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Changes in Cd and Zn bioavailability upon an experimental resuspension of highly contaminated coastal sediments from a tropical estuary

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Abstract Bioavailability evaluations can be an important tool to determine the quality of dredging sediments. Sequential extractions are commonly used to assess the different chemical forms of trace metals in coastal sediments; however, sometimes they are expensive and timeconsuming. Additionally, these analyses do not represent possible changes due to resuspension during and after dredging activity. Newer, easier options to evaluate bioavailability are necessary to understand and preview bioavailability changes resulting from trace metals in dredging and disposal areas. This study aims to evaluate changes in Cd and Zn bioavailability due to sediment resuspension in a highly contaminated area in Sepetiba Bay, Brazil. Twelve surface sediment samples from this location were submitted to a resuspension experiment during two different time intervals (1 and 24 h). The extraction of potentially bioavailable (1 mol L^{-1} HCl-extractable) fractions and strongly bound (concentrated HNO₃-extractable) fractions were sequentially carried out. More than 50 % of the concentrations were in potentially bioavailable fractions. Bioavailability change indexes were proposed; these were estimated as relative changes in bioavailability percentage after resuspension. However, two of these stations presented increases in the Cd and Zn HCl-extractable fractions after sediment resuspension above effects range low

and effects range medium National Oceanic and Atmospheric Administration which are the same limits adopted for Brazilian environmental jurisdiction. Positive correlation of Zn and Cd with TOC in strongly bound fractions evidenced the importance of organic matter binding to preserve metals in this fraction. Fe and Mn partitioning was a major geochemical control on bioavailability of Cd and Zn upon short-time resuspension periods.

Keywords Bioavailability · Coastal sediments · Resuspension · Sediment quality · Sepetiba Bay · Trace metals

Introduction

Sediment resuspension events in coastal environments can occur due to natural processes or be induced by human activities, which are known as factors affecting trace metal bioavailability and their associated environmental risks (Eggleton and Thomas 2004; Roberts 2012). This concern is particularly important for areas that combine metal contamination history with frequent sediment resuspension events, such as harbors, where periodical sediment dredging occurs to support navigation. Assessments of environmental risks associated with metal contamination in these areas can involve the use of sediment resuspension experiments combined with extraction techniques that allow metal bioavailability estimation (Caetano et al. 2003; Machado et al. 2011). Studies comparing strong chemical extraction data with sediment quality guidelines (SQGs) have been frequently done in sediments from dredging areas (Huerta-Diaz et al. 2008; Buruaem et al. 2012). However, the use of resuspension experiments can improve results and be a useful tool for the management of dredging sediments.

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Assessment of sediment quality is recognized as a critical step for estimating the risk associated with man-made pollution in aquatic systems (Castillo et al. 2013). Environmental regulatory agencies from many countries recognize the importance of sediment quality evaluation before dredging activities begin at an area or any other remediation activity at aquatic ecosystems (e.g., Chapman and Mann 1999). In Brazil, trace metals SQGs used for the licensing process of dredging activities were established in 2004 (CONAMA 2004), adopting the safety levels proposed by Long et al. (1995), where Level 1 corresponds to 1.2 and 150 mg/kg^{-1} for Cd and Zn, respectively (ERL). In 2012, the Brazilian legislation was reviewed and incorporated rules for the final disposal of dredged material (CONAMA 2012). The new restrictions drove environmental authorities to demand safer dredging procedures (Wasserman et al. 2013) and include new tests, such as bioaccumulation tests, when the sediment has total concentrations of trace metals above the safety levels. However, chemistry bioavailability tests or geochemistry mobility tests were not included in the legislation.

The effects of dredging on geochemical mobility of contaminants and their availability to biota are poorly known, especially in tropical ecosystems. To improve this knowledge, changes in metal geochemical mobility can be measured in resuspension assays, which simulate the dredging effects using different time intervals (Morse 1994; Van den Berg et al. 2001; Caetano et al. 2003; Cappuyns et al. 2006; Cantwell et al. 2008; Machado et al. 2011; Acquavita et al. 2012).

