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Dredging impact on trace metal behavior in a polluted estuary: a discussion about sampling design

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ABSTRACT

Studies involving coastal sediment resuspension have shown that trace metals could be released to the water column due to changes in physical-chemical conditions. Therefore, if environmental agencies adopt screening protocols with insufficient evaluations of contaminant mobilization risks for a given area, the prediction of environmental impacts caused by dredging may be limited. This work evaluates the influence of spatial variation on the geochemical mobility of trace metals (Cd, Cu, Ni, Pb, Zn) after artificial sediment resuspension, using as study case the Iguaçu River estuary (Guanabara Bay, Brazil). The Iguaçu River drains the industrial complex of the metropolitan area of Rio de Janeiro State, besides the presence of agriculture and the input of untreated domestic wastes. Surface estuarine sediments were submitted to resuspension experiments in an open system, during 1h and 24h of agitation on local water. A clear tendency of metals' solubilization was observed after resuspension, especially considering the dissolved concentrations of Cu (average: 8.0 $\mu g\ L^{-1}$) and Zn (average: 0.9 $mg\ L^{-1}$), especially for the samples from the transects 2 and 3. However, evaluations of water quality changes due to sediment resuspension are not requested by the legislation regulating the dredging activities. In the sediments, the results suggested a higher geochemical mobility of Cu, indicated by the massive increase on the bioavailable fraction after resuspension, mainly on the transect number 3, on the river's mouth. The effects of resuspension were distinct between samples, suggesting that even in a small scale, important differences on metals' mobility are found. Thus, the combined assessment of changes in metal concentrations in water and in the metal partitioning linked to the solid-phase was demonstrated to be a promising tool for predicting the environmental risks of dredging due to changes in the bioavailability of metals.

Descriptors: Bioavailability, resuspension, Guanabara Bay, remobilization, trace metals.

INTRODUCTION

Dredging activities are commonly used as a basic operation to maintain navigation channels and to remove contaminated sediments from aquatic ecosystems (Cappuyns et al., 2006). However, it is one of the human activities that cause sediment resuspension to the water column, which can change the geochemical mobility of trace metals, affecting the potential bioavailability of these toxic elements (Morse, 1994; Machado et al., 2011).

Resuspension experiments of contaminated sediments constitute important methods for evaluation of the effects of dredging in aquatic environments (Morse, 1994; Cappunys et al., 2006; Machado et al., 2011; Monte et al., 2015) and they have been used to contribute to the assessment of ecological risks linked to resuspension events (Cotou et al., 2005; Torres et al., 2009; Urban et al., 2010; Monte et al., 2015). For example, an increase in the copper (Cu) content in the potentially bioavailable geochemical phase by more than 10 times after resuspension of coastal sediments has been reported (Morse, 1994; Machado et al., 2011).

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Therefore, understanding the behavior of contaminants in dredged sediments is essential to manage their final disposal (Cappuyns et al., 2006).

The Brazilian legislation was reviewed in 2012 and incorporated rules for the final disposal of dredged material (CONAMA, 2012), including the obligation of ecotoxicological tests when the concentrations of trace metals are higher than the SQGs of Level 1. The new restrictions caused environmental authorities to demand safer dredging procedures (Wasserman et al., 2013) and include new tests, such as bioaccumulation tests. However, the metal bioavailability assessment, is not usually incorporated as criteria for environmental licensing of dredging activities, as occurs in Brazil. The Brazilian legislation that establishes the rules for dredging activities (CONAMA, 2012) demands a screening protocol suggested for the environmental impact evaluation, without considering the possible spatial variation of metal bioavailability.

There are currently several large dredging projects underway for rivers and port areas (harbors) in Brazil. Among these projects, some are held in Guanabara Bay, due to the presence of two harbors, and also as part of the projects for water quality recovery of its watershed that was part of the preparation for the Olympic Games of 2016. The Guanabara Bay is one of the largest bays of the country, with an area of 381 km^2. Domestic sewage contributes 75% of its organic pollution and 25% comes from industrial wastes. This complex ecosystem suffers from several impacts, including contamination by toxic metals that threaten the bay organisms (Bidone and Lacerda, 2004; Maddock et al., 2007). Therefore, dredged bay sediments are usually very contaminated (Barbosa and Almeida, 2001).

The Iguaçu River (drainage area of 726 km^2) is one of the most important rivers of the Guanabara Bay drainage basin, because it drains several heavily industrialized municipalities of the metropolitan area of Rio de Janeiro State, besides agriculture areas (JICA, 2003). The biggest oil refinery in Brazil is located at the mouth of Iguaçu River - the Duque de Caxias Refinery (REDUC). The Iguaçu-Sarapuí river system receives a significant load of non-treated domestic wastewater as well, due to absence of sanitation (Silveira et al., 2011).

The estuarine region of the Iguaçu River is silted, frequently showing areas with a maximum of just 50 cm of depth during high tide. In such cases, dredging is used as a remediation strategy for removal of accumulated sediments (Cappuyns et al., 2006). The Iguaçu Project, which is part of the Restoration Program of Guanabara Bay, dredged 5.58 million tons of contaminated sediment from tributaries of the Iguaçu River drainage area (SEA-RJ, 2012).

In this context, the present study aimed to evaluate the spatial variation (small scale) of toxic metals bioavailability in estuarine sediments and waters from the Iguaçu River (Guanabara Bay, Rio de Janeiro) after laboratory resuspension tests, simulating sediment resuspension events in an in vitro open system. The first hypothesis tested is that the dissolved concentration of trace metals in the water column increases with sediment resuspension, and the second hypothesis is that spatial variation exists in the solid phase geochemical partitioning of metals and other sediment characteristics (grain size and organic matter) between sampling stations, which can cause variation in the metal bioavailability responses to sediment resuspension.

MATERIAL AND METHODS

Sampling

Sediment and water sampling was carried out in March 2011 (wet season, during ebb tide), using four transects with 3 sampling points each, starting from the Iguaçu River and going in the direction of Guanabara Bay (Figure 1), composing a total of 12 sampling points. The quantity of sampling points was determined following the environmental impact evaluation procedure described by CONAMA Resolution 454/2012 (CONAMA, 2012). This Brazilian legislation specifies the number of samples to be analyzed according to the sediment volume that is intended to be dredged. Applying this protocol to the current study, was formulated the following dredging scenario: the study area is crossing the Iguaçu estuary, measuring 900m in length and 100m in width, a dredging to 2 m depth would yield a total of 180,000 m^3 of sediments to be removed. Using the resolution scale for dredging activities that involve volumes between 100,000 and 500,000 m^3 of sediments, 7 to 15 sampling points would be required.

The assessment of spatial variability in sediment quality and metal responses to resuspension was performed for surface sediment samples obtained using a van Veen sampler, which were stored in sealed plastic bags and cooled during the transport to the laboratory. For the resuspension experiments, surface water samples were collected nearby the transects (Figure 1), where oxic conditions were found (with a dissolved oxygen level as high as 11.5 mg L^{-1} recorded in this sampling).

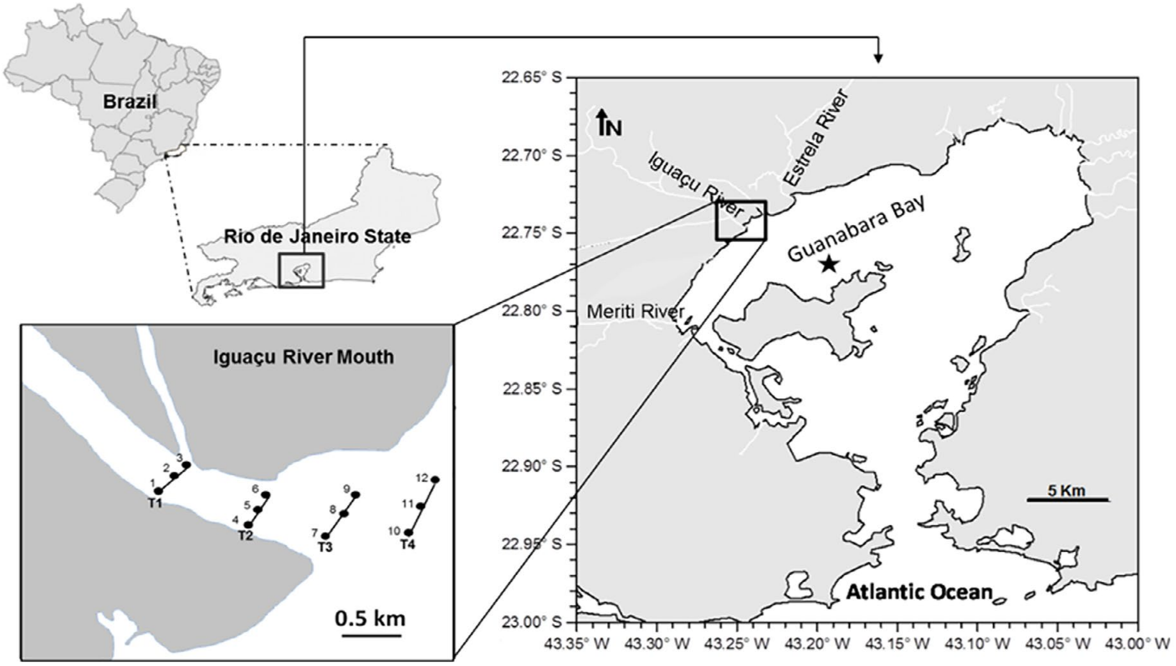

Figure 1. Localization of the 12 surface sediments sampling points, organized by transects (T1, T2, T3 and T4) starting from the Iguaçu River and going in the direction of Guanabara bay, at Rio de Janeiro State – Brazil. The star represents the water sampling point for resuspension experiments.

