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Influence of biological activity on ^{65}Zn and ^{109}Cd removal from tidal water by chronically-polluted mangrove sediments

M. N. Sondermann[1,2] · K. N. Suzuki[1] · E. C. Machado[3] · W. Machado[1] · L. F. Bellido[4] · R. T. Lopes[5] · A. V. B. Bellido[1]

Abstract

The biological activity influence on the mangrove sediment capacity to remove ^{65}Zn and ^{109}Cd from tidal water was evaluated in a site chronically polluted. Benthic Activity Indexes (BAI), corresponding to relative estimates of biological impact on radiotracer accumulation, were higher for ^{109}Cd ($\sim$ 38%) than for ^{65}Zn ($\sim$ 10%) in the top centimetre of sediment. However, BAI exceeded 96% for deeper sediment layers. This apparent decrease in radiotracer diffusion into deep sediments through biological activity inhibition is stronger than reported for much less polluted mangrove nearby, suggesting that benthic organisms tolerant of chronic metal pollution may affect metal sorption mechanisms.

Keywords Mangrove sediments · Radiotracers · Zinc · Cadmium · Biogeochemical barrier

Introduction

The role of mangrove systems as biogeochemical barriers for trace metals across the land–ocean interface is dependent on metal-sediment associations, which are affected by the affinity of these elements to sedimentary constituents such as organic matter, sulphides, clay minerals and metal oxides [1–4]. The mechanisms involved in determining the metal sorption by mangrove sediments can vary spatially and temporally in response to tidal flooding variability, plant cover, rhizosphere development, as well as sediment physical, chemical and mineralogical properties [5–7]. In addition, microbial activity affects the accumulation of metal-bearing compounds by driving redox processes, consuming organic matter and fuelling the production of diagenetic minerals [5, 8], thereby influencing the chemical speciation of metals [9]. Bioturbation may also play an important role in mixing reduced and oxidized metal-binding compounds [8, 10] and in determining the metal diffusion from tidal water to underlying sediments [11, 12]. Mangrove sediments can be sinks and sources of metals for coastal waters [1, 13], but their biological influence on metal trapping within sediments remains unclear.

Radiotracers have been employed to study metal transfer rates between overlying water and sediments in diverse marine systems [14–17]. Though the tidal flooding dynamics usually affect trace metal exchanges across the water–sediment interface by advection [18–20], radiotracers in core incubation and benthic chamber experiments have been helpful in elucidating the role of metal diffusion as a factor affecting the exchanges. For example, these experiments evidenced that bioturbation is an important driver controlling the water–sediment transfers in deep sea and coastal environments [17, 21, 22]. A previous core-incubation study showed that the diffusion of ^{65}Zn, ^{51}Cr

✉ M. N. Sondermann
melissa.sondermann@ics.ulisboa.pt

1 Programa de Pós-Graduação em Geoquímica, Instituto de Química, Universidade Federal Fluminense, Niterói, RJ 24020-007, Brazil

2 Programa Doutoral em Alterações Climáticas e Políticas de Desenvolvimento Sustentável, Instituto de Ciências Sociais, Universidade de Lisboa, 1600-189 Lisbon, Portugal

3 Instituto Federal de Educação, Ciência e Tecnologia do Rio de Janeiro, Nilópolis, RJ 26530-060, Brazil

4 Instituto de Radioproteção e Dosimetria/CNEN, Rio de Janeiro, RJ 22783-127, Brazil

5 Laboratório de Instrumentação Nuclear, COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21945-970, Brazil

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and ^{58}Co into mangrove sediments can be increased by biological factors, thereby affecting trace metal bioavailability and enhancing the role of mangrove sediments as metal sinks in a low-polluted area [12].

Our objective was to evaluate the relative influence of benthic organisms influence on the capacity of mangrove sediments to remove metals transported by tidal water from a tropical mangrove wetland heavily impacted by industrial waste. After decades of exposure to anomalously high levels of Zn and Cd, studies of this area, located in Sepetiba Bay (south-eastern Brazil), have improved our knowledge of the behaviour of metals in mangrove systems [23–25].