It is known that trace metals which typically undergo high incorporation into pyrite are susceptible to changes in their geochemical partitioning upon sediment resuspension in oxidizing water. The pyrite can become a source of these elements to the water column if oxidized (Morse 1994; Saulnier and Mucci 2000). However, potential changes in the bioavailability of trace metals that generally do not present elevated pyritization degree (such as Cd and Zn; Huerta-Diaz and Morse 1992), can be also an issue of concern in areas strongly contaminated by these elements. This is the case with sites affected by metallurgical activities, as observed in Sepetiba Bay (SE Brazil), a tropical coastal system influenced by combined effects of severe Cd and Zn contamination (principally due to past activities of a Zn smelting plant), urbanization and harboring activities (Barcellos et al. 1991; Machado et al. 2008; Ribeiro et al. 2013). Cd and Zn emissions from this major industrial source were estimated as 24 and 3660 t year⁻¹, respectively, until 1997 when the metallurgical plant was closed. Contaminants were mainly transferred to the bay by a tidal creek, Saco do Engenho Creek, which received the drainage from a large refuse pile of the past metallurgical plant (Molisani et al. 2004).

This study aimed to evaluate possible changes on trace metal bioavailability in coastal sediments due to resuspension events by simulating a scenario of final disposal of dredging material in which the highly contaminated sediment would be exposed to an oxidant water column. This exposure of anoxic sediment to an oxidant water column can increase the mobility and, consequently, the potential bioavailability of trace metals which could be a threat to local biota. The hypothesis was that the trace metals become more bioavailable after resuspension in an oxidant water column in a laboratory assay using Cd and Zn contaminated sediments samples from Sepetiba Bay as consequence of geochemical partitioning changes.

Materials and methods

The study area is highly impacted by Cd and Zn contamination, located between Saco do Engenho Creek (SEC) and Itaguaí Harbor, northern region of Sepetiba Bay, Rio de Janeiro Brazil. In March 2011, surface sediment samples (nearly 0–10 cm depth) were collected using a Van Veen grab at 12 sampling stations (Fig. 1), while surface estuarine water was sampled in station 12 at approximately 15 cm depth, using acid-cleaned glass bottles. Sampled water salinity was 32, pH was 8.1 and dissolved oxygen concentration was 5.77 mg L⁻¹, as measured using an YSI sonde. Resuspension experiments were carried out at room temperature (~25 °C). The experiment compared short and long time periods of resuspension (1 vs. 24 h). Wet sediment subsamples (7 g) were transferred to 125-mL



Fig. 1 Study area and sampling stations in Sepetiba Bay, Rio de Janeiro, SE Brazil. SEC, Saco do Engenho Creek

Erlenmever flasks and were shaken in 100 mL of unfiltered estuarine water in contact with atmosphere. The experiment was made in duplicate. As blanks, two Erlenmeyers containing only unfiltered estuarine water were used for each time period. Reactive geochemical phase of Cd and Zn were extracted by 16-h agitation in 1 mol L^{-1} HCl solution, a usual approach for metal bioavailability evaluation (Huerta-Diaz and Morse 1990). HCl-extracted subsamples were washed with deionized water and centrifuged three times to remove HCl residues prior to a second-step extraction of strongly bound metal fractions, as previously carried out by Machado et al. (2011). The strongly extraction bound metals method chosen was a microwaveassisted digestion in concentrated HNO₃ (USEPA method 3051A) (USEPA 1994). Cd, Zn, Mn and Fe concentrations were determined by ICP OES. The accuracy was checked using certified samples of NIST 2782. The detection limits were: Cd: 0.01 mg/kg, Fe: 3.00 mg/kg, Mn: 0.02 mg/kg and Zn: 0.01 mg/kg. Sediment grain size was characterized using a particle size analyzer CILAS 1064. After carbonate removal by acidification, total organic carbon (TOC) contents were determined using a Shimadzu TOC analyzer. Possible associations between studied variables were evaluated using correlation analysis. A significance level of 0.05 was accepted.

For the evaluation of possible differences in bioavailability after resuspension, the relative change in the percentage of trace metals in HCl-extractable fractions was calculated, hereafter called as bioavailability change index (BCI), as expressed by the formula:

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

where %HCl_{AR} is the percentage in the HCl-extractable fraction after resuspension, while %HCl_{BR} is the percentage in HCl-extractable fraction before resuspension.

Contamination factors (CF) were calculated in relation to mean background values (Håkanson 1980). These values were obtained from ²¹⁰Pb-dated sediment cores sampled in Sepetiba, as reported by Gomes et al. (2009) and Marques et al. (2006). The averages of background levels derived from these two studies were 0.27 and 72.5 mg/kg⁻¹ for Cd and Zn, respectively.

