ARTICLE IN PRESS

Marine Pollution Bulletin xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil)

Andreza Portella Ribeiro[a,b,*], Ana Maria Graciano Figueiredo[b,1], José Osman dos Santos[c,2], Elizabeth Dantas[b,1], Marycel Elena Barboza Cotrim[b,1], Rubens Cesar Lopes Figueira[d,3], Emmanoel V. Silva Filho[e,4], Julio Cesar Wasserman[f,5]

[a] Mestrado de Gestão Ambiental e Sustentabilidade, Universidade Nove de Julho (UNINOVE), Av. Francisco Matarazzo, 612, prédio C, andar térreo, Água Branca, São Paulo, SP 05001 100, Brazil
[b] Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear (IPEN-CNEN), PO Box 11049, 05422 970, Brazil
[c] Instituto Federal de Educação, Ciência e Tecnologia de Sergipe, (IFS-UNED-Lagarto), Povoado Carro Quebrado, CCHS, Lagarto, SE 49400 000, Brazil
[d] Instituto Oceanográfico, Universidade de São Paulo (IO-USP), Pça. do Oceanográfico, 191, Butantã, SP 05508 900, Brazil
[e] Programa de Pós-Graduação em Geoquímica, UFF, Outeiro de Sao Joao Batista s/n, Centro, Niteroi, RJ 24020 150, Brazil
[f] Universidade Federal Fluminense, Rede UFF de Meio Ambiente e Desenvolvimento, Av. Litorânea, s/n, Boa Viagem, Niterói, 24020 149, Brazil

ARTICLE INFO

Keywords:
Metals
Bioavailability
Mobility
SEM/AVS
Attenuation
Sepetiba Bay

ABSTRACT

This study proposes a new methodology to study contamination, bioavailability and mobility of metals (Cd, Cu, Ni, Pb, and Zn) using chemical and geostatistics approaches in marine sediments of Sepetiba Bay (SE Brazil). The chemical model of SEM (simultaneously extracted metals)/AVS (acid volatile sulfides) ratio uses a technique of cold acid extraction of metals to evaluate their bioavailability, and the geostatistical model of attenuation of concentrations estimates the mobility of metals. By coupling the two it was observed that Sepetiba Port, the urban area of Sepetiba and the riverine discharges may constitute potential sources of metals to Sepetiba Bay. The metals are concentrated in the NE area of the bay, where they tend to have their lowest mobility, as shown by the attenuation model, and are not bioavailable, as they tend to associate with sulfide and organic matter originated in the mangrove forests of nearby Guaratiba area.

1. Introduction

Inorganic and organic chemicals produced by various anthropic activities are one of the main contributors to the degradation of coastal environments (Cesar et al., 2006). These regions are prominently susceptible to human impacts as urbanization and industrialization affect the complex structure and dynamic characteristics of marine ecosystems (Celino et al., 2008; Raj and Jayaprakash, 2008).

Sediments are considered to be the main reservoir of metallic and organic pollutants for the marine environment (Chapman et al., 1999; Fukumoto, 2007; Ridgway and Shimmield, 2002). In human-impacted area, due to the fact that sediments constitute a significant storage compartment of pollutants from the water column, they can also be a potential source of these contaminants whenever they release it back to the free environment through wind resuspension, dredging, bioturbation or diffusion (Audry et al., 2004; Luiz-Silva et al., 2006).

As the sediment storages contaminants, benthic flora and fauna constitute an important link for the coastal marine food web (Wolff, 1980). Contaminants from the sediments absorbed by benthic organisms bioaccumulate and biomagnificate as they escalate the food chain, reaching fishes, birds, and eventually humans (Bargagli et al., 1998; Lawson and Mason, 1998; Silvério, 2003).

Knowledge regarding the chemical composition of sediments is of great relevance when studying environmental pollution, as it mirrors the historical inputs to the environment (Li et al., 2000; Ribeiro, 2006; Turner, 2000). Therefore, the contamination of coastal sediments became a focal study point to the world scientific community, as it is a major source of ecosystem health stress (Caeiro et al., 2005).

Since 1980s, these studies became more sophisticated, passing from the initial researches on causes and patterns of contamination, toward behavior, mobility and bioavailability evaluation of metallic elements (Zhigang and Pu, 2007). There is a large number

---

[*] Corresponding author at: Mestrado de Gestão Ambiental e Sustentabilidade, Universidade Nove de Julho (UNINOVE), Av. Francisco Matarazzo, 612, prédio C, andar térreo, Água Branca, São Paulo, SP 05001 100, Brazil. Tel.: +55 11 3665 9342.
E-mail address: andrezp@uninove.br (A.P. Ribeiro).

[1] Tel.: +55 11 3133 9977.

[2] Tel.: +55 79 3321 1500.

[3] Tel.: +55 11 3091 6610.

[4] Tel.: +55 21 27174189.

[5] Tel.: +55 21 2629 99745.

0025-326X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

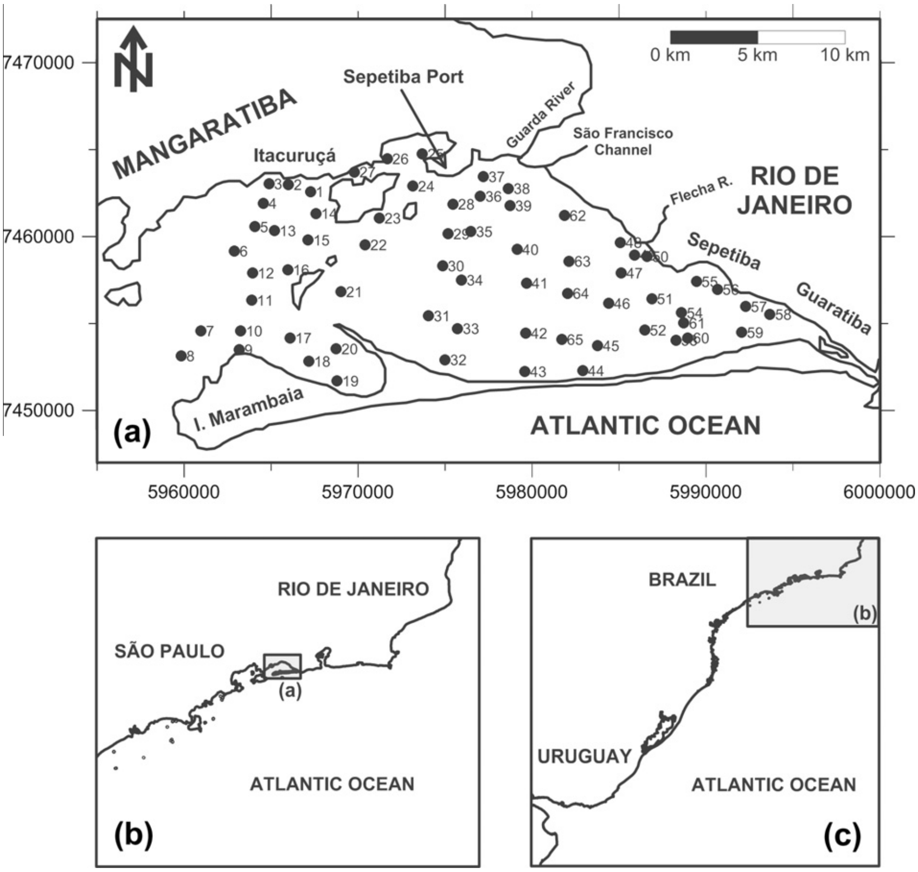

Fig. 1. Sampling sites at Sepetiba Bay (a), located in Rio de Janeiro state coast (b), and Southeast Brazil (c).

