Water Air Soil Pollut (2012) 223:3887–3892
DOI 10.1007/s11270-012-1157-x

Selenium, Chromium and Cobalt Diffusion into Mangrove Sediments: Radiotracer Experiment Evidence of Coupled Effects of Bioturbation and Rhizosphere

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Received: 6 January 2012 / Accepted: 20 March 2012 / Published online: 3 April 2012

Abstract Microcosm experiments on the behaviour of Se, Cr and Co were carried out with mangrove sediments from Sepetiba Bay, Brazil. Three 8-cm length sediment cores were covered with tidal water spiked with ^{75}Se, ^{51}Cr and ^{60}Co to evaluate its behaviour within the sediments. Two cores retained almost all activities (99–100 %) within the uppermost centimetre layer, while the third core presented a deeper penetration of all radiotracers, displaying a second activity peak at the 3–4-cm depth interval, which evidenced benthic fauna bioturbation influence. This influence extended the diffusion into depths in which mangrove rhizosphere can retain the elements, suggesting increased retention efficiency. This mechanism of retention enhancement was proposed in addition to previous conceptual models describing trace elements behaviour in mangrove sediments. Increased bioturbation and rhizosphere development will probably increase this effect, while mangrove plant cover losses may promote a less efficient retention of elements recently diffused from tidal water.

Keywords Mangrove · Trace elements · Radiotracers · Bioturbation · Rhizosphere

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1 Introduction

Radiotracer experiments are useful tools in elucidating the role of biogeochemical processes determining the behaviour of elements of environmental interest in sediments from coastal and marine environments (Barros et al. 2004; Hall et al. 1989; Santschi et al. 1984). As an important example, the extent in which bioturbation affects the trace element transport and accumulation within the sediment columns is largely unknown and difficult to be directly quantified, but it can be investigated by using radiotracer experiments (Cournane et al. 2010; Petersen et al. 1998; Osaki et al. 1997). Since the role of mangrove ecosystems as trace elements' sinks has been demonstrated in the last decades, mainly as a consequence of the uptake by fine-grained sulphidic and organic matter-rich sediments (Alongi et al. 2004; Clark et al. 1998; Marchand et al. 2006), experimental approaches have been employed to evaluate the trace element removal from overlaying water by mangrove sediments, as previously reported for ^{65}Zn (Machado et al. 2008a), ^{137}Cs, ^{54}Mn and ^{57}Co (Machado et al. 2012). Although bioturbation effects have not been identified in these previous radiotracer experiments, the crab burrowing activity importance for mangrove sediment biogeochemistry has been broadly recognised, for instance, by affecting oxygen and sulphate input from overlaying water into the sediments and mixing the reduced and oxidised forms of metals (Clark et al. 1998; Ferreira et al. 2007; Kristensen and Alongi 2006). Moreover, even in studies that sampled sediments without visible crab burrows (e.g. Alongi et al. 2004; Machado et al. 2008b), sediment bioturbation can occur due to burrowing activity of many other important benthic organisms not detected by visual inspection of sediment surface (e.g. benthic worms).

Radiotracer experiments on the behaviour of ^{75}Se (half-life 119.8 days), ^{51}Cr (half-life 27.7 days) and ^{60}Co (half-life 5.3 years) were carried out with three sediment cores taken from the mangrove ecosystem of Itacuruçá, located in Sepetiba Bay (SE Brazil). The X-ray microtomography of another short sediment core from Itacuruçá mangrove forest presented in Fig. 1 demonstrates benthic fauna activity within the upper sediment layers, as what typically occurs in coastal sediments (e.g. Osaki et al. 1997; Petersen et al. 1998). In a previous work, using mangrove and tidal creek sediments from the same site, it was demonstrated that mangrove-colonised sediments were more efficient in retaining ^{65}Zn than unvegetated tidal creek sediments, without evidences of bioturbation (Machado et al. 2008a).

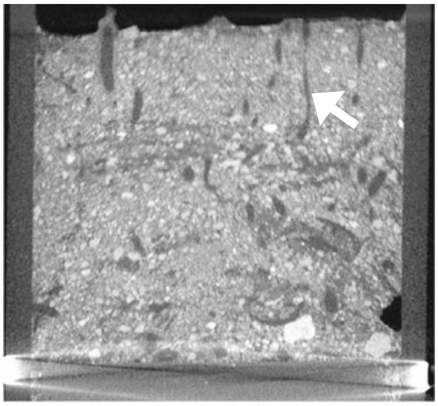

Fig. 1 X-ray microtomography of 0–4-cm depth sediment layers from Itacuruçá mangrove. Sediment structure complexity is demonstrated, evidencing density heterogeneity due to mineral and organic matter composition and biological activity. The *arrow* indicates an example of burrow structure

