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Removal efficiency of ^{75}Se, ^{51}Cr and ^{60}Co from tidal water by mangrove sediments from Sepetiba Bay (SE Brazil)

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Abstract Mangrove sediment cores sampled from Sepetiba Bay (SE Brazil) were covered with tidal water spiked with ^{75}Se, ^{51}Cr and ^{60}Co to evaluate the removal efficiency of these radiotracers by underlying sediments. Variable time-evolution trends were observed along 115 h experiments, with significant differences between removal efficiencies of all radiotracers observed only after 70 h (^{51}Cr > ^{60}Co > ^{75}Se). After an event of ^{60}Co release back to overlying water, there was a general trend of lower ^{60}Co removal than observed for other radiotracers during the period from 20 to 54 h. After this event, alternated periods of higher ^{60}Co and higher ^{75}Se removal trends were observed, attributed to behavioural differences expected for such anionic and cationic radiotracers. While ^{75}Se and ^{51}Cr showed uniform time-evolution curves, as typically found in the literature for most radiotracers, ^{60}Co removal rates presented oscillations, probably due to sensitivity to changes in redox conditions within underlying sediments. Results evidenced the role of mangrove sediments as trace element sinks, which have implications for coastal water quality and for possible uses of such sediments in wastewater treatment systems.

Keywords Radiotracers · Trace elements · Mangrove sediments · Removal efficiency · Sediment–water interface

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Introduction

Mangrove sediments have been frequently recognized as important trace element sinks in coastal environments from tropical regions, mainly due to accumulation of substantial amounts of organic and inorganic chemical compounds that can immobilize these elements in the sediment solid phase [1–3]. Unfortunately, relatively few studies have dealing with the transfers of trace elements between such intertidal environments and coastal waters under field conditions [4–6], as also observed for the distribution of trace elements between mangrove sediment solid phase and pore water [7, 8]. As helpful tools to improve our comprehension on trace elements behaviour in aquatic systems, radiotracer studies have been performed for a wide range of environments and experimental conditions [9–12], which have been recently extended to elucidate the extent and to evaluate the factors affecting the mangrove sediments capacity to remove trace elements from coastal water [13–15]. For example, Suzuki et al. [16] demonstrated that the

trace elements removal from overlying water by mangrove sediments and their burial within such sediments can be significantly dependent on activities of benthic organisms. However, radiotracer experiments have not been frequently applied to evaluate trace element behaviour in tropical aquatic ecosystems, being mostly found in the literature for temperate and subtropical environments [17–20].

In this study the adsorption of cobalt (Co), chromium (Cr) and selenium (Se) by mangrove sediments was evaluated by using corresponding radiotracers, allowing the estimation of their removal efficiency from overlaying tidal water by such sediments. Microcosm experiments on the behaviour of ^{75}Se (half-life 119.8 days) ^{51}Cr (half-life 27.7 days) ^{60}Co (half-life 5.3 years) were performed with surface sediments from the mangrove ecosystem of Itacuruçá, located in Sepetiba Bay (SE Brazil), in addition to previous experiments on water–sediment transfer of trace elements carried in this site [13] and in other mangrove area from south-eastern Brazil [14]. Sediment data (^{75}Se, ^{51}Cr and ^{60}Co activities) derived from these experiments were previously reported by Suzuki et al. [15], which observed a strong effect of benthic fauna bioturbation on the depth distribution of all radiotracers, as evidenced by subsurface activity peaks within just one of the experimental cores, even without the presence of visible burrows. Similar observations on bioturbation influences on radiotracer distribution have been reported for other sedimentary environments [17, 18].

Materials and methods

Tidal water and mangrove sediments were sampled within a fringe forest dominated by the red mangrove (*Rhizophora mangle* L.) located in Itacuruçá, northern coast of Sepetiba Bay (22°55′19″S, 43°53′09″W). Detailed information on Itacuruçá mangrove ecosystem characteristics and on trace metal biogeochemistry within this ecosystem have been reported elsewhere [5, 21–23]. Three short sediment cores (0–8 cm depth) were sampled by using Plexiglas tubes (4.4 cm diameter), within nearly 10 cm from each other. Surface tidal water was sampled, during the flooding period, by using a 25-L plastic container. The sampled cores were transported to the laboratory in a vertical position, maintaining a tidal water column of nearly 5 cm overlaying the sediments.