of environmental quality indicators and indices to assist the study and evaluation of contaminants present in environmental matrices such as sediments (Caeiro et al., 2005) that are based only in these elements concentrations, for example: concentration factor, enrichment factor and geochemical index (Laluraj and Nair, 2006; Mahiques et al., 2009; Ribeiro et al., 2011; Zhang et al., 2007).

In aquatic systems, metals undergo partition between water and suspended matter, ultimately reaching the sedimentary compartment. Di Toro et al. (1992) improved the understanding about partitioning of metals in sediments when noticing that their controlling agents in sediments are the acid volatile sulfides (AVS). AVS correspond to the solid phase of sulfides that are soluble in cold hydrochloric acid and are available for binding metals (TVA, 2009), consisting primarily of Fe and Mn sulfides (Di Toro et al., 1990; Mozeto, 2001; Ribeiro, 2006).

During extraction with cold hydrochloric acid, besides volatilization of the sulfides, a fraction of labile metals is extracted that is known as simultaneously extracted metals (SEM; Ribeiro, 2006). This fraction is an indicator of metals toxicity that can be estimated by simultaneously analyzing the SEM and the AVS, which is their main complexing agent in sediments (Allen et al., 1993; De Jonge et al., 2010; Teuchies et al., 2012).

The toxicity of metals capable of forming insoluble sulfides can be predicted by the ratio SEM/AVS (Di Toro et al., 1992). If this ratio is greater than one, that is, SEM > AVS, the excess metal can possibly be liberated to the interstitial water, where it can become toxic. Therefore, this ratio is used to evaluate the bioavailability and mobility of metals in sediments and has been applied to a variety of studies throughout the world (Brix et al., 2010; Machado et al., 2004; Vasconcelos et al., 2010).

Sepetiba Bay (Fig. 1), located 60 km from Rio de Janeiro metropolitan region (SE Brazil), suffered a considerable urban and industrial development in the last decades. Its basin presents about 400 industries, most of which metallurgic plants, releasing wastes rich in metals and other potentially toxic substances directly in the bay and in its waters (Cunha et al., 2009; Gomes et al., 2009; Paraquetti et al., 2004).

Itaguaí Harbor is located in Sepetiba Bay, occupying an area of over 10 million m^2 that can receive large vessels (Pellegatti et al., 2001). These portuary facilities brought intense economic development to the region, but also negative consequences to the surrounding environment, with direct contamination of the water or from the atmosphere (Pedlowsky et al., 1991; Silva-Filho et al., 1999; Wasserman et al., 2000).

This paper presents a new methodology to evaluate contamination, bioavailability and mobility of Cd, Cu, Ni, Pb and Zn by coupling a model of cold acid extraction of metals (SEM/AVS) and a geostatistical model (model of attenuation of concentrations) based on the spatial distribution of the metals in bottom sediments of Sepetiba Bay. Granulometry and organic carbon contents were determined to allow a better interpretation of the levels of metals and their mobility in the study area.

2. Materials and methods

2.1. Sampling

Sediment samples were collected with a stainless steel Van Veen bottom grab in 65 different sites distributed throughout Sepetiba Bay in 2003 (Fig. 1). These samples were frozen, lyophilized, weighted and transferred to plastic containers.

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

2.2. Granulometric and organic carbon contents determination

Granulometry and organic carbon content were determined in order to allow a better interpretation of the availability and mobility of metals, as the presence of metals in sediments depends strongly on its particle-size distribution and its relationship with organic matter (Fernandes et al., 2011). Granulometry was assessed using the sieving methodology proposed by Suguio (1973), and organic carbon was measured in a CHN analyzer (Perkin-Elmer, model 2400 CHN).

2.3. Total concentration of metals

The total concentrations of metals were determined via total digestion procedure with a mixture of strong acids in a microwave oven, as recommended by US-EPA (United States Environmental Protection Agency; US-EPA, 2003). Cd, Cu, Ni, Pb and Zn concentrations were determined by ICP-OES (induced coupled plasma – optical emission spectrophotometry; Spectro, model Spectro Flame M120E). All metal analyses were replicated and presented relative standard deviation (ratio between the mean and the standard deviation of the replicated measurements) lower than 10%.

The precision and the accuracy of the methodology was evaluated through the determination of Cd, Cu, Ni, Pb and Zn in certified reference materials NIST-SRM 2704 (National Institute of Standards and Technology, riverine sediment), MESS2 (National Research Council of Canada, estuarine sediment) and IAEA-Soil-7 (International Atomic Energy Agency, soil). The precision was checked using the relative standard deviation (RSD) and the accuracy was checked using the relative error (RE) of the data generated in these measurements.

2.4. SEM/AVS model

The acid extraction of metals from sediment to determine AVS and SEM was performed based on the technique adopted by the US-EPA (Allen et al., 1991, 1993; Machado et al., 2004).

In this methodology, the sulfides in the sample are converted into hydrogen sulfide (H_2S) by reaction with cold hydrochloric acid (HCl). The produced sulfide then reacts with DMPD (N,N-dimethyl-phenyl-p-diamine) in the presence of ferric chloride ($FeCl_3$) and is quantified with a UV–visible spectrophotometry. The remaining solution after the removal of sulfides is filtered and the targeted dissolved metals (Cd, Cu, Ni, Pb and Zn) are determined by ICP-OES (induced coupled plasma – optical emission spectrophotometry) (Spectro, model Spectro Flame M120E). From the molar concentrations of the sulfides (AVS) and the sum of the molar concentrations of the target metals (SEM), the ratio SEM/AVS is calculated.

2.5. Model of attenuation

The model of attenuation is a modified procedure that followed the study proposed by Wasserman and Queiroz (2004), and is based in the principle of the Fick diffusion law, assuming that the concentration of an element decays spatially from theoretical punctual sources (maximum concentrations, or hot spots). The attenuation of concentration can be determined with the following equation

$$A = \text{grad } F = (\partial E/\partial x) + (\partial E/\partial y) \qquad (1)$$

In which A is the attenuation of concentration of an element E (in $\text{mg kg}^{-1}\text{ m}^{-1}$); E is the concentration of an element E (in mg kg^{-1}); grad F is the gradient of the concentration of an element E (in $\text{mg kg}^{-1}\text{ m}^{-1}$). $\partial E/\partial x$ is the longitudinal derivative of the concentration of an element E (in $\text{mg kg}^{-1}\text{ m}^{-1}$); $\partial E/\partial y$ is the latitudinal derivative of the concentration of an element E (in $\text{mg kg}^{-1}\text{ m}^{-1}$).

