CONCENTRAÇÃO DE METAIS TRAÇO EM REGIÕES DA COSTA BRASILEIRA: UMA AVALIAÇÃO DA INFLUÊNCIA DA PLUMA DO RIO DOCE E OUTRAS ÁREAS COSTEIRAS ADJACENTES

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UNIVERSIDADE ESTADUAL DO NORTE FLUMINENSE – UENF

CAMPOS DOS GOYTACAZES - RJ

JANEIRO 2022

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Dissertação apresentada ao Centro de Biociências e Biotecnologia da Universidade Estadual do Norte Fluminense Darcy Ribeiro como parte das exigências para obtenção do título de Mestre em Ecologia e Recursos Naturais.

Orientador: Prof. Dr. Carlos Eduardo de Rezende (UENF/CBB/LCA)

Co-orientador: Profª. Drª. Cristiane dos Santos Vergilio (UFES/CCENS/DBIO)

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DECLARAÇÃO

Eu, Marina Satika Suzuki, coordenadora do Programa de Pós-Graduação em Ecologia e Recursos Naturais (PPG-ERN) da Universidade Estadual do Norte Fluminense Darcy Ribeiro (UENF), seguindo a Resolução CPPG nº2 de 2021, declaro validadas as assinaturas constantes da Folha de Assinaturas da Dissertação intitulada **“Concentração de metais traço em regiões da costa brasileira: uma avaliação da influência da pluma do rio Doce e outras áreas costeiras adjacentes”** de autoria de **Échily Sartori**, defendida no dia 31 de janeiro de 2022.

Campos dos Goytacazes, 01 de abril de 2022

Marina Satika Suzuki
Coordenadora PPG-ERN / UENF
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Dedico essa dissertação aos meus pais Aloísio e Rosana Sartori, que em mim confiaram e deram todo apoio para a concretização de mais uma etapa.

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SUMÁRIO

LISTA GERAL DE ABREVIAÇÕES E SIGLAS

Al – Alumínio
Au – Ouro
C – Carbono
Cu – Cobre
Fe – Ferro
H – Hidrogênio
Mn – Manganês
N – Nitrogênio
O – Oxigênio
S - Enxofre

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RESUMO

A bacia do rio Doce está localizada na região sudeste do Brasil e compreende uma área de drenagem de cerca de 86.715 km² de extensão. Devido as atividades desenvolvidas, a bacia é conhecida por sua grande importância socioeconômica, principalmente no âmbito da mineração. Devido ao elevado regime pluviométrico da bacia, o rio Doce é considerado um dos principais tributários da costa brasileira, carreando sedimentos, rejeitos e efluentes domésticos/industriais despejados ao longo de todo seu curso, para a plataforma continental. Especialmente após o rompimento da barragem de Fundão (Mariana – MG), ocorrido no dia 5 de novembro de 2015, que liberou 50 milhões de m³ de rejeito de minério de Fe no ambiente, causando um dos maiores desastres ambientais envolvendo barragens de mineração. Ao longo dos anos, diversos estudos ainda encontram concentrações de vários metais em desacordo com as legislações, tanto na água quando no sedimento. Com isso, o presente estudo tem como objetivo analisar a extensão dos impactos de longo prazo, além de fornecer um possível panorama da dispersão da pluma do rio Doce e suas respectivas concentrações de metais. Para isso, água e sedimentos superficiais foram coletados em 34 pontos ao norte e ao sul na foz do rio Doce, em algumas regiões da costa sudeste brasileira, para caracterização granulométrica, analises da composição elementar e isotópica e determinação de metais. Os resultados indicam que após 4 anos do rompimento da barragem de minério de ferro, as concentrações de metais no sedimento do estuário do rio Doce são menores do que as descritas em estudos de anos anteriores, sugerindo o transporte desse material para o litoral brasileiro. Esse resultado é evidenciado pelas maiores concentrações de metais nas proximidades de sua foz e nas áreas ao norte, juntamente com a composição isotópica e concentrações de carbono orgânico semelhante às encontradas no rio Doce. Assim, o presente estudo contribui para o monitoramento de longo prazo do Rio Doce e das áreas costeiras afetadas, destacando a necessidade de estudos contínuos para avaliação das condições dessas áreas, uma vez que os metais contribuem para a redução da qualidade do habitat, além de apresentarem potencial para se acumular nos organismos, causando efeitos tóxicos.

Palavras-chave: Composição isotópica, Rio Doce, Metal, Plataforma continental, Sedimento.

ABSTRACT

The Doce river basin is located in the southeastern region of Brazil and comprises a drainage area of approximately 86,715 km² of extension. In addition, due to the activities carried out, the basin is known for its great socioeconomic importance, especially in the field of mining. Due to the high rainfall in the basin, the Doce river is considered one of the main tributaries of the Brazilian coast, carrying sediments, tailings and domestic/industrial effluents discharged along its entire course, to a continental shelf. Especially after the collapse of the Fundão dam (Mariana – MG), which occurred on November 5, 2015, releasing 50 million m³ of iron ore tailings into the environment, causing one of the biggest environmental disasters involving mining dams. Over the years, several studies still find concentrations of several metals still in disagreement with legislation, both in water and in sediment. Thus, the present study aims to analyze the extent of long-term impacts, in addition to providing a possible overview of the dispersion of the Doce river plume and their respective metal concentrations. For this, surface sediments and water were collected at 34 points, in some regions of the southeast Brazilian coast, for the granulometric characterization, elemental and isotopic composition analysis and metal determination. The results indicate that four years after the collapse of the iron ore dam, the metal concentrations in the sediment of the Doce river estuary are lower than other studies carried out in previous years, suggesting the transport of this material to the Brazilian coast. This result is evidenced by the higher concentrations of metals near its mouth and in the northern areas, together with the isotopic composition and concentrations of organic carbon similar to those found in the Doce river. Thus, the present study contributes to the long-term monitoring of the Doce river and affected coastal areas, highlighting the need for continuous studies to monitor the conditions of these areas, since metals contribute to the reduction of habitat quality, in addition to have the potential to accumulate in organisms, causing toxic effects.

Key-words: Continental shelf, Doce river, Isotopic composition, Metal, Sediment.

1. INTRODUÇÃO GERAL

1.1. Rio Doce

A bacia hidrográfica do rio Doce localiza-se na região sudeste do Brasil, nos estados de Minas Gerais (MG) e Espírito Santo (ES). Sua área de drenagem compreende 86.715 km², sendo 86% em MG e 14% no ES. Sua nascente se encontra nas Serras da Mantiqueira e do Espinhaço, em Minas Gerais e percorre 879 km até atingir o Oceano Atlântico, no Espírito Santo (ANA, 2010). A bacia é reconhecida por sua grande importância socioeconômica, principalmente em relação as atividades industriais, agropecuárias e de mineração (Almeida et al., 2018). Seu regime pluviométrico é caracterizado por dois períodos bem distintos, com período chuvoso entre outubro a março, e seco entre abril a setembro, com variações na precipitação entre 900 a 1500 mm de média anual e vazão específica média de longo tempo de 950 m³/s (ANA, 2010).

O rio Doce é caracterizado como uma planície deltaica dominada por onda, onde suas praias são influenciadas pelo aporte fluvial, além da presença dos sedimentos locais. Além disso, as praias dessa região são extremamente expostas, resultando em uma maior variabilidade no perfil sedimentar, e um maior carreamento de sedimentos grosseiros.

Na porção superior da bacia, localiza-se o quadrilátero ferrífero, área onde se encontra as jazidas de ferro (Fe) de Minas Gerais, um dos depósitos minerais mais explorados do mundo. Desde o século XVII, a região constantemente é explorada para ouro (Au) e Fe, fazendo com que o Brasil ocupe posição de destaque na produção de Au e Fe (Azevedo *et al.,* 2012; Cagnin, 2018). Contudo, além das atividades de mineração de Au e Fe, a região também é rica em reservas de alumínio (Al) e manganês (Mn) (Costa, 2015).

O rio Doce é considerado um dos maiores tributários do litoral brasileiro, principalmente em função do seu regime pluviométrico nos meses chuvosos, o que aumenta a descarga de sedimentos na costa sudeste do Brasil (Cagnin, 2018). Em função disso, o rio é um grande responsável por transportar os rejeitos e efluentes produzidos ao longo de seu percurso para o litoral (ANA, 2016). No entanto, a elevada descarga de rejeitos no rio, além de impactar diretamente na qualidade da água do rio

Doce, e consequentemente, na água de abastecimento das cidades ao longo da bacia, também leva a um grande impacto à costa brasileira, principalmente após o rompimento da barragem de Fundão (Mariana – MG), ocorrido no dia 5 de novembro de 2015, que liberou 50 milhões de m³ de rejeito de minério de Fe no ambiente, levando a morte de 19 pessoas, além da fauna associada a bacia e áreas do entorno (Segura *et al.*, 2016).

O rejeito de minério foi classificado conforme a ABNT NBR 10.004/2004, que dispõe sobre a classificação de resíduos sólidos, como não-perigoso (não inflamável, não reativo, não tóxico, não patogênico) e não-inerte (biodegradáveis, solúveis em água) para Fe e Mn (IBAMA, 2015). No entanto, diversos estudos encontraram concentrações elevadas de diferentes metais tanto na água, quanto no sedimento, dias após o rompimento da barragem (Gomes et al., 2017; Hatje et al., 2017), o que acarretou em diversos efeitos tóxicos em diferentes organismos de níveis tróficos distintos (Vergilio et al., 2020). Além disso, segundo o Instituto Mineiro de Gestão das Águas (IGAM, 2019), mesmo após 4 anos, alguns metais como Al, cobre (Cu), Fe e Mn ainda se encontram em desconformidade com o máximo da série histórica para o rio Doce, fazendo-se necessário estudos de monitoramento dos impactos de longo prazo.

1.2. Metais

Os metais existem de diferentes formas, como solúveis, ligados a matéria orgânica, sulfetos, rede de minerais, carbonatos, oxi-hidroxido de Fe e Mn, e podem ser originados tanto por fontes naturais como intemperismo e erosão de rochas/solos, quanto por fontes antrópicas como descarga de efluentes domésticos/industriais, atividades de mineração, agricultura, dentre outros. (Davutluoglu et al., 2011; Hoang et al., 2020). Esses elementos, principalmente os metais, estão entre os contaminantes ambientais mais comuns, sendo conhecidos por sua elevada toxicidade, por sua capacidade de bioacumulação e biomagnificação, por não serem biodegradáveis e serem de alta persistência, permanecendo por anos no ambiente, especialmente nos sedimentos (Oliveira e Marins, 2011).

Cerca de 90% dos metais presentes nos ambientes aquáticos se encontram estocados nos sedimentos ou nas partículas suspensas na coluna d'água, principalmente devido aos processos de adsorção, floculação, sedimentação. Isso faz com que esses compartimentos sejam as principais fontes de contaminação, através da liberação dos metais, por processos de ressuspensão e alterações nas condições ambientais (alterações no pH, condições oxi-redox do meio e salinidade) (Davutluoglu et al., 2011; Oliveira e Marins, 2011; Zhang et al., 2014).

No caso dos estuários, esses processos são controlados através da complexa hidrodinâmica estuarina, onde as misturas de águas criam gradientes longitudinais e verticais, que influenciam nos processos de transporte de elementos para a plataforma continental, devido a distribuição dos elementos entre as fases dissolvidas, particulada e sedimentar (Oliveira e Marins, 2011).

1.3. Isótopos

Isótopos são átomos de um mesmo elemento químico com números de massa distintos, devido ao fato de possuírem o mesmo número de prótons e diferentes números de nêutrons (massa = número de prótons mais número de nêutrons). São conhecidos dois tipos, os isótopos radiogênicos (chamados instáveis), ou seja, que alteram sua massa ao longo do tempo devido a emissões de energia, e os isótopos conhecidos como estáveis, que não alteram sua massa ao longo do tempo (C, N, O, H e S) (Martinelli et al., 2009). Normalmente os isótopos mais leves como (^{12}C e ^{14}N) são mais abundantes na natureza, enquanto os mais pesados (^{13}C e ^{15}N) são mais raros (Martinelli et al., 2009).

Uma vez que a composição isotópica do elemento varia previsivelmente conforme o mesmo se move entre os compartimentos, as diferenças entre as composições isotópicas de diferentes fontes podem ser utilizadas como traçadores para entender os processos ecológicos, especialmente no âmbito de identificação de fontes, origens, sumidouros e transformação da matéria orgânica (Fry & Sherr, 1989; Martinelli et al., 2009; Bouillon et al., 2011).

2. HIPÓTESE

Através do sensoriamento remoto e análises isotópicas, Marta-Almeida et al. (2016) e Francini-Filho et al. (2019) identificaram diferentes zonas atingidas pela pluma do rio Doce entre os anos de 2016 e 2018, desde latitudes mais ao sul como ao norte da foz do rio Doce, se concentrando principalmente na plataforma continental entre sua foz em direção ao sul, próximo a cidade de Vitória-ES. Com isso, após 4 anos do rompimento da barragem de Fundão em Mariana-MG, ainda serão observadas composições isotópicas e concentrações de metais compatíveis com as do rio Doce, na plataforma continental entre sua foz e em direção ao sul, próximo a Vitória-ES, principalmente devido à predominância de ventos nordeste na região nas estações de primavera e verão, que estaria impulsionando o transporte dos rejeitos em direção ao sul.

3. OBJETIVO

O estudo visa avaliar a extensão da área impactada na foz do rio Doce após quatro anos do rompimento da barragem de minério de ferro através da determinação de metais e composição elementar e isotópica em diferentes compartimentos abióticos dos ecossistemas na interface continente - oceano.

4. RESULTADOS

ARTIGO

Trace metal concentration in regions of the Brazilian coast: an assessment of the influence of the Doce river plumes and other adjacent coastal areas

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Trace metal concentration in regions of the Brazilian coast: an assessment of the influence of the Doce river plumes and other adjacent coastal areas

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Abstract

In November 2015, the Fundão dam collapsed, releasing tons of iron ore tallings into the environment, being considered one of the biggest environmental disasters in Brazil. Even after 4 years, several studies still show that metal concentrations in the river are still in disagreement with legislation. This study analyzes the extension of long-term impacts, in addition to provide a possible scenario of the Doce river plume dispersion, and their respective metal concentrations. For this, water and surface sediment were sampled at 34 points along north and south of Doce river mouth, through 3 Brazilian coastal states, for analysis of elemental and isotopic composition and metal determination. The results indicate that even after 4 years of the iron ore dam collapse, the metal concentrations in the sediment of the Doce river estuary are lower than other studies carried out in previous years, suggesting the transport of this material to the Brazilian coast. This result is evidenced by the higher metal concentrations nearby its mouth and in north areas, together with the isotopic composition similar to those found in the Doce river. Thus, the present study contributes to the long-term monitoring of the Doce River and affected coastal areas, highlighting the need for continuous studies to monitor the conditions in these areas.

Key-words: Continental shelf, Environmental disaster, Metals, Isotopic composition, Sediment.

