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Zinc stable isotopes in mangrove crabs as tracers of anthropogenic contamination in a tropical estuary

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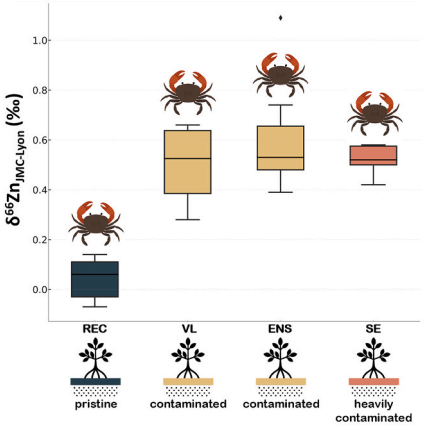
HIGHLIGHTS

- Zn isotopes trace electroplating-derived contamination in mangrove crabs.
- Bioaccumulation from diet and water drives isotopic shifts in crab tissues.
- Internal regulation causes Zn isotope differences among crab organs.
- Zn isotopes differentiate clean from polluted sites, but not contamination intensity.
- Study conducted in Sepetiba Bay, Brazil, impacted by electroplating waste.

GRAPHICAL ABSTRACT



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ABSTRACT

Our study presents a novel approach for tracing anthropogenic zinc (Zn) bioaccumulation in mangrove crabs using Zn stable isotope compositions (δ^{66}Zn). We analyzed δ^{66}Zn and elemental composition in crab tissues from Brazilian mangroves within a coastal lagoon historically impacted by electroplating waste. Crabs from the mangrove area near the old electroplating plant exhibited the highest Zn concentrations in both muscle and hepatopancreas, likely reflecting the high Zn bioavailability in these sediments. In contrast, crabs from other mangrove sites showed minimal variations in Zn concentrations, despite prominent differences in sediment Zn

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levels. This suggests that crabs regulate their internal Zn concentrations within a specific range, not correlating with external Zn bioavailability. The tissues of crabs from contaminated sites bore heavier δ^{66}Zn, consistent with the δ^{66}Zn left by industrial Zn pollution in sediments. However, δ^{66}Zn did not correlate directly with either bioaccumulated Zn or sediment Zn levels, making it challenging to distinguish between stations with varying contamination degrees. Shifting δ^{66}Zn in crab tissues toward lighter isotopes compared to sedimentary Zn indicates the influence of diet, internal biological fractionation, specific bioaccumulation pathways, or additional Zn sources. Biological fractionation within crabs likely caused muscle tissues to be isotopically lighter than the hepatopancreas, especially in moderately contaminated areas. This first systematic study of δ^{66}Zn within mangrove crabs highlights the need for further research to fully understand isotopic variations in crab tissues and their relationship with environmental, ecological, and physiological factors. Initial findings suggest that sources, bioaccumulation routes, and regulatory mechanisms shape δ^{66}Zn within crab tissues.

1. Introduction

Mangrove crabs are significant contributors to recycling sedimentary nutrients and organic matter (Méziane et al., 2006; Kristensen et al., 2008; Yong et al., 2011) and are important seafood resources for coastal populations. Most mangrove crabs are collector-gatherers and detritivores, feeding on sediment organic matter, microalgae, and decomposing plant litter, often by scraping or ingesting material from sediment surfaces and mangrove detritus (Lee, 1998; Kristensen et al., 2008; Méziane et al., 2006; Cannicci et al., 2008). However, they are frequently exposed to trace metals from anthropogenic emissions that accumulate in sediments (Pinheiro et al., 2012; Zhang et al., 2019). Among these metals, Zn is essential for biochemical processes but becomes toxic at elevated concentrations (Fosmire, 1990; Beltrame et al., 2010; Schoofs et al., 2024). Crabs bioaccumulate trace metals by ingesting sediment particles or absorbing dissolved metals, depending on metal speciation and bioavailability (Rainbow, 2002). Bioaccumulated metals may be transferred to higher trophic levels, including humans, posing ecological and health risks (Silva et al., 2024). Thus, developing efficient tools to monitor trace metal dispersion and pathways within marine ecosystems is critical, especially those involving these animals.

Due to their capacity of bioaccumulating high concentrations of trace metals, crabs are effective indicators for monitoring contamination and assessing bio-ecological risks in mangrove ecosystems (Harris and Santos, 2000; Pinheiro et al., 2012; Baki et al., 2018; Zhang et al., 2019). However, their utility as bioindicators faces challenges. Metal incorporation can vary significantly between crab species, driven by differences in diet preferences and metabolic processes (Amiard-Triquet et al., 1993). Local environmental conditions also influence the speciation of trace metals in sediments (Bianchi, 2007), affecting bioavailability and the extent of bioaccumulation. Additionally, species-specific depuration mechanisms—the ability to detoxify and eliminate accumulated metals—also impact the metal concentrations in crab tissues (Ettajani and Pirastru, 1992).