With the values of A, a distribution map can be created to evaluate how a given element behaves spatially and its range from its hot spot(s), information that is essential when assessing its mobility. According to this model, the generated maps can inform regions where metals retention is higher (higher values of A). For this purpose, softwares Excel (Microsoft, version 2010) and Surfer (Golden Software, version 9) were used to make the necessary calculations.

3. Results and discussion

3.1. Quality control

The quality control of the analytical data obtained for Cd, Cu, Ni, Pb and Zn was accomplished by analyzing the selected certified reference materials. The mean values and standard deviations obtained for replicated analyses of the certified reference materials are presented in Table 1.

The results of Table 1 shows an adequate precision with relative standard deviations ranging from 2.5% for Zn to 9.0% for Pb. Also, for all analyzed elements, the results were in good agreement with certified values, with relative errors never greater than 10%.

3.2. Granulometry and organic carbon content distribution in Sepetiba Bay

Granulometry is recognized as an important factor controlling metallic contents in sediments due to the fact that specific surface in fine grained sediments is larger than in coarse sediments (Förstner and Salomons, 1980). Therefore, these fine grained fractions tend to be more reactive than coarser sediments. The granulometric control drove some researchers to assume that a correction based on grain size percentage, normally the fraction smaller than 63 μm (fine grained sediments), would be necessary to interpret metallic concentrations (Clark et al., 1998; Loring and Rantala, 1992). Based on this concept, some authors carried out metal analyses on the <63 μm fraction, ignoring the other fractions (Kehrig et al., 2003; Wasserman et al., 2001).

Fig. 2 shows the granulometric distribution of fine grained sediments in Sepetiba Bay. This result showed that fine grained sediments are predominant in Sepetiba Bay, mainly in the eastern area. On the other hand, in the seaward side of the bay (west and southwest), there are higher amounts of coarse grained

Table 1

Concentrations of Cd, Cu, Ni, Pb and Zn (in mg kg^{-1}) in standard reference materials. Quality control through the evaluation of precision and accuracy of the methodology.

Metal	Reference material	Certified concentration (mg kg^{-1})[a]	Measured concentration (mg kg^{-1})[b]	Precision (RSD) (%)	Accuracy (RE) (%)
Cd	NIST-SRM 2704	3.45 ± 0.22	3.60 ± 0.26 (n = 14)	7.2	4.3
	IAEA-Soil-7	104[c]	100	[d]	3.8
Cu	MESS2	39.2 ± 2.0	35.5 ± 2.9 (n = 7)	8.2	9.4
Ni	MESS2	49.3 ± 1.8	45.6 ± 4.0 (n = 7)	8.8	7.5
Pb	MESS2	21.9 ± 1.2	19.9 ± 1.8 (n = 7)	9.0	9.1
Zn	NIST-SRM 2704	438 ± 12	475 ± 12 (n = 14)	2.5	8.4

[a] Concentration values represented in the form (median ± confidence interval).
[b] Concentration values represented in the form (mean ± standard deviation).
[c] Value of information.
[d] Value not determined.

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

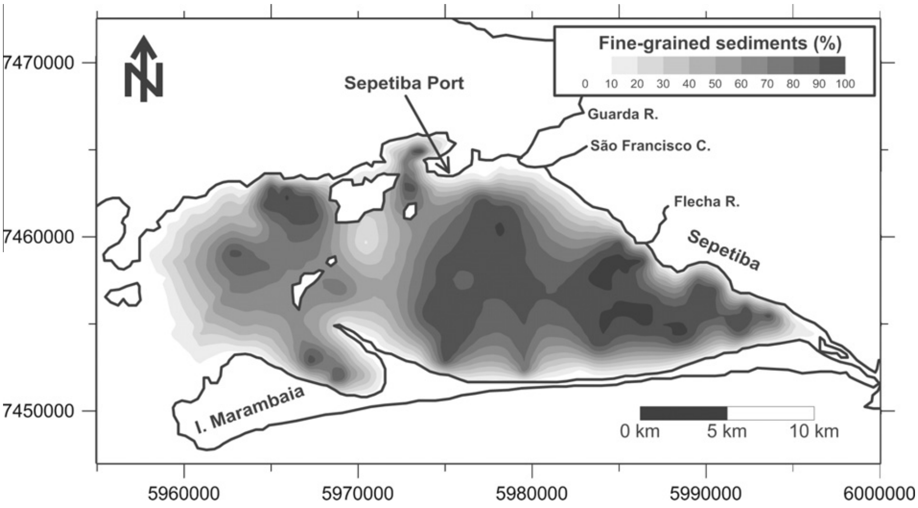

Fig. 2. Spatial distribution of fine-grained sediments (grain fraction smaller than 63 μm) (in %) in Sepetiba Bay (SE Brazil).

sediments. This area is subject to more intensive hydrodynamics (Molisani et al., 2006). Furthermore, the clockwise currents are predominant in Sepetiba Bay (Signorini, 1980). Therefore, less deposition and accumulation of metals are expected in the western portion of the bay.

The organic matter has a significant role in the destination of metal ions in the environment as it provides sorption or reaction sites, retaining these pollutants in the sediments or forming the more toxic organo-metallic complexes. Earlier studies showed that Cu^{2+} presents stronger affinity to organic matter compared with other heavy metals (Reimann and De Caritat, 1998). Therefore, in an organic rich environment, Cu may be less mobile than other metals. Also, in the presence of organic matter, the development of microorganisms may affect the chemical speciation of metal ions and control metal bioavailability and/or toxicity in aquatic systems (Wasserman et al., 2000).

The results obtained for organic carbon content in the sediment samples showed contents varying between 2% and 3% for most of the analyzed samples. As presented in Fig. 3, the highest values were observed in the southeastern portion of the bay due to the extensive mangrove forests in that region, which are considered significant sources of organic matter (Neves et al., 2006).

3.3. Total concentration of metals

Fig. 4 presents the spatial distribution of the total concentration of the analyzed metals in the sediments of Sepetiba Bay. The comparison with some reference and literature values for metal concentration in sediments indicates considerably high levels of Cd and Zn (Table 2). Pb concentrations are also slightly above the limits of the ISQG (Interim Sediment Quality Guidelines; CCME, 1999, 2002), that correspond to the threshold level effects below which adverse biological effects are not expected, and the average shale (Reimann and De Caritat, 1998). Also, the comparison with data from the neighboring Guanabara Bay (Perin et al., 1997) indicates similar concentrations except for Zn.

