August 2017	7.8 $\pm$ 8.1 (1.3–28.8)	3.6 $\pm$ 1.5 (0.6–7.1)	10.0 $\pm$ 3.4 (3.8–19.1)	47.4 $\pm$ 15.7 (18.0–71.1)	9.4 $\pm$ 4.1 (3.0–15.0)	539.8 $\pm$ 227.3 (148.7–1002.7)	15.4 $\pm$ 5.2 (7.0–26.2)	100.2 $\pm$ 48.9 (5.5–192.9)	38.7 $\pm$ 14.9 (18.2–78.1)
January 2018	1.8 $\pm$ 1.9 (0.2–6.9)	1.1 $\pm$ 0.6 (0.3–2.7)	3.3 $\pm$ 1.1 (1.7–5.7)	9.8 $\pm$ 7.0 (2.9–34.1)	2.7 $\pm$ 1.9 (0.4–7.3)	181.0 $\pm$ 63.6 (92.5–274.3)	2.1 $\pm$ 1.1 (0.9–5.0)	2.9 $\pm$ 1.1 (1.4–5.9)	11.0 $\pm$ 6.0 (3.8–25.6)
August 2018	5.1 $\pm$ 2.9 (0.3–11.0)	1.6 $\pm$ 0.6 (0.7–2.6)	7.0 $\pm$ 1.4 (4.6–9.4)	25.9 $\pm$ 9.3 (10.3–50.6)	3.6 $\pm$ 1.8 (0.6–6.3)	308.4 $\pm$ 100.9 (157.6–497.2)	9.8 $\pm$ 2.3 (5.9–14.9)	6.5 $\pm$ 1.5 (3.5–9.5)	25.5 $\pm$ 9.0 (13.4–44.5)
February 2019	5.0 $\pm$ 3.6 (0.7–14.4)	0.0	5.4 $\pm$ 6.2 (0.9–24.5)	11.1 $\pm$ 12.8 (0.6–42.3)	5.0 $\pm$ 6.4 (1.3–26.9)	167.9 $\pm$ 123.9 (54.5–430.5)	5.6 $\pm$ 6.1 (1.7–22.0)	95.5 $\pm$ 61.3 (14.7–257.3)	13.7 $\pm$ 13.4 (3.7–48.5)
January 2020	4.0 $\pm$ 2.4 (0.0–7.6)	0.1 $\pm$ 0.1 (0.0–0.6)	4.0 $\pm$ 5.2 (0.4–22.8)	14.0 $\pm$ 15.8 (0.2–63.0)	4.9 $\pm$ 7.0 (0.0–28.3)	142.9 $\pm$ 102.7 (57.2–461.2)	5.9 $\pm$ 7.9 (0.9–34.1)	135.4 $\pm$ 73.9 (9.3–271.5)	12.5 $\pm$ 14.2 (1.4–61.8)
TEL	7.2	0.7	–	52.3	18.7	–	15.9	30.2	124.0
PEL	41.6	4.29	–	160.4	108.2	–	42.8	112.2	271.0

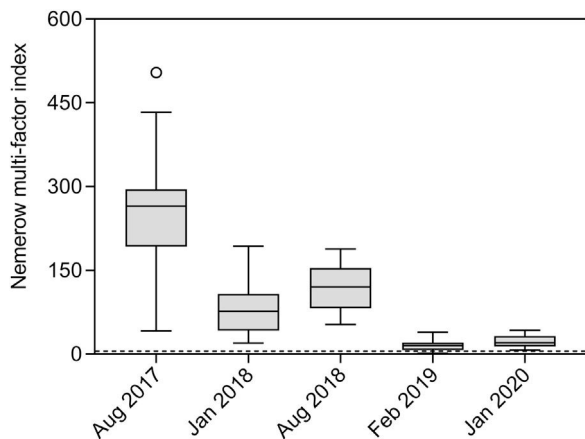
Sediment quality assessing based on multiple elements, the Nemerow multi-factor index results demonstrated that the sediments were classified as highly polluted in August 2017 ( $P_i = 257.1 \pm 104.9$ ), January and August 2018 ( $P_i = 79.6 \pm 44.7$  and  $117.7 \pm 43.4$ , respectively), February 2019 ( $P_i = 15.5 \pm 10.5$ ), and January 2020 ( $P_i = 22.4 \pm 10.9$ ), with values higher than 7 (Fig. 4). A high pollution rating was observed in all stations from 2017 to 2020, except in 2019 (February) when a low (5.9%), moderate (17.6%) and high (76.5%) pollution classification was observed between the stations.