Introduction

On November 5, 2015, the Fundão dam (Mariana-MG) collapsed, releasing 50 million m³ of iron ore tailings into the environment, causing the death of 19 people, destruction and damage to regions around the basin until the coastal area (Segura et al., 2016; Hatje et al., 2017; Almeida et al., 2018; Francini-Filho et al., 2019). The tailings reached the Santarém dam, the Gualaxo do Norte, Carmo and Doce rivers, reaching the Atlantic Ocean on November 21, 2015 (IBAMA 2015; Segura et al., 2016; Bastos et al., 2017), affecting fauna and flora of the adjacent coastal environment (Gomes et al., 2017), leading a major environmental disaster.

Initially, there was a high mortality of the associated fauna, due to the high concentration of suspended particulate matter (SPM) (Francini-Filho et al., 2019), where the turbidity levels presented by Vergilio et al. 2020 after 15 days (med = 2630) were 43 times higher than the maximum of the historical series, described by IGAM, 2015 (med = 61.2). The increase of turbidity, induced by high SPM concentration, are associated with other negative factors, such as interferences with aquatic metabolism habitats and biodiversity losses, especially in estuarine and coastal areas, since they are the final sedimentation regions (Rudorff et al., 2018, Viana et al., 2020).

Different studies have shown a high metal concentration in water along the river course, and in the estuarine zone one year after the disaster at levels above the maximum regulated by Brazilian legislation (Bastos et al., 2017; Gomes et al., 2017; Hatje et al., 2017). Even after 4 years of the dam rupture, some metals such as aluminum (Al), copper (Cu), iron (Fe) and manganese (Mn) are still in disagreement, and above the maximum of the historic recorded for Doce river water (IGAM, 2019). Trace metals are toxic elements, non-biodegradable and highly persistent in the environment, in addition their presence in high concentrations is associated with reduced water quality (Kim et al., 2015; Matos et al., 2017).

Metals in the water column are presented in dissolved or adsorbed to SPM can be removed from the water column through flocculation and/or coagulation processes and adhere to the bottom sediment. The sedimentation over time leads elements enrichment, however the physical-chemical changes in the environment can make them bioavailable (Aguiar et al., 2020), especially in case of the mine ore deposited through Doce river. This mining tailing can be remobilized, leading to risk of metal contamination for the aquatic biota and surrounding communities (Fernandes et al., 2016; Felizardo et al., 2021).

Just 25 days after the tailing's ocean arrival, Rudorff et al., (2018) demonstrated, through remote sensing, coastal regions affected by the plume at south of Doce river mouth, close to Vitória-ES city, and within a few months it reached distances close to Rio de Janeiro city (Marta-Almeida et al., 2016, Rudorff et al., 2018). However, climatic episodes such as cold and subtropical fronts, in the autumn-winter seasons, can reverse the wind direction to the northeast, which made the plume to reach the northernmost Doce river latitudes (INPE, 2015; Rudorff et al., 2018; Francini-Filho et al., 2019). Nevertheless, although the plume has reached different latitudes, its dispersion pattern has shown that the most affected regions are still on the continental shelf between the Doce river mouth and the Vitória-ES city (Marta-Almeida et al., 2016), due to changes in the wind field, towards the northeast and southeast (INPE, 2015).

Due to the space-time variability, stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopes ratios, have been used in the last decades as a tool to characterize sources and transfer pathways of organic matter (OM) and contaminants in the environment (Wiederhold, 2015). Thus, the isotopic composition, associated with the metals study, can be used as a tracer of sources and destinations of OM, in order to discriminate anthropogenic contamination. Few studies have worked with determination of isotopic composition in the Doce river and surrounding areas (Felizardo et al., 2021).

In this way, considering that the mine tailings released along Doce river present a geochemical signature distinct from the natural sediment, the assessment of the carbon and nitrogen isotopic composition in the sediment of coastal areas may be an important tool to help to discriminate the amplitude of the affected areas by the rupture of the iron ore dam at the Doce river mouth. The association of geochemical tools of isotopic composition of C and N, and their molecular ratio together with the metals determination can be applied to distinguish other areas with different sources of contamination.

Given the event environmental proportions and the complex characteristics of the released tailings, remain the need for further studies to assess the long-term impacts of the Doce river and the possible affected areas by the tailings. The results obtained through the isotopic composition, will provide a possible panorama of the plume's dispersion along the Brazilian coast, sideways with the metals results from the abiotic matrices, which will provide an overview of the different sampling sites conditions.

Material and Methods

Study area and sampling

Sediment and water samples were collected at the end of November 2019 (four years after the tailing rupture) in 34 locations at north and south of Doce river mouth (Fig. 1). The areas of Doce river plume influence were classified as beaches, other rivers estuaries, and the Doce river estuary (DRE). The sampling sites were chosen according to the plume dispersion patterns of the Doce river (Marta-Almeida et al., 2016; Rudorff et al., 2018; Francini-Filho et al., 2019), where the authors report distances from the Rio de Janeiro city to near the Abrolhos bank. Sediments and surface waters were collected in polyethylene bags and bottles, respectively and kept in thermal boxes, moreover part of water samples was acidified for metals determination and other part was stored in a freezer at -60 °C for elemental and isotopic composition of OM. The sediment was dried by lyophilization (L101 Liotop ®), and a fraction of was separated for granulometric characterization, while the rest, was sieved in the fractions <2.0 mm and <63μm, macerated and homogenized for metal and isotopic analysis. The both granulometric fractions were analyzed to verify the deposits of fine material in the influence areas of the Doce river mouth, and together with metal levels infer about the areas affected by the mining ore.

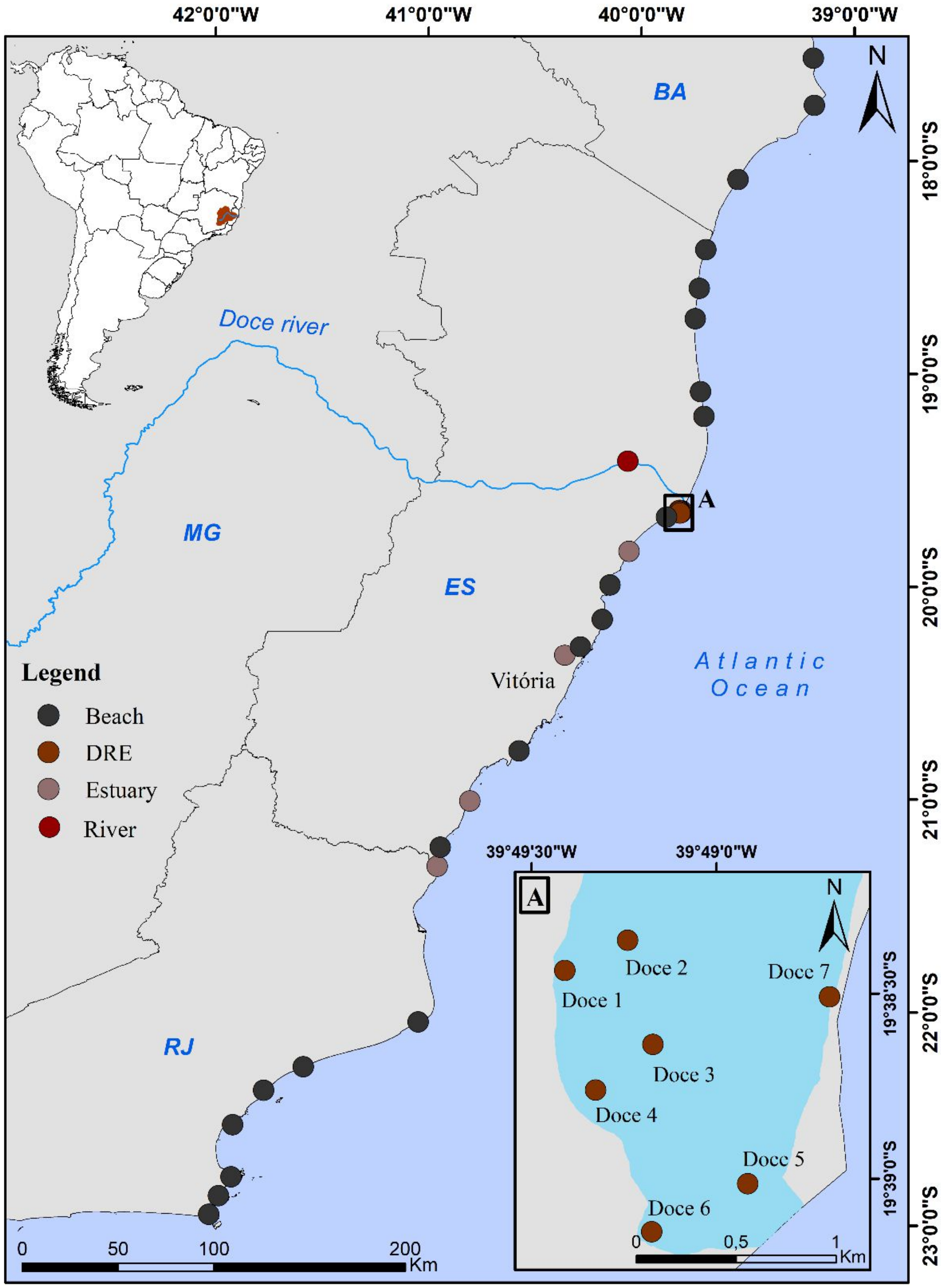

Figure 1: Sampling sites along the Brazilian coast. The figure was prepared using the software ArcGIS (ArcMap 10.5 version 10.5.0.6491; https://desktop.arcgis.com/en/).

To obtain SPM and dissolved fraction, estuarine water samples were filtered through a GF/F glass fiber filter (47 mm and 0.7 µm) (Whatman 40), through vacuum pump. Environmental parameters such as pH, dissolved oxygen, salinity, and temperature were measured in the water column before sediment sampling, using their respective probes (YSI-EcoSense).

Granulometric characterization

Lyophilized sediment samples were added to the granulometry up to a grain absorbance limit of 0.05 (sandy samples) for a period of 6 minutes, being washed for granulometric decontamination between each sample. The characterization (coarse sand, medium sand, fine sand, silt + clay) of grain size was performed by the particle size analyzer by laser diffraction (Shimadzu SALD-3101) and classified according to the scale of the Massachusetts Institute of Technology (MIT). Due to sensitivity issues, the granulometry percentages varied between 97.4 and 100%, and the variance obtained was not significant.

Table 1. Particle size classification according to MIT.

Classification		**Particle size**
Boulder		> 200 mm
Cobble		200 mm to 60 mm
Gravel	Coarse	60 mm to 20 mm
	Medium	20 mm to 6 mm
	Fine	6 mm to 2 mm
Sand	Coarse	2 mm to 0.6 mm
	Medium	0.6 mm to 0.2 mm
	Fine	0.2 mm to 0.06 mm
Silt	Coarse	0.06 mm to 0.02
	Medium	0.02 mm to 0.006 mm
	Fine	0.006 mm to 0.002 mm
Clay		< 0.002 mm

Metal determination

Metal determination in the sediment (<2.0 mm and <63µm) and SPM (for estuary and one beach) samples was carried out according to the method 3052 US EPA (1995). Approximately 0.5 g of the dry and homogenized sediment were dissolved in 9 mL of nitric acid (HNO_3 65%), 4 mL of hydrofluoric acid (HF 48%) and 4 mL of hydrochloric acid (HCl 37%) and digested with the microwave oven (Mars 5 Xpress

CEM-Corporation) at a temperature of 180 °C for 40 min. After digestion, a volume of 25 mL of 4% boric acid (H_3BO_3) was added to complex the HF, followed by heating with the microwave oven a temperature of 180 °C, as described. The final extract was filtered (Whatman 40) and a final volume of 50 mL was measured with 0.5 N HNO_3. For quality assurance of analyzes, a triplicate was performed for every five samples, where samples with a coefficient of variation lower than 15% were considered. One analytical blank was also used for every 10 samples. Metal determination in the sediment was performed for all 34 samples, while SPM was performed only in eight samples on the Doce river (1), DRE (2), other estuaries (4) and beach (1). To ensure the method accuracy, the estuarine standard reference material® NIST 1646a (National Institute of Standards and Technology – Certificate of Analysis) from Department of Commerce of United States of America was used (Table 1). The results of sediment were compared with the TEL (Threshold Effect Level) and PEL (Probable Effect Level) levels from the National Oceanic and Atmospheric Administration (NOAA; Buchman, 2008) reference.

Table 2. Recovery values for standard reference material (NIST 1646a). Concentrations are presented in µg.g^{-1}. * indicate concentration in mg.g^{-1}.

Metal	Mean ± SD	Recovery	NIST
Al*	22,9 ± 0,7	100%	23,0
As	4,6 ± 1,2	73%	6,2
Ba	186,2 ± 80,6	89%	210,0
Cr	34,1 ± 5,0	83%	40,9
Fe*	19,4 ± 0,2	97%	20,0
Mn	210,0 ± 4,2	90%	234,5
Mo	1,6 ± 0,5	92%	1,8
Ni	22,8 ± 8,3	99%	23,0
Pb	12,2 ± 1,1	105%	11,7
Sr	47,6 ± 3,6	70%	68,0
Ti*	3,8 ± 0,1	84%	4,6
V	54,3 ± 13,0	121%	44,9
Zn	44,1 ± 9,7	90%	49,0

Metal determination in water samples was carried out according to the method 3015a US EPA (1994). A volume of 22.5 mL of the sample was acidified with 2.5 mL of nitric acid (HNO_3) 65% and digested with the microwave oven (Mars 5 Xpress CEM-Corporation) at a temperature of 165 °C for 30 min. After digestion, the extract was filtered (Whatman 40) and the final volume of 25 mL was measured with ultra-pure water (Milli-Q ®, Merck Millipore). Metal determination in dissolved water followed metal determination of SPM (being performed in eight samples – 1 in Doce river, 2 in DRE, 4 in other estuaries and 1 in beach). The water results were compared with the maximum allowed for each class by Brazilian legislation (CONAMA 357, 2005). Metal determination (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Ti, V, Zn) were performed by optical emission spectrometry with coupled plasma (ICP-OES Varian model 720 ES).

Elemental and isotopic composition

The analyzes were carried out in three environmental matrices (dissolved, SPM and sediment). To obtain total carbon (C_{total}) and total nitrogen (N_{total}), 10 mg were weighed using a tin capsule. For organic carbon (C_{org}) determination, 10 mg were weighed using a silver capsule followed by decarbonation with five additions of 25 µL of HCl 2M, interspersed with heating in an oven at 60 °C for 30 minutes. After these procedures, the samples were heated at 110 ºC for 4 hours to evaporate the HCl in a muffle furnace.

For the dissolved fraction (C_{org}), estuarine water samples were filtered through a GF/F glass fiber filter (0.7 µm) (Whatman 40) and acidified with HCl pH 2 for increase the extraction efficiency of organic acids. To obtain the dissolved organic matter (DOM), the solid phase extraction method (SPE) was used (Dittmar *et al*., 2008). For adsorption of DOM, the samples were passed in a PPL column previously activated, due to gravity difference. For desalination, samples were washed twice with HCl pH 2 and dried with nitrogen (N_2) to eluate the OM with methanol in glass flasks. A volume of 1 mL of the sample was added in glass vials and dried in an oven at 60 °C, resuspended with 1 µL of methanol, transferred to silver capsules and dried in an oven at 60 °C. For the obtention of particulate organic matter (POM), the samples of particulate material retained on the filter were decarbonated in an acidic atmosphere HCl 65% for 48 hours and dried in a muffle oven at 110ºC for 4 hours. Filters were placed on tin disks.