Zn can be considered a pollutant in Sepetiba Bay, as its concentrations exceed the PEL (Probable Effect Level) limit (Table 2). Its contamination is the result of repeated accidental spillings of zinc ore wastes in the bay, and although this liability exists since the early 1980s, in 2005 the Federal Authorities began an environmental recovery program at the site (Pinto, 2005). Fig. 4e shows that the highest Zn contents were observed close to the mouth of São Francisco Channel and Guarda River, where most of the industrial wastes are dumped into the bay.

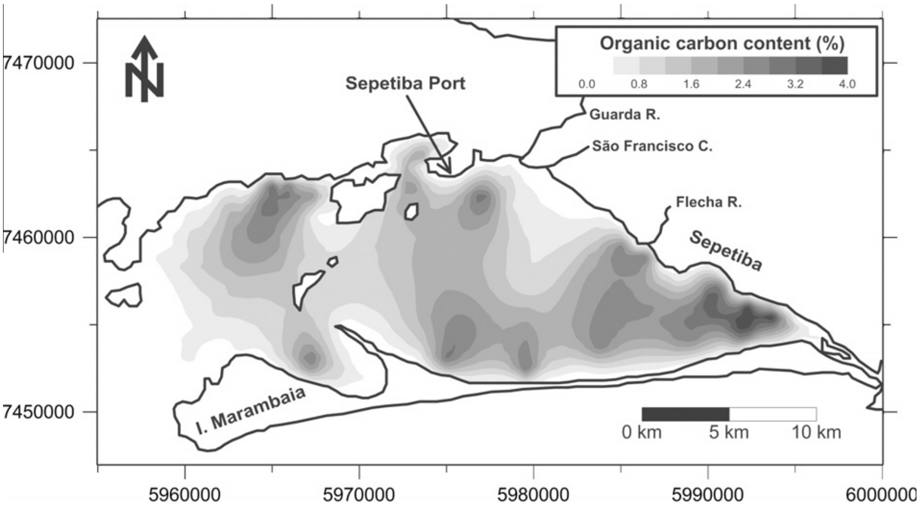

Fig. 3. Spatial distribution of organic carbon content (in %) in sediments of Sepetiba Bay (SE Brazil).

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

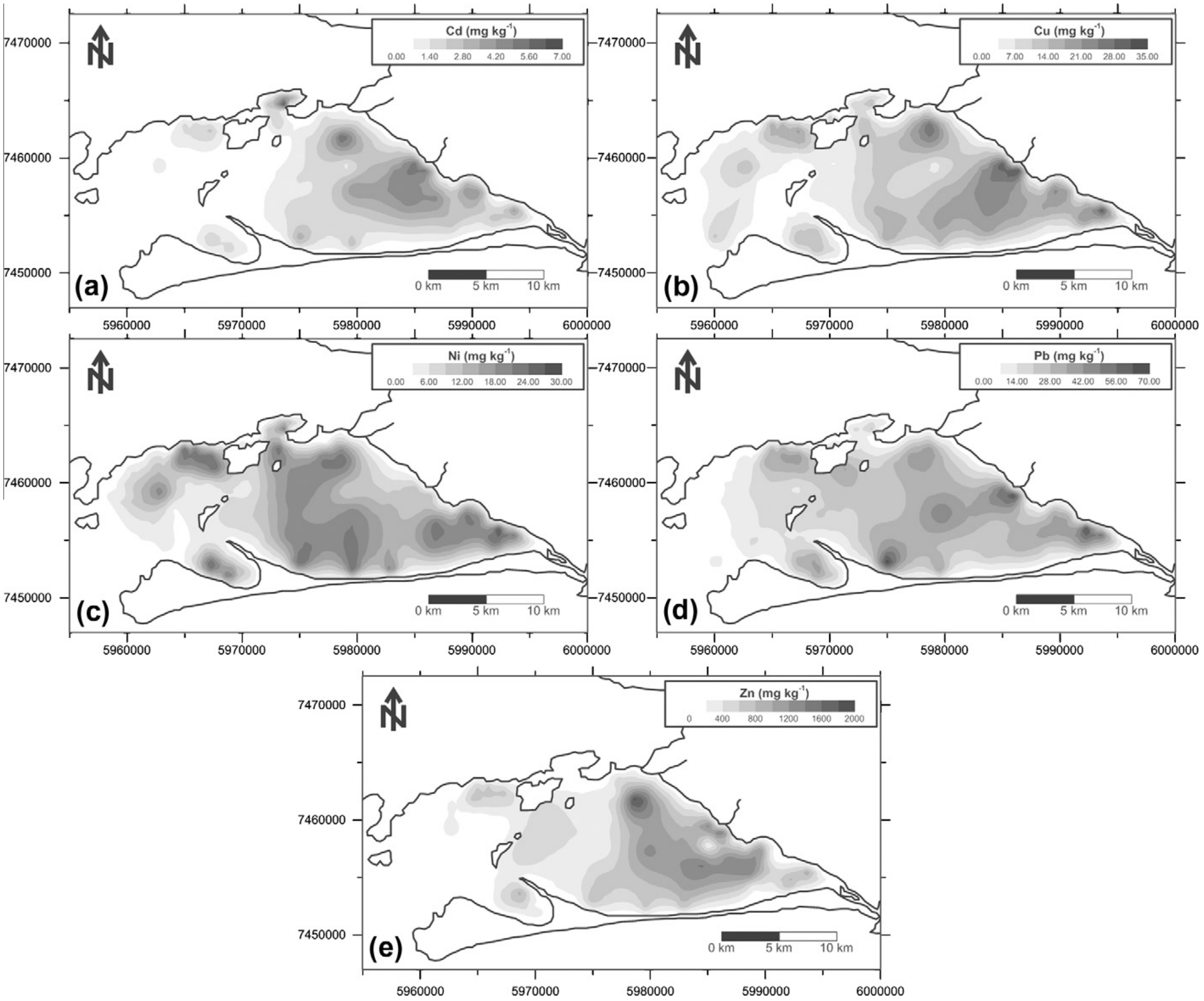

Fig. 4. Spatial distribution of the total concentration of metals (in mg kg^{-1}) in sediments of Sepetiba Bay (SE Brazil). (a) Cd, (b) Cu, (c) Ni, (d) Pb, and (e) Zn.

Table 2
Comparisons of metals concentration (in mg kg^{-1}) in sediments of Sepetiba Bay (SE Brazil) with the Canadian Environmental Quality Guideline (CCME, 2002).

Element	Concentration (mg kg^{-1})				
	This study			Canadian Environmental Quality Guideline	
	Minimum	Mean	Maximum	ISQG	PEL
Cd	0.85	3.30	7.62	0.70	4.20
Cu	0.92	7.56	18.17	18.70	108.00
Ni[*]	1.35	20.67	49.93	18.00	36.00
Pb	0.26	24.62	48.83	30.20	112.00
Zn	13.14	317.93	612.43	124.00	271.00

[*] The Quality Guidelines for Ni were provide by CCME, 1999.