Experimental

The performed microcosm experiments are similar to those described by Petersen et al. [22]. In brief, six short sediment cores (6 cm length) were collected in April 2014 by using Plexiglas tubes (4.4 cm i.d., 25 cm length), from a black mangrove (*Avicennia schaueriana*) forest at Saco do Engenho Creek (SEC), Sepetiba Bay (22°55′11.0″S, 43°49′05.98″W). Seawater was collected in a 5-L plastic container from a nearby site (22°55′42.9″S, 43°48′41.9″W) to represent incoming tidal water. The SEC mangrove forest was chosen because this creek is the major route for metal contamination from the electroplating industry into the bay [24]. Local water pH (8.23), salinity (31) and dissolved oxygen (88.7%) were measured by using a Hanna HI9828 m. Samples were immediately transported to the laboratory, and a tidal water layer of a few centimetres was maintained over the sediment cores. In the laboratory, the overlaying water in the sediment samples was replaced by a 10-cm layer of tidal water spiked with ^{109}CdCl$_2$ and ^{65}ZnCl$_2$ (Perkin Elmer Inc.). Initial activities of the radiotracers were 1150 ± 20 and 470 ± 12 Bq mL^{-1} for ^{109}Cd(II) and ^{65}Zn(II), respectively. These activities correspond to concentrations of 12 ± 0.21 and 1.5 ± 0.04 ng L^{-1}, respectively, which are close to the those reported in previous radiotracer studies [2, 13, 22, 26]. Oxygenation of the water columns was maintained during 48-h experiments by moist air pumping [22]. These experiments were carried out at room temperature (25 °C). Biocide (formaldehyde) was applied as described by Suzuki et al. [12]. Three of the sampled cores were initially treated with 16 mL of a 4% formaldehyde solution (added carefully without disturbing the sediment surface) to inhibit biological activity (microbial + faunal). After 2 h, the formaldehyde solution was removed by siphoning and the cores were covered with 16 mL of tidal water to dilute the remaining formaldehyde solution, which was also removed by siphoning. This dilution and removal procedure was carried out twice to minimize residual

formaldehyde levels. Further dilution of residual formaldehyde, by addition of radiotracer-spiked water, limited any possible chemical change due to formaldehyde degradation. Water overlying sediments was sampled at 12 min, and at 1, 2, 3, 4, 5, 6, 10, 24 and 48 h. After 48 h, sediment cores were sectioned in 1-cm intervals. Sediment slices were dried at 75 °C for 72 h. Radionuclide activities in these samples were determined by gamma-ray spectrometry using a high-purity Ge detector (Canberra). The detector was calibrated with standards (^{60}Co and ^{152}Eu) supplied by the Radiation Protection and Dosimetry Institute–Brazilian Nuclear Energy Commission (IRD/CNEN, Brazil). Measurements were corrected for background and physical decay of the radiotracers. The quantified γ-energies were 88.0 keV (^{109}Cd) and 1115.5 keV (^{65}Zn) and the obtained spectra were analysed using the Canberra Genie 2000 software. The uncertainty associated with the counting rate was less than 5%. Radiotracer activities in the sediments are expressed in a dry weight basis. Sediment porosity was estimated according to Ravichandran et al. [27].

A Benthic Activity Index (BAI) was estimated to evaluate relative radiotracer enrichment at various depths due to biological activity within sediments, as proposed by Suzuki et al. [12]. BAI values were determined, considering radiotracer contents from untreated ($C_{untreated}$) and formaldehyde-treated ($C_{treated}$) sediments, according to the calculation:

$$BAI(\%) = ((C_{untreated} - C_{treated})/C_{untreated})100$$

(1)

BAI values should be considered minimum estimates, since remaining chemical enrichments may have been influenced by biological effects that occurred before biocide addition (e.g., due to invisible burrows) [12].

