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Kinetics of trace metal removal from tidal water by mangrove sediments under different redox conditions

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HIGHLIGHTS

- Radiotracer experiments evidenced the role of mangrove sediments in trapping trace metals.
- Very contrasting removal kinetics from tidal water were observed for ^{65}Zn and ^{58}Co.
- Nearly 40%–50% of ^{58}Co activities and nearly 90% of ^{65}Zn activities in overlying water were removed.
- ^{65}Zn showed a stronger particle-reactive behaviour than observed for ^{58}Co.
- ^{58}Co was more sensitive to redox conditions in tidal water than observed for ^{65}Zn.

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ABSTRACT

The extent in which redox conditions can affect the removal kinetics of ^{58}Co and ^{65}Zn from tidal water by mangrove sediments was evaluated in microcosm experiments, simulating a tidal flooding period of 6 h. The average half-removal time ($t_{1/2}$) of ^{58}Co from overlaying water was slightly higher (7.3 h) under an N_2-purged water column than under an aerated water column (5.4 h). A lower difference was found for ^{65}Zn (1.9 h vs. 1.5 h, respectively). Average removals of ^{58}Co activities from water were 54.6% (N_2 treatment) and 43.5% (aeration treatment), whereas these values were 88.0% and 92.7% for ^{65}Zn, respectively. Very contrasting sorption kinetics of different radiotracers occurred, while more oxidising conditions favoured only a slightly higher removal. Average ^{58}Co and ^{65}Zn inventories within sediments were 30.4% and 18.8% higher in the aeration treatment, respectively. A stronger particle-reactive behaviour was found for ^{65}Zn that was less redox-sensitive and more efficiently removed by sediments than ^{58}Co.

1. Introduction

A substantial body of observational data has been accumulated on the role of mangrove sediments in trapping anthropogenic trace metals in inter-tropical regions, as supported by field studies (e.g., Clark et al., 1998) and laboratory experiments (e.g., Tam and Wong, 1996). In order to contribute to the knowledge on the mangrove sediments capacity to retain trace metals and on the behaviour of such elements within these sediments, radiotracer experiments have been recently carried out, comparing the metal sorption kinetics (Machado et al., 2012) and evaluating the controls on this sorption (Machado et al., 2008; Suzuki et al., 2012).

Since the application of radiotracer techniques can be useful in investigating metal behaviour in aquatic environments (Santschi, 1988; Bouchet et al., 2011), this study employed microcosm experiments to compare the kinetics of ^{58}Co (half-life 71.3 days) and ^{65}Zn (half-life 244 days) transfers across the water-sediment interface in a tropical mangrove ecosystem. The extent in which the removal kinetics is affected by different redox conditions was particularly evaluated.

2. Materials and methods

In a mangrove forest dominated by *Rhizophora mangle*, located at Sepetiba Bay, SE Brazil (22°55′19″S, 43°53′09″W), six sediment

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cores (0–6 cm depth) were sampled by using Plexiglas tubes (4.4 cm i.d., 25 cm length) and tidal water was sampled at a creek that drains the forest, using a 25 L container. Experimental procedures were similar to that employed by Petersen et al. (1998). There was no sieving or homogenisation of sediments prior to experiments, to preserve its natural structure. Water columns (nearly 5 cm height) that overlaid the sediments during the transport to the laboratory were substituted by a 10 cm height tidal water column already spiked with radiotracers, showing initial activities of 505–523 Bq ml^{-1} and 472–484 Bq ml^{-1} of ^{58}Co and ^{65}Zn, respectively. For three cores, the overlaying water was aerated by pumping moist air, simulating highly oxygenated flooding water (Petersen et al., 1998), while the water overlaying the other three cores was purged with N_2. A previous test showed that while air pumping caused nearly 100% dissolved O_2 saturation, the N_2 treatment caused nearly 30% dissolved O_2 saturation. Water was periodically sampled along 6 h. After this period, sediment cores were sectioned in 1 cm depth intervals. Radioactivity in the water and sediment samples was analysed by gamma-ray spectrometry with a high-purity Ge detector (ORTEC). Counting times were adjusted to give propagated counting errors below 5% for each isotope.