Cd behavior was similar to that of Zn ($r = 0.57$, $p < 0.05$), with the highest concentrations in the NE region near Itaguaí Harbor and Flecha River, where the domestic wastes from Sepetiba surroundings are dumped (Fig. 4a). For Ni, the results obtained were presented in Fig. 4c which show a more homogeneous distribution throughout the entire bay, apparently following the granulometric distribution (Fig. 2) ($r = 0.61$, $p < 0.05$). Most of the sediment samples presented Cd and Ni (Table 2), indicating that, even though adverse biological effects may be observed, their occurrence, nature and severity are difficult to predict, so, further investigation is recommended (CCME, 1999, 2002).

Fig. 4b and d indicate Cu and Pb accumulation in the NE (near the mouth of São Francisco Channel and Guarda River) and SE portions of the bay. The enrichment of the SE portion may be explained by the strong association of the metals with organic matter (Fig. 3) ($r = 0.48$, $p < 0.05$ for Cu; $r = 0.44$, $p < 0.05$ for Pb).

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

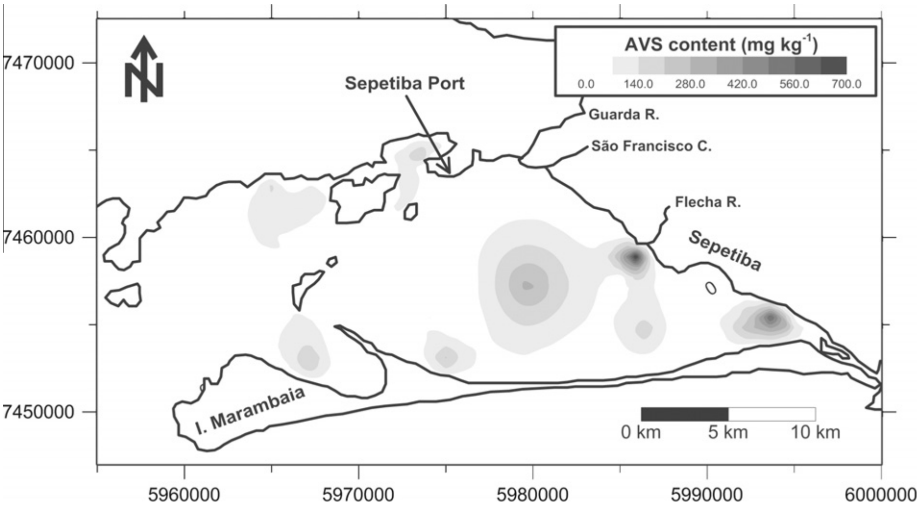

Fig. 5. Spatial distribution of AVS content (in mg kg^{-1}) in sediments of Sepetiba Bay (SE Brazil).

No predictable adverse biological effects to aquatic organisms can be expected due to Cu and Pb levels that present concentrations between ISQG and PEL limits (Table 2). These lower concentrations of Cu and Pb also do not seem to be bioavailable, because measurements in benthic organisms indicated values as low as those observed in the neighboring and pristine Ribeira Bay for Cu (Karez et al., 1994) and below the maximum permissible contents for human consumption for Pb (Molisani et al., 2004).

3.4. SEM/AVS model

There is a strong association between the sediment granulometry and its AVS content (Ankley et al., 1996), suggesting that a higher concentration of sulfides is associated with a stronger ability to retain metals in sediments. Nonetheless, it must be highlighted that the absence of AVS does not imply its toxicity (Di Toro et al., 1992). Fig. 5 represents the AVS content in the sediments of Sepetiba Bay, and it can be seen that the highest concentrations of sulfides are in the NE and SE regions near Reserva Biológica e Arqueológica de Guaratiba, with a broad mangrove forest (Neves et al., 2006) which favors the action of sulfate-reducing anaerobic bacteria (Casas and Crecelius, 1994), and also has finer sediments (Fig. 2).

In Fig. 6, that shows the spatial distribution of SEM/AVS ratio in Sepetiba Bay, it can be observed that the SW region of the bay presented the higher values of SEM/AVS. In this region the presence of sandy sediment dominates and AVS concentration is low (Fig. 5). Therefore, the high SEM/AVS values in this region indicated inexpressive metal retention in sulfides. Following the concept of the model SEM/AVS, whenever the values of the relationship is higher than 1.0, the metals may be more or less mobile as a function of their associations with organic matter (Casas and Crecelius, 1994).

The NE and SE region of the bay are the areas where the SEM/AVS ratio was the lowest, and the AVS content the highest, therefore indicating low toxicity in the region with an AVS concentration sufficient to immobilize the metals, as SEM/AVS ratio is around 1.

The SEM/AVS model provides information regarding the possible bioavailability of metals to the benthos. The use of the SEM/AVS model is attractive due to the faster and easier analysis than procedures with similar objectives, such as sequential extraction. Also, granulometry and organic carbon content are always important parameters when assessing sediment toxicity, mainly in the case of this methodology in which they are not considered in an acid extraction technique.

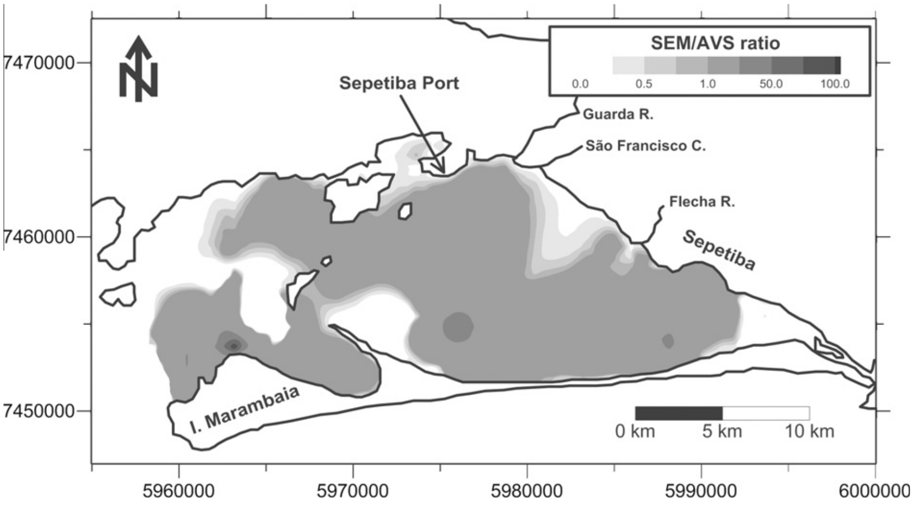

Fig. 6. Spatial distribution of the SEM/AVS ratio in sediments of Sepetiba Bay (SE Brazil).