### Ecological risks assessment

Ecological risk factor values indicated that estuarine sediments represent a low risk for As, Cr, Ni, Cu, Mn, and Zn in most stations over time (58–100%; Fig. 5). Cobalt represents a risk between low to considerable. In 2017 (August) 62.5% of the stations showed considerable risk while 70.6% moderate risk in 2018 (August). Lead presented considerable risk in 2017 (August), 2019 (February) and 2020 (January), with a low risk in 2018 (January and August). In contrast, Cd presented a very high risk in all stations in 2017 (August)



**Fig. 3.** Contamination factor ( $CF_i$ ) of metal(loid)s for sediments collected from the Rio Doce estuary in 2017 (August), 2018 (January and August), 2019 (February), and 2020 (January). Dashed lines determine classification limits:  $CF_i < 1$  Low;  $1 \leq CF_i < 3$  Moderate;  $3 \leq CF_i < 6$  Considerable; and  $CF_i \geq 6$  Very high contamination. Boxplots indicate minimum, maximum, median, quartiles, and outliers (circle).



**Fig. 4.** Nemerow multi-factor index ( $P_i$ ) of metal(loid)s for sediments collected from the Rio Doce estuary in 2017 (August), 2018 (January and August), 2019 (February), and 2020 (January). Dashed lines determine classification limits:  $P_i < 1$  Unpolluted;  $1 \leq P_i < 2.5$  Low;  $2.5 \leq P_i < 7$  Moderate; and  $P_i \geq 7$  High pollution. Boxplots indicate minimum, maximum, median, quartiles, and outliers (circle).

and 2018 (January and August), while in 2019 (February) and 2020 (January) the values were categorized as low risk.

In general, the period of August 2017 exhibited the highest index of ecological risk ( $R_i = 11,148 \pm 4490$ ) being categorized as “very high” for the estuarine ecosystem, as well as in August 2018 ( $R_i = 5106 \pm 1849$ ) and January 2018 ( $R_i = 3417 \pm 1902$ ; Fig. 6). In contrast, in February 2019, the overall classification exhibited