The experimental methods were adapted from Petersen et al. [24], according to Machado et al. [13]. There was no pre-treatment of sediments prior to experiments, in order to preserve the natural sediment structure. Water columns that overlaid sediments during transport were substituted by a 10-cm tidal water column already spiked with the radiotracers (Fig. 1). This overlaying water showed mean (±SE) initial activities of 22.0 ± 0.2, 10.7 ± 0.4 and 65.2 ± 3.3 Bq m L^{-1} for ^{75}Se, ^{51}Cr and ^{60}Co, respectively. Overlaying water columns were aerated by pumping moist air to ensure oxygen-saturation along the experiments, simulating the sediment flooding by oxygenated tidal water. The bottom of each tube was sealed with a rubber cap covered with a PVC film. Overlaying water of each replicate was periodically sampled (t = 0, 0.5, 4, 7, 20, 30, 44, 54, 69, 94 and 115 h) for ^{75}Se, ^{51}Cr and ^{60}Co activities determination, which was performed by gamma-ray spectrometry with a high-purity germanium detector (HPGe). Counting time errors were always below 5 %. Radiotracers were produced at the Instituto de Pesquisas Energéticas e Nucleares-Comissão Nacional de Energia Nuclear (IPEN-CNEN/SP). A one-way ANOVA followed by a post hoc Tukey's test was used to compare the results of percent remaining radiotracer activities in overlying water. Whenever necessary, statistical tests were performed on log-transformed data to meet the assumptions of parametric analysis.

Results and discussion

Radiotracer activities variability in tidal waters during the experiments is presented in Fig. 2. Most radiotracer experiments on trace element removal from overlying water by bottom sediments have found a pattern of fast initial removal, followed by a decreasing removal trend [9, 12, 24]. This typical tendency was also previously reported for ^{65}Zn [13], ^{137}Cs, ^{57}Co and ^{54}Mn [14] transfers from

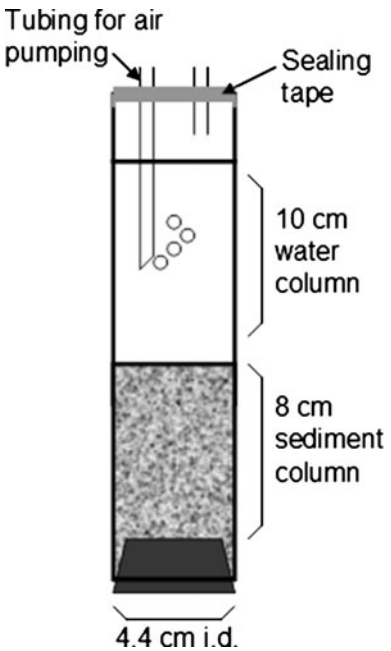

Fig. 1 Experimental apparatus employed, as adapted from Petersen et al. [24]

tidal water to mangrove sediments, as it was observed for the radiotracers evaluated in the present study. This general time-evolution trend is not expected to occur when some significant disturbance event affect the water system, such as sediment resuspension in the water column [25]. Although the radiotracers have followed an expected general trend, the time-curse evolution of ^{60}Co activity was different from the pattern followed by ^{75}Se and ^{51}Cr, as reflected by the similarity in the variability of removal rates of these later radiotracers in comparison with that from ^{60}Co (Fig. 3). Strong removal rate oscillations were often presented by ^{60}Co, showing a negative average removal rate within the 4–7 h interval. Moreover, the percents of remaining activities in overlying water demonstrated significantly different removal efficiencies (Tukey's test $p \leq 0.05$) in some time intervals (Fig. 4). Within the 20–25 h interval there was a significantly higher remaining activity of ^{60}Co in comparison with other radiotracers, while there were significant differences between all radiotracers after 70 h, indicating that the removal efficiency followed the order ^{51}Cr > ^{60}Co > ^{75}Se.