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

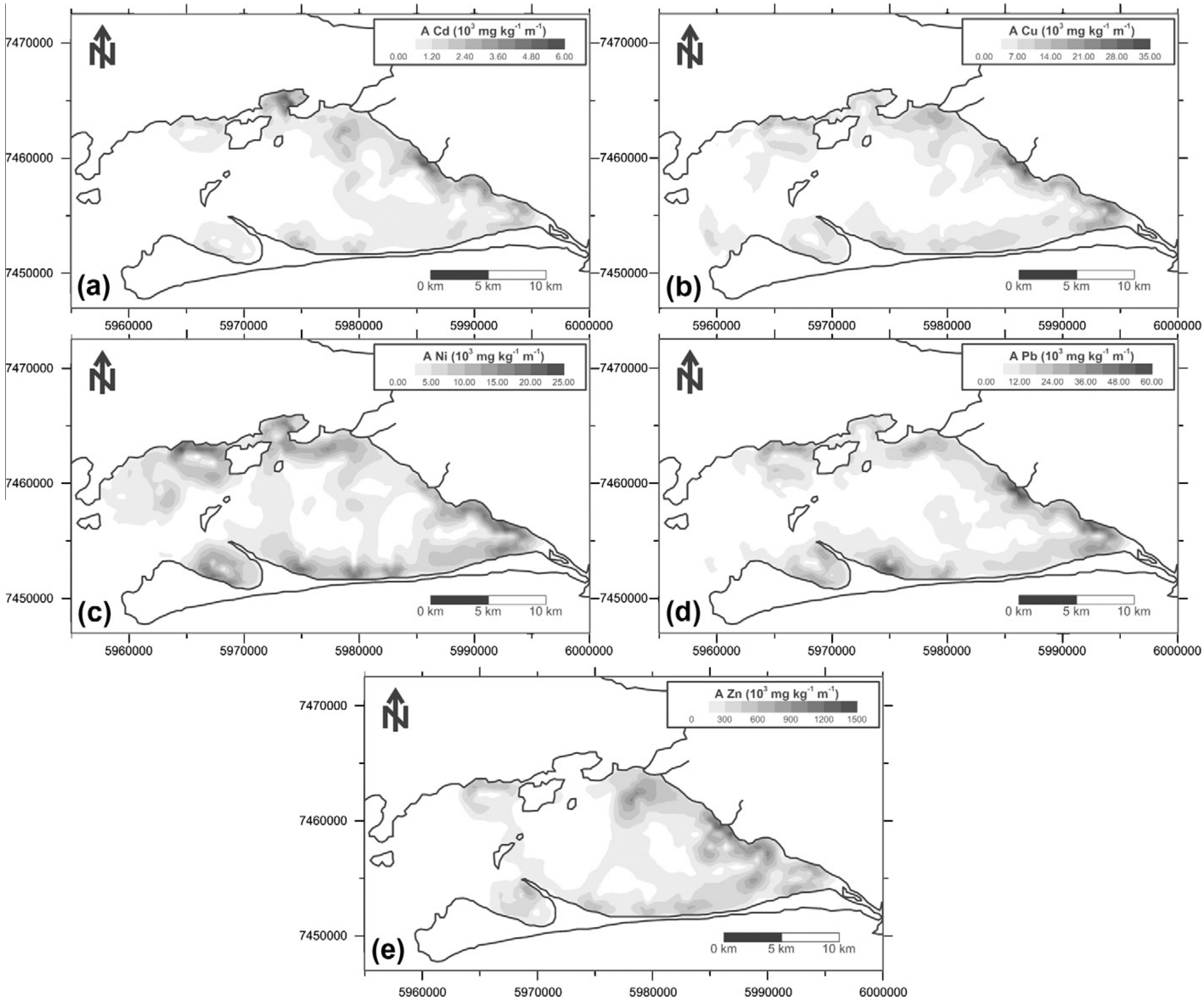

Fig. 7. Model of attenuation of concentrations (in 10^3 mg kg^{-1} m^{-1}) of the total concentration of metals (in mg kg^{-1}) in sediments of Sepetiba Bay (SE Brazil). (a) Cd, (b) Cu, (c) Ni, (d) Pb, and (e) Zn.

3.5. Model of attenuation of concentrations

Based on the data of total concentration of metals, the model of attenuation of concentration was applied. It provides information concerning metal mobility by the simulation of an element's behavior as it moves away from a hot spot (point of highest concentration). The maps made by this model show where metals retention is most intense (corresponding to the greatest values of *A*), and consequently with lowest availability.

According to Fig. 7, the greatest values of *A* for the metals are around the mouths of São Francisco Channel and Guarda River, the Sepetiba Port, and near Guaratiba, Sepetiba and Itacuruçá, coincident with the highest values of total concentrations of metals.

This strong retention of metals is indicated by the elevated values of *A*, which in turn mean low mobility, can be associated with their retention in the form of sulfides or organic matter. Therefore, the lower values of SEM/AVS ratio in the NE region of the bay, near São Francisco Channel, Guarda River and Sepetiba Port, agree with the high values of *A*, which means metal retention near their main sources to the system.

The hydrodynamics of Sepetiba Bay functions as a geochemical barrier to retain metals in the NE region (Wasserman et al., 2001), so, the areas that could present risk of adverse biological effects are the same one that presented high metal retention (according to the attenuation of concentrations model) and lower bioavailability (as shown by the SEM/AVS ratio).

4. Conclusions

The models of attenuation of concentrations and SEM/AVS ratio produce results that agree with each other. The areas that presented low SEM/AVS ratios (lower than one, indicating no risk of toxicity) has higher concentrations of metals because the metals are retained in the form of sulfides, and therefore unavailable and immobile. It is interesting to note the agreement between the models indicate that organic matter association is not a significant factor that immobilizes metals in Sepetiba Bay.

Thus, the maps of the attenuation of concentrations model successfully reproduce the behavior of metals in the acid extraction

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

model, generating a mirror image of the maps from the SEM/AVS model. It has to be underlined that the construction of the attenuation of concentrations model demands only the total concentration of metals, while SEM/AVS is a more time consuming procedure. Furthermore, SEM/AVS model does not consider the retention of metals with organic matter and the association of both procedures may be a good approach to metal mobility in sedimentary environments.

On the other hand, it must be considered that, due to sediment's resuspension, the continuous release of industrial and urban wastes and dredging activities, the metal mobility established in both models may change, thereby allowing for their release in the water column. So it can be concluded that the mobility may also change in a short range time scale. It is advisable that these models are periodically applied, in order to follow up the evolution of the behavior of the metals in contaminated sedimentary environments.

Acknowledgements

The authors acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support to this work. The authors are also greatfull to Ecologus Consultive Engineering Ltd. that supported part of the SEM/AVS analyses. JCW is thankful to CNPq for the productivity research support (Grant # 305241/2003-6).

References

Allen, H.E., Boothman, W., Di Toro, D.M., Mahony, J.D., 1991, US-EPA Report 821/12-91/100. Determination of Acid Volatile Sulfides and Selected Simultaneously Extractable Metals in Sediment. Washington DC, United States.

Allen, H.E., Fu, G., Deng, B., 1993. Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEMs) for estimation of potential toxicity in aquatic sediments. Environ. Toxicol. Chem. 12, 1441–1453.

