Seagrass losses concerns: does sediment metal pollution matter?

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Abstract

Seagrass losses result in the lost of well-known environmental services (*e.g.* nutrient retention and habitat functions). A potential additional loss is the enhanced trace metal retention capacity of sediments colonized by seagrasses. A preliminary study within a coastal lagoon in SE Brazil showed that upper layers of sediments colonized by the seagrass *Ruppia maritima* presented significantly higher reactive concentrations of Fe, Mn, Cu, and Zn than sediments from an adjacent bare area. Decreasing metal trapping capacity due to *R. maritima* removal deserves attention, since this is a potential implication for water quality.

Keywords: *Ruppia maritima*, seagrass services, trace metals.

Resumo

Perdas de áreas de fanerógamas marinhas resultam na perda de serviços ambientais bem conhecidos (por exemplo, a retenção de nutrientes e as funções de hábitat). Uma potencial perda adicional é a capacidade aumentada da retenção de metais-traço em sedimentos colonizados por estas fanerógamas. Um estudo preliminar realizado em uma lagoa costeira do Sudeste do Brasil mostrou que as camadas superiores dos sedimentos colonizados pela fanerógama marinha Ruppia maritima *apresentaram concentrações reativas de Fe, Mn, Cu e Zn significativamente maiores do que sedimentos de uma área adjacente sem cobertura vegetal. A capacidade reduzida da retenção de metais devido à remoção de* R. maritima *merece atenção, pois apresenta potenciais implicações para a qualidade da água.*

Palavras-chave: Ruppia marítima*, serviços de fanerógamas marinhas, metais-traço.*

1. INTRODUCTION

Seagrasses, a group of plants that are adapted to exist submerged in the sea, profoundly influence the physical, chemical and biological environments of coastal waters and provide numerous ecological services (Thangaradjou *et al.* 2013). They can affect coastal sediments biogeochemistry, *e.g.* by increasing the deposition of fine particles and sediment stabilization and adding organic matter, which fuel sulfide production (De Boer 2007, Viaroli *et al.* 1997). These effects are of particular interest in areas that receive anthropogenic metals input, which may also affect seagrass communities (Ward & Young 1983, Marín-Guirao *et al.* 2005). Several monitoring programmes have successfully used marine macrophytes to quantify contamination loads with trace metals (Haritonidis & Malea 1999). Indeed, because plants have a high capacity to accumulate a range of elements, their widespread use as indicators of marine pollution seems justified (Lytle & Lytle 2001).

Metal sulfides, organic matter, and oxidized forms of Fe and Mn are recognized as main controls on trace metal behavior in coastal sediments, which are also affected by sediment physicochemical conditions (Chapman *et al.* 1998). Therefore, the translocation of photosynthetically produced O_2 and its release by seagrass roots into the substrate may also be important (Hebert *et al.* 2007, Povidisa *et al.* 2009). This release has been observed for *Ruppia maritima* (Thursby 1984), which is the most widely distributed seagrass species (Short *et al.* 2007).

The distribution of acid-volatile sulfides (AVS) and simultaneously extracted metals (SEM) in sediments colonized by *R. maritima* was evaluated in Rodrigo de Freitas Lagoon (Rio de Janeiro State, Brazil), which is considered one of the most polluted coastal lagoons in SE Brazil, impacted by untreated sewage input and urban runoff. The lagoon is a semi-confined system making water renewal complex and the marine water flux is superficial, leaving deeper layers unaffected (Fonseca *et al.* 2014). Extreme reducing conditions within the lagoon are due to the high concentration of organic matter, low currents and limited exchanges with the sea, making ideal conditions for the accumulation of pollutants, such as trace metals (Kim *et al.* 2011).

Details on this eutrophicated system contamination history are available elsewhere (Lacerda & Gonçalves 2001, Loureiro *et al.* 2009). At least since nearly 2008, the government management policy to improve environmental and esthetical quality of the lagoon included the periodical removal of seagrass beds from its margins. We discuss here, based on preliminary analysis of seagrass bed sediments, the potential effects of the colonization by *R. maritima* on the sediment capacity to trap trace metal contaminants, such as Cu, Pb and Zn and possible implications of seagrass removal on this trapping (Loureiro *et al.* 2009).