Removal rates variability indicated that only ^{60}Co presented noticeable oscillations, while the other radiotracers showed a more uniform pattern. Incorporation by living organic matter (phytoplankton) is a common feature of "nutrient-type" trace elements, such as Se [25], while Cr behaviour has been previously evidenced as affected by associations with organic matter in the study site [21]. Therefore, it may be expected that ^{75}Se and ^{51}Cr have been strongly scavenged by suspended (living and non-living) organic matter. Although all studied radiotracers can be sensitive to particle scavenging and redox processes [25], there are substantial evidences that ^{60}Co behaviour is associated with the redox cycling of Mn [25], as confirmed by a previous study on radiotracer removal from tidal water

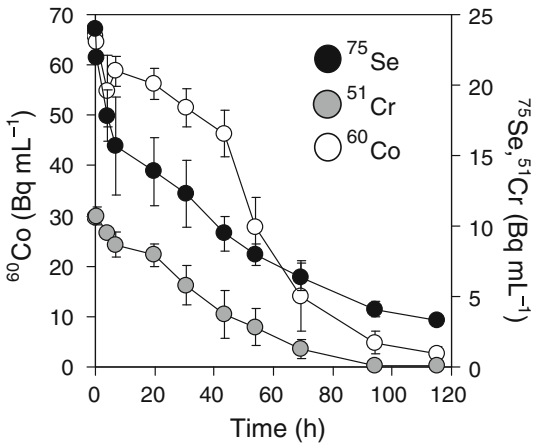

Fig. 2 Activities of ^{75}Se, ^{51}Cr and ^{60}Co in tidal water overlaying the mangrove sediments during the experiments (mean ± SE; $n = 3$)

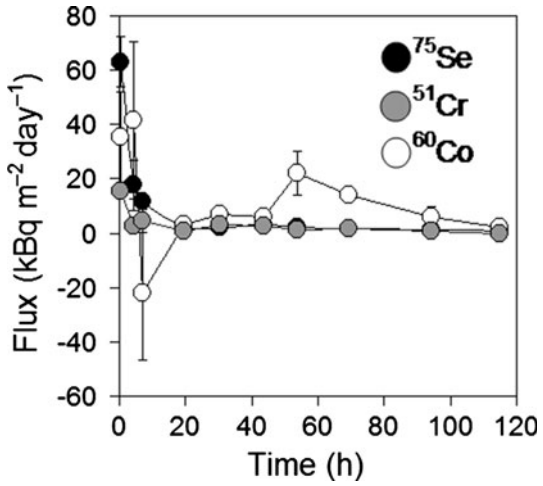

Fig. 3 Removal rates of ^{75}Se, ^{51}Cr and ^{60}Co from tidal water overlaying the mangrove sediments during the experiments (mean ± SE; $n = 3$)

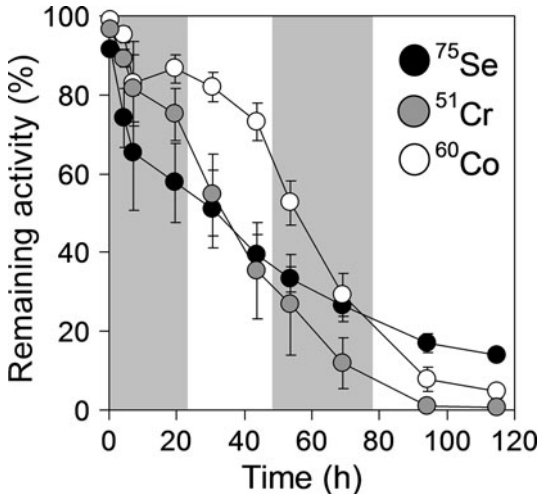

Fig. 4 Percent remaining activities of ^{75}Se, ^{51}Cr and ^{60}Co in relation to initial activities in tidal water overlaying the mangrove sediments during the experiments (mean ± SE; $n = 3$). Two periods showing not significant differences (*shaded*) and two periods showing significant differences (*not shaded*) between radiotracers were identified by statistical (Tukey's test) comparisons