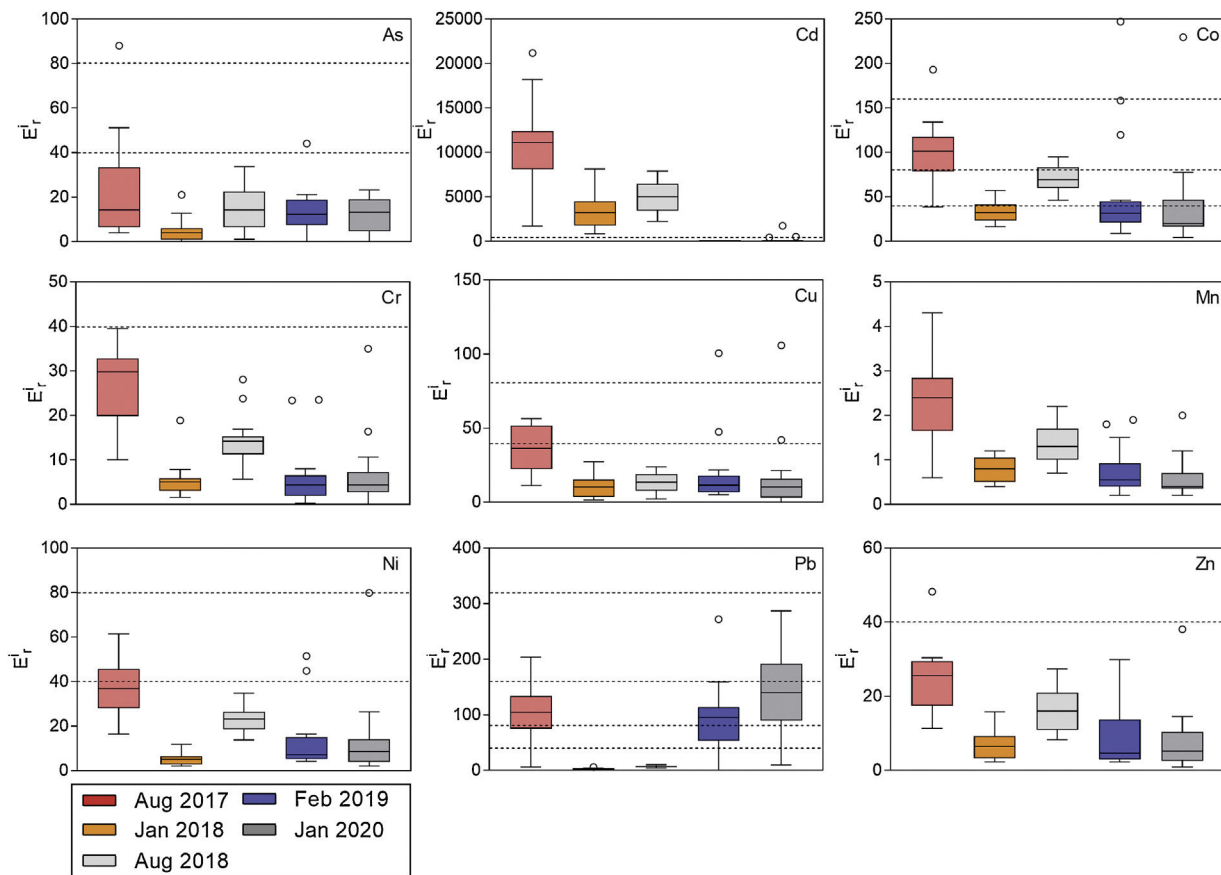
“moderate risk” ( $R_i = 186.5 \pm 121.5$ ), varying between stations in low ecological risk (41.2%) to considerable (23.5%). January 2020 was categorized as of “considerable risk” ( $R_i = 399.8 \pm 478.5$ ), given that 41.2% of the stations showed moderate, 23.5% considerable, and 17.6% low and very high risks.

#### Principal component analysis (PCA)

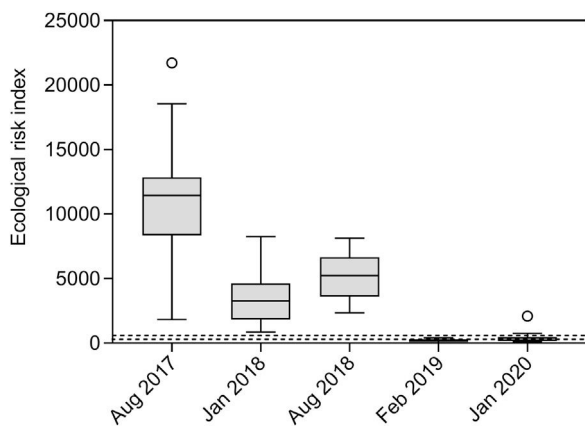
PCA was then used in the sediment dataset for all five sampling periods which showed a seasonal variability in contaminants and, consequently, in the contamination degree and ecological risk of the Rio Doce estuary (Fig. 7). Considering the F1 axis (43% of explanatory variables), we observed that Cd, Cr, Mn, and Zn were the elements that most contributed to the high degree of contamination in August 2017 and 2018 (Supplemental Data Table S3). On the other hand, the PCA supports changes in the metal(loid)s concentration in January 2018, February 2019, and January 2020, which was in agreement with the ecological risk and multi-factor Nemerow indices for the estuary. In addition, the second axis on the PCA segregated time periods with higher proportions of clay sediment particles (Aug-17, Aug-18 and Jan-18), and a second group with higher proportion of sand particles (Fev-19 and Jan-20); suggesting a temporal increase in mean grain size within the Rio Doce estuary.

#### Discussion

The contamination of the Rio Doce estuarine sediments changed during the 4.2 years since the disaster in 2015, with an observed



**Fig. 5.** Ecological risk factor ( $ER_i$ ) of metal(loid)s for sediments collected from the Rio Doce estuary in 2017 (August), 2018 (January and August), 2019 (February), and 2020 (January). Dashed lines determine classification limits:  $ER_i < 40$  Low;  $40 \leq ER_i < 80$  Moderate;  $80 \leq ER_i < 160$  Considerable;  $160 \leq ER_i < 320$  High; and  $ER_i \geq 320$  Very high ecological risk factor. Boxplots indicate minimum, maximum, median, quartiles, and outliers (circle).