The elemental (C and N) and isotopic composition ($\delta^{13}C$ and $\delta^{15}N$), were performed in the Flash 2000 Elemental Analyzer (Organic Elemental Analyzer - Thermo Scientific), coupled to the Conflo IV interface and Delta V Advantage (Isotope Ratio Mass Spectrometer -Thermo Scientific). The isotopic composition of carbon and nitrogen were expressed by conventional delta notation (δ) in parts per thousand (‰) relative to the reference standard material Pee Dee Belemnite (PDB) and atmospheric nitrogen, with detection limits of 0.05% and 0.02%, respectively, where R is equal to the ratio of the heavier isotope of the lighter (i.e., $^{13}C/^{12}C$ and $^{15}N/^{14}N$), according to the following equation:

$$\delta X = \left[\left(\frac{Rsample}{Rstandard}\right) - 1\right] \times 1000$$

Enrichment factor (EF)

The enrichment factor is used to assess levels of contamination by possible anthropogenic sources. The index was calculated for each group using the formula:

$$EF = \frac{\left(\frac{Metal}{Al}\right)\ sample}{\left(\frac{Metal}{Al}\right)\ background}$$

Aluminum was used as a normalizing element due to conservative characteristics and low mobility in the environment (Birch., 2020). The background values were obtained through the median of the sampling sites to north and south of the Doce river mouth for each metal. Values of EF < 1 indicates no enrichment; <3 is minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; and >50 is extremely severe enrichment (Sakan *et al*., 2009).

Statistical analysis

Sampling sites were divided in three different groups, according to environment type (estuary, DRE and beach). Two points located in Linhares-ES were not used in the statistical analysis for receive only the continental influence, being representative as Doce river source. The data from this site were considered only as sources of metals and OM for the coast, since the high metals concentrations could include errors in the statistics. Data from different metal concentration and physical-chemical parameter from different environmental matrices were submitted to ANOVA type III (unbalanced samples) for differentiation between groups (Anova, car package, R Core Team, 2020), followed by Tukey post-hoc (pairs, base package, R Core Team, 2020), assuming 95% of confidence level. When necessary, data were transformed to meet ANOVA premises (linearity, normality, homoscedasticity, leverege), using a maximum likelihood function (boxcox, MASS package, Venables and Ripley, 2002). For non-parametric variables Kruskal-Wallis test (kruskal.test, base package, R Core Team, 2020), followed by Dunn pos-hoc (dunn.test, dunn.test package, Dinno, 2017) was applied, assuming 95% of confidence level. Results were considered significant with p-value less than 0.05. For variables with only one data in the group, ANOVA was not performed.

To analyze association of variables (metal), Pearson's correlation (rcorr, Hmisc package, Harrell and Dupont, 2021) was used to identify clusters with the same behavior, assuming a correlation coefficient (r) > 0.7 and p-value < 0.05. To perform the correlation analysis, variables with missing data (less than 50%) were regressed with others and the values were stipulated using linear regression with determination coefficient (R^2) > 0.7.

To sediment graphical plot, the data were transformed to z-scale (normalized standard deviation from the mean, where the standard deviation is 1 unit and the mean is zero) to make the variables comparable. To plot the graphs according to associations verified in the Pearson's correlation, local polynomial regression was used, fitting with R Software (loess, base package, R Core Team, 2020). Total water, dissolved, SPM and sediment fraction <63 µm showed lower or no correlation, the data were not plotted.

To evaluate the distribution, associations and similarities of the variables among and within the clusters of sediment samples, multivariate principal component analysis (PCA) (PCA, FactoMineR package, Le et al., 2008) was performed. This analysis was conducted excluding missing data and variables with more than 40% of missing data.

The differences between sources and contributions to sediments from the DRE, other estuary and beaches influenced by its plume were estimated by the isotopic compositions of C and N, using Bayesian mixture models (MixSIAR, MixSIAR package, Stock and Semmens, 2016). Since the groups presented a different discrimination factor, their models were calculated separately. The discrimination factor for each source (dissolved DR: $\delta^{13}C$ = 1.010 ± 0.000, $\delta^{15}N$ = 0.514 ± 0.000; sediment DR: $\delta^{13}C$ = 1.025 ± 0.046, $\delta^{15}N$ = 0.811 ± 0.479; MPS DR: $\delta^{13}C$ = 1.106 ± 0.000, $\delta^{15}N$ = 1.062 ± 0.000) was calculated using the formula presented by Martinelli et al. (2009). Contributions were calculated for points within the main dispersion pattern observed by Marta-Almeida et al. (2016) (Doce river mouth and the Vitória-ES city). Furthermore, as isotopic signatures of iron ore tailings were observed towards the north by Francini-Filho et al. (2019), we assigned a point to the north for the contribution's calculation. All statistics and multivariate analysis were performed using R version 4.1.0 (R Core Team, 2020).

$$\varepsilon = \left(\frac{\delta source - \delta sample}{\delta sample + 1}\right)$$

The interpolation results were fitted using IDW (inverse distance weighting) method in ArcGIS software (ArcMap 10.5 version 10.5.0.6491;

https://desktop.arcgis.com/en/). The calculation is based on the tendency of the variables closer to each other to be more similar than those farther apart. Therefore, the IDW uses the values sampled around it to predict an unmeasured location. The points chosen for the interpolation are mainly based on the results found by Marta-Almeida et al. (2016) and Francini-Filho et al. (2019) for the dispersion pattern of the Doce river plume.

Results and Discussion

Physical chemical parameters

Water environmental parameters (Table 2) evidenced differences among the sampling areas. For pH, DRE showed the lowest median than beach and other estuaries (Kruskal-Wallis, $X^2 = 8.58$, $p = 0.0137$). DRE showed intermediate values of dissolved oxygen between beaches and other estuaries ($X^2 = 11.89$, $p = 0.0026$). The beaches showed the higher salinity compared to DRE and other estuaries ($X^2 = 16.11$, $p = 0.0003$). Although the pH values are in accordance with the Brazilian legislation for brackish water (6.5 – 8.5; CONAMA 357), the data are still below those found by Viana et al. (2020) and Gomes et al. (2017) in the Doce river estuarine zone before and after the dam rupture, being also below the historical average (6,9; IGAM, 2015).

Chou et al., (2018) reported that variations in physical chemical parameters such as pH, DO and salinity are linked to mobility and bioavailability of metals, where in general, under acidic and oxic conditions (pH's between 5-7; OD ~ 8 $mg.L^{-1}$) there is greater release of these elements to the water column, in addition to an increase in their concentrations over time. While under suboxic conditions (~5 $mg.L^{-1}$) there is release, but in lower concentrations. Regarding salinity, the authors observed variations in the concentration of the elements Cu, Zn and Pb under different systems (freshwater, seawater and estuary), where each element had a different behavior.

Regarding granulometric characterization (Table 2), coarse sand ($X^2 = 0.13$, $p = 0.9381$), medium sand ($X^2 = 0.91$, $p = 0.6346$), fine sand ($X^2 = 0.11$, $p = 0.9457$) and silt-clay ($X^2 = 3.52$, $p = 0.1725$) showed no statistical difference between the medians of the sampling areas. However, DRE had the highest median percentages of coarse sand (77.61%), followed by beaches and other estuaries, and the lowest percentages of the rest of the fractions, except for Doce 6, which was mostly composed of the finest sediment fractions (silt-clay; 81.53%). In fact, the sediments of the Doce river are mostly composed of the sand fraction, however, after the dam collapse, there were changes in the sediment composition, with greater appearances of fine sand fractions and silt fractions (Duarte et al., 2020). Nevertheless, although the river is returning to its granulometric composition prior to the dam's rupture, some sediment deposition sites still have large percentages of fine material, which can be remobilized through resuspension events, releasing the mud to the water column, enabling the elements accumulation, for the biota and their incorporation in the food web.

The granulometric composition along the Brazilian coast is mostly composed of coarse sand (~63% average), followed by medium (~17% average) and fine sand (~11% average), except for a few points in the extreme south (Búzios and Arraial do Cabo) and north (Caravelas and Itaúnas) of the Doce river mounth, with changes in composition to fine sand and silt+clay. The predominance of sand fraction (~65%, 17%, 8%), followed by silt+clay (~7%) was also observed by Marta-Almeida et al. (2016), in areas influenced by the Doce river plume. According to Zuo et al. (2021), wave-dominated environments generate different fractions of sediment, in addition to its transport being influenced by sedimentation processes and continental shelf shapes, since the concentration of sediments varies according to these characteristics, demonstrating that the transport and resuspension of sediment involve several complex factors.

Table 3: Physical-chemical parameters of water from different sampling sites and different areas (median and interquartile interval - IQR) along the southeastern Brazilian coast. Different letters indicate statistical difference between groups (p <0.05). Positive and negative km are north and south of the DRE central point (km 0), respectively. Coordinate system given in decimal degrees. Summary data are presented as median and IQR since the data were not normally distributed, and the statistic used is based on the calculation of differences between the medians and their interquartile ranges.

									Sediment			
					Water				**Sand**			
Site	**Type**	**km***	**Lat**	**Long**	**pH**	**Temp.**	**OD**	**Sal.**	**Coarse**	**Medium**	**Fine**	**Silt-Clay**
Alcobaça	Beach	265.02	-17.515778°	-39.192306°	8.14	28.00	5.81	35.50	78.16	19.32	0.99	1.41
Caravelas	Beach	236.5	-17.737917°	-39.187917°	8.04	29.30	5.27	36.30	23.68	26.11	31.45	17.74
Mucuri	Beach	180.31	-18.086444°	-39.546194°	8.06	27.30	5.43	32.50	95.54	4.23	0.03	0.00
Itaúnas	Beach	140.00	-18.414778°	-39.697611°	7.92	27.80	6.17	35.90	3.36	53.70	42.94	0.00
Conceição da Barra	Beach	120.00	-18.597361°	-39.728306°	8.06	27.90	5.69	33.40	71.84	23.21	4.87	0.00
Guriri	Beach	103.61	-18.739833°	-39.747417°	8.06	25.40	5.78	36.50	95.82	4.00	0.17	0.00
Urussuquara	Beach	65.56	-19.082056°	-39.722583°	7.85	23.60	6.79	33.60	63.78	27.72	2.42	6.06
Pontal do Ipiranga	Beach	52.61	-19.198528°	-39.706306°	7.51	23.80	6.30	33.90	56.39	42.46	1.16	0.00
Doce 7	DRE	1.00	-19.641833°	-39.811556°	6.65	27.40	5.37	0.30	77.61	20.81	1.46	0.00
Doce 2	DRE	0.21	-19.639222°	-39.820653°	6.83	27.40	5.70	0.00	74.12	23.86	1.91	0.00
Doce 3	DRE	0.13	-19.643899°	-39.819535°	-	-	-	-	88.75	10.57	0.41	0.00
Doce 5	DRE	0	-19.649721°	-39.815299°	6.78	29.00	5.93	0.20	87.48	11.72	0.68	0.00

Doce 1	DRE	-0.20	-19.640612°	-39.823624°	6.53	27.30	6.19	0.00	93.22	5.86	0.04	0.00
Doce 4	DRE	-0.30	-19.645940°	-39.822170°	-	-	-	-	75.81	14.28	1.94	7.92
Doce 6	DRE	-0.40	-19.650281°	-39.819449°	-	-	-	-	0.00	0.00	18.57	81.53
Comboios reserve	Beach	-7.44	-19.671278°	-39.882583°	-	-	-	-	95.13	4.63	0.12	0.00
Riacho	Estuary	-33.47	-19.831448°	-40.058818°	3.79	25.20	2.91	0.70	96.83	0.57	0.00	0.00
Formosa	Beach	-54.22	-19.989692°	-40.147786°	7.49	24.10	7.33	13.20	4.23	45.02	50.41	0.34
Jacaraipe	Beach	-72.74	-20.151267°	-40.184281°	7.85	24.10	7.40	6.60	21.54	31.40	45.82	1.22
Camburi	Beach	-92.38	-20.280783°	-40.287044°	7.95	22.30	6.70	30.00	89.04	8.26	0.22	0.00
Santa Maria de Vitória	Estuary	-96.90	-20.321250°	-40.360139°	7.85	22.70	4.72	21.00	61.89	26.78	1.71	9.63
Ubu	Beach	-154.39	-20.771083°	-40.574636°	7.79	22.50	7.60	35.90	85.54	13.41	0.92	0.00
Itapemirim	Estuary	-196.17	-21.005897°	-40.806239°	8.24	25.40	4.30	0.10	70.62	8.43	1.38	19.45
Presidente Kennedy	Beach	-224.90	-21.223225°	-40.945378°	7.87	24.00	6.36	33.80	73.08	24.00	2.79	0.00
Itabapoana	Estuary	-235.14	-21.312497°	-40.959742°	7.79	25.30	3.84	1.90	50.23	27.65	17.57	4.48
Farol de Sao Thomé	Beach	-325.84	-22.043142°	-41.049092°	8.00	23.60	6.87	33.40	98.12	1.25	0.00	0.00
Quissamã	Beach	-386.37	-22.252817°	-41.588089°	7.42	24.70	6.13	34.70	92.57	7.26	0.14	0.00
Macaé	Beach	-409.00	-22.363639°	-41.774472°	8.02	22.80	5.76	21.80	98.98	1.02	0.00	0.00
Rio das Ostras	Beach	-433.68	-22.525250°	-41.920572°	7.37	23.70	7.07	33.90	79.16	19.00	1.72	0.00
Búzios	Beach	-466.82	-22.770028°	-41.928194°	7.52	24.00	6.53	35.60	2.11	18.37	78.53	0.99
Cabo Frio	Beach	-479.72	-22.858294°	-41.986481°	7.64	22.40	6.10	35.80	97.86	2.09	0.02	0.00

Arraial do Cabo	Beach	-493.00	-22.946167°	-42.032558°	7.49	22.00	6.50	35.70	2.64	26.82	52.53	18.00
				Median (Beach)	7.86[a]	24.00[a]	6.33[a]	33.90[a]	78.16[a]	19.00[a]	1.16[a]	0.00[a]
				IQR (Beach)	0.51	2.48	1.01	2.55	73.60	22.20	31.30	0.99
				Median (DRE)	6.72[b]	27.40[a]	5.82[ab]	0.10[b]	77.61[a]	11.72[a]	1.46[a]	0.00[a]
				IQR (DRE)	0.17	0.42	0.38	0.22	13.20	9.33	1.38	3.96
				Median (Estuary)	7.82[a]	25.25[a]	4.07[b]	1.30[b]	66.25[a]	17.60[a]	1.54[a]	7.05[a]
				IQR (Estuary)	1.16	0.75	0.80	6.12	18.20	20.50	4.64	8.72

Temp = temperature (ºC) and DO = dissolved oxygen ($mg.L^{-1}$).