The distance of this water sampling station from sediment sampling points is explained by the need to have oxidizing water for resuspension experiments, to simulate oxidizing conditions of disposal (since the indication of final disposal, according to the regulation, is specific areas in the ocean). Dissolved oxygen (DO) and pH were monitored before and after resuspension experiments. DO was measured using an YSI probe, and pH using a 300M Analyzer. These parameters were also measured in situ in surface water at each sampling point.

RESUSPENSION EXPERIMENTS

The resuspension experiment was performed in a 125 mL Erlenmeyer flask by adding 7.0g of wet sediment and 100 mL of unfiltered water after 4 hours of sampling. The sediment resuspension was performed in analytical duplicates by agitation during two intervals (T1=1h; T2=24h), using a mechanical shaker, with a speed of 200 RPM, at 20°C. That is, for each sampling point, four Erlenmeyer flasks were prepared: two for 1 h of agitation and two for 24 h of agitation, being each one an independent system. The sediment**:** water proportion was chosen based on Morse (1994) and Machado et al. (2011), wherein the authors performed laboratory studies on trace metal bioavailability changes after resuspension events.

METALS DETERMINATION IN WATER AND SEDIMENT

After agitation, samples were transferred to 50 mL polypropylene tubes for centrifugation at 3,000 RPM during 5 min. Then the supernatant was filtered, acidified with three drops of HCl for preservation of samples and maintained under refrigeration until metals' determination (cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn)) using an inductively coupled plasma optical emission spectrometer (ICP-OES, brand Jobin Yvon Horiba).

The sediment samples were dried at 40^{o}C and homogenized for sequential extraction. The potentially-bioavailable and strongly-bound extractions were performed sequentially to determine metal concentrations (Pb, Cd, Ni, Zn, Cu, Fe and Mn). The potentially-bioavailable fraction was obtained using a 1 mol L^{-1} HCl solution, where 40 mL of this solution was added to a polypropylene tube containing 3.0 g of dried sediment. The tubes were stirred during 16h. After this period the samples were centrifuged (3,000 RPM, for 5 minutes), the supernatant was separated for metals determination and the sediment was washed three times with distilled water to remove the acid solution. This extraction was chosen based on Morse (1994), Machado et al. (2011) and Monte et al. (2015).

Furthermore, Peña-Icart et al. (2014) compared metal bioavailability using acetic acid 0.11vv, acetic acid 25% and 1 mol L^{-1} HCl with and without trypsin and pepsin extractions to simulate the digestive system of marine organisms and concluded that 1 mol L^{-1} HCl yielded the most efficient extraction.

After drying at 40°C and subsequent homogenization, the sediments were tested with the USEPA 3051A extraction method (USEPA, 1994), using 0.5 g of dried sample and 10 mL of HNO_3 (concentrated), heating in a microwave oven at 175°C for 5.5 min, and maintaining this temperature for an additional 4.5 min to complete the process (Machado et al., 2011). Metal determinations in both extracts (1 mol L^{-1} HCl and USEPA 3051A) were performed on an ICP-OES. In order to verify the accuracy of the methods, certified material was also analyzed (CRM NIST 2782). The detection limits for Cd, Cu, Fe, Mn, Ni, Pb and Zn were: 0.01, 0.01, 0.53, 0.01, 0.01, 0.03 and 0.31 mg/kg $^{-1}$, respectively, and the recovery ranged from 95.49 to 107.4%. To characterize the sediments before resuspension, the metals were also determined in (T0) samples, performing both extractions, to quantify the initial concentrations of these metals.

GRAIN SIZE, ORGANIC CARBON CONTENTS AND ACID VOLATILE SULFIDES

Factors that could possibly interfere with the geochemical mobility of metals, such as grain size, organic carbon (C) and sulfide contents were evaluated. The particle size of the samples was determined using approximately 1g of wet sample added to a 50 mL polypropylene tube with 40 mL of dispersant (sodium hexametaphosphate 40 g L^{-1}) and stirred during 24 h. After stirring, the particle size was determined in a particle analyzer by laser diffraction CILAS Shimadzu, model 1064, and the results were calculated using the software GRADSTAT 1.0. The determination of total organic carbon (TOC) was performed on a TOC-V with a SSM-5000A module (Shimadzu), using 20 mg of decarbonated sediment, obtained after 1 mol L^{-1} HCl extraction. The acid volatile sulfides (AVS) were measured only in T0 samples according to Allen et al. (1991), wherein a 6 mol L^{-1} HCl solution is added to wet sub-samples of sediments and the H_2S released during the agitation is trapped in a 0.5 mol L^{-1} NaOH solution. The AVS concentrations were determined by a colorimetric method (Cassella et al., 1999).

BIOAVAILABILITY CHANGES AFTER RESUSPENSION

The bioavailability change index (BCI) was proposed by Monte et al. (2015) and applied to the remobilization evaluation of trace metals after resuspension of different surface sediment samples and was calculated as follows:

$$BCI = ((\%HCl_{AR} - \%HCl_{BR}) / \%HCl_{BR}) \times 100$$

Where $\%HCl_{AR}$ is the percentage in the HCl extractable fraction after resuspension, and $\%HCl_{BR}$ is the percentage in HCl extractable fraction before resuspension. BCI could be negative or positive, which means that bioavailability could be decreased or increased (respectively) in surface sediments. The scale used to classify samples reflects the intensity of the changes on sediments after resuspension:

Increase on Bioavailability
- 0 to 15% = none or low
- 15 to 50% = moderate
- 50 to 100% = considerable
- > 100% = very high

Decrease on Bioavailability
- 0 to -15% = none or low
- -15 to -50% = moderate
- -50 to -100% = considerable
- > 100% = very high

The percentage of metal remobilization to water after resuspension was also assessed, as suggested by Rodrigues et al. (2017), using the following equation:

$$PRI = ((Me_{AR} – Me_{BR}) / Me_{BR} \times 100)$$

Where PRI is the potential remobilization index, Me_{AR} is metal concentration in water after resuspension (mg L^{-1}) and Me_{BR} is metal concentration in water before resuspension (mg L^{-1}). Similar to BCI, the PRI could be negative or positive, which means that metal concentrations in the dissolved phase could be decreased or increased (respectively) in water. The scale used to classify the changes after resuspension is:

Increase on Bioavailability
- 0 - 15 % = none or low
- 15 - 100 % = moderate
- 100 - 1,000 % = considerable
- > 1,000 % = very high

Decrease on Bioavailability
- 0 to -15 % = none or low
- -15 to -100 % = moderate
- -100 to -1,000 % = considerable
- > -1,000 % = very high

Additionally, the particle-water partition coefficient (*Kd*; kg L^{-1}) was calculated to understand the relative affinity of metals for dissolved and particulate phases (Hatje et al., 2003; Parquetti et al., 2004). An elevated *Kd* value indicates high affinity for the particulate phase. For this calculation, it was used the total concentrations in sediment (particulate phase) divided by metal concentrations in filtered water (0.45 µm; dissolved phase).

Data analysis

Statistical analysis was performed using STATISTICA 7.0 and SPSS 19. Nonparametric tests were used since our data did not follow a normal distribution. A Mann–Whitney test was applied to evaluate differences between intervals of resuspension and between transects. Spearman correlation was used to verify possible relationships between toxic metals and grain size, organic carbon contents, AVS, Fe, and Mn concentrations. The significance level was 0.05.