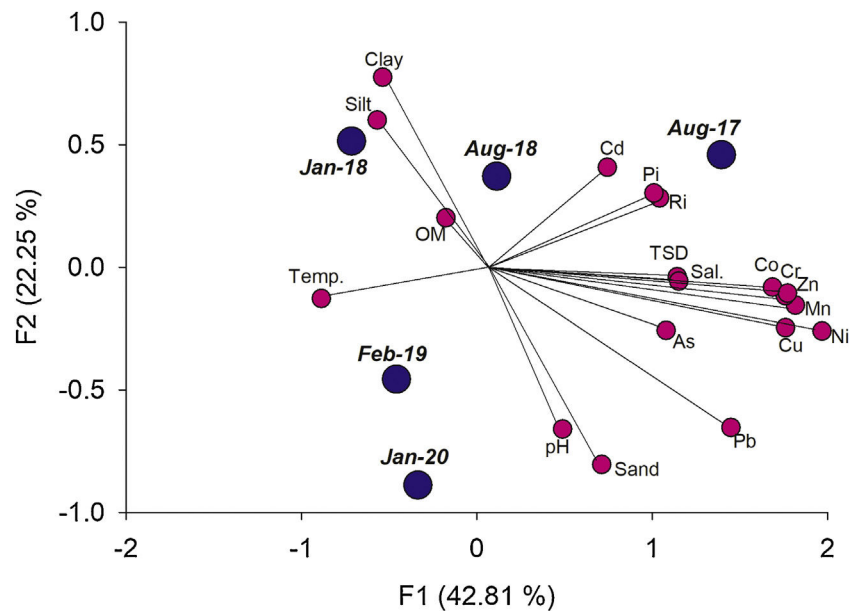
**Fig. 6.** Ecological risk index ( $R_i$ ) of metal(loid)s for sediments collected from the Rio Doce estuary in 2017 (August), 2018 (January and August), 2019 (February), and 2020 (January). Dashed lines determine classification limits:  $R_i < 150$  Low;  $150 \leq R_i < 300$  Moderate;  $300 \leq R_i < 600$  Considerable; and  $R_i \geq 600$  Very high ecological risk. Boxplots indicate minimum, maximum, median, quartiles, and outliers (circle).

peak of sediment metal(loid) concentrations in 2017, followed by a period of stability until 2020. The higher metal(loid) concentrations in 2017 evidenced that nearly two years after the disaster, the estuary was being a significant sink of tailings and associated metals from the upper river basin (Gabriel et al., 2020a). As a consequence of the disaster, significant amounts of tailings were accumulated along the river basin and riparian ecosystems, and our data support that part of those tailings was being continually transported

towards the estuary and bound to metals (Feng et al., 2011; Gabriel et al., 2020a; Queiroz et al., 2018). However, after the peak in 2017, the concentration of most metal(loid)s (except Pb) in the estuary decreased by an average 65.9%, with highest reductions in Cd (97.2%), Mn (73.5%), and Cr (70.5%). Our data then supports the continued transport of tailings and bound metals from the estuary to the Atlantic Ocean (Richard et al., 2020).

The decrease in metals concentrations may be associated with an increased grain size and a decrease in Fe content over time, which may suggest that there is a net transport of tailings outside the estuary, and biogeochemical transformation of tailings in estuarine soils. Based on satellite monitoring, there are multiple studies that suggest that the tailings are being continually transported to the coast after the disaster and potentially being accumulated on the inner shelf (Magris et al., 2019; Rudorff et al., 2018; Coimbra et al., 2019). Rudorff et al. (2018) reported an increase in coastal water turbidity after the disaster and suggested extensive plumes over the coastal zone that would be intensified during rainfall periods. We observed a temporal stability in estuarine contamination from 2018 to 2020 with limited evidence for a seasonal variability, which supports the hypothesis of a press disturbance over coastal ecosystems that are in short distances from the Rio Doce estuary (Magris et al., 2019). There has been so far limited evidence for the accumulation and ecological effects of tailings over the seafloor at distances of over 10 km from the Rio Doce mouth (Richard et al., 2020), even though tailings may be transported along with the river plume at greater distances.