2 Materials and Methods

The sampling site (22°55′19″ S, 43°53′09″ W) is located inside a fringe forest dominated by the red mangrove (*Rhizophora mangle* L.). Detailed information on Itacuruçá mangrove ecosystem characteristics and on trace metal biogeochemistry within this ecosystem is available in the literature (e.g. Lacerda et al. 1988, 1991; Silva et al. 1990). Three short sediment cores (0–8-cm depth) were sampled by using Plexiglas tubes (4.4-cm diameter, 25-cm length), within 10 cm from each other. Surface tidal water was simultaneously sampled, during the flooding period, at an adjacent tidal creek, by using a 25-l plastic container. The sampled cores (called A, B and C) were transported immediately to the laboratory, in a vertical position, maintaining a tidal water column of few centimetres overlaying the sediments.

The experimental methods were adapted from Petersen et al. (1998), according to Machado et al. (2008a). 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. 2). This overlaying water showed mean (±SD) initial activities of 22.0±0.6, 10.7±1.1 and 65.2±1.0 Bq ml^{-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 coastal water. The bottom of each tube was sealed with a rubber cap covered with a PVC film. After 115 h, sediment cores were sectioned in 1-cm intervals. The determination of radionuclide activities was performed by gamma-ray spectrometry with a high-

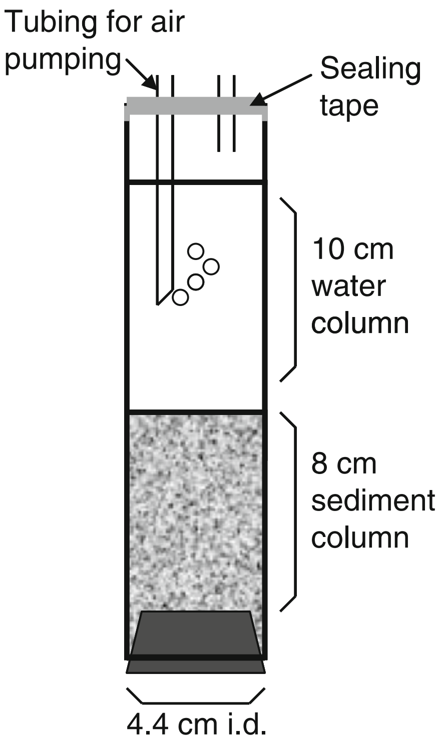

Fig. 2 Experimental apparatus employed to evaluate the behaviour of ^{75}Se, ^{51}Cr and ^{60}Co

purity Ge detector. Counting time errors were always below 5 %. Radiotracers were produced at the Instituto de Pesquisas Energéticas e Nucleares–Comissão Nacional de Energia Nuclear.

Inventories of radionuclide activities were calculated for each sediment depth interval as the product between activity (in Becquerels per gram), sediment density (in grams per cubic centimetre) and the thickness of the depth interval (in centimetre). The sediment density was determined after drying (50 °C for 72 h) and weighing the whole sediment core sections.

3 Results and Discussion

In most previous radiotracer experiments, the radionuclide distribution along sediment cores is characterised by a larger amount within a thin upper layer followed by a sharp activity decrease with depth, mainly due to radionuclide binding to sediment particles, deposition of particulate matter on the sediment surface and diffusion into pore water (Cournane et al. 2010; Barros et al. 2004; Hall et al. 1989; Machado et al. 2008a, 2012; Santschi et al. 1984). The radionuclide accumulations within cores A and B were in agreement with this trend, since all or almost all activities were retained in the uppermost centimetre layer, corresponding to 99.4 to 100 % of the total activities in each core. The

