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A critical examination of the possible application of zinc stable isotope ratios in bivalve mollusks and suspended particulate matter to trace zinc pollution in a tropical estuary☆

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A B S T R A C T

The application of zinc (Zn) isotopes in bivalve tissues to identify zinc sources in estuaries was critically assessed. We determined the zinc isotope composition of mollusks (*Crassostrea brasiliana* and *Perna perna*) and suspended particulate matter (SPM) in a tropical estuary (Sepetiba Bay, Brazil) historically impacted by metallurgical activities. The zinc isotope systematics of the SPM was in line with mixing of zinc derived from fluvial material and from metallurgical activities. In contrast, source mixing alone cannot account for the isotope ratios observed in the bivalves, which are significantly lighter in the contaminated metallurgical zone ($\delta^{66}Zn_{JMC} = +0.49 \pm 0.06‰$, 2σ, $n = 3$) compared to sampling locations outside ($\delta^{66}Zn_{JMC} = +0.83 \pm 0.10‰$, 2σ, $n = 22$). This observation suggests that additional factors such as speciation, bioavailability and bioaccumulation pathways (via solution or particulate matter) influence the zinc isotope composition of bivalves.

1. Introduction

Zinc isotopes are established as versatile tracers of sources in various environmental reservoirs and of different biogeochemical processes (Wiederhold, 2015). They undergo significant isotopic fractionations during industrial processes such as ore refining and coal combustion, resulting in byproducts and man-made materials that are isotopically distinct from those found naturally, and this has the promise to discriminate zinc from natural or anthropogenic origin (Ochoa and Weiss, 2015; Thapalia et al., 2015; Yin et al., 2016). Furthermore, stable metal isotopes are fractionated during low temperature processes, and hence can be used to determine reactions pathways in the environment such as adsorption on organic and inorganic solid surfaces, biological uptake, redox reactions, complexation and more (Cloquet et al., 2008 and references therein; Veeramani et al., 2015; Yin et al., 2016; Szynkiewicz and Borrok, 2016; Markovic et al., 2017).

The possible application of zinc isotope ratios as a biomonitoring tool for tracing metal bioavailability and sources in estuaries using tissues of bivalve mollusks has been recently assessed (Shiel et al., 2012, 2013; Petit et al., 2015). The findings, however, did not confirmed the applicability of Zn isotopes for source tracing using biomonitor organisms. One possible explanation for this is that these investigations were carried out in large estuaries, representing open systems mixing multiple point and diffuse anthropogenic sources and natural sources. This is making source identification challenging given the typically small isotope

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variability between zinc sources.

To get a better appreciation of the potential of zinc isotopes as biomonitoring tool in aquatic systems, we conducted a study in a small tropical estuary system, Sepetiba Bay, in southeastern Brazil. This bay is a good estuarine model system as it presents one single dominant anthropogenic zinc source (i.e., associated with old electroplating wastes) and the possible metal contaminants pathways are well-established by previous geochemical and biomonitoring studies (Molisani et al., 2004; Lacerda and Molisani, 2006). A first assessment zinc isotope compositions of sediment cores and suspended particulate matter (SPM) was performed recently in Sepetiba Bay, demonstrating that the stable isotopes signatures of sediments are reliable tracers of anthropogenic sources in the inner bay regions and, therefore, can be useful to reconstruct the temporal and spatial evolution of zinc contamination (Araújo et al., 2017a). In this companion work, we examine the applicability of zinc isotopes to trace anthropogenic sources signatures in oysters (*Crassostrea brasiliana*) and mussels (*Perna perna*) from Sepetiba Bay, using new data on SPM to extend our understanding on zinc source mixing along the fluvial-estuarine continuum.

2. Materials and methods

2.1. Study area

Sepetiba bay is a small semi-enclosed estuary about 519 km^2 located 60 km south of Rio de Janeiro city. It plays an important role as geo-economic center of Brazil, hosting an extensive industrial park with significant harbor activity, besides an increasing human occupation in its drainage basin (Fig. 1). Rivers, estuaries and extensive mangrove ecosystems occur in the northern and eastern portions of the bay. The watershed of approximately 2654 km^2 is drained by rivers crossing agricultural, industrial and urban areas. The São Francisco channel represent the main fluvial system, receiving transposed waters of a neighbor watershed located upstream and attending for over 86% of the total freshwater and most part of fluvial sediment load (Molisani et al., 2004).