Ankley, G.T., Di Toro, D.M., Hansen, D.J., Berry, W.J., 1996. Technical basis and proposal for deriving sediment quality criteria for metals. Environ. Toxicol. Chem. 15, 2056–2066.

Audry, S., Schäfer, J., Blanc, G., Jouanneau, J., 2004. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environ. Pollut. 132, 413–426.

Bargagli, R., Monaci, F., Sanchez-Hernandez, J.C., Cateni, D., 1998. Biomagnification of mercury in an Antarctic marine coastal food web. Mar. Ecol. Prog. Ser. 169, 65–75.

Brix, K.V., Keithly, J., SAntore, R.C., DeForest, D.K., Tobiason, S., 2010. Ecological risk assessment of zinc from stormwater runoff to an aquatic ecosystem. Sci. Tot. Environ. 408, 1824–1832.

Caeiro, S., Costa, M.H., Ramos, T.B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G., Painho, M., 2005. Assessing heavy metal contamination in Sado estuary sediment: an index analysis approach. Ecol. Indic. 5, 151–169.

Casas, A.M., Crecelius, E.A., 1994. Relationship between acid volatile sulfide and the toxicity of zinc, lead and cooper in marine sediments. Environ. Toxicol. Chem. 11, 529–536.

CCME, Canadian Council of Ministers of the Environment, 1999, Report CCME-EPC-98E. Protocol for Derivation of Canadian sediment Guidelines for Protection of Aquatic Life. Update 1999.

CCME, Canadian Council of Ministers of the Environment, 2002. Canadian sediment quality guidelines for the protection of aquatic life: Summary Tables. Updated In: Canadian envrironmental quality guidelines, 1999. Update 2002.

Celino, J.J., Oliveira, O.M.C., Hadlich, G.M., Queiroz, A.F.S., Garcia, K.S., 2008. Assessment of contamination by trace metals and petroleum hydrocarbons in sediments from the tropical estuary of Todos os Santos Bay. Brazil. Rev. Bras. Geol. 38, 753–760.

Cesar, A., Pereira, C.D.S., Santos, A.R., Abessa, D.M.S., Fernández, N., Choueri, R.B., DelValls, T.A., 2006. Ecotoxicological assessment of sediments from the Santos and São Vicente estuarine system – Brazil. Braz. J. Oceanogr. 54, 55–63.

Chapman, P.M., Wang, F., Adams, W., Green, A., 1999. Appropriate applications of sediment quality values for metalsand metalloids. Environ. Sci. Technol. 33, 3937–3941.

Clark, M.W., McConchie, D., Lewis, D.W., Saenger, P., 1998. Redox stratification and heavy metal partitioning in Avicennia-dominated mangrove sediments: a geochemical model. Chem. Geol. 149, 147–171.

Cunha, B.C.A., Rocha, D., Geraldes, M.C., Pereira, S.D., Almeida, A.C., 2009. Pb isotopic signatures in sediments of a subtropical coastal lagoon: anthropogenic sources for metal contamination in the Sepetiba Bay (SE - Brazil). J. Coast. Res. 56, 797–801.

De Jonge, M., Blust, R., Bervoets, L., 2010. The relation between acid volatile sulfides (AVS) and metal accumulation in aquatic invertebrates: implications of feeding behavior and ecology. Environ. Pollut. 158, 1381–1391.

Di Toro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mayr, S.M., Redmond, M.S., 1990. Toxicity of cadmium in sediments: the role of acid-volatile sulfide. Environ. Toxicol. Chem. 9, 1487–1502.

Di Toro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Carison, A.R., Ankley, G.T., 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. Environ. Sci. Technol. 26, 96–101.

Fernandes, L., Nayak, G.N., Ilangovan, D., Borole, D.V., 2011. Accumulation of sediment, organic matter and trace metals with space and time, in a creek along Mumbai coast. India. Estuar. Coast. Shelf Sci. 91, 388–399.

Förstner, U., Salomons, W., 1980. Trace metals analysis on polluted sediments. Part I: Assessments of sources and intensities. Environ. Technol. Lett. 1, 495–505.

Fukumoto, M.M., 2007. Determinação da história deposicional recente do Alto Estuário Santista, com base nos teores de metais e na susceptibilidade magnética dos sedimentos. PhD thesis. Instituto Oceanográfico, Universidade de São Paulo, São Paulo, Brazil.

Gomes, F.C., Godoy, J.M., Godoy, M.L.D.P., Carvalho, Z.L., Lopes, R.T., Sanchez-Cabeza, J.A., Lacerda, L.D., Wasserman, J.C., 2009. Metal concentrations, fluxes and inventories and chronologies in sediments from Sepetiba and Ribeira Bays: a comparative study. Mar. Pollut. Bull. 59, 123–133.

Karez, C.S., Magalhães, V.F., Pfeiffer, W.C., 1994. Trace metal accumulation by algae in Sepetiba Bay. Brazil. Environ. Pollut. 83, 351–356.

Kehrig, H.A., Pinto, F.N., Moreira, I., Malm, O., 2003. Heavy metals and methylmercury in a tropical coastal estuary and a mangrove in Brazil. Org. Geochem. 34, 661–669.

Laluraj, C.M., Nair, S.M., 2006. Geochemical index of trace metals in the superficial sediments from the western continental shelf of India. Arabian Sea. Environ. Geochem. Health 28, 509–518.

Lawson, N.M., Mason, R.P., 1998. Accumulation of mercury in estuarine food chains. Biogeochemistry 40, 235–247.

Li, X., Wai, O.W.H., Li, Y.S., Coles, B.J., Ramsey, H., Thornthon, I., 2000. Heavy metal distribution in the sediment profiles of the Pearl river estuary, South China. Appl. Geochem. 15, 567–581.

Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analysis of marine sediments and suspended particalte matter. Earth Sci. Rev. 32, 235–283.

Luiz-Silva, W., Matos, R.H.R., Kristosch, G.C., Machado, W., 2006. Variabilidade espacial e sazonal da concentração de elementos-traço em sedimentos do sistema estuarino de Santos-Cubatão (SP). Quim. Nova 29, 256–263.

Machado, W., Carvalho, M.F., Santelli, R.E., Maddock, J.E.L., 2004. Reactive sulfides relationship with metals in sediments from a eutrophicated estuary in Southeast Brazil. Mar. Pollut. Bull. 49, 89–92.

Mahiques, M.M., Burone, L., Figueira, R.C.L., Lavenére-Wanderley, A.A.O., Capellari, B., Rogacheski, C.E., Barroso, C.P., Santos, L.A.S., Cordero, L.M., Cussioli, M.C., 2009. Anthropogenic influences in a lagoonal environment: a multiproxy approach at the Valo Grande mouth, Cananéia-Iguape systems (SE Brazil). Braz. J. Oceanogr. 57, 325–337.

Molisani, M.M., Marins, R.V., Paraquetti, H.H., Bidone, E.D., Lacerda, L.D., 2004. Environmental changes in Sepetiba Bay. SE Brazil. Reg. Environ. Change 4, 17–27.