Results

Sediment grain size and TOC content results are presented in Table 1, while metal concentrations observed before and after resuspension experiments are shown in Table 2. Studied sediments are essentially composed of fine particles (upper 70 % of the silt and clay), while TOC contents ranged from 1.66 to 4.23 %. There was a clear trend of higher Cd and Zn concentration at the stations closer to the

Table 1 Grain size and total organic carbon (TOC) contents of sediments, per sampling station

Station	Sand (%)	Silt (%)	Clay (%)	TOC (%)
1	5.0	87.3	7.6	4.23
2	0.0	79.7	20.3	2.84
3	1.3	87.3	11.4	2.85
4	0.3	81.2	18.4	3.28
5	0.3	83.0	16.7	3.03
6	20.5	70.6	8.9	1.66
7	2.4	86.5	11.1	1.69
8	0.4	82.1	17.6	3.07
9	0.9	80.8	18.2	2.64
10	1.2	81.2	17.6	2.60
11	0.3	80.5	19.2	2.75
12	0.4	82.3	17.3	2.81

shore and to SEC (reaching values one order of magnitude above concentrations found in other stations), partly coinciding with a generally higher HCl-extractable concentration of Mn in stations 1 and 2. These trends were not observed for Fe; that was the only metal showing lower concentration at station 6, which had a more relevant sand content, suggesting sand dilution effect. There was no significant correlation of Cd and Zn concentrations with grain size data. Cadmium and Zn HNO3-extractable phases were significantly correlated with sediment TOC content (r = 0.62 to 0.78), while Cd HCl-extractable phases were significantly correlated with HCl-extractable Mn (r = 0.63to 0.82) for all datasets. Zinc HCl-extractable phases were significantly correlated with HCl-extractable Mn before resuspension and after 1-h resuspension (r = 0.64 and 0.80, respectively). Cadmium HCl-extractable phases were correlated with Fe HCl-extractable before resuspension (r = 0.59) and after 1-h resuspension (r = 0.64).

The relative contributions of HCl-extraction phase to the total concentration are presented in Table 3. All metals presented a general tendency of slight increases in the relative contributions of HCl-extractable phase after sediment resuspension for both time intervals. There was a decreasing tendency in contributions from the closest stations to SEC. Cd showed percentages in HCl-extraction phase above 55 % after resuspension, whereas these estimates were above 80 %.

Relative changes in metal bioavailability are represented in Table 4 estimated as BCI values. These values were up to 16 % for Cd and 20 % for Zn after 1-hr resuspension, and up to 13 % for Cd and 18 % for Zn after 24-h resuspension, which indicate a low relative susceptibility of Cd and Zn to become more bioavailable after resuspension. The spatial distribution, according to the study, were characterized by a clear trend of increasing values with the **Table 2** Concentrations of Fe (mg g⁻¹) and trace metals (μ g g⁻¹) before and after sediment resuspension, per sampling station