RESULTS

Sample characterization

In the field, surface water pH ranged from 6.58 to 8.66, and salinity ranged from 2.0 to 11.0. The DO results indicated a range from intense consumption to intense photosynthetic oxygen release (ranged from 2.4 to 11.46 mg L^{-1}). The strongly-bound concentrations of Pb were correlated to salinity (Spearman, 0.60, $p<0.005$ n=12) and pH (Spearman, 0.66, $p<0.005$ n=12). Surface sediments were composed mainly by fine fractions (i.e., the sum of silt and clay fractions), which generally corresponded to more than 80% (dry weight) of grain size data (Table 1). Sand was present in all samples, but always in low percentages (less than 10% of sand), excepted the sampling point number 5 that presented a relatively higher value of 24.7% of sand. The strongly-bound concentrations of Cd, Ni, Fe and Mn were correlated positively to clay contents (Spearman, 0.7, $p<0.005$, n=12). In the case of Ni, the potentially-bioavailable phase was negatively correlated with clay contents (Spearman, -0.61, $p<0.05$, n=12), other non-evaluated factors, such as acid-volatile sulfide contents and mineralogical variability, may cointribute for determining the Ni distribution. TOC contents in sediments were above 4.0% at almost all sampling points (ranged from 3.34 to 6.91%). AVS concentrations ranged from 6.0 to 59.3 µmol g^{-1}. These moderate to high AVS concentrations indicate reducing conditions of these surface sediments. The AVS concentrations were correlated negatively with the bioavailability of Mn concentrations in T0 samples (Spearman, -0.69, $p<0.05$, n=12), which may be attributed to AVS consumption in reaction with HCl-extractable Mn oxides (e.g., Machado et al., 2008).

Since metal's determinations were held sequentially, the sum of both fractions was performed to compare the results with Brazilian sediment quality guidelines (SQG), which indicates as standard the EPA 3051a method for metal determination (see supplementary material).

Table 1. Characterization of the surface sediment and physical-chemical parameters from the mouth of the Iguaçu River at Guanabara Bay-RJ, Brazil.

Sampling Points	Sand (%)	Silt (%)	Clay (%)	TOC (%)	AVS (µmol g-1)	DO* (mg L-1)	Salinity*	pH*
1	0.6	86.3	13.1	4.6	13.26	2.4	2.0	6.8
2	3.5	87.5	9.0	5.4	17.18	2.7	2.0	6.9
3	9.0	81.1	9.9	6.0	13.22	1.8	1.0	6.6
4	1.9	84.8	13.3	4.4	18.5	4.8	6.0	7.5
5	24.7	68.5	6.8	3.9	14.6	3.0	4.0	7.2
6	2.4	85.8	11.8	5.0	39.7	5.3	5.0	7.3
7	2.9	86.4	10.7	6.9	34.5	4.8	7.0	7.4
8	0.3	83.1	16.6	4.1	17.2	5.7	7.0	7.5
9	0.3	81.5	18.2	5.4	54.6	7.9	8.5	7.9
10	0.6	86.4	13.0	5.1	59.3	8.2	9.0	7.9
11	3.2	84.8	12.0	4.6	59.3	7.8	10.0	7.9
12	1.1	79.9	19.0	3.3	6.0	11.5	11.0	8.7

*measured in water; TOC: total organic carbon; AVS: acid volatile sulfide; DO: dissolved

The SQG were defined for the licensing process of dredging activities in 2004 (CONAMA, 2004), adopting the safety levels proposed by Long et al. (1995), where Level 1 is similar to the ERL (Effects Range Low), which represents the minimum effect range (Long et al., 1995). Level 2 is similar to ERM (Effects Range Medium), representing the range where more probable effects could be found (Long et al., 1995) (Table 2). Cd and Cu concentrations were above level 1 of the SQG in 92% of the samples. Pb and Zn concentrations were also above level 1, but in lower proportions of the samples (58.3 % and 75 %, respectively). Only one sample showed Ni concentration above level 1. None of the samples had metal concentrations above level 2 of the SQG.

The ERL and ERM definition is based on strongly-bound extraction (Long et al., 1995). However, in the current study was also compared the potentially-bioavailable fraction with the safety reference levels, since this reactive phase represents the risks associated with biota exposure to bioavailable metals.

Additionally, in the current study was also compared the potentially-bioavailable fraction with the safety reference levels, since this reactive phase (which includes exchangeable ions and/or linked to carbonates) represents the risks associated with biota exposure to bioavailable metals. However, metal mobility and bioavailability tests were not included in the legislation, which represents a key weakness to support the decisions on performing dredging activities. Note that the bioavailable fraction can itself exceed sediment quality guidelines (as exemplified in the Figure 2 for Cu and Zn), even evidencing larger environmental risks than in the cases in which the guidelines are exceeded by total concentrations, but not exceeded by the respective bioavailable factions (Machado et al., 2011).

RESUSPENSION EXPERIMENTS: CHANGES IN METAL CONCENTRATIONS IN SEDIMENT

Potentially-bioavailable concentrations of Fe (Mann-Whitney, U=33.0, Z=2.25, $p<0.05$, n=12), Pb (Mann-Whitney, U=38.0, Z=1.96, $p<0.05$, n=12) and Zn (Mann-Whitney, U=33.0, Z=2.25, $p<0.05$, n=12) decreased after 1h of resuspension, and in the case of Zn, it continued to decrease, with the lowest concentrations found after 24 h of resuspension (Mann-Whitney, U=25.0, Z=2.71, $p<0.01$, n=12). The decrease in this geochemical phase was also significant for Cd in T2 (Mann-Whitney, U=25.0, Z=2.71, $p<0.01$, n=12). The strongly bounded fraction showed no significant differences in trace metals concentrations before and after resuspension.

The TOC ranged from 3.34 to 6.91% in T0, 3.48 to 5.97% in T1 and 3.62-6.05% in T2 (Table 3), and presented a tendency of slightly higher concentrations after resuspension, but no significant differences were found. Also, there was no correlation between the TOC contents and metal concentrations in sediment before resuspension, but after 1 h resuspension, the TOC contents were correlated with potentially-bioavailable concentrations of Cd (Spearman, 0.92, $p<0.001$, n=12) and both geochemical phases of Mn (Spearman, - 0.6, $p<0.05$, n=12).

Table 2. Trace metal concentrations adopted as sediment quality guidelines for dredging activities in Brazil (CONAMA 454/2012) and water quality guidelines (CONAMA 357/2005).

	CONAMA 454/2012		CONAMA 357/2005	
Metals	Level 1 (mg kg^{-1})	Level 2 (mg kg^{-1})	Class 1 (µg/l^{-1})	Class 2 (µg/l^{-1})
Cadmium	1.2	7.2*	5.0	40
Copper	34	270	5.0	7.8
Iron	-	-	300	-
Lead	46.7	210	10	-
Manganese			100	74
Nickel	20.9	51.6	25	210
Zinc	150	410	90	120

*Levels 1 and 2 of CONAMA 454/12 use the same values of ERL and ERM (Long et al., 1995), respectively.

* Environmental Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec. Criteria for the Assessment of Sediment Quality in Quebec and Application Frameworks: Prevention, Dredging and Remediation.

* Fe and Mn do not have established safety limits for Class 2. If the safety levels from Class 2 are not satisfied, the water uses allowed are those from Class 3 in CONAMA 357/2005.

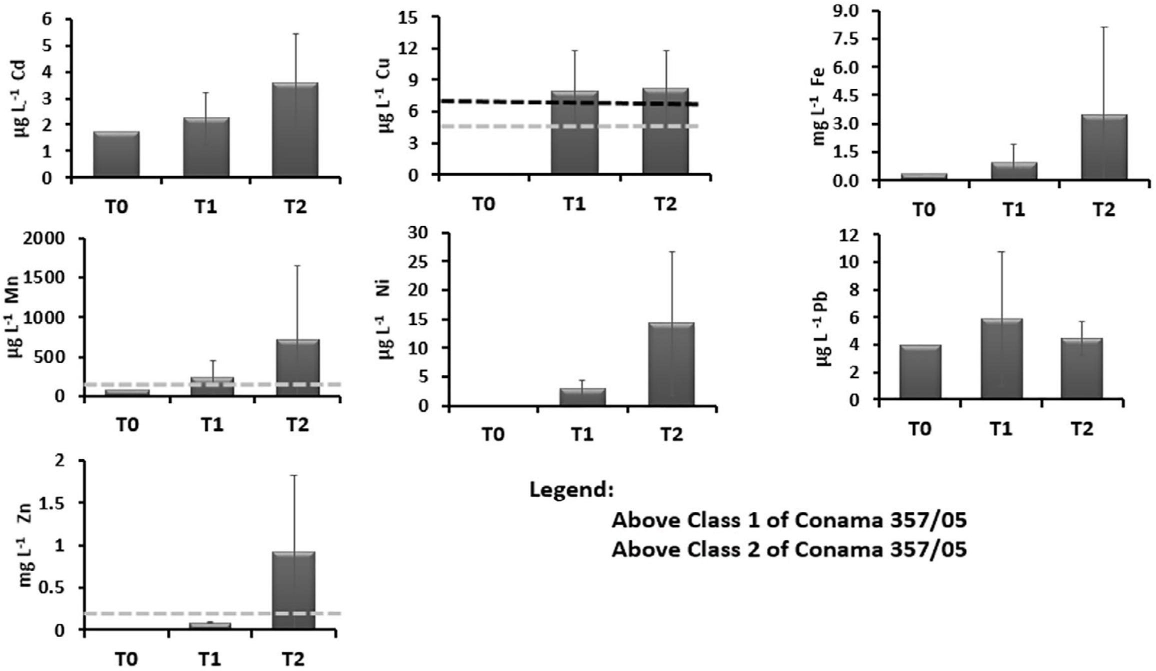

Figure 2. Metal concentrations in water before (T0) and after the resuspension experiments (1h - T1 and 24h - T2) ($\mu g\ L^{-1}$).