Sources and contributions of Doce river to sediment of DRE, beach and other estuaries

Carbon and nitrogen isotopic composition can be used as proxy for tracking the iron ore plume in the marine environment (Francini-Filho et al., 2019). For this evaluation, the analysis was performed using sediment the fraction <63 µm, since the fraction <2 mm had many values below the detection limit for N. The comparison of the isotopic rations of $\delta^{13}C$ from DRE ($\delta^{13}C$ -26.2‰ to -24.3‰ / $\delta^{15}N$: 1.4‰ to 8.1‰ / C:Na: 10.8‰ to 16.7‰) and beaches areas at north and south of Doce river mouth ($\delta^{13}C$ -26.1‰ to -16.1‰ / $\delta^{15}N$: 1.6‰ to 6.9‰ / C:Na: 5.0‰ to 19.8‰) indicate the dilution of organic material coming from the continental sources.

The C and N isotopic composition can also indicate the deposition of the mud from fluvial, estuarine and marine areas. The most negative $\delta^{13}C$ and $\delta^{15}N$ values observed in mud ($\delta^{13}C$: -28.0‰ / $\delta^{15}N$: 3.0‰) was followed by SPM ($\delta^{13}C$: -27.7‰ / $\delta^{15}N$: 5.6‰), sediment ($\delta^{13}C$: -26.5‰ to -24.9‰ / $\delta^{15}N$: 2.5‰ to 6.1‰) and dissolved fractions ($\delta^{13}C$: -25.3‰ / $\delta^{15}N$: 2.7‰) indicating the geological matrices involved in the transport of OM in direction to the ocean (Fig 2).

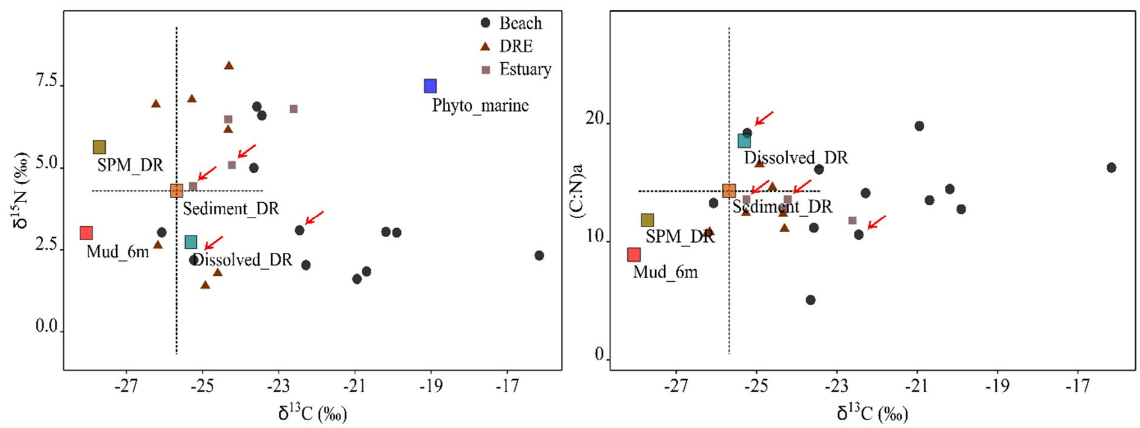

Figure 2. Relationship between $\delta^{13}C$ and $\delta^{15}N$ (A); $\delta^{13}C$ and (C:N)a (B) from surface sediment <63 µm. The isotopic values for marine phytoplankton source (represented by Phyto_marine) were retrieved from Gatts et al. (2020). The 6-month tailings values (represented by Mud_6m) were obtained from internal data. Other sources values were obtained through the Linhares-ES point of the present work. Boxes represent fonts and dotted line represents standard deviation. This graphical plot represents all sample sites, only in order to assess their distribution. Arrows indicate beaches and other estuaries within the Doce river plumes.

The Baysian mixture model (MixSIAR) was used to estimate the contribution of the Doce river plume to the sediments of the DRE, beaches and other estuaries according to the results of Marta-Almeida et al. (2016) and Francini-Filho et al. (2019). For DRE, the SPM and sediment acted as main matrices involved in transport of the mud, while in case of the areas at north and south of Doce river mouth, the material transported occurred mainly in the dissolved fraction. In this sense, the results show that even after 4 years of the dam's failure, the environmental matrices (sediment, dissolved and particulate) from the Doce river still contribute to the proportions of OM in the DRE and beaches, and consequently, to the increased of metals concentration in these locations. Furthermore, the mud from the dam failure is still among the main OM contributors to the Doce river plume, as resuspension events can still release this material into the water column, allowing its transport to the continental shelf. Our results indicate that after the tailing deposition in the sediment of DRE, the main part of the material was transported as dissolved fraction reaching north and south marine areas.

Due to the similarity in isotopic signatures between other estuaries and the DRE, we cannot say that the estuaries close to the dispersion of the Doce river plume are influenced or only have similar signatures due to the proximity of the drainage basins. Furthermore, since the Santa Maria de Vitória river is directly influenced by the port presence (with iron ore shipments), the isotopic signatures can also be similar to those found in DRE after the dam rupture. In fact, our results are in agreement with those found by Felizardo et al. (2021), where it shows the presence of mining residues and their long-term dispersion along the Brazilian coast, in addition to not showing the dispersion of tailings to other estuaries to the north and south of the Doce river mouth.

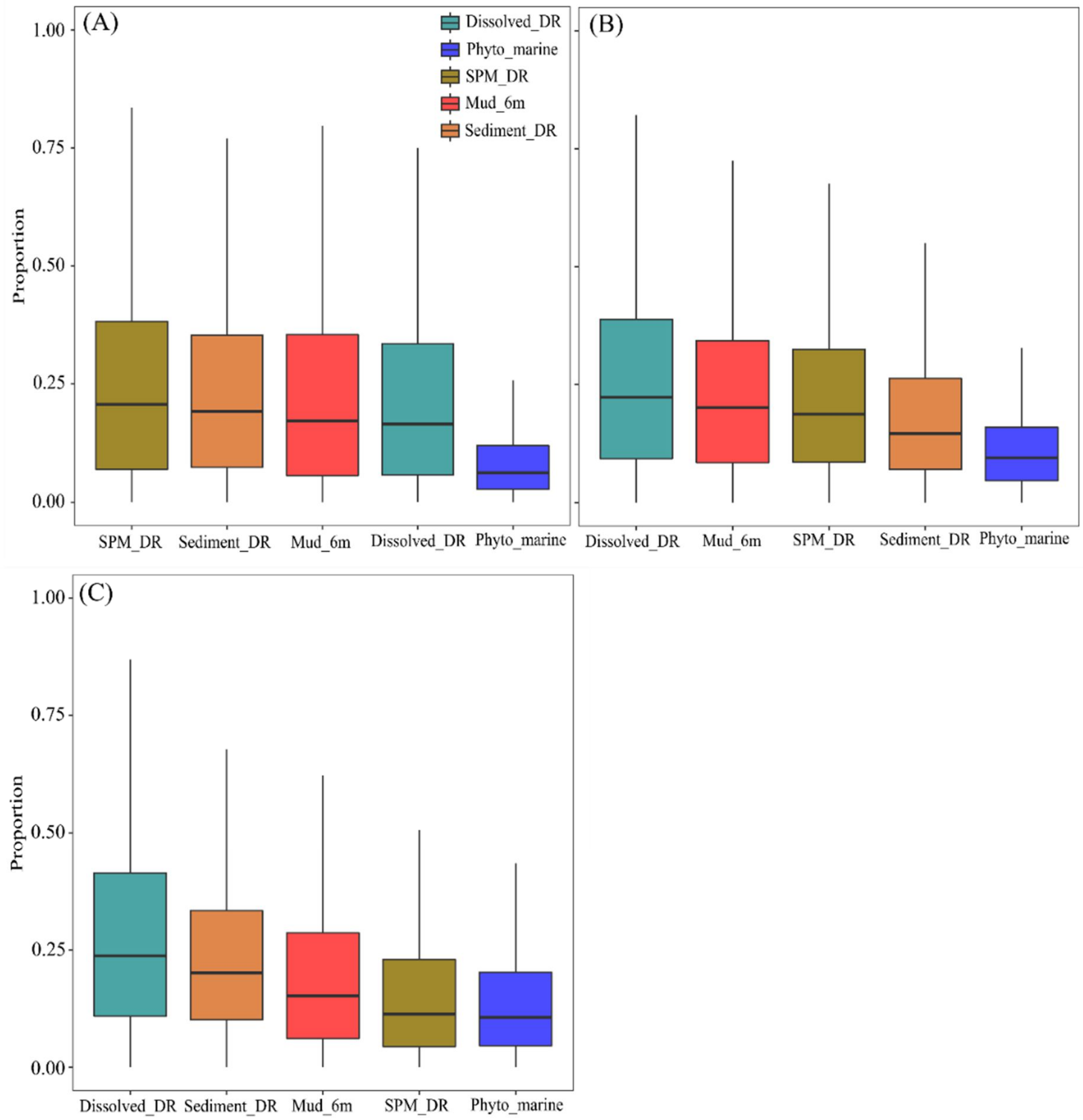

Figure 3. Mixing model results using MixSIAR (MixSIAR package R). for the organic matter proportion contribution to surface sediment of DRE (A), estuaries (B) and beaches (C). The data were organized only with the results of C and N within the main dispersion pattern of the Doce river plume (Marta-Almeida et al., 2016; Francini-Filho et al., 2019) to avoid errors in the mixture model. The isotopic values for marine phytoplankton source (represented by Phyto_marine) were retrieved from Gatts et al. (2020). The 6-month tailings values (represented by Mud_6m) were obtained from internal data. Other sources values were obtained through the Linhares-ES point of the present work.

Dynamic and concentration of elements in water column

Almost all elements remained below the detection limit for total water (As, Cd, Mo, Ni, Pb, Se, Sr, Ti and Zn) and for dissolved fraction (As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Ti and Zn) (Table S3 and S4; supplementary material). For the elements that were quantified in total water, the highest concentrations remain in Al and Fe for the DRE, and Fe, Al, Cu, Ba, Mn, and V for the beach and other estuaries areas (Table S4). The presence of higher level of elements in marine areas at north and south of Doce river, is another evidence of the transport of OM together with metals occurs through the water. In addition, some studies also indicate deleterious actions, or increase of these elements in the trophic chain (Vergilio et al., 2020; Andrades et al., 2021). For the dissolved fraction, high levels of Ba and Al was observed for DRE, while beach and other estuaries areas, the high levels were observed in Ba and V (Table S3).

The same trends regarding the dissolved Ba and Al were found in the DRE by Viana et al. (2020). The low concentrations of the other elements in the dissolved fraction were attributed by the author to processes such as flocculation, coagulation, exchanges between the SPM and the dissolved phase, which may have removed the elements to the sediment. Nonetheless, sediment remobilization processes, especially in the rainy season, may have released the elements to the water column, mainly to the particulate fraction, which explains higher concentrations in the particulate fraction in relation to other fractions on the water column.

The SPM, presented values below the detection limit for almost all elements (As, Cd, Cr, Cu, Ni, Pb, Ti, V and Zn) (Table S3). For the elements that were quantified in suspended solids, the highest concentrations of Al, Fe and Sr were observed for the DRE and beach, and Al, Fe, Ba and Sr for the other estuarine areas. Besides that, only Fe ($F = 7.33$, $p = 0.0326$) statistical differs among DRE and beach (Table S3), showing higher means on other estuaries. The present work found values 7 times higher to those of Vergilio et al. (2020) for Al (average 9.2 $mg.L^{-1}$), and values 0.7 lower for Fe 6 months (18.10 $mg.L^{-1}$) after the tailing's arrival in the DRE, respectively. The same pattern of the reduction of Fe levels was observed by Queiroz et al. (2021) between the years 2015-2017. Our result indicates that both dissolved and particulate fractions also act in the transport of metals from resuspend sediments even four years of the tailing rupture

After four years of the dam rupture, the levels of total and dissolved metals in water remained below the maximum regulated by Brazilian legislation for almost sampling sites (CONAMA 357) for brackish and saline waters, except for one beach at the north and one beach at the south of the DRE that presented values above 0.1

$mg.L^{-1}$ for total Mn (Mn = 0.119 and Mn = 0.168; Table S4), and all water samples from DRE remained below the maximum values of the historical series of the Doce river (IGAM, 2015). However, despite the values being below the legislation, the average of metal levels in water of DRE remained almost always higher than beach and other estuarine areas, and may also be associated with contamination by mining tailings from the Fundão dam.

Regarding the element's distribution in water along the Brazilian coast, according to local polynomial regression, Al, Ba and Mn show similar distribution patterns around the Doce river mouth, slightly increasing concentrations on the beaches at north of the DRE in relation the south (data not ploted). Iron and V showed opposite distribution. According to images retrieved from NASA's MetOP-A/ASCAT satellite, the direction of the ocean surface wind during the sampling period may have contributed to the increased concentrations of some elements at north of the Doce river mouth. Abnormal water metal values for beaches outside the influence of the Doce river plume may be associated with contamination from other hydrographic basins, and consequently its estuaries such as Santa Maria de Vitória river (Martins et al., 2019), Itapemirim river (Queiroz et al., 2018), Paraíba do Sul river (Molisani et al., 1999), among others.

Dynamic and concentration of elements in sediment

The highest concentration in the surface sediment for almost all metals were present in the fraction <63 µm (Fig. S1). Only the metals Al, Ba, Cd and Sr showed no statistical difference between the fractions. Furthermore, like the other elements, all of them showed an increase tendency in metal concentrations in the finest sediment fraction, due to the larger contact surface of the grains, in addition to the negative presence of charges in the sediment, which favors the metals binding.

For the surface sediment metal concentration only Mo and Se remain below de detection limit for <2mm sediment fraction (Table S1). For the elements that were quantified, the highest concentrations were in Fe, Al, Ti, Mn, Ba, V, Cr, Zn, Sr, As, Ni, Cu, Pb, Cd for DRE; Fe, Al, Ba, Ti, Mn, Sr, V, Zn, Cu, Cr, Pb and Ni for other estuaries and Al, Fe, Sr, Ba, Ti, Mn, As, V, Cr, Zn, Cu, Ni and Pb for beaches. Furthermore, only the elements Cr ($F = 4.69$, $p = 0.0183$), Fe ($F = 4.90$, $p = 0.0147$), Mn ($F = 6.70$, $p = 0.0041$), Ti ($F = 5.65$, $p = 0.0084$), V ($F = 5.49$, $p = 0.0095$) and Zn ($F = 7.33$, $p =$

0.0034) statistically differs between DRE and beach, showing higher concentrations for all metals in the DRE. While Al ($F = 5.98$, $p = 0.0067$) and Cu ($F = 10.99$, $p = 0.0010$) differs from beach to the DRE and other estuaries, showing higher concentrations on beaches, and Ba ($F = 3.40$, $p = 0.0472$) differs between beach and other estuaries, with higher values on other estuaries (Table S1).