2. MATERIALS AND METHODS

Two short sediment cores (0 to 20 cm depth) were sampled in May 2009, by driving acrylic tubes into the sediments near the edge of an approximately two-year-old *R. maritima* bed in the lagoon margin (Figure 1; 22°58'0.07"S, 43°12'58.06"W). The first core was collected inside the seagrass bed (core R) and the second one in the bare adjacent area (core U), both distanced nearly 3 m from the bed edge. Live and dead roots and rhizomes were observed within the upper 10 cm depth of core R. The sediments were sub-sampled in 0 to 2, 2 to 4, 4 to 6, 6 to 8, 8 to 10, 12 to
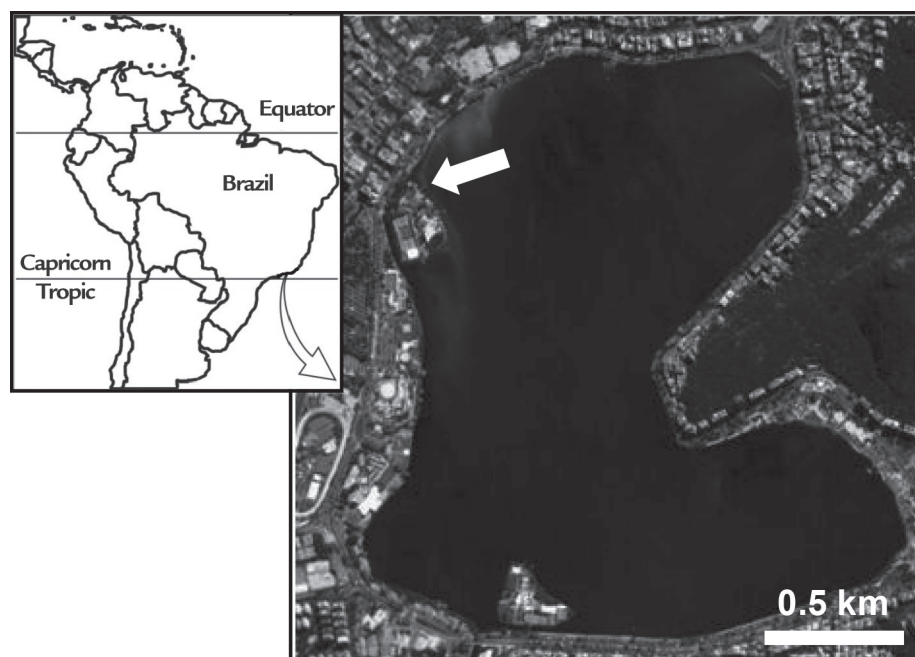

Figure 1

Location of sampling site (indicated by an arrow) within Rodrigo de Freitas Lagoon, SE Brazil.

14 and 16 to 18 cm depth intervals and kept refrigerated until analyses. AVS and SEM extractions were carried out in duplicates, according to the acid (6 mol l–1 HCl) distillation method (Allen *et al.* 1991). AVS levels were determined gravimetrically after precipitation of the evolved sulfide (H_2S) as Ag_2S (Allen *et al.* 1991). Simultaneously extracted Fe, Mn, Cu, Pb and Zn levels were determined by ICP OES.

Reproducibility was within 30 (AVS) and 15% (metals). Sediment water content was determined after drying to constant weight (60°C, 48 hours). Visual examination evidenced grain size differences between cores and a sediment grain size analysis was carried out for some representative depth intervals (0 to 2, 4 to 6, 8 to 10 and 16 to 18 cm) by using a CILAS particle size meter. Data were treated using the software XLSTAT-Pro7.0©. The significance of the observed differences in concentrations between cores and surface and deeper layers in each core was tested using Mann-Whitney's test (p<0.05) and Spearman's correlation analyses (p<0.05).