Table 3. Total Organic Carbon (%) in surface sediments at the estuary of Iguaçu River, Guanabara Bay-RJ, Brazil, before and after 1h (T1) and 24h (T2) of resuspension in oxic water.

Sampling Points	T0	T1	T2
1	4.56	4.30	5.08
2	5.35	5.19	5.81
3	6.00	5.97	6.51
4	4.43	4.42	4.92
5	3.93	4.54	5.22
6	5.02	4.93	5.69
7	6.91	4.49	6.01
8	4.06	4.09	4.57
9	5.40	5.29	6.05
10	5.05	5.83	5.92
11	4.62	5.37	5.39
12	3.34	3.48	3.62

Additionally, after 24 h resuspension, TOC contents were correlated with Cd (Spearman, -0.60, $p<0.05$, n=12) and Zn (Spearman, 0.59, $p<0.05$, n=12) concentrations in the strongly-bound phase and also with both fractions of Mn (Spearman, 0.63 $p<0.05$, n=12). These results suggest that changes in the geochemical partitioning induced by resuspension can affect the relative importance of TOC as a geochemical carrier for metals.

With respect to a possible influence of Fe and Mn on bioavailability of trace metals, before resuspension, the Fe concentrations in the potentially-bioavailable fraction were positively correlated to Ni and Zn (Spearman, 0.67; $p<0.05$, n=12). After the resuspension, for both intervals, Cd, Cu and Zn correlated negatively with bioavailability of Fe and Mn (Spearman, -0.64; $p<0.05$, n=12). Additionally, positive correlations between strongly-bound Fe and Mn and trace metals were found for Cu (only in the T1 interval), and for Cd and Ni (Spearman, 0.71; $p<0.05$, n=12) for both time intervals. Therefore, the results also suggest important changes in the trace metal associations with Fe and Mn compounds, after resuspension.

BCI showed a general behavior of potential remobilization of trace metals, with a change from the occurrence of negative values after 1h resuspension (T1) to higher (always positive) values after 24 h resuspension (T2) (Table 4). The bioavailability of Cd and Ni decreased after resuspension (Table 4). Especially in T2, when 67 % and 33 % of the samples, respectively, presented negative BCI values between -15 % and -50 % (Moderate changes). On the other hand, Cu showed the highest positive results (2 samples classified as very high changes: BCI > 100 %) for both resuspension time intervals, thus making Cu a possible cause for concern for environmental management, due to a high geochemical partitioning sensitivity to

Table 4. Bioavailability Change Index (BCI) (%) in metal concentrations in surface sediments from Guanabara Bay-RJ, after 1h (T1) and 24h (T2) of resuspension in oxic water.

Sampling Points	T1					T2				
	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn
1	**-25.1**	-10.9	-4.4	-6.8	-1.2	**-25.5**	-13.7	-3.3	-3.8	-0.5
2	-3.9	1.9	-0.1	-1.0	-2.8	**-26.7**	-3.5	**-24.4**	-6.5	-11.8
3	-8.9	5.5	-3.6	-1.9	-2.9	**-30.5**	-0.6	-14.5	0.1	-14.2
4	-13.5	**-25.3**	**-15.3**	-11.0	-10.2	**-20.4**	**-19.3**	-11.7	-8.1	-4.3
5	-12.8	**17.4**	-2.1	-1.8	-2.1	**-24.6**	10.4	**-21.4**	-2.8	-7.6
6	-12.6	**-18.0**	**-21.9**	-7.0	-4.4	-14.6	-1.7	-9.3	-7.2	-4.2
7	**-24.7**	**166.1**	-14.3	-3.3	0.1	**-25.1**	**149.9**	**-16.1**	-1.1	-6.1
8	**19.7**	**808.0**	7.3	**28.5**	-6.8	**34.6**	**1,228.8**	**61.6**	**66.6**	**15.0**
9	-9.1	-6.5	-8.6	-3.5	-1.8	-6.6	-3.9	1.4	-1.2	-2.6
10	1.3	**27.7**	**-22.0**	-10.3	-5.1	**-31.0**	**21.5**	**-27.4**	-7.1	-13.7
11	8.9	-13.0	**-16.1**	-11.9	-5.0	**-22.5**	-9.8	-9.7	-7.0	-3.5
12	**-22.5**	7.8	-4.7	-2.9	-3.7	-2.5	**20.6**	7.8	4.2	-1.5

The bold values correspond to results at least 15% different from metal concentrations in surface sediments before resuspension. This criterion was established in Monte et al. (2015).

sediment resuspension in oxidizing water. Pb and Zn showed basically none or low changes (both negative and positive scales) in BCI, with only one exception (point number 8), where Ni and Pb positive changes were classified as considerable (50 to 100%) and Zn, classified as moderate (15 to 50%), representing a increment on these metals' bioavailability in sediment. In general, the experiment showed higher potential of bioavailability at the sampling points from transects 3 and 4, closer to the river's mouth and in the shallowest areas, which may be possibly more affected by previous resuspension events by natural processes in the estuary.

Resuspension experiments: changes in metal concentrations in water

An increase in metal concentrations in water after resuspension was generally found, except for Pb which did not show significant variation. Interestingly, metal concentrations varied along the sampling points. After 1h of resuspension, Fe concentrations ranged from 301 to 3,225 µg L^{-1} (Figure 2) and Mn ranged from 36.0 to 759 µg L^{-1}. On the other hand, after 24h, the variation was more expressive, where Fe concentrations ranged from 276 to 15,377 µg L^{-1}, Mn from 46 to 2,842 µg L^{-1} and Zn ranged from 72 to 2,014 µg L^{-1}. These results express the difference of remobilization for each sampling points, showing the heterogeneity of samples in a small area.

The main increase was found after 24h of resuspension for Cu, Fe, Mn, Ni and Zn (Mann-Whitney, U=16.0, Z=-2.58 $p<0.05$, n=12). Cd concentrations were higher in T1 (Mann-Whitney, U=24.0, Z=-2.77, $p<0.001$, n=12), suggesting that through time, Cd concentrations in water tended to return to lower values, but are still different from initial concentrations (Mann-Whitney, U=12.0, Z=-3.46, $p<0.01$, n=12). TOC contents in sediment were correlated to Fe concentrations in water after 1h of resuspension (Spearman, 0.74, $p<0.01$, n=12) and to Cd, Fe, Mn and Zn after 24h (Spearman, 0.68 $p<0.05$, n=12). No correlation of trace metals in water with AVS or grain size was found.

The criteria adopted for surface water quality in Brazil is described in CONAMA Resolution Number 357/2005. This resolution includes three classes of estuarine waters based on their possible uses (Table 2). If the water quality is classified as Class 1, the following uses are allowed: recreation, aquiculture and fishing. If it is Class 2, the water could be used only for indirect contact through recreation and angling. For Class 3 waters, only navigation and landscaping are allowed.

Comparing the observed concentrations in water with those established as thresholds, while these limits were not exceeded before sediment resuspension, results above the guidelines occurred after both time intervals (Fig. 3). After 1h of resuspension, Cd, Cu, Fe and Mn concentrations were above class 1. After 24h of agitation, Cu and Zn were above class 2; Fe and Mn were above class 1 in all sampling points.