by mangrove sediments, which showed a high correlation between ^{57}Co and ^{54}Mn activities in overlying water [14]. Therefore, the observed contrast between ^{60}Co and other radiotracers can be partly due to different responses to particle-scavenging (including phytoplankton uptake) and redox-driven removal from water column. Besides scavenging processes by particulate matter (e.g., by adsorption processes onto organic compounds [26] and metal oxides [27]) and removal by deposition, the direct sorption from aqueous phase by bottom sediment particles and diffusion into pore water are other probable factors affecting the observed results [13, 16, 24].

The continuing aeration of overlying water implies in a continuous oxidation of uppermost sediment layers, favoring radiotracer sorption by Fe and Mn oxides, while the consumption of organic matter by microorganisms can partly decompose such compounds, releasing part of the associated radiotracers back to water column [25, 28]. This is the most probable explanation for the negative ^{60}Co flux reported above, as previously reported for Co elsewhere [25]. Such radiotracer remobilization can also contribute to explain the less-efficient removal observed during the period from 20 to 54 h (just after the negative flux event), in which significantly lower ^{60}Co removals were found during intermediate time intervals (Fig. 4). It is interesting to note that this release back to overlying water can eventually occur even with radiotracers of known "particle-reactive behaviour", such as ^{65}Zn [13]. On the other hand, the examination of radiotracer activities in overlying water from individual experiments (data not shown) did not indicate higher radiotracer removal from overlying water in the replicate that presented strong bioturbation effects within sediments, reported by Suzuki et al. [15]. Although there is a substantial body of evidences that bioturbation can increase the transport of radionuclides into the sediments [18, 23, 24], there was no noticeable effect of bioturbation on ^{75}Se, ^{51}Cr and ^{60}Co transfer from water to underlying sediments, whereas their distribution within the bioturbated core was sufficiently affected to promote deeper penetration into the rhizosphere, indicating more efficient retention [15].

The observed results confirmed that mangrove sediment biogeochemical processes can promote an elevated retention of trace elements. This role has been used to support proposals of using mangrove sediments for wastewater treatment in the last decades, e.g. as evidenced by sediment column leaching experiments [29, 30]. Constructed mangrove wetlands have also been recommended for this purpose recently, as a potentially feasible technology for nutrient contaminants removal [31, 32], which may possibly be extended to trace element contaminants. Radiotracer techniques can be useful in elucidating the potential efficiency of this kind of treatment systems. Moreover, the reverse process (i.e., how and how much the elements preconcentrated within mangrove sediments used for water treatment can be recovered before disposal) has not been quantified to our knowledge, which may also deserve attention in further studies, as can also be investigated by radiotracer experiments.

Conclusions

Radiotracer experiments performed to estimate trace element removal efficiency from overlaying tidal water by mangrove sediments resulted in time-evolution trends with significant differences in removal efficiencies only after 20 h. There were significant differences between removal efficiencies of all radiotracers after 70 h, following the order ^{51}Cr > ^{60}Co > ^{75}Se. Within the 20–54 h interval there was a general trend of lower ^{60}Co removal than observed for other radiotracers, after an event of ^{60}Co release back to overlying water. This suggests that post-depositional remobilization from bottom sediments affected these results, possibly contributing to explain the significant difference observed within this time interval. Alternated periods of higher ^{60}Co and higher ^{75}Se removal trends were observed, attributed to behavioural differences between such cationic and anionic radiotracers (e.g., expected strong associations of Se with organic matter and Co with metal oxides). Results are in agreement with previous data found in the literature on the role of mangrove sediments as trace elements sinks, which have implications for coastal water quality in polluted tropical areas and for possible uses of such sediments in wastewater treatment systems.

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