Results and discussion

Figure 1 presents the temporal variability of radiotracer activities within overlying water along the experiments, while raw data are available in the Supplementary Material. Untreated and formaldehyde-treated mangrove sediments exhibited contrasting radiotracer removal from overlying water (Fig. 1), reflecting second-order removal kinetics, with correlation coefficients (R^2) between time and 1/activity of at least 0.97. This contrasts with the first-order removal kinetics frequently reported in other radiotracer studies [13, 15, 28]. All experimental scenarios presented the same removal trend, with radiotracers going from faster initial sorption kinetics to slower sorption kinetics. This trend can be explained by binding to settling
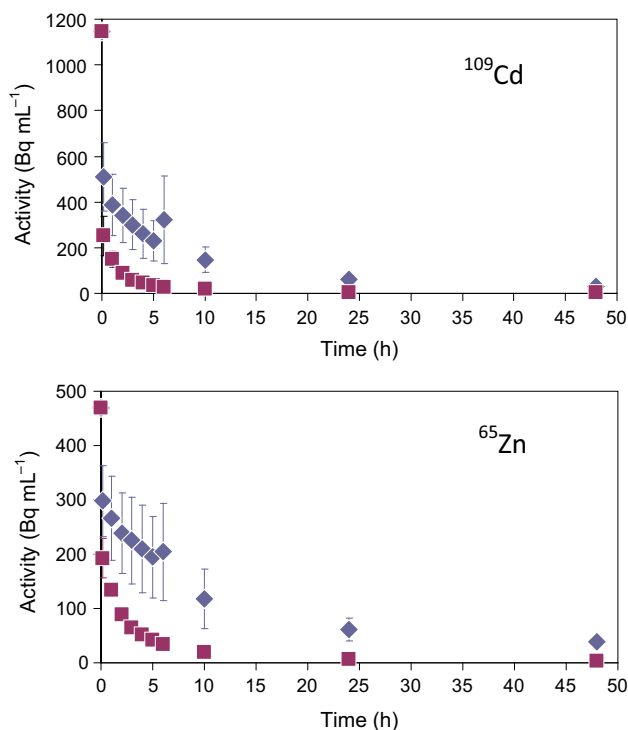
Fig. 1 Radiotracer activities in overlying water for formaldehyde-treated (diamonds) and untreated (squares) sediment experiments. Symbols represent average values of triplicate experiments. Error bars represent standard deviations. Note that error bars may be obscured symbols

estimate ^{65}Zn half-removal times of $\sim$ 7–9 days from water by underlying sediments in benthic chamber experiments performed on the Swedish coast. These data correspond to removal kinetics three orders of magnitude slower than our calculations for untreated experiments (^{65}Zn $T_{1/2} = 0.35 \pm 0.14$ h). Two previous microcosm experiments using mangrove sediments from Sepetiba Bay established ^{65}Zn half-removal times ranging from 2 to 9 h [13, 31], which are more consistent with our results. However, ^{65}Zn removal by sediments from these two studies was less efficient then observed for SEC sediments.

Radiotracer activities, assessed at the end of experiments, varied according to depth within the sediment cores (Fig. 2). Raw data are presented in the Supplementary Material. The uppermost sediment layer (0–1 cm depth) exhibited the highest radiotracer retention, which is unsurprising, since radiotracer diffusion is negatively correlated with increasing sediment depth [11, 21, 22]. However, almost all radiotracer activities ($\sim$ 98%) were retained in the uppermost layer of sediments in which biological influence had been inhibited (by formaldehyde treatment), whereas the uppermost layer of untreated
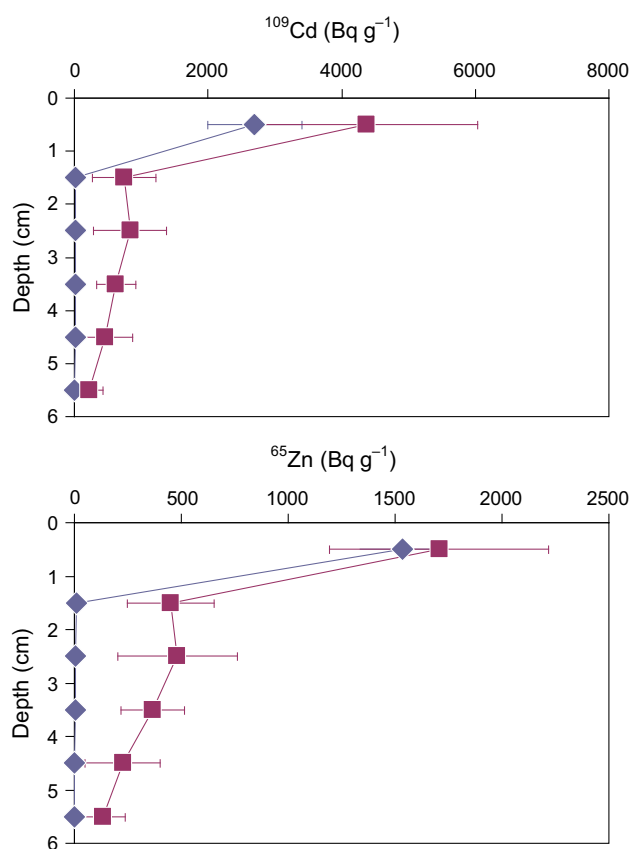
particulate matter, sorption by underlying sediment particles and diffusion into sediment pore water, as reported elsewhere (e.g., [11, 21, 29]). However, the formaldehyde treatment resulted in longer half-removal times of ^{65}Zn ($T_{1/2} = 4.4 \pm 0.89$ h vs. 0.35 ± 0.14 h) and ^{109}Cd ($T_{1/2} = 1.35 \pm 0.44$ h vs. 0.12 ± 0.02 h) from tidal water. These results suggests that inhibition of biological activity is responsible for the variability in radiotracers half-removal times, with radiotracer sorption processes being affected by benthic organisms, perhaps due to sediment bioturbation [11, 12, 30].