The potential remobilization index (PRI) showed few negative results (Table 5) after both agitation intervals, corresponding to 19.0% and 14.3% of the results found for T1 and T2, respectively. None or low changes on concentrations

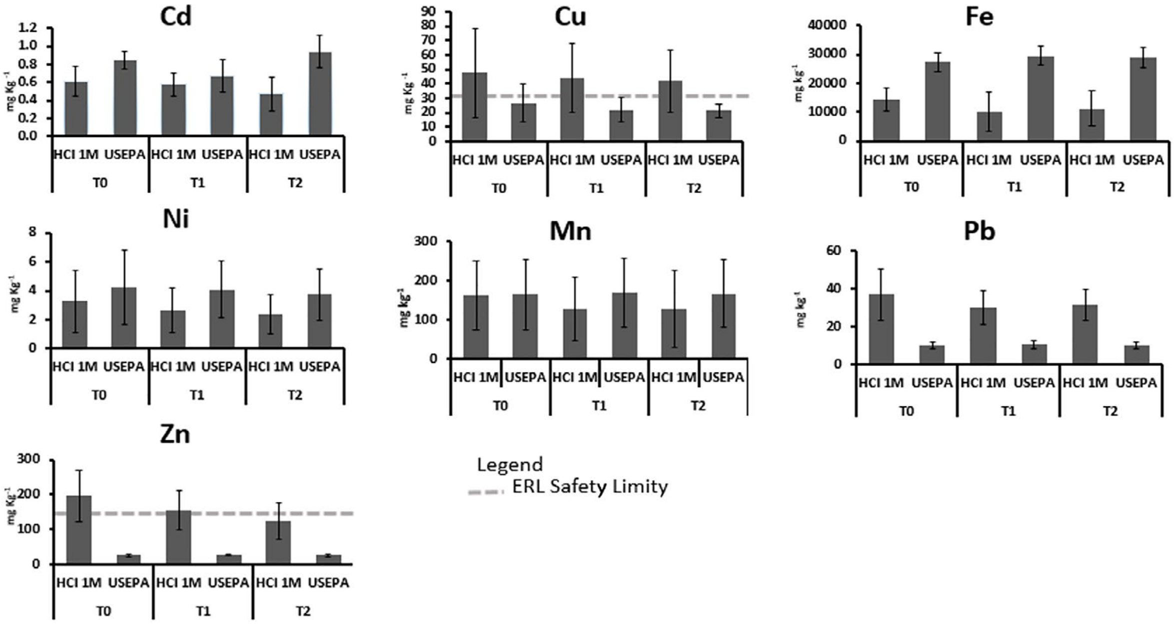

Figure 3. Extraction by HCl (1M) and by USEPA 3051 A methods. Metal concentrations in superficial sediment before (T0) and after the resuspension experiments (1h - T1 and 24h - T2) (mg kg $^{-1}$).

Table 5. Potential remobilization index (PRI) for metals to the water column after 1h (T1) and 24h (T2) of sediment resuspension and the average of the distribution coefficient (Kd; kg L^{-1}) of each metal.

Sampling Points	T1							T2						
	Cd	Cu	Fe	Mn	Ni	Pb	Zn	Cd	Cu	Fe	Mn	Ni	Pb	Zn
1	**27.5**	**79.5**	-4.2	**-55.2**	**258.0**	**202.8**	0.0	11.0	**77.5**	**18.4**	**-22.1**	**879.0**	**31.9**	**51.4**
2	**157.0**	**124.0**	**37.2**	**848.5**	**466.0**	**393.1**	28.6	**182.5**	**123.8**	**1,081**	**3,452**	**2,829**	0.0	**2,305**
3	**-18.5**	8.0	**707.8**	**494.3**	**162.0**	1.8	0.0	**221.0**	**155.2**	**4,559**	**1,292**	**1,939**	**54.3**	**2,776**
4	**-18.5**	**22.0**	8.9	**198.3**	**242.0**	**-22.2**	0.0	**19.0**	**216.8**	13.6	**330.5**	**940.0**	**21.4**	3.4
5	6.0	**185.2**	4.5	**350.5**	**360.0**	7.1	**28.6**	**111.5**	**295.0**	**1,664**	**2,853**	**4,354**	**35.7**	**2,715**
6	-9.0	0.0	**34.0**	10.4	**40.0**	**-25.0**	0.0	**17.0**	**54.0**	**31.4**	**52.6**	**513.0**	2.6	**42.8**
7	11.5	0.0	**408.2**	**80.4**	**161.0**	**-15.8**	0.0	**162.0**	**112.5**	**1,822**	**402.6**	**1,507**	**50.3**	**2,396**
8	-10.0	0.0	-8.7	**133.2**	**60.0**	-5.1	0.0	-9.0	**29.5**	-5.5	**299.8**	**255.0**	**-26.0**	0.0
9	-4.5	**25.5**	**29.8**	**86.0**	**71.0**	**17.9**	0.0	**25.0**	**19.5**	6.2	**515.8**	**391.0**	-7.1	**429.6**
10	4.0	**64.8**	**877.3**	**179.3**	**329.0**	**15.8**	0.0	**218.5**	**59.0**	**2,164.**	**509.5**	**1,658**	**54.3**	**2,606**
11	-9.5	0.0	**32.2**	-3.9	**37.0**	-9.9	0.0	8.0	**18.0**	**-16.2**	**-18.0**	**356.0**	**-18.1**	4.1
12	**12,778**	**285.0**	12.4	**-17.7**	**203.0**	**42.9**	0.0	**-16.5**	0.0	-14.0	**-34.6**	**273.0**	**-33.4**	**79.9**
Kd	*0.007*	*0.12*	*0.85*	*0.03*	*0.03*	*0.09*	*0.02*	*0.005*	*0.09*	*0.77*	*0.02*	*0.01*	*0.10*	*0.01*

The bold values correspond to results at least 15% different from the results obtained before resuspension.

of metal in water corresponded to 16.7% of the results for 1 h of resuspension and, only 3.6% of the results for T2. Then, the majority of the PRI values (64.3% in T1; 84.1% in T2) was positive, indicating a release of these metals from sediments to water. The most expressive difference on PRI values between T1 and T2 was found for Ni and Zn, which increased significantly in T2 (Mann-Whitney, Z= -3.58, *p*< 0.001). After 24 h of agitation, PRI classification was considerable or very high for all metals (except Pb) for at least 42% of the samples.

The BCI and PRI are new proposals of indices to observe changes in sediments and water after resuspension, presented by Monte et al. (2015) and Rodrigues et al. (2017). When they are used together, it may improve the assessment of the aquatic system quality change. Comparisons of BCI and PRI data suggest that there is an exchange between sediment and water, since negative results for BCI could reflect losses of the metal from reactive phase in sediment to water and that positive results for PRI reflects gains on concentration of a metal in water (independently of the magnitude of BCI and PRI values). At T1, more than 50 % of the samples presented negative BCI and positive PRI results for Fe (83.3%), Mn (66.7%), Ni (91.7%), Pb (58.3%) and Zn (75%).This relation between BCI and PRI results was even more frequent at T2, and including cases for Cd (83.3%) and Cu (58.3%), whose cases frequencies at T1 were lower than 40%.

This transfer also could be observed when the distribution coefficient (*Kd*) was applied (see supplementary tables). Before resuspension, the *Kd* values for each metal (Cd, Cu, Fe, Mn, Ni, Pb and Zn, respectively) were 0.007, 0.19, 1.27, 0.04, 0.07, 0.12 and 0.03 kg L^{-1} x 10^5. Fe showed the highest *Kd*, not surprisingly, since Fe is an abundant element on several minerals and generally is found in strongly bounded geochemical phases (Figure 2). After resuspension, these coefficients showed a trend of a slightly decrease (Table 5) (all *Kd* were different from T0; Kruskal-Wallis, $p<0.05$). The most expressive reductions of *Kd* were found for Cu and Fe, being almost half of the initial *Kd*.

SPATIAL ANALYSIS

The physical-chemical characteristics of the surface water showed significant differences from the transect 1 to the transect 4, what is, pH (Kruskal-Wallis; 2.89, $p<0.05$) and DO (Kruskal-Wallis; 2.94, $p<0.05$) increased in the direction of the river's mouth. Especially, the left margin sampling points that showed higher concentrations in relation to the right margin and central channel. This may be related to the proximity of the points to two channels (that appears in Figure 1), and to the dry season characteristics (Monte et al., 2017).The others parameters, include metals, not show significant difference between transects.

In general, the experiment showed higher potential of bioavailability at the sampling points from transects 3 and 4, more distant from the river's mouth and in the shallowest areas, which may be possibly more affected by previous resuspension events by natural processes in the estuary. All points from the first transect showed only negative changes on bioavailability or no changes at all. Only one sample (sampling point: 8) had positive BCI results for all metals in T2, showing the highest potential risk associated to metal's mobility in sediment after resuspension, which could be related to the lower AVS and TOC contents in this sample.