Station	HCl-e	xtractal	ble fraction	on	HNO ₃ -extractable fraction				Sums of the two fractions			
	Fe	Mn	Cd	Zn	Fe	Mn	Cd	Zn	Fe	Mn	Cd	Zn
Before r	esuspen	sion										
1	13.6	285	15.72	1982	22.7	70	1.40	212	36.3	354	17.1	2194
2	11.9	234	17.77	3854	25.8	85	1.41	193	37.6	319	19.2	4047
3	11.6	194	8.80	1614	23.3	85	1.28	163	34.9	280	10.1	1777
4	10.5	159	2.59	443	26.2	127	1.10	89	36.7	287	3.69	532
5	12.0	184	4.31	713	27.1	105	1.27	128	39.1	289	5.58	841
6	7.6	119	4.12	580	16.1	52	0.62	64	23.6	171	4.74	644
7	7.9	104	4.10	419	23.4	87	0.66	40	31.3	191	4.76	459
8	12.8	190	2.73	409	27.5	116	0.82	66	40.3	306	3.54	475
9	8.9	150	1.26	205	24.9	166	0.83	82	33.8	317	2.09	287
10	7.7	165	0.78	124	26.0	146	0.70	50	33.7	311	1.47	174
11	9.2	169	0.84	135	24.4	120	0.63	38	33.6	289	1.47	173
12	10.5	195	1.28	199	26.6	115	0.81	47	37.1	310	2.09	246
After 1-l	h resusp	ension										
1	14.4	295	16.74	2103	20.9	48	1.16	169	35.3	343	17.9	2273
2	13.5	305	22.08	4772	23.8	47	0.97	93	37.3	352	23.0	4865
3	11.6	202	7.99	1424	21.3	50	0.86	89	32.9	253	8.85	1513
4	10.4	158	2.02	333	19.9	80	0.54	39	30.3	238	2.57	372
5	12.1	194	4.81	775	24.5	73	0.79	71	36.5	267	5.60	846
6	10.9	164	6.59	778	16.8	46	0.53	44	27.8	210	7.12	822
7	9.9	128	4.72	486	18.7	49	0.47	21	28.6	177	5.19	506
8	13.2	202	2.91	425	23.9	70	0.72	44	37.1	272	3.63	469
9	10.6	168	1.47	250	21.3	137	0.66	42	31.9	305	2.14	292
10	9.9	193	0.83	150	20.9	97	0.57	27	30.9	289	1.41	177
11	11.1	187	0.92	153	19.2	79	0.46	19	30.4	266	1.37	171
12	13.0	209	1.49	212	23.0	72	0.63	30	36.1	280	2.12	242
After 24	-h resus	pension	L									
1	13.1	263	14.72	1845	18.7	44	1.18	169	31.8	307	15.9	2014
2	12.3	280	19.13	4215	24.5	60	0.93	106	36.8	340	20.1	4321
3	10.2	176	7.79	1424	23.7	58	1.00	125	33.9	234	8.79	1549
4	10.4	153	2.02	326	21.1	82	0.73	51	31.6	235	2.75	377
5	11.0	169	4.34	682	24.5	72	0.99	86	35.5	241	5.32	767
6	7.6	118	3.97	532	12.5	30	0.42	44	20.1	147	4.39	576
7	7.6	110	4.04	408	19.1	52	0.48	19	26.7	162	4.52	428
8	17.4	269	3.56	579	23.4	69	0.74	54	40.8	338	4.30	633
9	10.0	166	1.42	229	23.0	134	0.69	53	33.1	300	2.11	282
10	9.3	189	0.81	138	19.4	93	0.55	26	28.7	281	1.36	164
11	9.8	170	0.82	148	20.4	85	0.57	24	30.1	255	1.40	172
12	11.7	196	1.39	194	23.1	72	0.64	33	34.8	268	2.03	227

distance from SEC for Zn. Cadmium followed this trend to a less accentuated extent. Zinc bioavailability changes were correlated with those of Fe after both resuspension times (r = 0.62 and 0.67 for 1- and 24-h resuspension times, respectively). Cadmium bioavailability changes were also correlated with Fe bioavailability changes after 24-h resuspension (r = 0.63), but not for the 1-h resuspension experiment. The anthropogenic contribution of Cd and Zn were calculated as the ratio between metal concentrations in superficial sediments from the sampling stations and the respective background levels. The results obtained for these contamination factors (CF) can be classified, according to Håkanson (1980), as follows:

CF < 1 = there is no contamination or it is low.

CF 1 > 3 = moderate contamination.

Table 3 Percent contribution of HCl-extractable phase to determine the sums of HClextractable and HNO₃extractable phases, before and after sediment resuspension, per sampling station

Station	Before	e resuspe	ension		After 1-h resuspension				After 24-h resuspension			
	Fe	Mn	Cd	Zn	Fe	Mn	Cd	Zn	Fe	Mn	Cd	Zn
1	37.4	80.4	91.8	90.3	40.8	86.1	93.5	92.6	41.3	85.6	92.6	91.6
2	31.6	73.4	92.6	95.2	36.3	86.5	95.8	98.1	33.4	82.5	95.4	97.5
3	33.2	69.5	87.3	90.8	35.3	80.0	90.3	94.1	30.1	75.3	88.6	91.9
4	28.6	55.5	70.1	83.3	34.4	66.4	78.8	89.6	33.0	65.1	73.3	86.4
5	30.7	63.6	77.3	84.8	33.0	72.6	86.0	91.6	31.0	70.0	81.5	88.8
6	32.0	69.3	87.0	90.0	39.4	78.2	92.6	94.6	37.9	79.9	90.5	92.4
7	25.3	54.4	86.1	91.4	34.7	72.4	90.9	95.9	28.3	67.8	89.3	95.5
8	31.7	62.1	76.9	86.0	35.6	74.2	80.2	90.6	42.7	79.5	82.7	91.5
9	26.3	47.4	60.2	71.4	33.2	55.1	68.9	85.7	30.3	55.3	67.4	81.1
10	22.8	53.0	52.6	71.3	32.2	66.6	59.3	84.6	32.4	67.0	59.3	84.1
11	27.4	58.5	57.3	77.9	36.7	70.4	66.7	89.1	32.4	66.6	59.1	86.3
12	28.3	63.0	61.3	81.0	36.1	74.5	70.3	87.8	33.6	73.2	68.3	85.5