The $T_{1/2}$ difference between untreated and biocide-treated experiments were used for dimensioning the effects of biological activity on the radiotracer removal kinetics. The ratios between the average $T_{1/2}$ from formaldehyde-affected experiments and average $T_{1/2}$ from untreated experiments were 12.4 and 11.7 for ^{65}Zn and ^{109}Cd, respectively. These results evidence a large predominance of biological influence in determining the sediment capacity to remove metals from overlying water, reflecting similarity of kinetics behaviour responses of different metals.

Direct comparisons with other studies are problematic, given their highly different treatments and specific responses of reaction kinetics. For example, Hall et al. [15]

Fig. 2 Radiotracers activities in sediment cores for formaldehyde-treated (diamonds) and untreated (squares) experiments. Symbols represent average values of triplicate experiments. Error bars represent standard deviations

sediments only showed ∼ 50–60% retention of radiotracer activities. These activities in subsurface layers (1-6 cm depth) were 1–2 orders of magnitude greater in untreated sediments than treated sediments, for both metals (Fig. 2).

Substantial influence of benthic organisms' activity in determining metal removal from tidal water by sediments was evidenced. Our results are linked to alterations in radiotracer removal kinetics, with both faunal and microbial activities being limited by the formaldehyde treatment [32, 33]. This biological influence on metal sorption likely contribute to determining trace element exchanges across the water–sediment interface [34, 35]. Benthic fauna bioturbation has been associated to higher ^{109}Cd removal rate from overlying water by coastal sediments [22], indicating that organisms may have a more pronounced impact on metal sorption kinetics than usually considered [30].

Greater oxidation of upper sediment layers by overlying oxygenated water is likely after the formaldehyde treatment [33, 36], due to inhibition of microbial oxygen consumption and biological mixing of surface sediments [12, 32]. These processes could have contributed to the varied radiotracer removal rates between treatments. Trace metals usually present an affinity for (oxy)hydroxides, which retain metals under oxidizing conditions in mangrove sediments [6, 10]. However, under reducing conditions, the metal-bearing sulphides can occur in coastal sediments, as reported for the study area [23, 37], which may also retain the trace metals [1, 38]. Therefore, changes in the predominant physicochemical conditions at the sediment–water interface, associated with inhibition of biological activity, can affect the processes involved in determining the metal removal rates from overlying water, as observed here for ^{65}Zn and ^{109}Cd.

Molecular-level speciation of trace metals in mangrove sediments have been applied to elucidate the affinity of these metals to different primary and neoformed minerals, using K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy in combination with Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM–EDXS), which demonstrate the role of metal incorporation into pyrite (FeS_2) and metal remobilization after pyrite oxidation [3]. The sulfur re-oxidative cycling is recognized as a common process that can affect the sediment capacity to retain trace metals within mangrove environments [6].