For the fraction <63 µm (Table S2), there was a predominance of Fe, Al, Ti and Mn for DRE and other estuaries. Regarding the other elements DRE followed with the highest concentrations in Cr, V, Ba, Zn, Ni, Sr, Pb, As, Cu, Mo and Cd, while Cu, Ba, Cr, Sr, V, Zn, Ni, Pb, As, Mo and Cd were higher in other estuaries; beaches showed the predominance of Fe, Ti, Al, Cr, Mn, Ni, Sr, V, Ba, Pb, Mo, Zn, As, Cu, Se and Cd. Besides that, only Al ($F = 3.54$, $p = 0.0413$) and Fe ($F = 3.70$, $p = 0.0362$) were different between the DRE and beach, showing higher concentrations on DRE, while Cu ($F = 4.65$, $p = 0.0177$) and Sr ($F = 3.54$, $p = 0.0022$) in other estuaries and DRE differs from the rest, respectively.

The presence of some minerals (i.e kaolinite, gibbsite, goethite and hematite) in the finer sediment fraction, as well as the presence of OM and the larger contact surface increase the metal retention capacity for this compartment (Silva et al., 2018; Vane et al., 2020). In fact, according to Duarte et al. (2020), the finest sediment fractions of the Doce river were composed of quartz, kaolinite, muscovite and gibbsite, and after the dam rupture there was the appearance of hematite and goethite minerals. However, the sediment of the Doce river is mostly composed of the sand fraction (Silva et al., 2018; Duarte et al., 2020), and they are under negative ΔpH values (the authors obtained the values by the difference between the pH in KCl and the pH in H_2O), which favors the prevalence of negative charges on the sediment surface, allowing the adsorption of metals even in gross sediments (Silva et al., 2018). These results may explain the fluctuation in the concentrations found in our study for the metals between the fractions (Fig. 4).

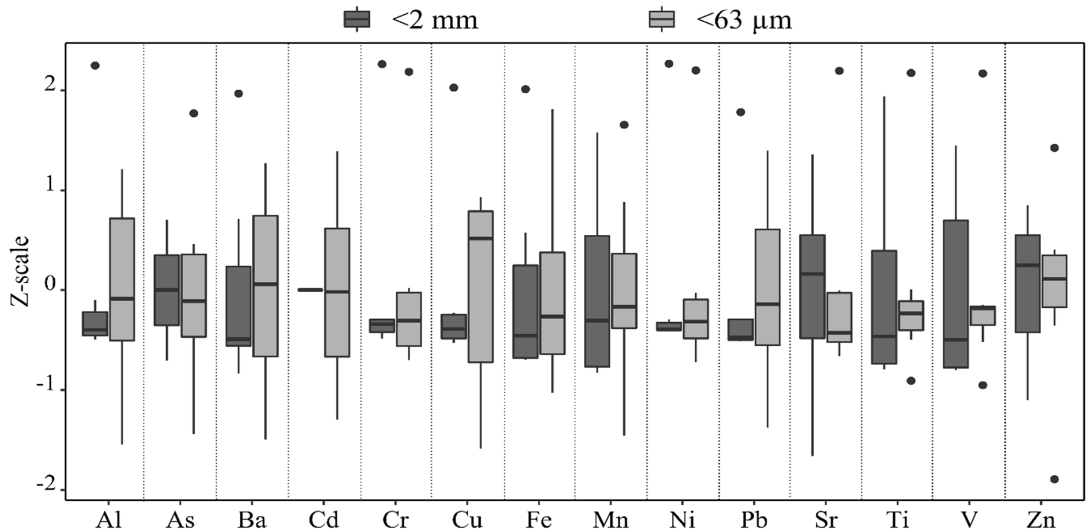

Figure 4. Variation of total metal concentration between sediment fractions of DRE. Data were transformed to Z-scale to make the variables comparable. Since the metals Mo and Se presented values <DL the data where no plotted.

The levels of metals in the sediment (<2mm) observed in the present study are higher than those found by Gomes et al. (2017) 2 days after tailings arrival in the estuary for Al, Ba, Cr, Fe and Zn elements, suggesting that most elements were still in suspension in the water column, and suffered deposition over time, increasing their concentrations. However, they are considerably lower than those found by Vergilio et al. (2020) 15 days and 6 months across the river, and Viana et al. (2020) 30 days after the tailing's arrival in the estuarine zone. This indicates that the estuarine area suffers resuspension processes that are acting transporting the metals to the marine areas, mainly as dissolved fraction.

Nevertheless, despite the values being below those found by the authors, some elements are still in disagreement with the values describe by the National Oceanic and Atmospheric Administration (NOOA; Buchman. 2008) of TEL (Ba, Cd and Cu) and PEL (As and Cr) for in the fraction <2 mm, and TEL (As, Cd, Ni, Pb and Zn) and PEL (As, Cr and Ni) for in the fraction <63 µm (Table S1 and S2) in DRE. Nonconformity levels were also observed in marine areas at north and south of Doce river mouth, above TEL (As and Ba) for fraction <2mm and above TEL (As, Ba, Cd, Cr, Cu, Ni, Pb and Zn) or PEL (As, Cr, Cu, Ni and Pb) for fraction <63 µm. The data indicate the transport of elements to the coast, mainly by the particulate and dissolved fraction after sediment resuspension events. These results alert for the risk of induction of toxic effects for biota from Doce river estuary and adjacent areas.

Models of OM and metals transport for marine areas with Doce river influence

The carbon isotopic composition of the sediment along the Doce river plume (Fig. 5), shows the dispersion pattern mainly to the north but also in areas closer to south of the Doce river mouth. Although the dispersion pattern of the isotopic composition of the sediment is relatively similar between the two fractions, it is still possible to observe the enrichment of $\delta^{13}C$ in the finer fraction, mainly due to the larger contact surface of the grain, according to Bai et al. (2012), who observed a positive and significant correlation of $\delta^{13}C$ values with silt+clay grains, and negative and significant correlation with sand. Thus, a greater dispersion of the <63 µm fraction is expected, especially as they are finer sediments and capable to travel longer distances (Fig. 5b).

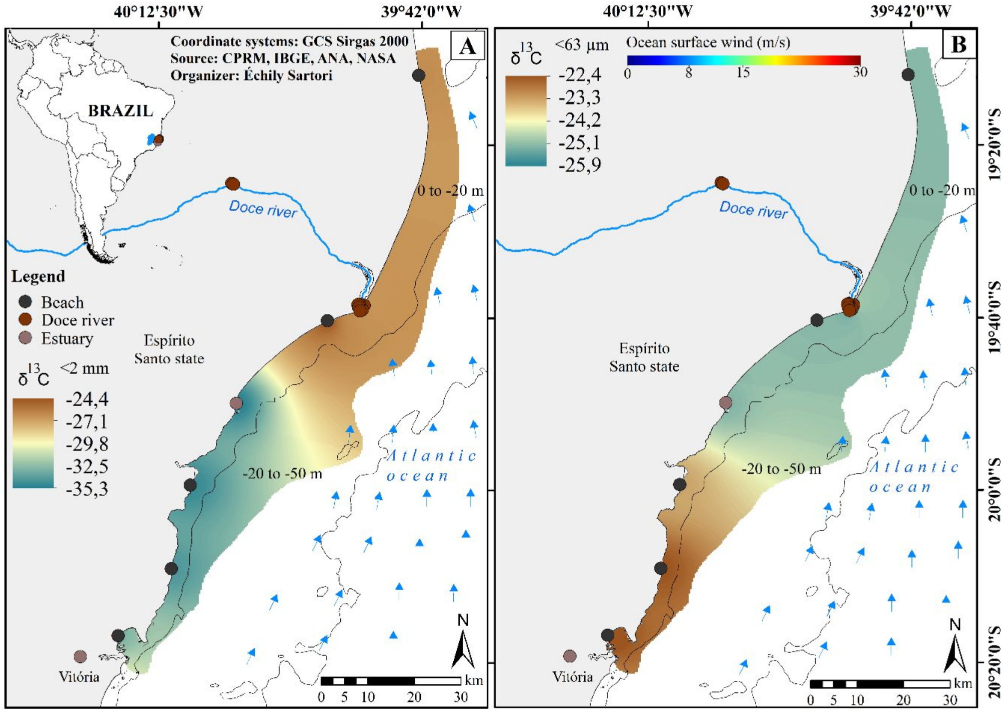

Figure 5. δ^{13}C distribution along the Doce river plume influence zone. In (A) sediment fraction <2 mm and (B) <63 µm. The interpolation results were fitted using IDW in ArcGIS software (ArcMap 10.5 version 10.5.0.6491; https://desktop.arcgis.com/en/). Ocean surface wind vector (L2. 12.5 Km) data were retrieved from MetOP-A/ASCAT.

In addition, the DRE had the highest Corg means in sediment fraction <2 mm (0.55 ± 1.24), and the second highest mean for a fraction <63 µm (1.02 ± 0.68), being behind other estuaries (1.86 ± 0.29). Besides, the dispersion pattern was similar to Fig 5, evidencing the plume's transport to the north and the closest areas of the Doce river mouth. The distribution of fine sediments (Fig 6a) and Corg (Fig 6b, c) along the coast plays an important role in the dispersion and bioavailability of trace elements, due to the affinity that these elements have to the finer sediments, in addition to their ability sorption of metallic ions to Corg, directly influencing the bioavailability of the elements, where it acts mainly as a sink of metals, affecting the dispersion of the elements (Iftikhar et al., 2021).

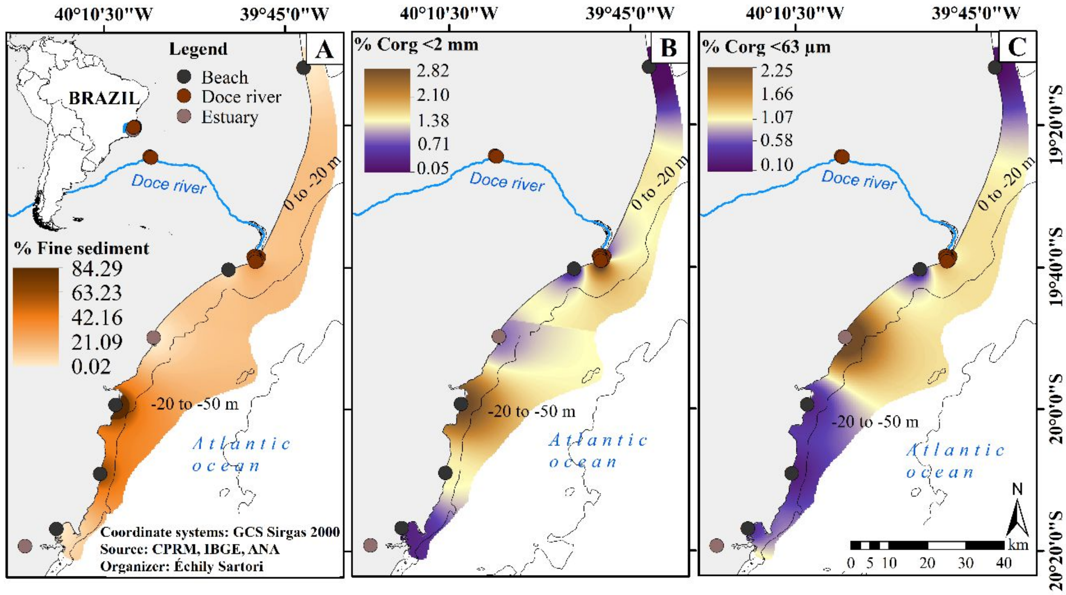

Figure 6. Distribution of the finest sediments (fine sand and Silt+Clay) (A) and Corg <63µm (B) along the Doce river plume influence zone. IDW in ArcGIS software (ArcMap 10.5 version 10.5.0.6491; https://desktop.arcgis.com/en/).

Moreover, the multi-elementary analysis (Fig. 7) shows the same behavior observed by the distribution of $\delta^{13}C$ for most elements (Fig. 7a and 7b) with a slight increase in concentrations near the Doce river mouth, especially towards the north, while only Sr (Fig. 7c) showed a different behavior. Our study found similar patterns to those found by Richard et al. (2020) between the years 2015 and 2017, where metal concentrations are tending to decrease in the DRE over the years, through its transport to the continental shelf. In addition, the author observed finer sediment compositions, especially in the areas closest to the Doce river mouth, being associated with the tailing's composition, since Golder (2016) finds a material with orange features, directly related to the characteristics of iron ore tailings, which may be contributing to the release of metals in this region. Moreover, Quaresma et al. (2021) in study in the continental shelf of Espírito Santo state before and after the dam rupture (6 months and 1 year later) noticed the enrichment of some metals (Zn, Pb, Ni, Cr, Cu and Fe), classifying the areas as ultrahigh contaminated according to modified degree of contamination. These results are supported by our principal component analysis (Fig. 8), where an association of most elements in the both sediment fractions (<2 mm and <63 µm), and the grains of the silt-clay fraction with the points located in the DRE was observed, while the other metals were associated especially with beach points and Santa Maria de Vitória river. Fluctuations and increases of metal concentrations in other estuaries and nearby areas, especially the Santa Maria de Vitória river are seen by Martins et al. (2019). The authors attribute that the high concentrations of Pb, Cu, Cr and As are mainly caused by human activities in the port area of the region.

Thus, the Doce river has been shown to be a major contributor to the increase in metal concentrations along the Brazilian coast after the dam collapse, mainly on the continental shelf of the Espírito Santo state, indicating the importance of long-term monitoring studies, since the elements have the ability to cause toxic effects to organisms, in addition to their capacity to bioaccumulate and biomagnify along to the trophic chain.