In the resuspension experiment, the concentrations of metal in water presented an important variation according to the sediment samples, what is, the sample points. The highest PRI values were found for samples from transect 1, which is the opposite trend observed for BCI. Four samples from the margins (sampling points: 3, 4, 7 and 10) and two samples from the central channel (points: 2 and 5) showed positive results for PRI of all metals. This way, PRI results expressed a large heterogeneity of metal sensitivity to be remobilized to water for different sampling points.

It is important to highlight some specific samples that showed extremely high changes on bioavailability. As mentioned before, the sampling point number 8 presented only positive results for BCI, reaching 1,228.8% of increase on Cu bioavailability, besides the increases on 66.6% on Pb, 61.6% on Ni and 34.6% on Cd bioavailabilities. The water changes were even more significant, reaching an increase of 12,778.5% on Cd concentrations at the sampling point 12. It is important to remember that Cd concentrations in this sediment were above the safety limit and that this sample presented negative BCI values, which suggests the Cd transference from sediment to water.

These results reinforce the effect of spatial variation on the metals' geochemical response to resuspension events, even within a relatively small scale.

DISCUSSION

In this study, all samples presented fine grain size predominance (Table 1) and this fraction was correlated with trace metal concentrations in the strongly bounded phase, suggesting the occurrence of metal complexation processes. Silt and clay have a particularly important influence on the transport and storage of heavy metals within fluvial sediments (Zhang et al., 2014), and fine fractions play a significant role in water and sediment quality, especially in the dynamics of adsorption/desorption of metals, and even in biological accumulation (De Jonge et al., 2009; Zhang et al., 2014). Trace metals adsorbed on surface sediments can return to the water column, due to dissolution process caused by physical-chemical changes after resuspension (Maddock et al., 2007; Machado et al., 2011).

The negative correlations with Ni and physical-chemicals factors in weakly bound can be attributed to pH. In pH < 6.5 part of compounds formed may became soluble, therefore the pH regulated the bioavailability of Ni in the sediments (Kabata Pendias and Pendias, 2001).

This experiment showed correlations between trace metals and Fe and Mn, which may have led to oxidation of sulfides and precipitation of Fe and Mn oxides, which are important regulators of metal bioavailability due to sorption or co-precipitation (Calmano et al., 1994; Saulnier and Mucci, 2000; Caetano et al., 2003). This suggests that Fe and Mn precipitation is an important process affecting metal mobility.

Another process that may explain the increase of trace metals in reactive forms or even in the dissolved phase in water is the oxidation of metal mono-sulfides (Caetano et al., 2003). The same observation was described by Maddock et al. (2007) who carried out the first experimental study on contaminated sediments resuspension in Guanabara Bay. These authors suggested a combination of trace metal inputs characterization and retention mechanisms with the assessment of its potential remobilization to better understand the processes that determine the metals´ partitioning between solid and dissolved phases.

Furthermore, the majority of metals showed higher concentrations in the sediment at T0 in the potentially-bioavailable fraction (Figure 3). However, there were changes in bioavailability (negative and positive) after resuspension, for both intervals. After one hour of resuspension, most samples showed relevant changes and after 24h all samples showed changes in bioavailability (Table 4). The oxidation of sulfides and precipitation of Mn and Fe oxides suggest the release of metals into water (Simpson et al., 1998; Cappuyns et al., 2006), however in a few minutes the metals released, but also quickly scavenged and removed by Fe oxyhydroxide (Zhang et al., 2014). Van den Berg et al. (2001) indicated that trace metals were released into water during oxidation in laboratory experiments.

The changes in trace metals concentrations were significant only in the bioavailability fraction (no changes in strongly-bound concentrations were observed). This may be related to TOC contents after resuspension. Organic matter complexation with trace metals such as Cd, Cu, Ni and Zn is well known and described in the literature for eutrophic regions such as the present study area (Kehrig et al., 2002; Covelli et al., 2012). Although no significant difference on concentrations of metal along the transects was found, in a previous work (Monte et al., 2017), the differences on concentrations found in the central channel of the river and the margins were clearer and significant, indicating the interference of hydrodynamics.

Organic carbon is well known as an efficient binder of metals, and its concentrations have been demonstrated to reduce the solubility and toxicity of metals (Zhang et al., 2014). It is important to highlight that the potentially-bioavailable methodology used in this work is not able to extract metals linked to organic matter (Morse, 1994).

In general, the results of BCI (Table 4) showed no extensive remobilization. The sampling station 8 showed remobilization for three metals in T1 (Cd, Cu and Pb), and in T2, for (Cd, Cu, Ni and Pb). A possible explanation for these specific results may be the fact that the sampling points are close to two channels that come from the oil refinery, which may be a source of more bioavailable phases of metals for this area. Also, Silveira et al. (2011) studied the Iguaçu-Sarapuí River system and conclude that the Sarapuí River is responsible for most trace metals found in the Iguaçu River's mouth, using a mass balance methodology.

The possible explanation for negative results for the BCI (Table 4) is the influence of oxidation of contaminants adsorbed to sediment, causing their mobilization to the water column, mainly at T1 (1 h). Monte et al. (2015) observed positive results of BCI using surface sediments from Sepetiba Bay (Rio de Janeiro, Brazil), a mesotrophic system, indicating a remobilization of trace metals to the bioavailable phase. In other words, an increase in potentially-bioavailable fraction concentrations after resuspension was found, which was not observed in this work, where the concentrations decrease suggests that the potentially-bioavailable trace metals were possibly oxidized and dissolved in water. The concentrations in water had an important increase, and no changes in the strongly-bound phase were observed, which may be due to the high TOC contents in sediments of Guanabara bay (Table 3) (Lacerda and Gonçalves, 2001; Covelli et al., 2012), an eutrophic environment (Kjerfve et al., 1997), forming complexes with strongly-bound trace metals.

Moreover, the heterogeneity of sampling points contributed to the results for water and sediment. The effects of resuspension on the water column was distinct between samples, suggesting the influence of hydrodynamics, since the northwest sector of Guanabara bay has low water renovation, with high influence of continental inputs (Kjerfve et al., 1997). Monte et al. (2017), showed the difference between the central channel and sediment banks of the Iguaçu River in the distribution of contaminants.

Acquavita et al. (2012) tested the effects of resuspension using an open system and contaminated sediments from Grado and Marano Lagoons (Italy), which are known for their high levels of mercury pollution due to a chlor-alcali plant that discharges its effluents to the drainage basin. An increase in methylmercury in water after resuspension was related to Fe and Mn oxides and hydroxides formation, releasing mercury in solution. The same pattern seemed to occur in our experiment, where negative correlations were observed; suggesting that when there is less bioavailable iron and manganese, there are higher trace metals in strongly-bound forms. Monte et al. (2015) showed positive correlations between trace metals and Fe and Mn concentrations, which were found in our study only for trace metals and Fe and Mn in strongly-bound forms.

Comparing the observed concentrations in water with those established as thresholds for surface water quality in Brazil (CONAMA resolution 357/2005), while these limits were not exceeded before sediment resuspension, results above the guidelines occurred after both time intervals of agitation in coastal water (Fig. 3). After 1 h of resuspension, Fe and Mn concentrations were above class 1, and Cd and Cu were above class 2. After 24 h of agitation, Cu and Zn were above class 2; Fe and Mn were above class 1 in all sampling points.

Choppala et al. (2018), shows an increase of Cu and Zn after resuspension, moreover their results for dissolved were similar with this study for Cu and Ni. Burton et al. (2006), performed a laboratorial study experiment of resuspension and found an increase of Mn, Ni and Zn after resuspension with concentrations similar to this study.

Moreover, it was clear that, even in a small scale, different patterns of trace metals remobilization were observed, with dissolved concentration results that were above the Brazilian guidelines. Although the results not shows significant differences between transects for metals and others parameters, this study presented a significant difference for physical-chemical parameters, demonstrating the importance of the study of spatial variability in dredging areas. Is suggested that temporal variability in the metal bioavailability should be incorporated in the planning and monitoring of dredging activities, coupled with spatial variability assessments.

CONCLUSIONS

The sampling points presented large differences in remobilization of trace metals, mainly in relation to the metal release into water column. Considering the small area of 90,000 m^2 sampled in this estuary, a great heterogeneity can exist in the composition and physical-chemical process. The necessity of integrate the use of current guidelines in the legislation with analyses of dissolved concentrations and solid phase bioavailability evaluations in the environmental assessments of dredging impacts was evidenced. The results showed, in some cases, concentrations above ERL and ERM levels after resuspension, suggesting possible risks to biota. The BCI and PRI indices showed significant changes in bioavailability of trace metals and can be important tools for trace metals behavior prediction after resuspension. The increase of Cu and Zn in water column suggests the oxidation of sulfides after resuspension. The particle-water partition coefficients obtained for Cu, Fe and Pb were higher than for others metals, demonstrating the importance of particulate study after resuspension, whereas can affect the bioavailability of trace metals after dredging activities.