3. RESULTS AND DISCUSSION

Vertical distributions of AVS and metals were consistently different between cores, frequently showing inverse trends, with higher contents observed in upper layers of core R for all metals (Figure 2). These metals presented relatively few significant correlations (p<0.05) with studied sediment properties, as indicated by Spearman's correlation analyses. In the core, R, Pb and Zn were correlated (rs=0.89), as well as Fe and Mn (rs=0.96), while Cu was correlated with Fe (rs=0.89) and Mn (rs=0.86). In the core U, there were correlations of Fe with Mn (rs=0.96) and Pb with Zn (rs=0.96), and Pb was also correlated with Fe (rs=0.79) and Mn (rs=0.86), while Zn was correlated with Mn (rs=0.82).

This evidenced an association of trace metals with reactive Fe and Mn, without significant correlations with AVS, indicating that reactive Mn and Fe compounds are main geochemical carriers. Metal contaminant associations with Fe and Mn are frequently observed in coastal sediments, as reported for other parts of Rodrigo de Freitas Lagoon (Loureiro *et al.* 2009). The correlations between trace metals can indicate similar geochemical behavior and metal source similarity, as previously found for Cu, Pb and Zn that are mostly affected by urban effluents inputs to Rodrigo de Freitas Lagoon (Loureiro *et al.* 2009).

Despite any possible sand dilution effect due to a coarser grain size in vegetated sediments than in bare sediments (11 to 23% *versus* 27 to 45% sand contents, respectively, for the analyzed depth intervals), core R presented levels that are similar to or higher than those found in core U for all elements within the 0 to 8 cm depth (Figure 2). For this interval, a Mann-Withney U test indicated significant (p=0.02 to 0.04) differences for all metals, with the exception of Pb. Besides the seagrass stabilization of sediments against resuspension (De Boer 2007), a coupled effect of the observed reactive Fe, Mn and AVS enrichments near the sediment-water interface is expected to occur, favoring metal retention in the solid-phase (Keene *et al.* 2010, Nizolo & Luiz-Silva 2012).
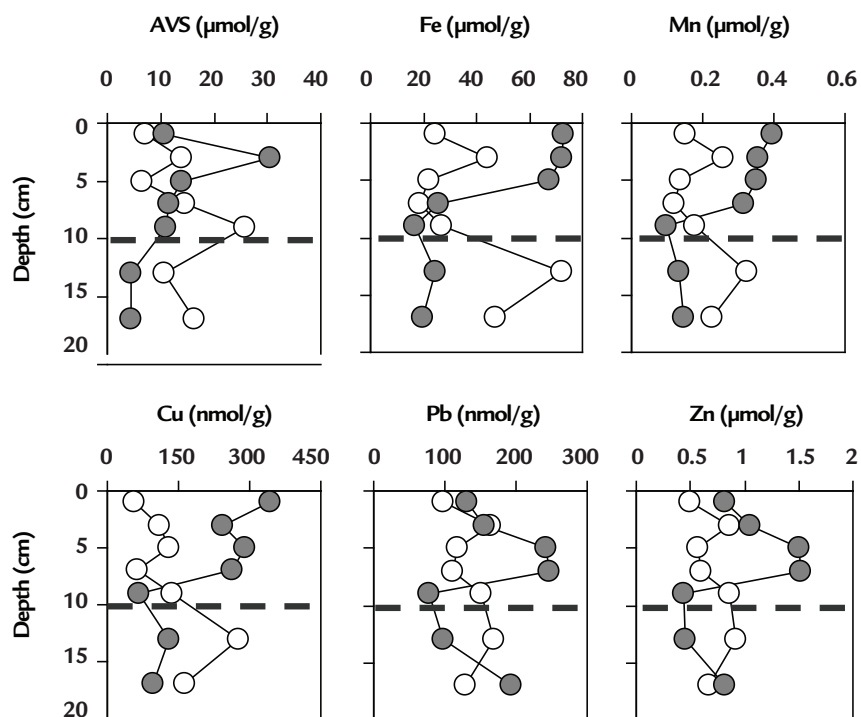
Figure 2

Depth variability in acid-volatile sulfides (AVS) and reactive (HCl-extractable) metal concentrations from the seagrass-covered (core R, filled symbols) and unvegetated (core U, open symbols) sediments. Dashed horizontal lines represent the approximated maximum rhizosphere depth observed in core R sediments.