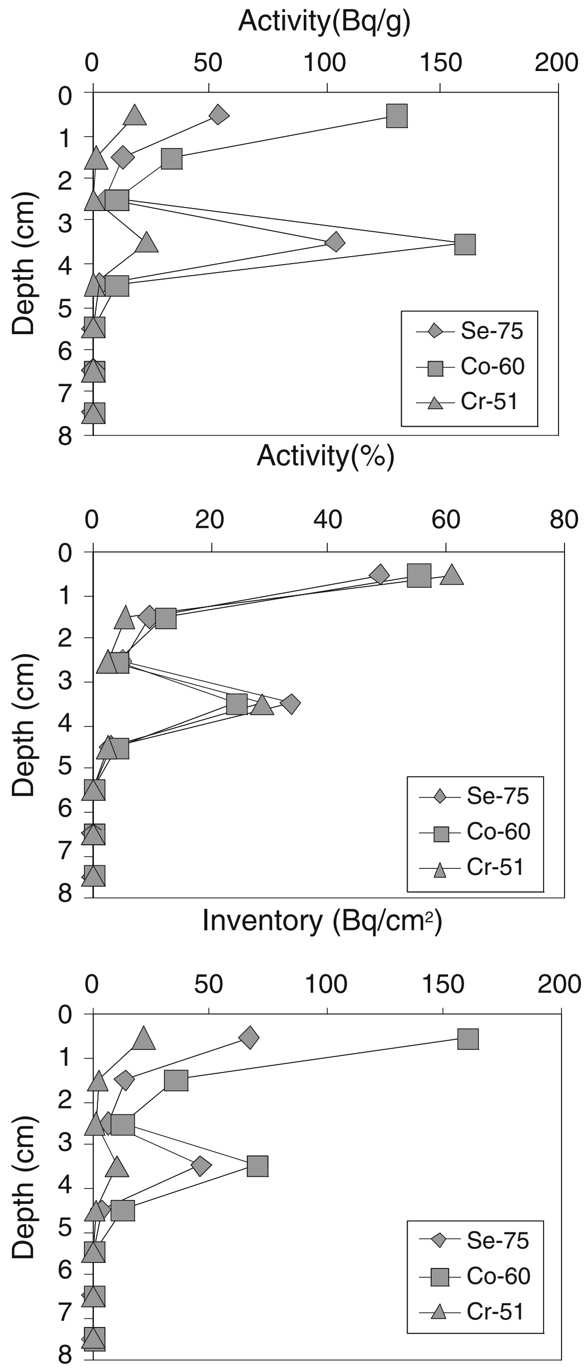

Fig. 3 Activities of ^{75}Se, ^{51}Cr and ^{60}Co in the sediment core C

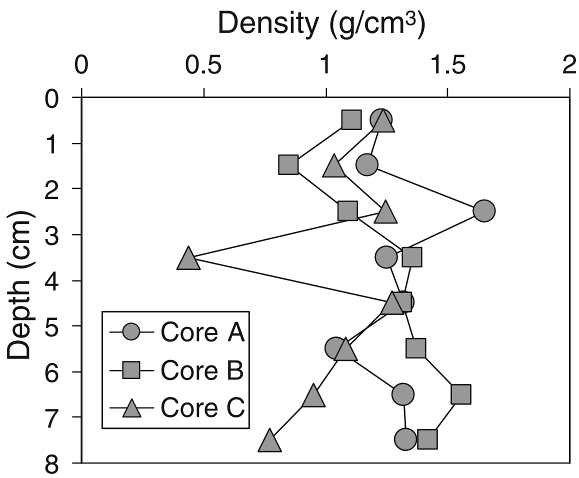

Fig. 4 Sediment density in the studied sediment cores

remaining activities were found in the following depth interval (1–2 cm). This limited diffusion into the sediments was probably due to adsorption processes onto mineral phases, such as metal oxides, iron sulphides and organic compounds (e.g. Clark et al. 1998; Machado et al. 2008b; Marchand et al. 2006). A previous study with Itacuruçá mangrove sediments emphasised the role of organic matter in determining the chromium accumulation (Lacerda et al. 1991).

In core C, all radiotracers were detected within the 0–5-cm depth, showing two depth intervals with activity peaks (Fig. 3). Besides the uppermost layer peaks, there was a subsurface (3–4-cm depth) layer that presented often larger activity peaks. However, the surface layers accumulated the larger percents of the total activity within the cores, as well as the larger activity inventories. The 0–1-cm depth interval retained 48.7, 55.2 and 61.0 % of the total ^{75}Se, ^{60}Co and ^{51}Cr activities, while the 3–4-cm depth interval retained 33.6, 24.2 and 28.6 % of these activities, respectively. Although there was no visible evidence of faunal burrowing in the studied cores, there are evidences in the literature that bioturbation can promote this transport into subsurface layers. Osaki et al. (1997) showed that one or two subsurface peaks of the radionuclides ^{54}Mn, ^{59}Fe, ^{57}Co and ^{65}Zn were observed (between 1- and 4-cm depth) in intertidal sediments when it contained living benthic fauna, whereas Santschi et al. (1984) found that, at only one of their studied deep sea sites, the transport of particle-reactive radionuclides (such as ^{54}Mn, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{113}Sn, ^{7}Be and ^{141}Ce) occurred to a depth of 4–5 cm in a core taken around a 'hole', identified as burrowing activity. The knowledge on this behaviour is particularly important in the case of known toxic elements, susceptible to be transferred across food chains, such as selenium (e.g. Alquezar et al. 2007; Xu and Wang 2002).