The transport of tailings out of the estuary may be facilitated by the absence of bottom vegetation, which would help to capture the finer fractions (i.e., silt and clay; Sand-Jansen, 1998). As a result



**Fig. 7.** Principal Component Analyses (PCA) of salinity (Sal.), pH, temperature (Temp.), and total solid dissolved (TSD) in the water column and metal(loid)s, organic matter (OM), and grain size (sand, silt, and clay) for the sediment samples collected in the Rio Doce estuary. Samples collected in August 2017 (Aug-17), January 2018 (Jan-18), August 2018 (Aug-18), February 2019 (Feb-19), and January 2020 (Jan-20).

of strong bottom transport in the Rio Doce estuary, the lower contents of finer particles decrease the sediment binding capacity due to elevated sand and low organic matter content. It is important to highlight that the metal binding to sediments of the Rio Doce estuary occurs by adsorption and complexation processes, mainly in sediments with fine particles and/or with a high organic matter (Rainbow, 2007; Wang et al., 2015). Likewise, metal(loid) mobility and availability in the superficial sedimentary layer are associated with the sediment granulometry, salinity, organic matter content and Fe oxides from tailings (Machado et al., 2016; Queiroz et al., 2021c). Given that metal(loid) contamination is continually higher than baseline levels, the hypothesis of the arrival of more tailings that have been retained along the banks and channel of the Rio Doce through rainfall-runoff events is further supported (Rudorff et al., 2018).

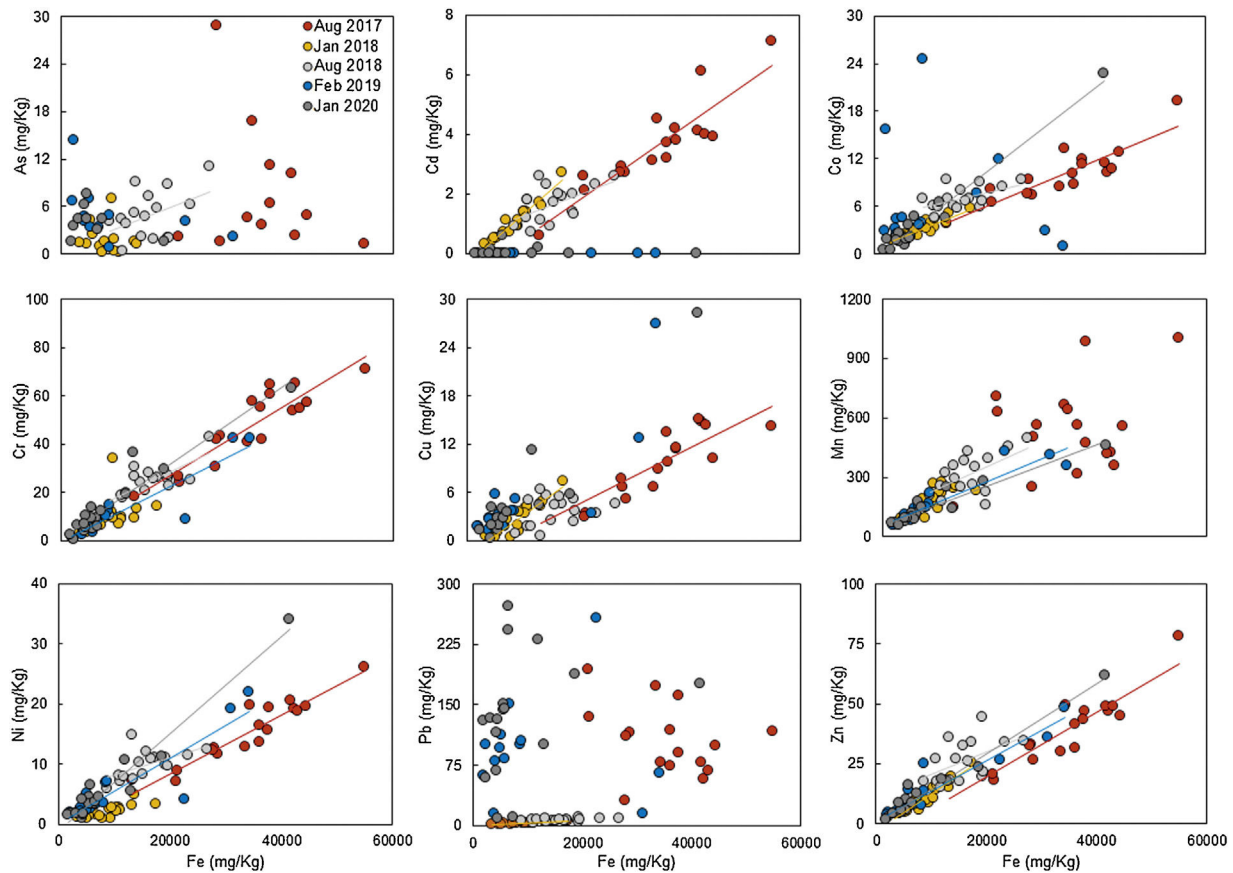
Even with an overall temporal stability, the metal(loid)s concentrations in the estuarine sediment persisted above the pre-impact reference values reported by Gomes et al. (2017). Thus, considering that Fe oxides are a geochemical marker for the tailings that were deposited in the Rio Doce estuary and its significant correlation with other metal(loid)s, there is strong evidence that the deposited tailings are maintaining a chronic contamination of the estuary for over 4.2 years (Fig. 8, Supplemental data Table S4). According to Queiroz et al. (2018), the deposited tailings on the estuary are mostly composed of Fe oxyhydroxides with a high concentration of associated metals. In addition, this mineral fraction is susceptible to mineral dissolution under suboxic/anoxic conditions, commonly found in estuarine sediments and soils (Lovley and Phillips, 1986; Du Laing et al., 2009). As a result of the dissolution of Fe oxyhydroxides (i.e., dissimilatory Fe reduction), the associated metals are released increasing their bioavailability (Bonneville et al., 2004; Lambais et al., 2008; Queiroz et al., 2018, 2021a, 2021b, 2021c). This mechanism of dissimilatory Fe reduction poses a risk of contamination since it may expose aquatic organisms and probably cause lethal or sub-lethal biological effects (He et al., 2018; Worms et al., 2006).