For example, while there is sufficient AVS to react with SEM, these metals (that form monosulfides more stable than FeS, assumed as the main AVS constituent) will not be accumulated in the pore water due to removal in re-action with AVS (Chapman *et al.* 1998). The molar ratios between SEM (Cu, Pb and Zn, in this case) and AVS were up to 0.13 and 0.18, for cores U and R, respectively, thus the sediment capacity to retain these metals in the form of AVS was not exhausted.

Organic matter input from the seagrass debris must fuel sulfide production close to the sediment-water interface (Viaroli *et al.* 1997). In the study site, there was probable additional organic matter input from the observed extensive epiphytic cover of *R. maritima* leaves (mainly by filamentous alga *Cladophora sp.*), while rhizosphere oxidation was not evident by visual examination (e.g. reddish iron plaque cover on the seagrass roots) (Povidisa *et al.* 2009), possibly due to a recent colonization. Hebert *et al.* (2007) did not see a 'ventilation' effect by seagrasses, so bioturbation may mask this observation.

Figure 3 presents the relative differences between trace metal concentrations for each sediment layer in *R.*
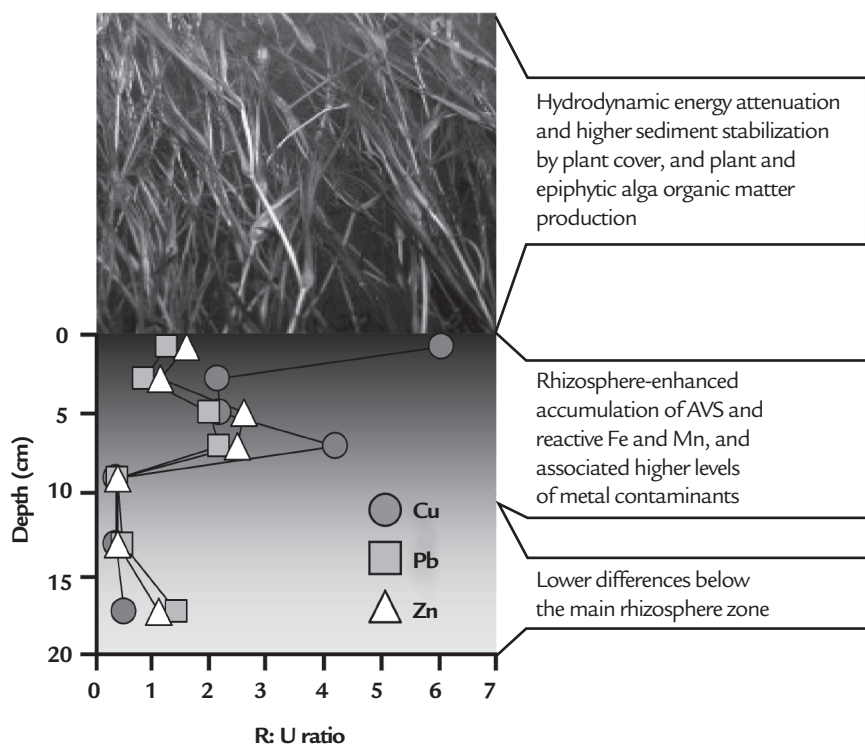

Hydrodynamic energy attenuation and higher sediment stabilization by plant cover, and plant and epiphytic alga organic matter production

Rhizosphere-enhanced accumulation of AVS and reactive Fe and Mn, and associated higher levels of metal contaminants