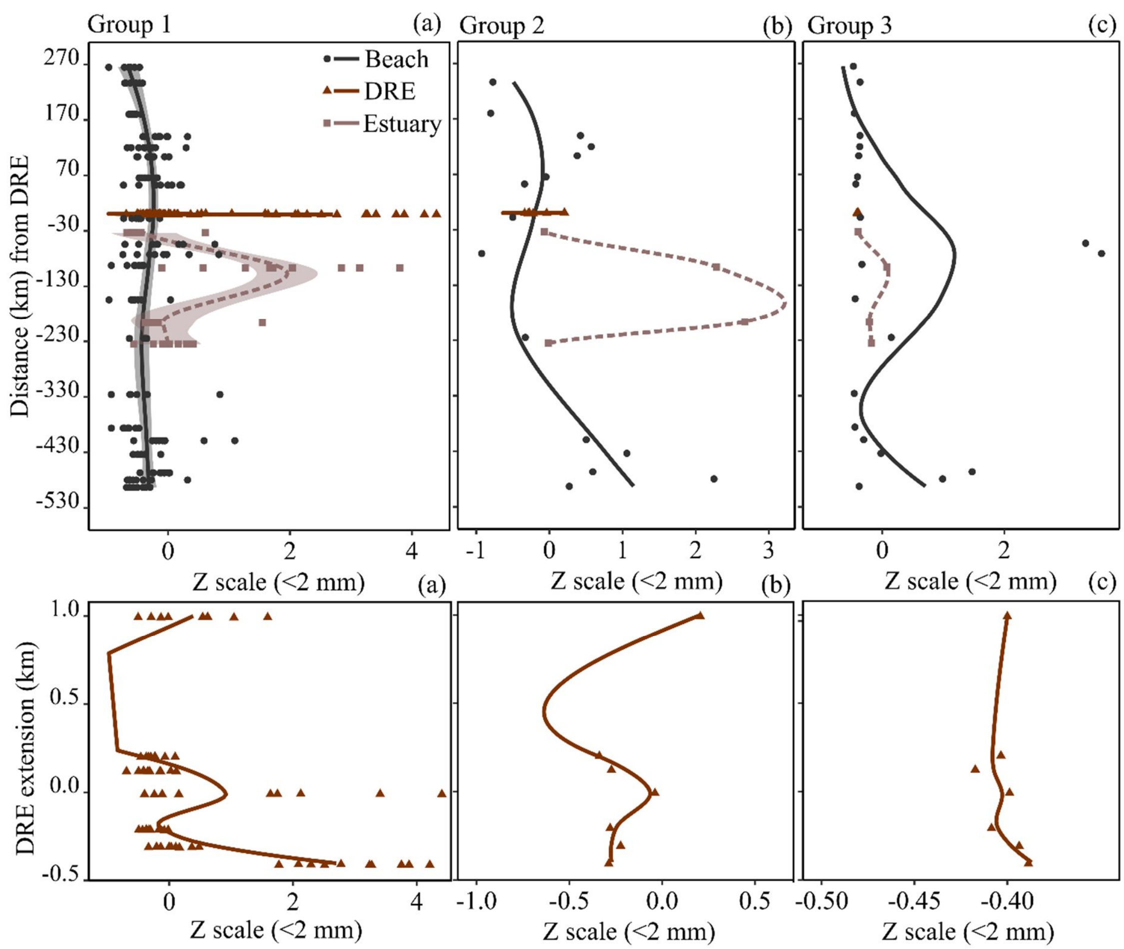

Figure 7. Association and dynamic of surface sediment metals along the Brazilian coast and DRE extension. Data were transformed to z-scale to make the variables

comparable. Positive and negative km are north and south of the DRE central point (km 0), respectively. Group 1 is composed of Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn; group 2 of Ba, and group 3 of Sr. Shadow indicates 95% of confidence interval. Since the other plot have only one value per site, it was not possible to construct the confidence interval.

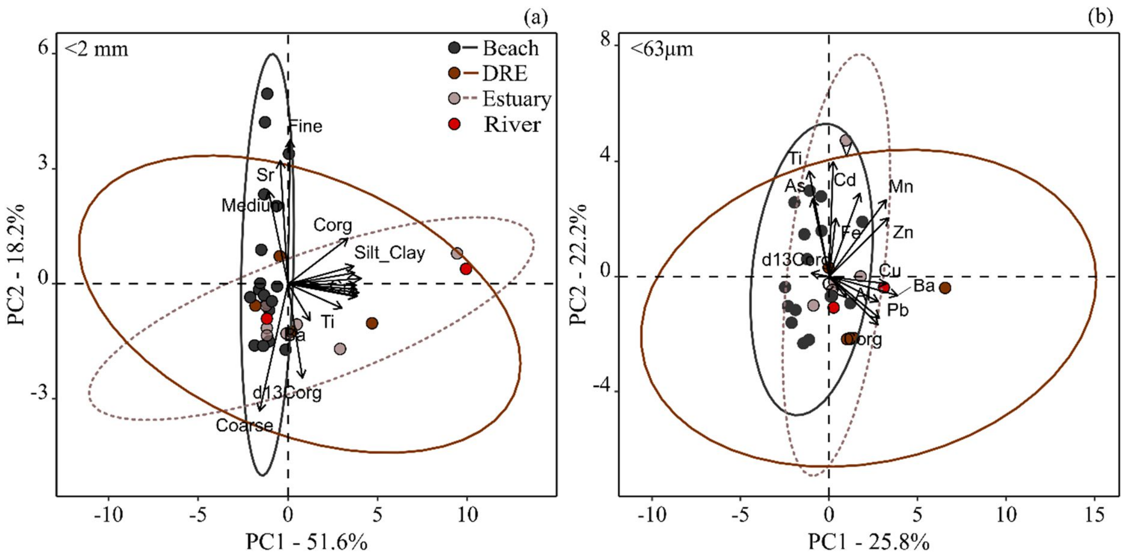

Figure 8. Principal component analysis (PCA) using the total metal concentrations of the two sediment fractions, particle size characterization (coarse, medium, fine sand and silt-clay), Corg and δ^{13}C. In (a) sediment fraction <2 mm and (b) <63 μm Ellipses were constructed using a 95% of confidence interval.

Enrichment factor

Regarding the enrichment factor for fraction <2 mm, both north and south of the Doce river mouth presented mostly low to moderate enrichment for almost all metals, except for some beaches to the south with enrichments of moderate-severe for Fe, Zn, Mn and Cu, and very severe for Sr (Table S5). The enrichment of metals characteristic of iron ore tailings from beaches at south of the Doce river, especially close to the Vitoria capital, may be associated with the city's port presence, where the main export cargoes are minerals. While, the fraction <63 μm already presents enrichment values from moderate to severe for almost all metals in areas mainly north of the Doce river mouth (Table S6). The results of the enrichment values are in agreement with those found in the present work, where the main areas affected after 4 years of the dam failure are located mainly in areas close to the river mouth and to the north, especially for the thinnest sediment fraction, characteristic of the tailings. Furthermore, values with enrichment above 1.5 suggest that the sources of those elements are more linked to be anthropogenic (Ghrefat et al., 2010), corroborating our results in relation to the elements enrichment in regions close to the Doce River mouth after the dam rupture.

Conclusion

The present study demonstrated that even after 4 years of the Fundão dam collapse in Mariana-MG, the Doce river continues with high metal concentrations in the sediment and continues to contribute to the enrichment of these elements on the continental shelf, especially towards the north and nearby its mouth, mainly through the tailings that were settled in sediment deposition zones, and that were probably resuspended and released to the water column, being available for transport and deposition in the coastal region, specially through SPM and dissolved fractions. Furthermore, our results showed low elements concentrations in the dissolved and particulate fraction in relation to the sediment, evidencing the deposition of the material over time. However, when compared to other studies, the metal concentrations in the DRE sediment remain lower than the concentrations found by other authors, suggesting the transport of this material along the Brazilian coast.

Our results show the OM transport from the DRE to the continental shelf, through Corg concentrations and carbon and nitrogen isotopic composition, where DRE and marine regions to the north and close to its mouth showed similar Corg concentrations and isotopic signature. These data reinforce the application of the C and N isotopic signature a tool for differentiate the areas impacted by the mining tailing in marine environment in the case of Doce river.

In this way, our results contribute to the monitoring of the Doce river and nearby regions after the collapse of an iron ore dam, highlighting the continuous need for long-term studies, especially due to the probability of resuspension of this fine material deposited in dams along the river and other deposition zones, since this material contains high metal concentrations metals, which contribute to the habitat quality reduction, in addition to having the potential to accumulate in organisms, causing toxic effects.

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Supplementary material

Figure S 1: Variation of total metal concentration between sediment fractions. Data were transformed to Log_{10} to make the variables comparable. Since the metals Mo and Se presented values <DL for <2 mm fraction, the data where no plotted. Different letters indicate statical difference among the sediment fractions.

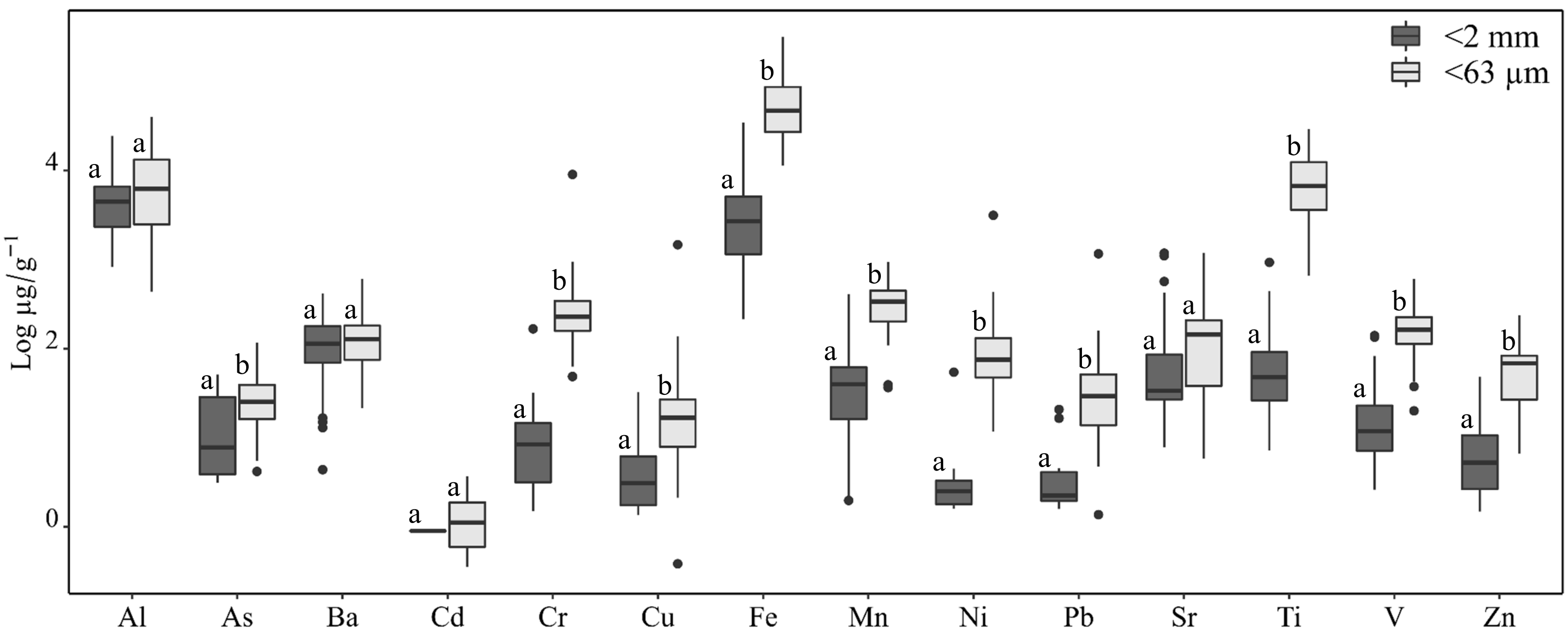

Table S 1. Sediment metal (<2 mm) concentration from different sampling sites and different groups (mean and SD) along the southeastern Brazilian coast. Different letters indicate statistical difference between groups ($p < 0.05$). Concentrations are presented in $\mu g.g^{-1}$. Bold indicate concentrations in $mg.g^{-1}$. Orange and red values are above TEL (Threshold Effect Level) and PEL (Probable Effect Level) levels respectively.

Site	Group	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Ti	V	Zn
Alcobaça	Beach	**0.82**	<DL	13.02	<DL	<DL	1.36	**0.47**	1.97	<DL	<DL	7.73	27.42	5.67	2.58
Caravelas	Beach	**2.01**	<DL	56.77	<DL	2.30	<DL	**1.25**	10.61	<DL	<DL	39.17	26.85	6.44	2.02
Mucuri	Beach	**2.42**	<DL	53.74	<DL	1.57	1.67	**1.07**	19.57	<DL	<DL	12.35	9.46	3.90	2.62
Itaúnas	Beach	**6.67**	8.54	180.22	<DL	14.66	<DL	**5.02**	52.09	3.06	<DL	39.04	89.36	19.62	5.88
Conceição da Barra	Beach	**6.57**	4.16	195.51	<DL	8.65	1.45	**2.98**	32.58	2.52	3.11	37.82	42.25	10.84	4.55
Guriri	Beach	**5.30**	<DL	175.65	<DL	7.77	<DL	**4.76**	36.81	1.59	1.98	32.70	70.40	13.91	4.17
Urussuquara	Beach	**4.37**	<DL	131.69	<DL	9.56	<DL	**2.69**	28.06	1.62	2.21	27.08	44.67	11.10	4.64
Pontal do Ipiranga	Beach	**4.30**	3.10	101.46	<DL	21.41	2.46	**6.74**	72.14	4.21	<DL	19.11	149.65	30.85	10.28
Doce 7	DRE	**5.27**	<DL	157.65	<DL	10.74	<DL	**9.80**	115.72	2.05	1.93	29.09	406.33	59.68	17.81
Doce 2	DRE	**5.67**	<DL	101.56	<DL	7.86	5.75	**2.95**	46.42	2.03	2.24	28.08	51.10	11.98	<DL
Doce 3	DRE	**4.58**	3.87	108.41	<DL	18.07	6.51	**2.60**	53.14	1.76	2.03	24.16	36.79	10.67	<DL
Doce 5	DRE	**4.70**	<DL	132.54	<DL	19.36	3.08	**17.47**	258.03	2.69	<DL	29.42	923.39	139.83	31.68
Doce 1	DRE	**5.01**	<DL	107.63	<DL	12.42	3.59	**2.65**	51.89	1.80	<DL	26.60	59.09	12.24	<DL
Doce 4	DRE	**7.41**	<DL	113.49	<DL	16.16	3.61	**5.39**	99.73	4.01	3.73	30.86	143.49	28.06	<DL
Doce 6	DRE	**24.27**	51.18	106.58	0.90	166.41	32.45	**34.20**	292.71	54.45	20.82	32.32	438.90	134.13	37.80
Comboios reserve	Beach	**3.87**	3.15	84.82	<DL	10.78	1.54	**1.85**	26.72	1.77	1.84	40.16	24.94	8.06	<DL
Riacho	Estuary	**3.22**	<DL	128.98	<DL	1.49	11.16	**1.14**	14.95	<DL	<DL	30.42	7.14	3.86	2.22
Formosa	Beach	**2.03**	28.67	18.24	<DL	7.26	<DL	**7.05**	82.11	<DL	<DL	1095.35	24.96	18.08	8.28
Jacaraipe	Beach	**1.87**	29.77	41.01	<DL	8.35	<DL	**5.03**	97.48	<DL	<DL	1169.63	57.76	21.79	4.25
Camburi	Beach	**1.01**	<DL	16.71	<DL	2.84	<DL	**1.14**	16.64	<DL	<DL	47.77	34.26	8.01	2.25
Santa Maria de Vitória	Estuary	**12.79**	<DL	371.70	<DL	32.17	19.95	**26.47**	408.22	4.47	16.60	165.15	346.38	82.58	48.21
Ubu	Beach	**0.84**	<DL	4.35	<DL	1.71	1.92	**0.67**	9.94	<DL	<DL	16.16	22.55	5.52	10.84
Itapemirim	Estuary	**12.24**	<DL	412.00	<DL	5.36	3.91	**2.53**	52.03	<DL	3.67	83.26	49.92	11.66	7.63
Presidente Kennedy	Beach	**3.64**	<DL	102.53	<DL	3.15	<DL	**2.22**	33.36	<DL	<DL	185.39	43.65	12.17	2.71