Figure 4 presents the sediment density variability (0.44 to 1.65 g cm^{-3}), which ranged in agreement with the values found by Silva et al. (2003) for mangrove sediment cores from the same site (0.45 to 1.22 g cm^{-3}), but the most noticeable data are the abrupt density decrease in the 3–4-cm depth layer, which explain why it presented lower inventories and

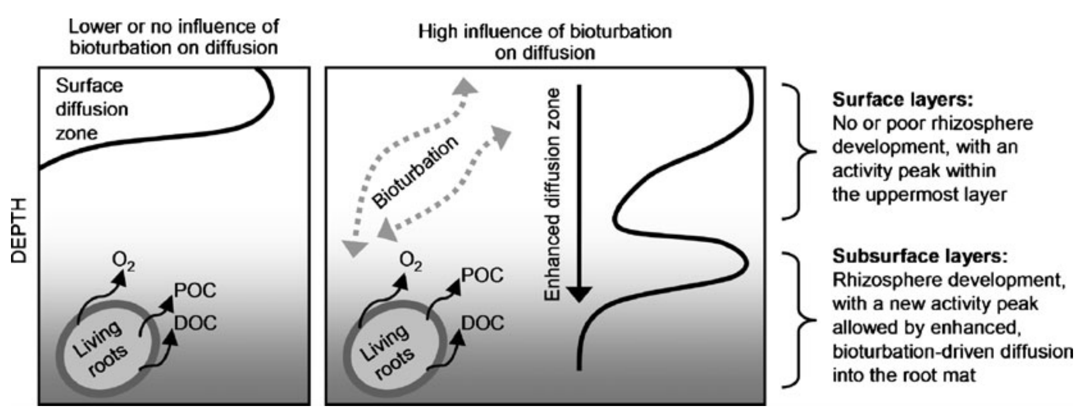

Fig. 5 Schematic diagram illustrating the relative influence of bioturbation on the distribution of trace elements recently diffused into upper layers (0–5 cm) of Itacuruçá mangrove sediments. According to the proposed complementary effects of bioturbation and mangrove roots, the *grey shading* indicates the increasing rhizosphere influence in subsurface layers. Root-derived oxygen, dissolved organic carbon (*DOC*) and particulate organic carbon (*POC*) are considered as main rhizosphere processes (see text)

percents of total activities than the surface layer. A visual examination of the sediments from the 3–4-cm layer showed a dense root mat, not observed above this depth. Since, mangrove rhizospheres are widely recognised as trace elements' sinks (e.g. Machado et al. 2002; Zhou et al. 2011), it appears that sediment layers containing mangrove root mats can form a barrier against diffusion into deeper layers, explaining the position of the subsurface activity peaks. The results indicate that bioturbation can promote the diffusional transport of trace elements into depths in which mangrove rhizosphere can retain these elements, enhancing the sink effect. This retention occurs below the less stable upper sediment layers, which are more exposed to physical and biological disturbances.

Conceptual models on trace element behaviour have considered a coupling between mangrove rhizosphere processes and bioturbation, being the transfers across the sediment–water interface favoured by burrow surfaces (Clark et al. 1998). The geochemical fraction that diffuses from tidal water into the sediments deserves additional consideration, since elements recently diffused from overlaying water can be particularly important because they could occur in forms weakly bound to sediment particles, which are more readily susceptible to remobilization, as it was observed for ^{65}Zn in an experiment with tidal creek sediments from Itacuruçá (Machado et al. 2008a). *R. mangle* roots can transport atmospheric O_2 and release it into the sediments (generating metal oxides in the sediments), as indicated by redox potential measures (Otero et al. 2006) and iron plaque deposits (mainly composed of iron oxides) on root surfaces (Silva et al. 1990). Root mats also release organic carbon (that can stimulate sulphate reduction and metal sulphide formation) by root tissue decay which can affect the trace element trapping (Alongi et al. 2004; Marchand et al. 2006). A schematic diagram on the association of these processes with the distribution of trace elements recently diffused into the sediments is presented in Fig. 5. Since mangrove fauna bioturbation frequently occurs in upper layers (Ferreira et al. 2007; Machado et al. 2002), bioturbation-driven diffusion into subsurface rhizospheres may be a frequent phenomenon.

4 Conclusions

The use of radiotracer experiments allowed the identification of the bioturbation effect on trace element downward diffusion within a mangrove sediment profile. Bioturbation can extend the diffusional transport of trace elements of environmental interest into depths in which the mangrove rhizosphere can retain it more efficiently than in upper layers. Therefore, it is expected that the accumulation of elements recently diffused from overlaying water into subsurface rhizosphere layers increases the whole-sediment retention efficiency. Complementary effects of bioturbated and rhizosphere sediment layers on this diffusional behaviour are proposed as a retention mechanism in addition to previous conceptual models describing trace element behaviour in mangrove sediments, even for environments without visible burrows. Enhanced bioturbation and rhizosphere development will probably enhance the importance of this mechanism, while losses of mangrove plant cover (e.g. due to deforestation) may result in a less efficient retention of trace elements recently diffused from overlaying water.

Acknowledgments K.N. Suzuki thanks the Brazilian Ministry of Education (CAPES) for her post-doctoral grant.

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