The study area has been impacted for almost five decades by a stack of wastes (estimated at 600,000 tons) from a zinc electroplating plant. These wastes exposed to the open air and lixiviated during rainfalls reached surrounding mangroves and the bay through a small tidal creek located in the Saco do Engenho mangrove, considered as the *hot spot* area (Fig. 1) (Molisani et al., 2004). Large loads of zinc and cadmium remobilized from the wastes were estimated about 24 t y^{-1} of Cd and 3660 t y^{-1} for Zn (Molisani et al., 2004). High zinc content in oysters have been reported along the last four decades, often exceeding 80,000 μg g^{-1} (Lacerda and Molisani, 2006). Despite the end of zinc refining activities in 1997, the continuous wastes lixiviation by pluvial waters kept the high inputs of metal loads for more than a decade later as confirmed in other studies (Marques et al., 2006; Gomes et al., 2009). The stack of wastes was definitively removed in 2012. However, Zn-enriched sediment particles from the *hot spot* continue to be remobilized throughout the bay during tidal cycles.

2.2. Sampling and sample preparation

In 2014, oysters samples (*Crassostrea brasiliana*) were collected at five different locations within the Sepetiba Bay to obtain a transect between the channel located in the Saco do Engenho mangrove (the *hot spot* area of electroplating impacts, P1; Fig. 1) and the open sea at the southwestern area of the bay (P5; Fig. 1). About 17 to 21 individual oyster samples were collected in each one of the location P1 to P5, accounting to a total of 91 oysters sampled in the bay. Mussels (*Perna perna*) were found only at P5, where 10 individuals were collected to evaluate possible inter-specific differences on Zn isotope compositions, as well as possible differences of gender. For mussels, male and female individuals were identified according to the tissue color, i.e. white for male and orange for female.

Oysters and mussels were depurated under 48 h in local water, and their tissues were extracted with plastic spatula, rinsed and stored frozen individually in polyethylene little flasks for 48 h, prior

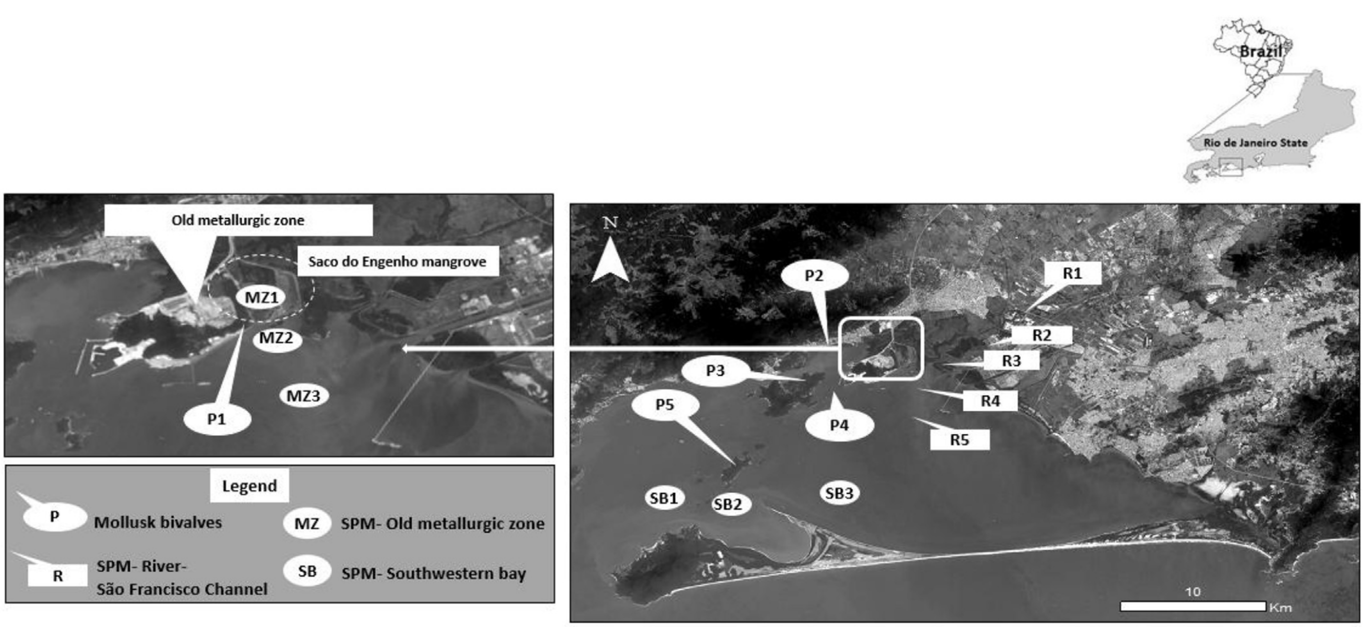

Fig. 1. Map showing the sampling locations at the Sepetiba bay. At left, it is shown a zoom in the old metallurgic zone, where the electroplating activity operated from 1960's to end of 1990's. The dashed circle line highlight the Saco do Engenho mangrove, one site heavily impacted by the wastes lixiviated from the old wastes produced by the electroplating processes. Bivalve sampling stations: P1-Saco do Engenho; P2- Gato; P3-Martins; P4-Itacurussá; P5- Jaguanum. The SPM samples were collected at diferente zones: R (rivers); MZ (old metallurgic zone); and SB (southwest of the bay).