Itabapoana	Estuary	**7.11**	<DL	134.78	<DL	7.60	<DL	**5.34**	58.83	<DL	1.58	92.46	169.71	29.82	10.14
Farol de São Thomé	Beach	**1.01**	<DL	0.29	<DL	<DL	13.09	**0.58**	10.05	<DL	<DL	11.93	50.91	6.93	<DL
Quissamã	Beach	**1.02**	<DL	15.01	<DL	<DL	2.47	**0.21**	2.18	<DL	<DL	14.95	15.11	2.60	1.48
Macaé	Beach	**7.90**	<DL	188.35	<DL	8.96	1.78	**4.09**	43.30	2.48	4.55	55.92	97.22	22.51	23.53
Rio das Ostras	Beach	**4.68**	<DL	245.61	<DL	3.44	<DL	**1.85**	22.17	<DL	<DL	136.76	21.00	9.34	3.43
Búzios	Beach	**4.08**	7.72	197.58	<DL	15.51	<DL	**4.74**	56.66	2.71	4.47	564.09	88.88	24.43	10.66
Cabo Frio	Beach	**6.68**	<DL	368.36	<DL	2.60	<DL	**0.54**	6.43	<DL	1.84	425.56	7.79	2.63	7.07
Arraial do Cabo	Beach	**3.89**	<DL	164.39	<DL	2.50	1.71	**0.49**	8.97	<DL	<DL	34.90	45.92	7.16	2.14
Mean (Beach)		**3.57** a	12.16 a	112.16 a		7.39 a	2.95 a	**2.64** a	31.90 a	2.49 a	2.86 a	191.12 a	47.38 a	11.98 a	5.97 a
SD (Beach)		**2.20**	11.85	97.24		5.58	3.58	**2.17**	26.93	0.88	1.21	344.16	34.99	7.93	5.23
Mean (DRE)		**8.13** b	27.53 a	118.27 ab	0.90	35.86 b	9.16 b	**10.72** b	131.09 b	9.83 a	6.15 a	28.65 a	294.16 b	56.66 b	29.09 b
SD (DRE)		**7.18**	33.45	20.01		57.71	11.49	**11.67**	102.45	19.69	8.24	2.70	324.74	57.49	10.24
Mean (Other estuary)		**8.84** b		261.86 b		11.65 ab	11.67 b	**8.87** ab	133.51 ab	4.47 a	7.28 a	92.82 a	143.29 ab	31.98 ab	17.05 ab
SD (Other estuary)		**4.54**		151.01		13.91	8.03	**11.86**	184.15		8.14	55.43	151.88	35.45	21.03
TEL freshwater (ppm)			5.90		0.60	37.30	35.70			18.00	35.00				123.00
TEL marine (ppm)			7.24	130.00	0.68	52.30	18.70			15.90	30.24				124.00
PEL freshwater (ppm)			17.00		3.53	90.00	197.00			36.00	91.30				315.00
PEL marine (ppm)			41.60		4.21	160.0	108.00			42.80	112.0				271.00

Mo and Se showed values below of the detection limit (DL; <0.012 and <0.009).
DL of As <0.009; Cd <0.001; Cr <0.004; Cu <0.004; Ni <0.004 ; Pb <0.004 and Zn <0.003.

Table S 2. Sediment (<63 µm) metal concentration from different sampling sites and different groups (mean and SD) along the southeastern Brazilian coast. Different letters indicate statistical difference between groups ($p < 0.05$). Concentrations are presented in $\mu g.g^{-1}$. Bold indicate concentrations in $mg.g^{-1}$. Orange and red values are above TEL (Threshold Effect Level) and PEL (Probable Effect Level) levels respectively.

Site	Group	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se
Alcobaça	Beach	**3.36**	19.78	35.28	<DL	**0.22**	2.93	**16.42**	**0.11**	8.06	99.82	4.70	<DL
Caravelas	Beach	**3.70**	54.80	78.68	1.67	**0.23**	5.37	**111.26**	**0.35**	<DL	70.34	50.98	<DL
Mucuri	Beach	**6.06**	23.18	108.83	0.39	**0.54**	13.54	**27.29**	**0.23**	<DL	202.89	39.64	<DL
Itaúnas	Beach	**10.53**	38.27	123.16	0.86	**0.18**	7.85	**114.49**	**0.15**	5.47	63.15	7.89	<DL
Conceição da Barra	Beach	**6.41**	117.02	105.63	3.67	**0.57**	21.81	**68.60**	**0.44**	<DL	192.89	37.31	<DL
Guriri	Beach	**14.00**	33.92	141.74	1.76	**0.15**	15.06	**309.49**	**0.40**	<DL	50.19	20.52	<DL
Urussuquara	Beach	**0.89**	44.98	35.41	2.51	**0.54**	10.83	**204.48**	**0.26**	<DL	190.40	36.78	<DL
Pontal do Ipiranga	Beach	**2.27**	68.84	64.67	2.05	**0.25**	23.16	**129.53**	**0.58**	5.23	80.04	1.37	<DL
Doce 7	DRE	**23.88**	44.11	215.39	1.37	**0.55**	18.47	**114.90**	**0.32**	<DL	195.29	40.16	<DL
Doce 2	DRE	**6.92**	22.10	146.15	1.18	**0.20**	9.52	**44.00**	**0.37**	4.33	67.33	17.01	<DL
Doce 3	DRE	**24.13**	28.81	235.94	2.08	**0.21**	17.64	**78.33**	**0.71**	<DL	59.61	42.31	<DL
Doce 5	DRE	**11.81**	19.85	178.61	2.34	**0.16**	7.87	**150.30**	**0.93**	<DL	49.60	15.43	<DL
Doce 1	DRE	**0.43**	6.52	31.51	<DL	**0.13**	3.60	**72.41**	**0.04**	<DL	50.80	5.20	<DL
Doce 4	DRE	**15.92**	26.41	100.90	1.77	**0.12**	17.60	**58.28**	**0.41**	<DL	32.75	23.40	<DL
Doce 6	DRE	**12.96**	15.98	84.61	1.69	**0.10**	16.02	**58.63**	**0.41**	<DL	27.55	21.69	<DL
Comboios reserve	Beach	**0.84**	13.18	100.79	<DL	**0.28**	0.39	**16.08**	**0.15**	16.29	111.71	8.93	<DL
Riacho	Estuary	**13.30**	30.34	134.21	0.90	**0.64**	82.26	**69.49**	**0.31**	8.59	223.05	149.45	<DL

Formosa	Beach	**3.23**	39.60	54.68	0.46	**0.05**	31.17	**30.22**	**0.20**	<DL	13.97	9.17	<DL
Jacaraípe	Beach	**1.94**	41.83	35.02	0.61	**0.07**	28.39	**51.71**	**0.43**	<DL	11.99	16.40	<DL
Camburi	Beach	**2.51**	22.53	55.14	0.55	**0.20**	17.98	**38.19**	**0.19**	6.96	84.34	9.10	<DL
Santa Maria de Vitória	Estuary	**13.13**	13.78	606.46	1.82	**0.19**	1456.10	**124.54**	**0.82**	12.08	41.64	159.61	<DL
Ubu	Beach	**0.92**	<DL	21.47	0.55	**0.36**	10.06	**11.29**	**0.04**	5.30	131.91	15.83	<DL
Itapemirim	Estuary	**31.07**	13.94	294.81	0.78	**0.24**	36.99	**42.00**	**0.27**	11.64	100.21	37.36	<DL
Presidente Kennedy	Beach	**0.82**	8.35	119.79	1.05	**0.31**	7.17	**23.64**	**0.16**	<DL	130.74	140.41	<DL
Itabapoana	Estuary	**4.10**	34.92	145.63	2.47	**0.06**	19.79	**49.09**	**0.48**	4.22	24.41	23.46	<DL
Farol de São Thomé	Beach	**18.86**	43.33	187.91	3.25	**0.22**	41.34	**14.16**	**0.49**	<DL	67.41	65.56	<DL
Quissamã	Beach	**39.45**	17.11	277.67	0.83	**0.94**	88.81	**32.10**	**0.45**	77.01	429.80	52.83	4.58
Macaé	Beach	**13.01**	5.48	224.24	0.65	**0.23**	7.64	**25.50**	**0.49**	<DL	32.27	54.88	<DL
Rio das Ostras	Beach	**2.34**	24.38	139.94	0.39	**0.34**	<DL	**33.54**	**0.22**	<DL	119.79	88.30	<DL
Búzios	Beach	**6.84**	37.26	132.02	<DL	**9.00**	136.45	**42.59**	**0.35**	410.89	3108.31	1152.46	11.94
Cabo Frio	Beach	**4.45**	4.16	144.34	0.46	**0.05**	2.11	**16.56**	**0.25**	<DL	11.83	10.10	<DL
Arraial do Cabo	Beach	**4.56**	<DL	272.58	0.35	**0.27**	<DL	**14.69**	**0.12**	<DL	92.04	38.45	4.39
Mean (Beach)		**7.00** a	34.63 a	117.09 a	1.23 a	**0.71** a	24.84 a	**63.42** a	**0.29** a	66.90 a	252.18 a	88.65 a	6.97
SD (Beach)		**8.90**	26.34	74.25	1.03	**1.91**	33.70	**74.97**	**0.15**	141.13	660.92	246.02	4.30
Mean (DRE)		**13.72** b	23.40 a	141.87 a	1.81 a	**0.21** a	12.96 a	**82.41** b	**0.46** a	4.33 a	68.99 a	23.60 a	
SD (DRE)		**8.60**	11.70	73.89	0.43	**0.16**	5.90	**37.42**	**0.29**		57.42	13.40	
Mean (Other estuary)		**15.40** ab	23.24 a	295.28 a	1.61 a	**0.28** a	398.79 b	**71.28** ab	**0.47** a	9.14 a	97.33 a	92.47 a	
SD (Other estuary)		**11.29**	10.99	219.98	0.81	**0.25**	705.37	**37.37**	**0.25**	5.44	89.87	72.00	
TEL freshwater (ppm)			5.90		0.60	**0.04***	35.70				18.00	35.00	

TEL marine (ppm)	7.24	130.00	0.68	**0.05***	18.70				15.90	30.24
PEL freshwater (ppm)	17.00		3.53	**0.09***	197.00				36.00	91.30
PEL marine (ppm)	41.60		4.21	**0.2***	108.00				42.80	112.0

Site	Group	Sr	Ti	V	Zn
Alcobaça	Beach	**0.59**	**6.95**	95.65	16.16
Caravelas	Beach	**0.13**	**19.85**	276.92	60.70
Mucuri	Beach	**0.14**	**1.38**	59.34	31.41
Itaúnas	Beach	**0.06**	**5.01**	82.06	29.06
Conceição da Barra	Beach	**0.04**	**14.51**	242.67	86.45
Guriri	Beach	**0.01**	**13.17**	230.08	78.35
Urussuquara	Beach	**0.11**	**8.59**	141.30	52.68
Pontal do Ipiranga	Beach	**0.06**	**22.19**	313.75	82.65
Doce 7	DRE	**0.02**	**9.06**	163.48	92.07
Doce 2	DRE	**0.02**	**4.42**	100.71	66.73
Doce 3	DRE	**0.04**	**6.84**	162.64	96.57
Doce 5	DRE	**0.04**	**28.97**	599.45	136.39
Doce 1	DRE	**0.14**	**0.66**	20.09	6.61
Doce 4	DRE	**0.01**	**6.18**	162.72	85.01
Doce 6	DRE	**0.01**	**6.87**	168.75	81.10
Comboios reserve	Beach	**0.15**	**0.81**	37.56	25.36
Riacho	Estuary	**0.20**	**2.58**	134.11	89.30
Formosa	Beach	**1.18**	**12.13**	235.11	26.66

Jacaraipe	Beach	**1.05**		**27.12**		529.52		73.84	
Camburi	Beach	**0.18**		**8.70**		175.33		34.62	
Santa Maria de Vitória	Estuary	**0.21**		**5.60**		203.10		169.61	
Ubu	Beach	**0.10**		**0.87**		42.86		10.46	
Itapemirim	Estuary	**0.18**		**3.99**		120.05		81.45	
Presidente Kennedy	Beach	**0.21**		**6.56**		117.29		25.15	
Itabapoana	Estuary	**0.37**		**6.41**		223.24		79.02	
Farol de Sao Thomé	Beach	**0.01**		**3.20**		383.17		236.09	
Quissamã	Beach	**0.21**		**13.86**		222.21		70.24	
Macaé	Beach	**0.06**		**13.11**		194.26		74.47	
Rio das Ostras	Beach	**0.31**		**3.26**		136.22		26.87	
Búzios	Beach	**0.17**		**3.69**		123.82		53.60	
Cabo Frio	Beach	**0.23**		**8.38**		119.18		23.19	
Arraial do Cabo	Beach	**0.16**		**1.87**		59.27		14.42	
Mean (Beach)		**0.25**	a	**9.30**	a	181.79	a	53.93	a
SD (Beach)		**0.32**		**7.35**		122.73		48.60	
Mean (DRE)		**0.04**	b	**9.00**	a	196.84	a	80.64	a
SD (DRE)		**0.05**		**9.19**		185.66		39.13	
Mean (Other estuary)		**0.24**	a	**4.65**	a	170.13	a	104.85	a
SD (Other estuary)		**0.09**		**1.70**		50.70		43.40	
TEL freshwater (ppm)								123.00	
TEL marine (ppm)								124.00	

PEL freshwater (ppm)	315.00
PEL marine (ppm)	271.00

*TEL and PEL values were converted to $mg.g^{-1}$ for results comparison for the bold values.
DL of Cd <0.001; Mo <0.012 and Se <0.009.

Table S 3. Suspended particulate matter and dissolved metal concentration from different sampling sites and different groups (mean and SD) along the southeastern Brazilian coast. Different letters indicate statistical difference between groups ($p < 0.05$).

		Dissolved (mg.L^{-1})			SPM (mg.L^{-1})			
Site	**Group**	**Al**	**Ba**	**V**	**Al**	**Ba**	**Fe**	**Sr**
Caravelas	Beach	<DL	0.030	0.002	24.13	<DL	6.81	0.54
Doce 2	DRE	0.042	0.085	0.002	59.71	<DL	11.76	1.51
Doce 1	DRE	0.057	0.059	0.002	70.71	<DL	14.88	1.69
Riacho	Estuary	<DL	0.026	0.002	49.85	1.49	30.47	1.49
Santa Maria de Vitória	Estuary	<DL	0.034	0.002	22.03	<DL	11.81	0.29
Itapemirim	Estuary	<DL	0.022	0.002	89.94	2.14	14.82	2.50
Itabapoana	Estuary	<DL	0.030	0.002	84.40	1.33	21.82	1.83
	Mean (Beach)		0.030^{ab}	0.002^{a}	24.13^{a}		6.81^{a}	0.54^{a}
	SD (Beach)							
	Mean (DRE)	0.049	0.072^{a}	0.002^{a}	65.21^{a}		13.32^{b}	1.60^{a}
	SD (DRE)	0.011	0.019	0.000	7.78		2.20	0.13
	Mean (Other estuary)		0.028^{b}	0.002^{a}	61.55^{a}	1.66	19.73^{b}	1.52^{a}
	SD (Other estuary)		0.005	0.000	31.76	0.43	8.30	0.92
	CONAMA 357 brackish waters	0.1						

Dissolved As (<0.0062), Cd (<0.0001), Cr (<0.0003), Cu (<0.0006), Fe (<0.0006), Mn (< 0.0004), Mo (<0.0014), Ni (<0.0005), Pb (<0.0022), Se (<0.0132), Sr (<0.0002), Ti (<0.003) and Zn (<0.0018) showed values below of the detection limit (DL).
SPM detection limits values are the same of sediment.
DL of dissolved Al < 0.0009.