Lower differences below the main rhizosphere zone

Cu
Pb
Zn

Figure 3

Depth variability of the relative enrichment in trace metal concentrations in R. maritima- colonized sediments (core R) in relation to unvegetated sediments (core U) in the study site (R:U ratios), and schematic synthesis of main processes involved in determining such enrichments. Upward gray shading indicates the increasing effect of R. maritima rhizosphere and input of plant and epiphytic alga debris on upper sediment layers.

maritima-colonized sediments (core R) in relation to un-vegetated sediments (core U) in the study site (hereafter referred to as R:U ratios), demonstrating that these metals presented highly variable sensitivities (Cu>>Zn>Pb) to plant cover influence. Within the upper 8 cm depth, Cu presented R:U ratios between 2.2 and 6.0 in comparison to values ranging in 0.9 to 2.2 (Pb) and 1.2 to 2.6 (Zn) showed by other trace metals, whereas all amounts below this depth (*i.e.* bellow the main rhizosphere influence zone) ranged from 0.5 to 1.5 for the three metals. Although all elements have an affinity to sulfides (Marín-Guirao *et al.* 2005), the well-recognized affinity of Cu to organic matter (*e.g.* as previously found in seagrass-colonized sediments) can contribute to explaining the observed higher sensitivity to plant colonization, in addition to the observed associations with reactive Fe and Mn (Ward & Young 1983).

Daby (2003) reported that seagrass removal caused high turbidity in waters overlying a destabilized lagoon seabed and complete loss of benthic fauna, rendering the ecosystem more vulnerable to environmental change and extreme events. The preliminary study presented here suggests that a less evident role of seagrass beds may also be lost, *i.e.* the influence on the sediment capacity to retain trace metals. This function loss may increase sediment release of metals, *e.g.* due to enhanced resuspension of sediments, which may have implications for water quality (Morse 1994, Machado *et al.* 2011). In fact, seagrass-colonized sediments have been recently evidenced as potential long-term sinks for trace metals, as recorded in a long sediment core from a Mediterranean site (Serrano *et al.* 2011).

4. CONCLUSIONS

Although the seagrass-colonized sediments showed a coarser nature, its upper layers presented AVS and metal levels similar to or higher than those found in the unvegetated core, indicating the influence of seagrass colonization. Besides the physical stabilization of sediments and organic matter input (well-known in segrass ecosystems), this preliminary study indicated that an enrichment in reactive Fe, Mn and AVS near the sediment-water interface also favors metal retention in sediments under the *R. maritima* influence, occurring a high variability in the sensitivity of metals to these effects. While there is already a concern with the loss of enviromental services (*e.*g. nutrient retention and habitat functions) due to seagrass removal worldwide because of anthropogenic pressures (Orth *et al.* 2006, Short *et al.* 2007), investigation on a potential additional service loss regarding trace metal mobility is recommended.

5. ACKNOWLEDGEMENTS

6. REFERENCES

Allen H.E., Fu G., Boothman W., Di Toro D., Mahony J.D. 1991. Determination of acid volatile sulfides and selected simultaneously extractable metals in sediment. *Environmental Protection Agency*, Narragansett, RI (United States), 1-22.

Chapman P.M., Wang F., Janssen C., Persoone G., Allen H.E. 1998. Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. *Canadian Journal of Fisheries and Aquatic Science*, **55**:2221-2243.

Daby D. 2003. Effects of seagrass bed removal for tourism purposes in a Mauritian bay. *Environmental Pollution*, **125**:313-324.

De Boer W.F. 2007. Seagrass-sediment interactions, positive feedbacks and critical thresholds for occurrence: A review. *Hydrobiologia*, **591**:5-24.

Fonseca E.M, Baptista Neto J.A., McAlister J.J., Smith B.J., Crapez M.A.C. 2014. Bioavailability of pollutants in bacterial communities of Rodrigo de Freitas Lagoon, Rio de Janeiro, Brazil. *Brazilian Journal of Microbiology*, **45**(3):953-962.

Haritonidis S. & Malea P. 1999. Bioaccumulation of metals by the green alga *Ulva rigida* from Thermaikos Gulf, Greece. *Environmental Pollution*, **104**:365-372.