Total inventories were estimated as the sums of inventories from each sediment layer, calculated as product between activity (Bq g^{-1}), sediment density (g cm^{-3}) and the depth interval thickness (cm). Sediment density was determined after drying (50 °C for 72 h) and weighing the sediment core sections. Radiotracers were produced at the Instituto de Pesquisas Energéticas e Nucleares–Comissão Nacional de Energia Nuclear (IPEN-CNEN/SP).

3. Results and discussion

The activities of different radiotracers in overlying water presented strong differences in their temporal variability, while smaller differences between water column treatments were observed for each radiotracer (Fig. 1). The average (±SD) half-removal time ($t_{1/2}$) of ^{58}Co from overlaying water was slightly higher (7.3 ± 1.3 h) under the N_2-purged water column than under the aerated water column (5.4 ± 1.6 h). Closer $t_{1/2}$ values were found for ^{65}Zn between N_2 (1.9 ± 0.5 h) and aeration treatments (1.5 ± 0.3 h). Final average (±SD) removals from water

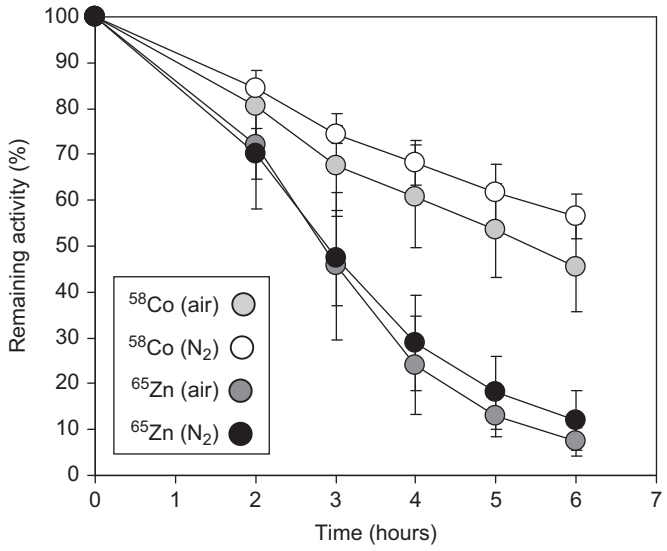

Fig. 1. Variability of ^{58}Co and ^{65}Zn activities in tidal water overlaying the mangrove sediments during the 6 h experiments under air and N_2 pumping (averages ± SD; n=3).

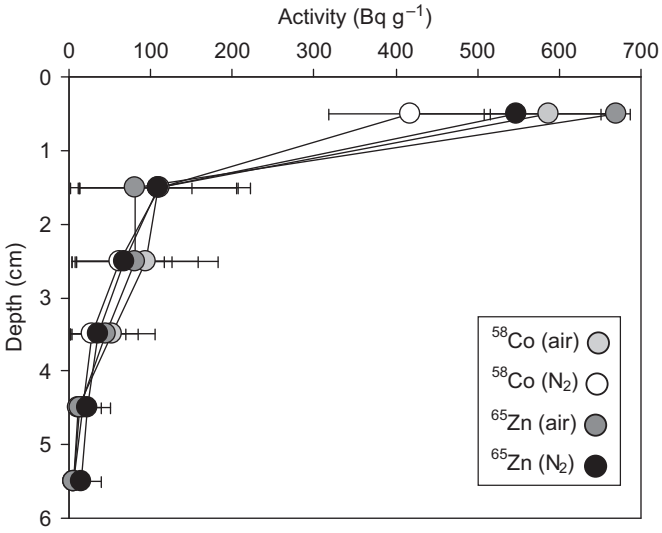

Fig. 2. Variability of ^{58}Co and ^{65}Zn activities in mangrove sediments at the end of 6 h experiments under air and N_2 pumping into overlaying water (averages ± SD; n=3).

were 54.6 ± 9.6% (N_2 treatment) and 43.5 ± 4.9% (aeration treatment) for ^{58}Co activities and 88.0 ± 6.4% (N_2 treatment) and 92.7 ± 3.1% (aeration treatment) for ^{65}Zn activities. Zinc and Co radiotracers have presented particle-reactive behaviours in previous studies (Santschi 1988; Machado et al., 2008, 2012), but the very contrasting sorption kinetics observed evidenced a stronger reactivity of ^{65}Zn to studied mangrove sediments.