The overall health of the Rio Doce estuary has declined significantly. The concentrations of metals that are now deposited in the Rio Doce estuary is comparable to other heavily polluted estuar-

ies in Brazil, including urbanized estuaries in the region (Hadlich et al., 2018). The high concentration of metal(loid)s in sediments impacts benthic assemblages as several species may be intolerant to their toxicity (Bernardino et al., 2019). Benthic assemblages are a critical component of estuarine food webs and may transfer contaminants to higher trophic levels through bioaccumulation and biomagnification processes, for instance, humans (Gabriel et al., 2020b; Jędruch et al., 2019; Tarras-Wahlberg et al., 2001). As a result, the sediments from the Rio Doce estuary may be considered polluted and chronic effects on sedimentary organisms are expected since Cd and Pb values exceed the PEL level and As, Cr, Cu, and Ni of the TEL level according to Canadian sediment quality guidelines (Table 2). However, such comparative method with guideline values for temperate environments may underestimate the assessment by not considering the local natural geochemical background, and complementary ecotoxicological assessments are necessary to assess possible metal toxicities for the environment.

In this sense, ecological risk indices ( $CF_i$ ,  $P_i$ , and  $R_i$ ) (Figs. 3, 4 and 6), and effects-based sediment quality guidelines (SQG) can support the hypothesis of long-term sediment contamination of the Rio Doce estuary since the impact in 2015. The Cd, Cr, Mn, and Zn in 2017 (August) and 2018 (January and August) induced a general increase in ecological risk exceeding the very high ecological risk limit ( $R_i \geq 600$ ; Fig. 7). Our data support that estuarine sediments may cause adverse effects on aquatic life and human health, even 4.2 years after the disaster. Our results also support the possibility of contamination of the biota by metal(loid)s such as As, Cr, Cu, Mn, and Zn. The effects of metal bioaccumulation and oxidative stress in fish have been detected in the Rio Doce estuary and in contaminated areas upstream (Ferreira et al., 2020; Gabriel et al., 2020b; Weber et al., 2020). Current high levels of Cr, Cu, Mn, and Zn may lead to toxic effects in other organisms (Li et al., 2013). On another hand, episodic peaks in sediment Pb are also of concern as the observed concentrations were significantly above the reference values for the Rio Doce estuary (Gomes et al., 2017). These peaks differ from the overall pattern of other metal(loid)s studied and may be related to other human-related sources, likely from a combination of heavily industrial and agricultural uses of the Rio Doce upper basin. It is also important to note that all forms of Pb are extremely toxic to humans