Hebert A.B., Morse J.W., Eldridge P.M. 2007. Small-scale heterogeneity in the geochemistry of seagrass vegetated and non-vegetated estuarine sediments: causes and consequences. *Aquatic Geochemistry*, **13**:19-39.

Keene A.F., Johnston S.G., Bush R.T., Burton E.D., Sullivan L.A. 2010. Reactive trace element enrichment in a highly modified, tidally inundated acid sulfate soil wetland: East Trinity, Australia. *Marine Pollution Bulletin*, **60**:620-626.

Kim K.T., Ra K., Kim E.S., Yim U.H., Kim J.K. 2011. Distribution of Heavy Metals in the Surface Sediments of the Han River and its Estuary, Korea. *Journal of Coastal Research,* **64**:903-907.

Lacerda L.D. & Gonçalves, G.O. 2001. Mercury distribution and especiation in waters of the coastal lagoons of Rio de Janeiro, SE Brazil. Marine Chemistry. *Marine Chemistry*, **76**:47-58.

Lytle J.S. & Lytle T. F. 2001. Use of plants for toxicity assessment of estuarine ecosystems. *Environmental Toxicology and Chemistry*, **20**:68-83.

Loureiro D.D., Fernandez M.A., Herms F.W., Lacerda L.D. 2009. Heavy metal inputs evolution to an urban hypertrophic coastal lagoon, Rodrigo De Freitas Lagoon, Rio De Janeiro, Brazil. *Environmental Monitoring and Assessment*, **159**:577-588.

Machado W., Rodrigues A.P.C., Bidone E.D., Sella S.M., Santelli R.E. 2011. Evaluation of Cu potential bioavailability changes upon coastal sediment resuspension: an example on how to improve the assessment of sediment dredging environmental risks. *Environmental Science and Pollution Research.*, **18**:1033-1036.

Marín-Guirao L., Atuch, A.M., Barba J.L., López E.M., Fernández A.J.G. 2005. Effects of mining wastes on a seagrass ecosystem: metal accumulation and bioavailability, seagrass dynamics and associated community structure. *Marine Environmental Research*, **60**:317-337.

Morse J.W. 1994. *Mar. Chem.*, **46**:1-6.

Orth, R.J., Carruthers,T.J.B., Dennison,W.C., Duarte,C.M., Fourqurean, J.W., Heck Jr., K.L., Hughes A.R., Kendrick G.A., Kenworthy W.J., Olyarnik S., Short F.T., Waycott M., Williams S.L. 2006. A global crisis for seagrass ecosystems. *BioScience*, **56**:987-996.

Povidisa K., Delefosse M., Holmer M. 2009. The formation of iron plaques on roots and rhizomes of the seagrass Cymodocea serrulata (R. Brown) Ascherson with implications for sulphide intrusion. *Aquatic Botany*, **90**:303-308.

Serrano O., Mateo M.A., Dueñas-Bohórquez A., Renom P., López-Sáez J.A., Martínez Cortizas A. 2011. The *Posidonia oceânica* marine sedimentar record: a holocene archive of heavy metal pollution. *Science of the Total Environment,*, **409**:4831-4840.

Short F., Carruthers T., Dennison W., Waycott M. 2007. Global seagrass distribution and diversity: a bioregional model. *Journal of Experimental Marine Biology and Ecology,* **350**:3-20.

Thursby G.B. 1984. Nutritional requirements of the submerged angiosperm *Ruppia marítima* in algae-free culture. *Marine Ecology Progress Series*, **16**:45-50.

Viaroli P., Bartoli M., Fumagalli I., Giordani G. 1997. Relationship between benthic fluxes and macrophyte cover in a shallow blackish lagoon. *Water, Air, and Soil Pollution*, **99**:533-540.

Ward T.J. & Young P.C. 1983. Effects of sediment trace metals and particle size on the community structure of epibenthic seagrass fauna near a lead smelter, South Australia. *Marine Ecology Progress Series*, **9**:137-146.