At the end of the experiments, the retention of radiotracers was greatest in the topmost sediment layer, as reported in other studies [13, 15, 21], but diffusion into deeper layers was greatly restricted by formaldehyde treatment (and thus by the inhibition of biological activity) (Fig. 2). Moreover, in relation to untreated sediments, the diffusion depth of radiotracers was higher than observed for ^{65}Zn, ^{51}Cr and ^{58}Co for sediments from a low-polluted

mangrove site located nearby [12]. Pennafirme et al. [39] indicated that the exposure of bacterial communities from SEC sediments to elevated metal levels could improve their capacity to promote sediment accumulation of these elements. This finding suggests that microorganisms adapted to long-term exposure to metal contamination may be more efficient at metal sorption from overlying water.

Estimated BAI results (Fig. 3) revealed that biological activity had a comparatively low impact on radiotracer accumulation in the uppermost centimetre of sediments (just ∼ 10 and ∼ 38% for ^{65}Zn and ^{109}Cd, respectively), compared to estimates for below this layer (exceeding 96%). Thus, depth penetration of radiotracers is essentially biologically-mediated, as evidenced by Osaki [30]. These findings suggest that biological activity is highly influential in determining the role of mangrove sediments as trace metal sinks under the chronically-polluted condition, since deeper trace metal diffusion into the sediments can improve their retention through diminished erosion and greater immobilization within mangrove rhizospheres [11, 40].

Variability in sediment porosity for all studied samples was limited (ranging from 0.72 to 0.83), indicating similar permeability for untreated and formaldehyde-treated sediments. Previous studies on intertidal sediments have indicated that metal transport by advection is more significant than by diffusion into the pore waters [41, 42], which is also expected for mangrove wetlands, since metal sorption by the sediment solid phase is likely to be efficient [1, 5]. However, the influence of biological activity on trace metal diffusion into the sediments warrants further study, particularly considering the adaptive mechanisms of benthic organisms to elevated metal exposure (e.g., metal tolerance development by benthic microbial community) [39].

The variability of water pH, salinity and suspended particulate matter (SPM) is important for determining the trace metal removal from solution in aquatic systems. Batch experiments showed that the general effect of
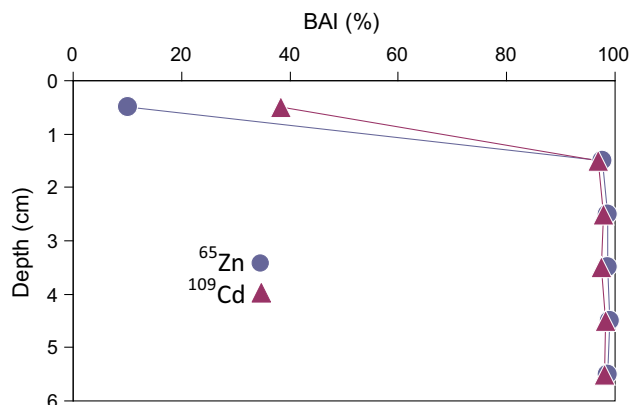

Fig. 3 Biological activity indexes (BAI) for ^{109}Cd and ^{65}Zn

salinity variability is to move the adsorption edge to higher pH values, with a generally increased metal uptake by particles as a function of time and SPM concentrations [26]. These experiments also evidenced a greater desorption of ^{109}Cd, ^{60}Co and ^{65}Zn in seawater than in freshwater. Therefore, further research on trace metals responses to the variability of physical–chemical conditions in mangrove water–sediment interfaces, along with metal percolation within the sediments, is recommended for supporting better predictions on the mangrove role as biogeochemical barriers for trace metals.

Conclusions

The activity of benthic organisms in the studied mangrove sediments favored their capacity to remove trace metals from overlying tidal water, as reflected in the faster removal kinetics for ^{65}Zn and ^{109}Cd under the formaldehyde treatment. Most radiotracer activities within the sediments were concentrated in the uppermost centimetre, but diffusion below this layer (where more efficient metal trapping may occur) was essentially driven by activities of benthic organisms (BAI values above 96%). Therefore, we have provided evidence that biological activity is a key factor influencing the role of mangrove sediments as biogeochemical barriers for the metals transported by tidal water in the chronically-polluted study area. These results demonstrated a stronger capacity of pollution-impacted sediments to trap trace metals from tidal water than previously observed for low-polluted mangrove sediments from a nearby area, possibly due to a more efficient removal capacity by organisms more tolerant to metal pollution.

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