Table S 4. Water metal concentration from different sampling sites and different groups (mean and SD) along the southeastern Brazilian coast. Different letters indicate statistical difference between groups ($p < 0.05$). Concentrations are presented in $mg.L^{-1}$.

Site	Group	Al	Ba	Cr	Cu	Fe	Mn	V
Alcobaça	Beach	0.014	0.033	0.001	0.038	0.350	0.026	5.670
Caravelas	Beach	0.300	0.062	<DL	0.070	0.941	0.021	6.438
Mucuri	Beach	0.109	0.059	<DL	0.080	0.283	0.013	3.904
Itaúnas	Beach	0.064	0.026	<DL	0.082	0.865	0.016	19.625
Conceição da Barra	Beach	0.191	0.043	0.001	0.083	0.788	0.119	10.838
Guriri	Beach	0.567	0.050	0.001	0.084	0.425	0.035	13.909
Urussuquara	Beach	0.614	0.016	<DL	0.026	0.237	0.046	11.097
Pontal do Ipiranga	Beach	0.280	0.050	<DL	0.084	0.457	0.039	30.849
Doce 7	DRE	0.056	0.026	<DL	0.081	0.676	0.025	59.681
Doce 2	DRE	0.387	0.097	<DL	<DL	0.268	0.028	11.977
Doce 3	DRE	0.820	0.108	<DL	<DL	0.316	0.031	10.673
Doce 5	DRE	0.519	0.047	<DL	0.146	0.322	0.058	139.829
Doce 1	DRE	0.585	0.098	<DL	<DL	0.182	0.020	12.241
Doce 4	DRE	0.699	0.146	<DL	<DL	0.217	0.020	28.057
Doce 6	DRE	1.689	0.213	<DL	<DL	0.388	0.028	134.129
Comboios reserve	Beach	0.006	0.104	<DL	<DL	0.171	0.031	8.058
Riacho	Estuary	0.005	0.026	<DL	0.125	0.518	0.023	3.855
Formosa	Beach	0.163	0.051	<DL	0.181	0.684	0.039	18.079
Jacaraípe	Beach	0.338	0.059	<DL	0.104	0.673	0.017	21.787
Camburi	Beach	0.078	0.072	<DL	0.094	0.103	0.051	8.013
Santa Maria de Vitória	Estuary	0.059	0.074	<DL	0.082	0.585	0.020	82.582
Ubu	Beach	0.256	0.050	<DL	0.093	0.433	0.015	5.515
Itapemirim	Estuary	0.372	0.055	<DL	0.094	0.648	0.053	11.661
Presidente Kennedy	Beach	0.478	0.071	0.004	0.099	0.461	0.057	12.167
Itabapoana	Estuary	<DL	0.052	<DL	<DL	<DL	0.003	29.817
Farol de São Thomé	Beach	0.046	0.038	<DL	<DL	0.158	0.013	6.927
Quissamã	Beach	0.059	0.043	<DL	0.093	0.465	0.094	2.601
Macaé	Beach	0.027	0.062	<DL	0.036	0.258	0.098	22.507
Rio das Ostras	Beach	0.016	0.085	<DL	0.058	0.122	0.014	9.340
Búzios	Beach	0.015	0.071	<DL	0.104	0.220	0.011	24.434
Cabo Frio	Beach	0.019	0.033	<DL	0.050	0.377	0.168	2.634
Arraial do Cabo	Beach	0.097	0.047	0.001	0.097	0.276	0.064	7.165
	Mean (Beach)	0.178 [a]	0.053 [a]	0.002	0.082 [a]	0.417 [a]	0.047 [a]	11.979 [a]
	SD (Beach)	0.189	0.020	0.001	0.034	0.246	0.041	7.935
	Mean (DRE)	0.679 [b]	0.105 [b]		0.113 [a]	0.339 [a]	0.030 [a]	56.655 [a]
	SD (DRE)	0.508	0.062		0.046	0.164	0.013	57.489
	Mean (Other estuary)	0.145 [ab]	0.052 [ab]		0.100 [a]	0.584 [a]	0.025 [a]	31.979 [a]

SD (Other estuary)	0.198	0.019		0.022	0.065	0.021	35.445
CONAMA 357 brackish waters			0.050			0.100	
CONAMA 357 saline waters		1.000	0.050			0.100	

As, Cd, Mo, N, Pb, Se, Sr, Ti and Zn showed values <DL. Total water detection limits values are the same of dissolved.
DL of total Al < 0.0009, Cr <0.0003, Cu <0.0006 and Fe <0.0006.

Table S 5. Enrichment factor from different sampling sites along the southeastern Brazilian coast for the sediment fraction <2 mm. Background values were taken from the median of the DRE data and points north and south of its mouth, due to the shape of its plume dispersion.

Site	Group	As	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Ti	V	Zn
Alcobaça	Beach					4.59	0.88	0.34			1.37	3.34	2.73	3.13
Caravelas	Beach				0.57		0.95	0.76			2.83	1.33	1.27	1.00
Mucuri	Beach				0.33	1.92	0.67	1.16			0.74	0.39	0.64	1.07
Itaúnas	Beach	1.3			1.10		1.15	1.12	0.79		0.85	1.34	1.16	0.88
Conceição da Barra	Beach	0.7			0.66	0.61	0.69	0.71	0.66	0.93	0.83	0.64	0.65	0.69
Guriri	Beach				0.73		1.37	0.99	0.52	0.73	0.89	1.32	1.04	0.78
Urussuquara	Beach				1.10		0.94	0.92	0.64	0.99	0.90	1.02	1.00	1.06
Pontal do Ipiranga	Beach	0.75			2.50	1.59	2.39	2.40	1.69		0.64	3.47	2.84	2.38
Doce 7	DRE		1.45		0.66		1.82	1.16	1.00	0.86	1.00	2.83	2.13	0.56
Doce 2	DRE		0.87		0.45	1.14	0.51	0.43	0.92	0.93	0.90	0.33	0.40	
Doce 3	DRE		1.15		1.28	1.60	0.56	0.61	0.98	1.04	0.95	0.29	0.44	
Doce 5	DRE		1.37		1.34	0.74	3.63	2.90	1.47		1.13	7.21	5.59	1.12
Doce 1	DRE		1.04		0.81	0.81	0.52	0.55	0.92		0.96	0.43	0.46	
Doce 4	DRE		0.74		0.71	0.55	0.71	0.71	1.39	1.18	0.75	0.71	0.71	
Doce 6	DRE		0.21	0.22	2.24	1.51	1.38	0.64	5.76	2.02	0.24	0.66	1.04	0.26
Comboios reserve	Beach	0.17	0.64		2.01	0.62	1.00	0.89	0.68	0.50	0.48	0.57	0.86	
Riacho	Estuary		1.18		0.33	5.44	0.74	0.60			0.44	0.20	0.50	0.38
Formosa	Beach	3.01	0.26		2.59		7.27	5.22			25.12	1.09	3.70	2.24
Jacaraipe	Beach	3.38	0.64		3.22		5.62	6.70			29.02	2.73	4.82	1.24
Camburi	Beach		0.49		2.03		2.36	2.13			2.20	3.01	3.30	1.22
Santa Maria de Vitória	Estuary		0.85		1.82	2.45	4.33	4.11	0.52	1.37	0.60	2.40	2.68	2.06
Ubu	Beach		0.15		1.47	3.59	1.67				0.89	2.38	2.72	7.06
Itapemirim	Estuary		0.99		0.32	0.50	0.43	0.55		0.32	0.32	0.36	0.39	0.34
Presidente Kennedy	Beach		0.83		0.62		1.27	1.18			2.36	1.06	1.38	0.41

Itabapoana	Estuary		0.56		0.77		1.57	1.07		0.23	0.60	2.12	1.74	0.78
Farol de Sao Thomé	Beach					20.28	1.21	1.28			0.55	4.45	2.83	
Quissamã	Beach		0.43			3.81	0.44	0.28			0.68	1.32	1.06	0.80
Macaé	Beach		0.70		0.82	0.35	1.08	0.71	0.47	0.61	0.33	1.09	1.18	1.63
Rio das Ostras	Beach		1.54		0.53		0.82	0.61			1.36	0.40	0.83	0.40
Búzios	Beach	0.40	1.42		2.75		2.43	1.79	0.99	1.16	6.42	1.93	2.48	1.43
Cabo Frio	Beach		1.62		0.28		0.17	0.12		0.29	2.96	0.10	0.16	0.58
Arraial do Cabo	Beach		1.24		0.47	0.69	0.26	0.30			0.42	1.05	0.76	0.30

The metals Mo and Se present values <DL. Al was removed since it was used as normalizing. EF < 1 indicates no enrichment ▭; <3 is minor enrichment ▭; 3–5 is moderate enrichment ▭; 5–10 is moderately severe enrichment ▭; 10–25 is severe enrichment ▭; 25–50 is very severe enrichment ▭.

Table S 6. Enrichment factor from different sampling sites along the southeastern Brazilian coast for the sediment fraction <63 µm. Background values were taken from the median of the DRE data and points north and south of its mouth. due to the shape of its plume d

Site	Group	As	Ba	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Sr	Ti	V	Zn
Alcobaça	Beach	0.69	0.56		1.37	0.35	0.21	0.52	2.14	1.61	0.24		10.06	0.93	0.75	0.41
Caravelas	Beach	1.74	1.13	1.25	1.28	0.58	1.30	1.50		1.03	2.35		2.05	2.41	1.97	1.41
Mucuri	Beach	0.45	0.95	0.18	1.82	0.89	0.19	0.62		1.82	1.11		1.35	0.10	0.26	0.45
Itaúnas	Beach	0.43	0.62	0.23	0.36	0.30	0.47	0.22	0.46	0.33	0.13		0.31	0.21	0.20	0.24
Conceição da Barra	Beach	2.14	0.87	1.58	1.83	1.36	0.46	1.11		1.63	0.99		0.33	1.01	1.00	1.16
Guriri	Beach	0.28	0.54	0.35	0.22	0.43	0.96	0.45		0.19	0.25		0.05	0.42	0.43	0.48
Urussuquara	Beach	5.94	2.11	7.80	12.49	4.88	9.95	4.75		11.63	7.05		7.05	4.34	4.18	5.10
Pontal do Ipiranga	Beach	3.55	1.51	2.50	2.22	4.08	2.46	4.08	2.06	1.91	0.10		1.54	4.38	3.63	3.13
Doce 7	DRE	1.08	0.80	0.43	1.85	0.63	0.86	0.43		2.09	1.00		0.53	0.72	0.55	0.59
Doce 2	DRE	1.87	1.87	1.28	2.30	1.11	1.14	1.69	1.87	2.48	1.47		1.87	1.21	1.16	1.47
Doce 3	DRE	0.70	0.87	0.65	0.71	0.59	0.58	0.94		0.63	1.05		1.15	0.54	0.54	0.61

Doce 5	DRE	0.99	1.34	1.48	1.10	0.54	2.28	2.51		1.07	0.78		2.21	4.65	4.04	1.76
Doce 1	DRE	8.79	6.42		23.64	6.70	29.80	2.67		29.80	7.14		241.18	2.86	3.68	2.32
Doce 4	DRE	0.97	0.56	0.83	0.58	0.89	0.66	0.82		0.52	0.88		0.43	0.73	0.81	0.81
Doce 6	DRE	0.72	0.58	0.98	0.62	1.00	0.81	1.00		0.54	1.00		0.37	1.00	1.04	0.95
Comboios reserve	Beach	3.11	3.83		6.31	0.07	2.66	2.86	7.44	6.45	1.23		3.95	0.77	1.47	2.51
Riacho	Estuary	0.45	0.32	0.46	0.90	0.97	0.72	0.38	0.25	0.81	1.30		0.33	0.15	0.33	0.56
Formosa	Beach	2.42	0.54	0.98	0.28	1.51	1.30	1.04		0.21	0.33		8.11	2.99	2.38	0.69
Jacaraipe	Beach	4.27	0.57	2.16	0.64	2.30	3.70	3.62		0.30	0.98		11.96	11.12	8.93	3.16
Camburi	Beach	1.77	0.70	1.50	1.45	1.12	2.11	1.27	1.06	1.63	0.42		1.58	2.76	2.28	1.15
Santa Maria de Vitória	Estuary	0.21	1.47	0.95	0.27	17.37	1.31	1.02	0.35	0.15	1.41		0.35	0.34	0.51	1.07
Ubu	Beach		0.74	4.10	7.29	1.71	1.70	0.70	2.20	6.92	1.99		2.32	0.75	1.52	0.94
Itapemirim	Estuary	0.09	0.30	0.17	0.14	0.19	0.19	0.14	0.14	0.16	0.14		0.13	0.10	0.13	0.22
Presidente Kennedy	Beach	2.02	4.66	8.78	7.16	1.37	4.01	3.24		7.73	19.87		5.61	6.37	4.69	2.55
Itabapoana	Estuary	1.68	1.13	4.13	0.29	0.76	1.66	1.92	0.39	0.29	0.66		2.01	1.24	1.78	1.60
Farol de Sao Thomé	Beach	0.45	0.32	1.18	0.22	0.34	0.10	0.43		0.17	0.40		0.01	0.13	0.66	1.04
Quissamã	Beach	0.09	0.22	0.14	0.44	0.35	0.11	0.19	0.75	0.53	0.15	0.11	0.12	0.28	0.18	0.15
Macaé	Beach	0.08	0.55	0.34	0.33	0.09	0.27	0.61		0.12	0.49		0.10	0.80	0.49	0.48
Rio das Ostras	Beach	2.06	1.90	1.13	2.68		1.99	1.58		2.48	4.37		2.95	1.11	1.90	0.95
Búzios	Beach	1.08	0.61		24.54	3.13	0.86	0.84	22.96	21.97	19.50	1.69	0.54	0.43	0.59	0.65
Cabo Frio	Beach	0.18	1.03	0.71	0.20	0.07	0.52	0.94		0.13	0.26		1.12	1.50	0.87	0.43
Arraial do Cabo	Beach		1.90	0.53	1.10		0.45	0.45		0.98	0.98	0.93	0.78	0.33	0.42	0.26

The metals Mo and Se present values <DL. Al was removed since it was used as normalizing. EF < 1 indicates no enrichment ; <3 is minor enrichment ; 3–5 is moderate enrichment ; 5–10 is moderately severe enrichment ; 10–25 is severe enrichment ; 25–50 is very severe enrichment . and >50 is extremely severe enrichment .