 Table 4
 Percent changes in metal bioavailability after sediment resuspension, per sampling station

Station	After	1-h resu	ispensic	n	After 24-h resuspension				
	Fe	Mn	Cd	Zn	Fe	Mn	Cd	Zn	
1	9.2	7.1	1.8	2.5	10.5	6.5	0.8	1.4	
2	14.9	17.9	3.4	3.0	5.7	12.3	3.0	2.4	
3	6.4	15.1	3.5	3.6	9.1	8.4	1.5	1.2	
4	20.2	19.5	12.5	7.5	15.4	17.3	4.6	3.6	
5	7.7	14.2	11.2	8.0	1.1	10.1	5.4	4.8	
6	23.1	12.8	6.5	5.1	18.6	15.2	4.0	2.7	
7	37.4	33.1	5.5	4.9	12.1	24.6	3.8	4.5	
8	12.4	19.5	4.3	5.3	34.5	28.0	7.6	6.3	
9	26.4	16.2	14.4	20.0	15.2	16.6	12.0	13.5	
10	41.3	25.8	12.7	18.7	42.1	26.6	12.7	18.1	
11	33.8	20.3	16.4	14.4	18.0	13.8	3.1	10.7	
12	27.5	18.2	14.7	8.4	18.7	16.2	11.5	5.6	

CF 3 > 6 = considerable high contamination.

CF > 6 = very high contamination.

Table 5 presents CFs results. For Cd, the maximum CF was found to be 71 (very high contamination) at station 2, and the minimum was 5.4 (considerable high contamination) at station 11. There was a trend of decreased CF values with the distance from SEC mouth. Zinc showed a similar pattern, with the maximum CF value found at station 2 (55.8; very high contamination) and the minimum found at station 11 (2.4; moderate contamination). Stations 10 and 11 were classified as moderate contamination and stations 9 and 12 were (classified as considerable high contamination; all the other stations showed very high contamination. CFs were significantly correlated with relative contributions of potentially bioavailable phases for Cd (r = 0.78) and Zn (r = 0.67).

Discussion

In cases of dredging activities, the first evaluation is the comparison of the results with the safety levels established on actual legislation. According to Brazilian Federal Legislation, the studied samples presented Cd and Zn levels (Table 2) exceeding CONAMA Level 1, indicating they may promote adverse effects. Sums of HCl and HNO₃ extractions were up to 16-times higher the SQG for Cd and 27-times higher the SQG for Zn, with HCl-extractable phase predominant for both metals. For the SQG of Level 2, 7.2 and 410 mg/kg⁻¹ for Cd and Zn, respectively, values correspond to the threshold above which there is major probability of adverse effects occurring on biota. Sampling stations 1, 2 and 3 exceeded the limit for Cd, and stations 1 to 8 exceeded the limit for Zn, being 1.4-2.7 times higher the SQG for Cd, and 1.1-9.9 times higher than the SQG for Zn. According to these regulations, such results request additional investigation if dredging is intended, such as toxicity tests and/or bioaccumulation assays (CONAMA 2012).

Two of twelve sampling stations presented an increase on HCl-extractable Cd (3.86 and 2.38 mg/kg⁻¹ in stations 2 and 6, respectively) and Zn (819 and 178 mg/kg⁻¹ in stations 2 and 6, respectively) above the referred SQGs after 1-h resuspension. This pattern was also observed for Zn (275 and 158 mg/kg⁻¹ in stations 2 and 6, respectively) after 24-h experiments. Even then with a slight increase after resuspension, this increase was enough to exceed the safety levels and transform into potentially bioavailable forms a significant amount of Cd and Zn that were strongly bound to sediments before. This may exemplify situations in which small relative differences correspond to environmentally relevant absolute differences. **Table 5** Contamination factors (CF) and its classification according to Håkanson (1980), per sampling station

Station	[Cd]	CF Cd	Classification	[Zn]	CF Zn	Classification
1	17.1	63.4	Very high	2194.3	30.3	Very high
2	19.2	71.1	Very high	4046.7	55.8	Very high
3	10.1	37.3	Very high	1776.8	24.5	Very high
4	3.7	13.7	Very high	531.5	7.3	Very high
5	5.6	20.7	Very high	840.9	11.6	Very high
6	4.7	17.5	Very high	644.3	8.9	Very high
7	4.8	17.6	Very high	458.8	6.3	Very high
8	3.5	13.1	Very high	474.9	6.6	Very high
9	2.1	7.8	Very high	287.4	4.0	Considerable high
10	1.5	5.5	Considerable high	173.8	2.4	Moderate
11	1.5	5.4	Considerable high	173.2	2.4	Moderate
12	2.1	7.8	Very high	245.8	3.4	Considerable high