**Fig. 8.** Correlation between total Fe and metal(loid)s concentrations in bottom estuarine sedimentary samples from the Rio Doce estuary in 2015 (November; [Gomes et al., 2017](#)), 2017 (August), 2018 (January and August), 2019 (February), and 2020 (January).

as well as most other living organisms ([Sayadi et al., 2010](#); [WHO, 2019](#)). In addition, there is no level of exposure to lead that is known to be unarmful, since, even at low concentrations, it can pose a greater threat to aquatic life compared to other metals ([Bastami et al., 2014](#); [WHO, 2019](#)).

Toxic effects in aquatic environments may cause serious consequences to human health, especially when coastal communities depend on fish protein for their subsistence ([Bashir et al., 2020](#); [Zhou et al., 2008](#)). Bioaccumulation effects of tailing-associated metals in the Rio Doce have been detected in bottom dwelling fish ([Gabriel et al., 2020b](#); [Queiroz et al., 2021a](#)), which allied to a continued ecological risk assessment of the estuary and supports the maintenance of the prohibition of fishing activities. There is urgent need to access and quantify other potential sources of contaminants to local populations near the Rio Doce estuary, as these will be key for determining long-term health risks.

Besides the risks for the aquatic life and human health, the Fundão dam failure can be considered the largest dam disaster in terms of the volume of spilled tailings, the size of the affected area, and the extent of socio-environmental impacts, when compared to other major environmental disasters involving mining dams ([Table 3](#)). The large proportion of the disaster and the ineffective strategies to retain the mine tailings spilled in aquatic environments led to severe environmental impacts and likely infeasible clean-up strategies ([Carmo et al., 2017](#)). Therefore, without an effective initial action to remove the deposited tailings, terrestrial, riverine and coastal ecosystems will be continually under the effects of tailings ([Carmo et al., 2017](#); [Gabriel et al., 2020a,b](#)). The consequence of the lack of short-term actions brought ecological implications to the aquatic environments from the molecular to the community level, having a direct impact on ecosystem ser-

vices and, therefore, on the subsistence and food security of the affected regions ([Gabriel et al., 2020b](#); [Gomes et al., 2017](#); [Quadra et al., 2019](#); [Weber et al., 2020](#)). This experience shows that efforts should be placed on prevention rather than reacting after the event. Therefore, the Rio Doce disaster has raised global concern and alarm about the pollution of natural environments caused by mining and dam failures.

Effective decontamination action plans and restoration of ecological integrity are crucial to improving the long-term environmental status of affected aquatic environments. Some experimental initiatives using different soil amendments seem promising in removing metal(loid)s from inundated soils on the estuary ([Ferreira et al., 2021](#)). It is clear that further research into recovery processes is urgently needed and will be crucial for food and water security of impacted communities, and protection of the biodiversity. In addition, recovery actions would help to protect the ecosystem services that the local region provide ([Brito et al., 2021](#)). Although plans for short, medium, and long-term recovery actions for the Rio Doce basin were determined by a Term of Transaction and Conduct Adjustment (TTAC) signed by Samarco (Vale and BHP), the Brazilian federal and state governments, recovery actions on the estuarine part of the basin were never put in place. According to the document that defines the repair actions, the Renova foundation is responsible for executing recovery actions, including the implementation of tailings containment systems and in situ treatment of rivers impacted (see [Fundação Renova, 2021](#)).