The different behavior between samples, mainly in the water column, reflects the high heterogeneity of metal behavior in sediments and water even in a small area in the estuary, which should be considered in assessing the risks to aquatic biota. The proposed mechanisms involved in the metals mobilization can be verified with analysis of such end products (e.g. organo-metals, metal sulfides, metal oxides) in future studies.

This transfer was better observed when the proposed integration was applied. Considering the respective contributions from water and sediment to the metal concentrations in the resuspension system, the importance of sediment is evident, containing more than 90% of the metal concentrations. Also, important modifications in the contribution of water to the concentrations in the system highlighted the transfer of metals from sediment to water after resuspension (see Supplementary Material).

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SUPLEMENTARY MATERIAL

Table 1. Original data of Cd concentrations. T0: before resuspension, T1: after 1 h of resuspension, T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (L kg^{-1})
1	T0	0.65	0.96	1.61	0.002	805
2	T0	0.76	0.70	1.46	0.002	730
3	T0	0.61	0.64	1.25	0.002	625
4	T0	0.52	1.03	1.55	0.002	775
5	T0	0.59	0.54	1.13	0.002	565
6	T0	0.61	0.84	1.45	0.002	725
7	T0	0.58	0.68	1.26	0.002	630
8	T0	0.20	1.07	1.27	0.002	635
9	T0	0.76	1.07	1.83	0.002	915
10	T0	0.83	0.83	1.66	0.002	830
11	T0	0.69	0.95	1.64	0.002	820
12	T0	0.52	0.87	1.39	0.002	695
1	T1	0.49	1.13	1.62	0.003	635
2	T1	0.60	0.60	1.20	0.005	233
3	T1	0.60	0.75	1.35	0.002	828
4	T1	0.38	0.93	1.31	0.002	804
5	T1	0.56	0.67	1.23	0.002	580
6	T1	0.57	0.98	1.55	0.002	852
7	T1	0.52	0.98	1.50	0.002	673
8	T1	0.23	0.99	1.22	0.002	678
9	T1	0.60	0.99	1.59	0.002	832
10	T1	1.14	1.11	2.25	0.002	1082
11	T1	0.77	0.91	1.68	0.002	928
12	T1	0.49	1.20	1.69	0.258	7
1	T2	0.46	1.07	1.53	0.002	689
2	T2	0.5	0.81	1.31	0.006	232
3	T2	0.39	0.76	1.15	0.006	179
4	T2	0.39	1.07	1.46	0.002	613
5	T2	0.48	0.74	1.22	0.004	288
6	T2	0.55	0.98	1.53	0.002	654
7	T2	0.40	0.76	1.16	0.005	221
8	T2	0.32	1.19	1.51	0.002	830
9	T2	0.57	0.90	1.47	0.003	588
10	T2	0.40	0.76	1.16	0.006	182
11	T2	0.61	1.26	1.87	0.002	866
12	T2	0.58	1.01	1.59	0.002	952

Table 2. Original data of Cu concentrations. T0: before resuspension, T1: after 1 h of resuspension, T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (kg L^{-1})
1	T0	114.57	19.50	134.07	0.004	33518
2	T0	72.27	22.32	94.59	0.004	23648
3	T0	47.07	20.88	67.95	0.004	16988
4	T0	26.53	15.78	42.31	0.004	10578
5	T0	49.39	26.17	75.56	0.004	18890
6	T0	49.36	25.82	75.18	0.004	18795
7	T0	23.74	61.31	85.05	0.004	21263
8	T0	0.08	10.05	10.13	0.004	2533
9	T0	63.36	26.92	90.28	0.004	22570
10	T0	55.08	39.10	94.18	0.004	23545
11	T0	63.21	21.64	84.85	0.004	21213
12	T0	6.50	27.56	34.06	0.004	8515
1	T1	84.47	26.52	110.99	0.007	15458
2	T1	56.34	16.02	72.36	0.009	8076
3	T1	46.96	17.27	64.23	0.004	14868
4	T1	17.08	19.38	36.46	0.005	7471
5	T1	55.59	16.83	72.42	0.011	6347
6	T1	48.08	41.17	89.25	0.004	22313
7	T1	51.83	17.94	69.77	0.004	17443
8	T1	0.73	9.45	10.18	0.004	2545
9	T1	51.87	27.2	79.07	0.005	15751
10	T1	54.71	18.56	73.27	0.007	11118
11	T1	50.39	27.37	77.76	0.004	19440
12	T1	6.29	24.30	30.59	0.015	1986
1	T2	73.06	25.97	99.03	0.007	13948
2	T2	56.56	20.17	76.73	0.009	8573
3	T2	43.97	19.88	63.85	0.010	6254
4	T2	18.76	18.30	37.06	0.013	2925
5	T2	51.66	19.93	71.59	0.016	4531
6	T2	46.52	25.55	72.07	0.006	11700
7	T2	49.64	21.53	71.17	0.008	8373
8	T2	1.02	8.70	9.72	0.005	1876
9	T2	49.73	23.97	73.70	0.005	15418
10	T2	52.87	21.53	74.40	0.006	11698
11	T2	52.14	25.49	77.63	0.005	16447
12	T2	7.19	24.05	31.24	0.004	7810

Table 3. Original data of Fe concentrations. T0: before resuspension, T1: after 1 h of resuspension, T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (kg L^{-1})
1	T0	15902.7	33758.4	49661.1	0.33	150488
2	T0	18424.5	24449.6	42874.2	0.33	129922
3	T0	15797.6	20822.2	36619.8	0.33	110969
4	T0	20053.8	31597.4	51651.2	0.33	156519
5	T0	15257.8	17751.4	33009.2	0.33	100028
6	T0	7703.4	28903.1	36606.6	0.33	110929
7	T0	14774.9	23425.5	38200.3	0.33	115759
8	T0	10897.8	32538.8	43436.5	0.33	131626
9	T0	12452.1	32294.6	44746.7	0.33	135596
10	T0	20957.8	24938.3	45896.1	0.33	139079
11	T0	9070.7	29005.2	38076.0	0.33	115382
12	T0	11081.0	29613.0	40693.9	0.33	123315
1	T1	9589.0	34460.7	44049.7	0.32	139265
2	T1	11665.3	22842.1	34507.4	0.45	76243
3	T1	13854.6	23691.0	37545.6	2.67	14085
4	T1	13496.8	33968.3	47465.1	0.36	132104
5	T1	12661.2	20427.4	33088.6	0.34	95965
6	T1	5591.7	34260.7	39852.3	0.44	90102
7	T1	8637.5	26990.0	35627.5	1.68	21242
8	T1	11292.5	33839.1	45131.6	0.30	149839
9	T1	8033.7	32945.5	40979.2	0.43	95656
10	T1	11844.9	27153.7	38998.6	3.23	12093
11	T1	6588.8	30438.6	37027.4	0.44	84906
12	T1	9432.5	31700.9	41133.3	0.37	110872
1	T2	10832.1	34523.9	45355.9	0.39	116089
2	T2	11630.1	24936.6	36566.7	3.90	9378
3	T2	12868.5	22091.7	34960.1	15.38	2274
4	T2	12915.7	31394.8	44310.4	0.37	118224
5	T2	12304.8	20391.7	32696.5	5.82	5614
6	T2	5176.6	32520.3	37696.9	0.43	86939
7	T2	8099.5	26323.3	34422.9	6.35	5425
8	T2	21138.7	32851.4	53990.1	0.31	173045
9	T2	9418.1	32907.1	42325.2	0.35	120722
10	T2	12086.7	26710.4	38797.1	7.47	5192
11	T2	6856.5	29975.6	36832.1	0.28	133256
12	T2	10169.3	32079.6	42248.9	0.28	148921