Molisani, M.M., Kjerfve, B., Silva, A.P., Lacerda, L.D., 2006. Water discharge and sediment load to Sepetiba Bay from an anthropogenically-altered drainage basin, SE Brazil. J. Hydrol. 331, 425–433.

Mozeto, A.A., 2001. Critérios de qualidade de sedimentos (CQS) para metais pesados: Fundamentos teóricos e técnicos para implementação. Report EESC-USP.

Neves, L.M., Pereira, H.H., Costa, M.R., Araújo, F.G., 2006. Uso do manguezal de Guaratiba, Baía de Sepetiba, Rio de Janeiro, pelo peixe-rei *Atherinella brasiliensis* (Quoy e Galmard) (Atheriniformes, Atherinopsidae). Rev. Bras. Zool. 23, 421–428.

Paraquetti, H.H.M., Lacerda, L.D., Ayers, G.A., Mounier, S., Almeida, M.D., 2004. Mercury speciation and dissolved organic carbon characterization in the surface waters of Sepetiba Bay, SE Brazil. Geochem. Brasil. 18, 28–37.

Pedlowsky, M.A., Lacerda, L.D., Ovalle, A.R.C., Watts, P.P., Silva-Filho, E.V., 1991. Atmospheric inputs of Zn, Fe and Mn into Sepetiba Bay, Rio de Janeiro. Ciên. Cult. 43, 380–382.

Pellegatti, F., Figueiredo, A.M.G., Wasserman, J.C., 2001. Neutron activation analysis applied to determination of heavy metals and other trace elements in sediments from Sepetiba Bay (RJ). Braz. J. Geostand. Geoanal. 25, 307–315.

Perin, G., Fabris, R., Manente, S., Rebello-Wagener, A., Hamacher, C., Scotto, S., 1997. A five-year study on the heavy metal pollution of Guanabara Bay sediment (Rio de Janeiro, Brazil) and evaluation of the bioavailability by means of geochemical speciation. Water Res. 31, 3017–3028.

Pinto, L.M.O., 2005. Implicações da contaminação por metais pesados no meio ambiente da baía de Sepetiba e entorno: o caso da Cia. MSc dissertation, Universidade Federal Fluminense, Niterói, Brazil, Mercantil Ingá.

Raj, S.M., Jayaprakash, M., 2008. Distribution and enrichment of trace metalsin marine sediments of Bay of Bengal, off Ennore, south-east coast of India. Environ. Geol. 56, 207–217.

Reimann, C., De Caritat, P., 1998. Chemical elements in the environment: factsheets for the geochemist and environmental scientist. Springer-Verlag, Heidelberg, 398p.

Ribeiro, A.P., 2006. Procedimento de fracionamento comparado ao modelo de atenuação para a avaliação de mobilidade de metais pesados em sedimentos da

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023

Baía de Sepetiba, Rio de Janeiro. PhD thesis. Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, São Paulo, Brazil.

Ribeiro, A.P., Figueira, R.C.L., Martins, C.C., Silva, C.R.A., França, E.J., Bícego, M.C., Mahiques, M.M., Montone, R.C., 2011. Arsenic and trace metals contents in sediment profiles from the Admiralty Bay, King George Island. Antarctica. Mar. Pollut. Bull. 62, 192–196.

Ridgway, J., Shimmield, G., 2002. Estuaries as repositories of historical contamination and their impacts on shelf seas. Estuar. Coast. Shelf Sci. 55, 903–928.

Signorini, S.R., 1980. A study of the circulation in bay of the Ilha Grande and Bay of Sepetiba. Part II. An assessment of the tidally and wind-driven circulation using a finite element numerical model. Bol. Instit. Oceanogr. 29, 57–68.

Silva-Filho, E.V., Pedlowski, M.A., Paiva, R.P., Wasserman, J.C., Lacerda, L.D., 1999. Atmospheric inputs to ecosystems of the East coast, State of Rio de Janeiro, Brazil. In: Knoppers, B.A., Bidone, E.D., Abrão, J.J. (Eds.), Environmental geochemistry of coastal lagoon systems. Rio de Janeiro.

Silvério, P., 2003. Bases técnico-científicas para a derivação de valores-guias de qualidade de sedimentos para metais: experimento de campo e laboratório. PhD thesis. Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, Brazil.

Suguio, K., 1973. Introdução à sedimentologia. Edgard Blücher, São Paulo, 317p.

Teuchies, J., De Jonge, M., Meire, P., Blust, R., Bervoets, L., 2012. Can acid volatile sulfides (AVS) influence metal concentration in the macrophyte *Myriophyllum aquaticum*? Environ. Sci. Technol. 46, 9129–9137.

Turner, A., 2000. Trace metals contamination in sediments from U.K. estuaries: an empirical evaluation of the role of hydrous iron and manganese oxides. Estuar. Coast. Shelf Sci. 50, 355–371.

US-EPA, United States Environmental Protection Agency, 2003, Method 3052. Microwave Assisted Digestion of Sediments, Sludges, Soils and Oils. Revision 0. December, 1996.

Vasconcelos, F.M., Almeida, D.F., Santos, L., Moreira, T.T., 2010. Caracterização do potencial de biodisponibilidade de metais (Zn, Cd, Pb, Cu e Ni) em sedimentos de corrente do Rio São Francisco. Geonomos 18, 28–32.

Wasserman, J.C., Queiroz, E.L., 2004. The attenuation of concentrations model: a new method for assessing Mercury mobility in sediments. Quim. Nova 27, 17–21.

Wasserman, J.C., Freintas-Pinto, A.P., Amouroux, D., 2000. Mercury concentrations in sediment profiles of a degraded tropical coastal environment. Environ. Technol. 21, 297–305.

Wasserman, J.C., Figueiredo, A.M.G., Pellegatti, F., Silva-Filho, E.V., 2001. Element composition of sediment cores from a mangrove environment using neutron activation analysis. J. Geochem. Explor. 72, 129–146.

Wolff, W.J., 1980. Biotic aspects of the chemistry of estuaries. In: Olausson, E., Cato, I. (Eds.), Chemistry and Biogeochemistry of Estuaries. Wiley-Interscience, New York, pp. 263–295.

Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., Liang, R., Gao, C., Chen, W., 2007. Heavy metal contamination in western Xiamen Bay sediments and its vicinity China. Mar. Pollut. Bull. 54, 974–982.

Zhigang, Y., Pu, G., 2007. Heavy metal research in lacustrine sediment: a review. Chin. J. Oceanol. Limnol. 25, 444–454.

Please cite this article in press as: Ribeiro, A.P., et al. Combined SEM/AVS and attenuation of concentration models for the assessment of bioavailability and mobility of metals in sediments of Sepetiba Bay (SE Brazil). Mar. Pollut. Bull. (2013), http://dx.doi.org/10.1016/j.marpolbul.2012.12.023