Our results show the persistence of potentially toxic elements in the Rio Doce estuary, and restoration actions need to consider environmental and human health improvements ([Couto and Brandesim, 2020](#); [WHO, 2016](#); [Zhou et al., 2008](#)). These actions

**Table 3**  
Major failures of mining tailings dams and some of their reported impacts.

Location and date of failure	Volume M (m <sup>3</sup> )	Company	Mine type	Impacts	References
Stava (Italy)	0.18	Prealpi Mineraria	Fluorite	Water contamination, killed 268 people and completely destroyed hotels, bridges, homes and industrial buildings.	<a href="#">Pirulli et al. (2017)</a>
19 July 1985 Merriespruit (South Africa)	0.60	Harmony Gold Mine	Gold	Houses were largely swept away and/or severely damaged, seventeen people were killed.	<a href="#">Van Niekerk and Viljoen (2005)</a>
22 February 1994 Marinduque (Philippines)	2–4	Marcopper Mining Corporation	Gold	Siltation up the watercourses, water and soil contamination, buried houses, vegetation, and animals.	<a href="#">Fatalla (2019)</a>
24 March 1996 Aznalcóllar (Spain)	6	Boliden–Apirsa	Copper, silver, lead, zinc	Water contamination, pollution of thousands of hectares of farmland covered, and dead of fish, crustaceans, and terrestrial vertebrates.	<a href="#">Grimalt et al. (1999)</a>
25 April 1998 Brumadinho (Brazil)	12	Vale S.A.	Iron	Decreased water quality, killed more than 250 people and devastated huge forest and agricultural areas.	<a href="#">Rotta et al. (2020)</a>
25 January 2019 British Columbia (Canada)	25	Mount Polley Mining Corporation	Copper, gold	Decreased water quality, valley morphology was significantly altered in the main receiving watercourse.	<a href="#">Byrne et al (2018)</a>
04 August 2014 Mariana (Brazil)	43	Samarco (Vale S.A./BHP Billiton)	Iron	Siltation up the watercourses, water and soil contamination, buried houses, vegetation, and animals, and 19 human casualties. The tailings traveled approximately 650 km towards the ocean.	<a href="#">Carmo et al. (2017)</a> and <a href="#">Fernandes et al. (2016)</a>
05 November 2015					

will need to be aligned with the Integrated Water Resources Plan (PIRH) prepared for the Rio Doce basin, which has as one of the objectives the promotion of a water quality for human health, aquatic life, and environmental quality (see [CBH-Doce, 2016](#)). However, the plan actions and investments involve the creation of additional protected areas and basic sanitation, but these will be largely ineffective to cease the effects of tailings in the estuarine biota. We envision no recovery for the estuarine health unless strategies that promote a removal of tailings and their associated metal(oids) in soils are implemented.

In summary, the Rio Doce estuary continues to be heavily impacted by the tailings and the associated contaminants nearly 5 years after the short-term impacts, with significant ecological and human health risks. Management measures have never been put in place on this particular region, but the source-to-sea system and the landscape approach can be the entry point for implementing restoration programs ([Brito et al., 2021](#)). The source-to-sea system offers an alternative to integrate the different issues that affect the quality of the watershed, as well as its adjacent coastal and marine areas; while the landscape approach seeks to integrate policies and practices for multiple land uses through the implementation of adaptive and integrated management ([Brito et al., 2021](#); [Mathews et al., 2019](#)). Given the long path of the tailings to reach the Atlantic Ocean and the socio-environmental impacts associated, it will be necessary to deal with land and sea together to face the long-term consequences of the disaster, offering a better basis for environmental management and governance.

## Conclusion

Our findings reveal that the Rio Doce estuary is working as a sink of tailings from the Samarco disaster for nearly 5 years, and will likely be a source of contaminants to the biota for decades to come. Despite a temporal stability in metal(loid)s concentrations from 2018 to 2020, the levels still remain well above the baseline reference values for the estuary and often reach sediment quality thresholds. Therefore, the potential health risks to the environment, biota, and consequently, to local communities remain at unacceptable levels and effective actions for decontamination of the Rio Doce estuary are a priority. Fe-rich tailings will likely bind and release metal(loid)s for a long period of time within the estuary and will offer great risk to humans through consumption of contaminated fish. For that reason, our results support the maintenance of the fishing bans, the need to monitor public health near the estuarine region, as well as implementation of recovery and decontamination actions along with integrated coastal and freshwater management.

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## Declaration of interests

The authors declare that there is no conflict of interest regarding the publication of this article.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.pecon.2021.09.001>.

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