[] = Concentration of Cd and Zn obtained by the sum of the two fractions (HCl- and HNO₃-extractable fractions)

Considering the severity of this contamination, bioavailability-based data can be additional tools to identify management priorities related to activities that promote sediment resuspension, since relatively small changes in high concentrations can imply in ecological risks and increasing biological metals uptake. For example, during resuspension events, metals may become partly available in the dissolved phase (which may often be of short duration; e.g., Maddock et al. 2007) and metals recently associated to the solid phase can present a weaker association than occurred before resuspension (e.g., by adsorption to particles surfaces; e.g., Caetano et al. 2003). The mechanisms involved in such transition between geochemical phases are frequently related to the production of metal oxides and hydroxides upon sediment resuspension, e.g., as a consequence of sulfides oxidation (Simpson et al. 2000; Cantwell et al. 2008). The observed correlations between Cd and Zn data with Mn and Fe data support that these mechanisms were important geochemical controls on the behavior of studied metal contaminants. Morse (1994) and Machado et al. (2011) showed also in their results after resuspension that the Cu in sediments was in a bioavailable phase.

The study of trace metals bioavailability is of great interest for management decisions concerning dredging activities and the final disposal of their residuals. However, high trace metals concentrations in sediment will not always be a consequence of dredging activity. Many other physical-chemical factors might capture metals from the water column. Carvalho and Lacerda (1992) found very low trace metals concentrations on biota of Guanabara Bay, despite the extremely high trace metal contamination due to anthropogenic activities in this ecosystem. The authors also compared the results with trace metals found in organisms from other two non-contaminated areas, Arraial do Cabo and Angra dos Reis, both located in Rio de Janeiro State. Here, higher concentrations were described to both uncontaminated areas. The reasons pointed by the authors for this difference are the high organic matter which regulates the bioavailability of trace metals in Guanabara Bay. The same result was found by Kehrig et al. (2002) when they analyzed MeHg and THg in fish species in Guanabara Bay. Rodrigues et al. (2011) have found similar results to Carvalho and Lacerda (1992), where Guanabara Bay had lower mercury concentrations in fish species than Ribeira bay, an uncontaminated site.

Considering that environmental legislations are revised periodically, the coupled use of different lines of evidence has been recognized as important tools to be incorporated, e.g., toxicity tests and bioavailability (Torres et al. 2009). The results discussed above also evidence that additional studies concerning geochemical partitioning may improve risk assessment, such as utilizing conventional uses of total (or near-total) metal concentration comparison together with SQGs. While fluctuations in environmental physicalchemical characteristics which influence metal bioavailability can be used to adapt SQGs (Hübner et al. 2009), the use of bioavailability-based sediment quality analysis in addition to current uses of SQGs would be an alternative and advantageous approach.

Conclusions

Low relative changes in the bioavailability of studied trace metals were found in the study site. Two of twelve sampling stations presented relevant increases in the Cd and Zn HCl-extractable fractions after sediment resuspension, being above SQGs adopted in the ERL and ERM. The positive correlation of Zn and Cd with TOC in strongly bound forms evidenced the importance of organic matter binding to preserve metals in this fraction. Fe and Mn partitioning was a major geochemical control on bioavailability of Cd and Zn upon short-time resuspension periods, but this role seems to be dependent on resuspension time, as observed for Cd. The formation of oxy-hydroxides after resuspension regulated the bioavailability of trace metals in bioavailable fraction.

The use of BCI showed a important and efficient tool for showing changes in bioavailability of trace metals before and after resuspension and can be used in evaluation of ecological risk of sites. The prediction of behavior of trace metals in sediment on site is a form for relatively quickly assessing the risks associated with dredging before the activity occurs. Good planning can decrease the environmental problems associated with bioavailability of trace metals in sediment or in water column after dredging activities.

The use of different tools for bioavailability prediction in contaminated areas susceptible to resuspension is a way to improve the SQGs, to support the management decisions for contaminated areas and to bring new possibilities for reviewing regulatory legislation.

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Compliance with ethical standards

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Informed consent Informed consent was obtained from all individual participants included in the study.

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