The vertical distribution trends within sediments (Fig. 2) evidenced a higher accumulation of each radiotracer in uppermost layers under the aeration treatment, while there was a close similarity of results in all other depth intervals for both treatments. Considering that the removal from water column occurs due to sorption by bottom sediments, deposition of particulate matter and diffusion into pore water, the first centimetre depth have generally accumulated over 50% of total activities within sediments in previous radiotracer experiments (Santschi 1988; Petersen et al., 1998; Suzuki et al., 2012), as also observed in this study (Fig. 2).

Average ^{58}Co inventories within sediments were 30.4% higher in the aeration treatment (1118 ± 230 Bq cm^{-2} vs. 777 ± 254 Bq cm^{-2}), whereas average ^{65}Zn inventories were 18.8% higher in the aeration treatment (1185 ± 21 Bq cm^{-2} vs. 962 ± 296 Bq cm^{-2}). Sediment variability in grain size, organic matter content and metal oxides concentrations are possible factors affecting the efficiency of trace metal trapping within mangrove sediments (Clark et al., 1998; Gueiros et al., 2003), which probably contributed to determine the observed results.

4. Conclusions

Considering the semidiurnal frequency of tidal flooding in the study area, the results evidenced the role of mangrove sediments in removing trace metals from tidal waters, since nearly 50% of initial ^{58}Co activities and nearly 90% of ^{65}Zn initial activities in overlying water were removed in 6 h experiments. Very contrasting removal kinetics were observed for ^{65}Zn and ^{58}Co, while more oxidising conditions favoured slightly its removal by sediments. A stronger particle-reactive behaviour was found for ^{65}Zn, which was less redox-sensitive and more efficiently removed by sediments than ^{58}Co.

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References

Bouchet, S., Bridou, R., Tessier, E., Rodriguez-Gonzalez, P., Monperrus, M., Abril, G., Amouroux, D., 2011. An experimental approach to investigate mercury species transformations under redox oscillations in coastal sediments. Mar. Environ. Res. 71, 1–9.

Clark, M.W., McConchie, D.M., 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.

Gueiros, B.B., Machado, W., Lisboa Filho, S.D., Lacerda, L.D., 2003. Manganese behaviour at the sediment-water interface in a mangrove dominated area in Sepetiba Bay. SE Braz. J. Coastal Res. 19, 550–559.

Machado, E.C., Machado, W., Bellido, L.F., Patchineelam, S.R., Bellido, A.V.B., 2008. Removal of zinc from tidal water by sediments of a mangrove ecosystem: a radiotracer study. Water Air Soil Pollut. 192, 77–83.

Machado, E.C., Machado, W., Bellido Jr, A.V., Bellido, L.F., Patchineelam, S.R., 2012. Cesium, manganese and cobalt water—sediment transfer kinetics and diffusion into mangrove sediments inferred by radiotracer experiments. J. Radioanal. Nucl. Chem. 292, 349–353.

Petersen, K., Kristensen, E., Bjerregaard, P., 1998. Influence of bioturbating animals on flux of cadmium into estuarine sediments. Mar. Environ. Res. 45, 403–415.

Suzuki, K.N., Machado, E.C., Machado, W., Bellido, A.V., Bellido, L.F., Osso Jr., J.A., Lopes, R.T., 2012. Selenium, chromium and cobalt diffusion into mangrove sediments: radiotracer experiment evidence of coupled effects of bioturbation and rhizosphere. Water Air Soil Pollut. 223, 3887–3892.

Santschi, P.H., 1988. Factors controlling the biogeochemical cycles of trace elements in fresh and coastal marine waters as revealed by artificial radioisotopes. Limnol. Oceanogr. 33, 848–866.

Tam, N.F.Y., Wong, Y.S., 1996. Retention and distribution of heavy metals in mangrove soils receiving wastewater. Environ. Pollut. 94, 283–291.