Table 4. Original data of Mn concentrations. T0: before resuspension, T1: after 1 h of resuspension, T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (kg L^{-1})
1	T0	305.5	263.4	568.9	0.08	7112
2	T0	238.5	88.7	327.2	0.08	4091
3	T0	112.7	87.4	200.1	0.08	2501
4	T0	283.5	245.9	529.4	0.08	6617
5	T0	164.2	80.1	244.2	0.08	3053
6	T0	66.5	128.6	195.1	0.08	2438
7	T0	87.0	97.3	184.3	0.08	2303
8	T0	134.5	221.0	355.5	0.08	4444
9	T0	97.2	150.5	247.7	0.08	3096
10	T0	111.3	109.9	221.2	0.08	2765
11	T0	78.6	144.2	222.8	0.08	2785
12	T0	262.6	361.0	623.6	0.08	7795
1	T1	214.9	275.9	490.8	0.04	13680
2	T1	147.8	86.0	233.8	0.76	308
3	T1	84.5	90.9	175.4	0.48	369
4	T1	202.6	252.3	454.9	0.24	1906
5	T1	132.8	83.2	216.0	0.36	599
6	T1	53.4	143.4	196.9	0.09	2230
7	T1	54.1	117.0	171.1	0.14	1185
8	T1	166.3	199.3	365.6	0.19	1959
9	T1	67.1	160.9	228.0	0.15	1532
10	T1	58.7	113.8	172.4	0.22	772
11	T1	60.0	152.9	213.0	0.08	2769
12	T1	299.6	362.0	661.6	0.07	10050
1	T2	214.0	255.9	470.0	0.06	7538
2	T2	97.2	88.7	185.8	2.84	65
3	T2	60.9	88.2	149.1	1.11	134
4	T2	196.1	238.2	434.3	0.34	1261
5	T2	84.5	83.9	168.4	2.36	71
6	T2	48.9	148.2	197.1	0.12	1614
7	T2	46.4	111.2	157.6	0.40	392
8	T2	308.7	199.2	507.9	0.32	1588
9	T2	62.0	149.5	211.5	0.49	429
10	T2	53.9	115.5	169.3	0.49	347
11	T2	62.7	148.3	211.0	0.07	3215
12	T2	298.4	372.1	670.5	0.05	12822

Table 5. Original data of Ni concentrations. T0: before resuspension, T1: after 1 h of resuspension, T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (kg L^{-1})
1	T0	9.31	12.12	21.43	0.001	21430
2	T0	4.30	2.60	6.90	0.001	6900
3	T0	2.58	2.85	5.43	0.001	5430
4	T0	2.52	4.83	7.35	0.001	7350
5	T0	4.32	2.64	6.96	0.001	6960
6	T0	2.11	3.10	5.21	0.001	5210
7	T0	2.80	3.35	6.15	0.001	6150
8	T0	1.10	3.49	4.59	0.001	4590
9	T0	2.33	4.26	6.59	0.001	6590
10	T0	3.59	3.89	7.48	0.001	7480
11	T0	2.73	3.63	6.36	0.001	6360
12	T0	1.58	3.66	5.24	0.001	5240
1	T1	6.97	9.82	16.79	0.004	4690
2	T1	3.36	2.04	5.40	0.006	954
3	T1	2.40	2.84	5.24	0.003	2000
4	T1	1.96	4.79	6.75	0.003	1974
5	T1	3.86	2.49	6.35	0.005	1380
6	T1	2.09	4.52	6.61	0.001	4721
7	T1	2.22	3.47	5.69	0.003	2180
8	T1	1.27	3.67	4.94	0.002	3088
9	T1	1.88	3.94	5.82	0.002	3404
10	T1	2.19	3.66	5.85	0.004	1364
11	T1	2.27	4.03	6.30	0.001	4599
12	T1	1.46	3.62	5.08	0.003	1677
1	T2	6.62	9.14	15.76	0.010	1610
2	T2	2.38	2.67	5.05	0.029	172
3	T2	1.71	2.50	4.21	0.020	206
4	T2	1.72	3.96	5.68	0.010	546
5	T2	2.35	2.47	4.82	0.045	108
6	T2	2.13	3.67	5.80	0.006	946
7	T2	1.93	3.12	5.05	0.016	314
8	T2	1.96	3.10	5.06	0.004	1425
9	T2	1.89	3.38	5.27	0.005	1073
10	T2	1.85	3.46	5.31	0.018	302
11	T2	2.34	3.70	6.04	0.005	1325
12	T2	1.70	3.53	5.23	0.004	1402

Table 6. Original data of Pb concentrations. T0: before resuspension, T1: after 1 h of resuspension, T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (kg L^{-1})
1	T0	60.8	8.9	69.8	0.004	17793
2	T0	41.7	9.7	51.4	0.004	13117
3	T0	34.3	8.4	42.7	0.004	10883
4	T0	27.9	10.0	38.0	0.004	9686
5	T0	40.2	9.6	49.9	0.004	12719
6	T0	36.5	8.5	45.0	0.004	11469
7	T0	40.8	10.7	51.5	0.004	13128
8	T0	6.6	10.3	16.9	0.004	4301
9	T0	40.4	11.8	52.2	0.004	13321
10	T0	50.0	9.7	59.7	0.004	15217
11	T0	41.3	9.1	50.4	0.004	12867
12	T0	23.3	15.3	38.6	0.004	9844
1	T1	43.4	10.0	53.4	0.012	4500
2	T1	31.8	7.8	39.7	0.019	2051
3	T1	31.8	8.6	40.4	0.004	10133
4	T1	21.0	11.1	32.1	0.003	10534
5	T1	34.8	9.1	43.9	0.004	10443
6	T1	33.1	10.8	43.9	0.003	14939
7	T1	33.9	10.4	44.3	0.003	13412
8	T1	8.5	8.5	17.0	0.004	4578
9	T1	32.4	11.0	43.4	0.005	9390
10	T1	32.3	10.7	43.0	0.005	9474
11	T1	33.7	13.0	46.7	0.004	13235
12	T1	21.8	15.3	37.1	0.006	6623
1	T2	45.8	8.8	54.6	0.005	10553
2	T2	32.8	10.5	43.3	0.004	11033
3	T2	32.5	7.9	40.4	0.006	6678
4	T2	19.3	9.3	28.5	0.005	5994
5	T2	37.8	10.4	48.2	0.005	9064
6	T2	31.2	10.2	41.4	0.004	10289
7	T2	33.8	9.3	43.1	0.006	7324
8	T2	14.6	8.0	22.6	0.003	7793
9	T2	33.5	10.3	43.8	0.004	12033
10	T2	35.8	10.2	46.0	0.006	7602
11	T2	35.0	10.9	45.9	0.003	14290
12	T2	24.4	14.3	38.8	0.003	14854

Table 7. Original data of Zn concentrations. T0: before resuspension. T1: after 1 h of resuspension. T2: after 24 h of resuspension.

Sampling Points	Time Interval	1M HCl (mg kg^{-1})	EPA 3051a (mg kg $^{-1}$)	Sum of 1M HCl and EPA 3051a fractions	Water (mg L^{-1})	Kd (kg L^{-1})
1	T0	287.4	30.5	317.8	0.07	4540
2	T0	228.8	26.3	255.1	0.07	3644
3	T0	194.5	23.4	217.9	0.07	3113
4	T0	111.0	24.9	135.9	0.07	1941
5	T0	209.3	25.1	234.5	0.07	3349
6	T0	204.3	21.6	225.9	0.07	3227
7	T0	208.4	33.8	242.2	0.07	3460
8	T0	26.3	20.5	46.8	0.07	668
9	T0	237.0	29.4	266.4	0.07	3806
10	T0	279.8	30.1	309.9	0.07	4427
11	T0	238.1	23.8	261.9	0.07	3742
12	T0	123.4	23.2	146.6	0.07	2094
1	T1	214.7	25.6	240.2	0.07	3432
2	T1	170.0	25.1	195.1	0.09	2167
3	T1	161.2	24.8	186.0	0.07	2657
4	T1	70.5	25.6	96.1	0.07	1373
5	T1	178.8	25.7	204.5	0.09	2273
6	T1	179.0	28.1	207.0	0.07	2958
7	T1	179.6	29.0	208.6	0.07	2980
8	T1	24.6	22.4	47.0	0.07	672
9	T1	190.5	27.6	218.1	0.07	3116
10	T1	172.7	28.9	201.6	0.07	2880
11	T1	191.7	30.2	222.0	0.07	3171
12	T1	107.0	25.0	131.9	0.07	1885
1	T2	203.1	22.7	225.9	0.11	2131
2	T2	116.0	30.7	146.7	1.68	87
3	T2	76.9	23.6	100.5	2.01	50
4	T2	76.3	21.3	97.6	0.07	1348
5	T2	117.7	25.0	142.7	1.97	72
6	T2	177.0	27.2	204.2	0.10	2043
7	T2	113.8	27.1	140.9	1.75	81
8	T2	34.7	19.0	53.6	0.07	766
9	T2	168.3	26.0	194.4	0.37	524
10	T2	101.4	28.7	130.1	1.89	69
11	T2	196.7	27.5	224.2	0.07	3077
12	T2	107.8	22.2	130.0	0.13	1032