The mobility and bioavailability of Zn in sediments are determined more by its speciation than its total concentration. Variations in Zn speciation often led to changes in Zn stable isotope compositions, which make them valuable tools for tracing Zn sources, its behavior across geochemical compartments, and mechanisms of bioaccumulation (Sivry et al., 2008; Shiel et al., 2010; Ochoa Gonzalez and Weiss, 2015; Araújo et al., 2017a; Tonhá et al., 2020). Since the work of Maréchal et al. (1999), Zn isotope biogeochemistry has emerged as a powerful tool for tracing Zn within the critical zone and has been applied to various domains, including aquatic invertebrates such as bivalves (Shiel et al., 2012, 2013; Jeong et al., 2021) and corals (Little et al., 2021). A recent study successfully used Zn isotopes in brown crabs from fjord ecosystems impacted by mine tailings to apportion contamination sources (Bank et al., 2024). However, challenges remain in using metal isotopes to trace bioavailability, as factors such as geochemical reactivity, biological uptake mechanisms, and internal transport processes may influence Zn stable isotope compositions within organisms to a greater extent than the δ^{66}Zn of the original contamination source (Petit et al., 2015; Araújo et al., 2017a).

This study investigates Zn stable isotope ratios in mangrove crab tissues to explore their potential as tracers of Zn bioaccumulation in a tropical estuary affected by anthropogenic contamination. Sepetiba Bay (southwest Brazil), a coastal lagoon that has historically experienced severe pollution due to the release of electroplating wastes near local mangroves, provides an excellent scenario for addressing this gap. Spatial Zn concentrations in sediments along the bay were extensively studied (e.g., Lacerda et al., 1987; de Carvalho Gomes et al., 2009; de Souza et al., 2012; Ribeiro et al., 2013), revealing extremely high contents of bioavailable Zn (defined here as acid-acetic extractable Zn, following the BCR method; Tonhá et al., 2020). The electroplating source imparts a dominant influence over the Zn isotope distribution, yielding distinguishable Zn stable isotope compositions in sediment and suspended particulate matter (SPM) samples in different ecosystems of the bay (Araújo et al., 2017a, 2017b, 2018; Tonhá et al., 2020, 2021; Cunha et al., 2022; Garnier et al., 2024).

Here, we analyzed Zn stable isotope compositions and elemental concentrations in tissues from burrowing crabs and surrounding sediments in Sepetiba Bay's mangroves. Our objectives were: (1) to evaluate the potential of Zn stable isotope compositions as a tracer for anthropogenic Zn bioaccumulation, and (2) to discuss the influence of diet, bioaccumulation pathways, and internal regulation on the Zn stable isotope compositions in these benthic organisms.

2. Material and methods

2.1. Study area

Sepetiba Bay is a partially enclosed estuarine lagoon in southeastern Brazil, covering an area of approximately 519 km^2, with a mean surface area of 427 km^2, a volume of 2.56×10^9 m^3, and an average depth of 6 m (Molisani et al., 2004). The bay's watershed supports a population of around 1.4 million people, primarily from the metropolitan Rio de Janeiro area, and hosts Brazil's largest steel industry complex.

In the early 1960s, a Zn silicate ore electroplating plant was established on the northeastern shoreline. The facility produced and disposed large quantities of waste enriched with toxic metals, including Zn, Cd, and Pb, in open-air sites (Lacerda et al., 1987). Surface runoff transported these materials into nearby mangrove ecosystems, creating a contamination hotspot known as "Saco de Engenho" (SE). From SE, the contamination dispersed across the bay, facilitated by the high mobility of anthropogenic Zn (e.g., Lacerda et al., 1987; Ribeiro et al., 2013; Rodrigues et al., 2020). Studies on local biota, such as oysters, demonstrated significant Zn bioaccumulation (Lacerda and Molisani, 2006; Araújo et al., 2017b).

Despite the shutdown of the electroplating plant in 1997 and the encapsulation of its waste, sediments in SE continue to release Zn during tidal cycles. These remobilized Zn compounds - whether dissolved, bound to geogenic particles, or associated with organic matter - are transported from SE into the bay (Rodrigues et al., 2020). Sepetiba Bay also receives secondary Zn inputs from anthropogenic sources, predominantly urban untreated sewage (Molisani et al., 2004). The Valão

River (VL) is the main conduit for sewage-derived Zn, with its outlet located near the mangrove station "Enseada das Garças" (ENS; Garnier et al., 2024). For further details on the physical and environmental characteristics of the region, refer to Barcellos (1995), Araújo et al. (2017a, b), and Tonhá et al. (2020).

2.2. Crabs and sediment sampling

We collected paired crab and sediment samples from four mangrove sampling stations representing varying contamination levels (Fig. 1). These areas included Saco de Engenho (SE): A contamination hotspot in Sepetiba Bay; Enseada das Garças (ENS): A nearby mangrove adjacent to SE; Valão River (VL): A mangrove influenced by urban sewage inputs; Praia do Recife (REC): A nearby pristine mangrove chosen as a reference site, given the widespread contamination in Sepetiba Bay.

A total of 92 burrowing crabs from four species (*Uca rapax*, *Neohelice granulata*, *Aratus pisonii*, and *Panopeus lacustris*) were collected during low tide in June 2017, coinciding with the rainy season. Crabs were sampled from all four stations: REC (20), SE (28), VL (16), and ENS (28) (Fig. 1). These species are omnivorous, with *Uca rapax*, *Neohelice granulata*, and *Panopeus lacustris* primarily detritivorous, while *Aratus pisonii* is predominantly herbivorous. *Uca rapax* was the only species collected across all stations. Sampling aimed at crabs with similar sizes, from ~3.5 to ~4.5 cm width for all species.

Crabs were frozen immediately after collection and transported to the laboratory for analysis. There, muscles and hepatopancreas tissues were dissected and pooled to create 23 composite samples, each consisting of tissues from four individuals (Table 1).

Surface sediments (0–2 cm) were collected using metal-free plastic containers, freeze-dried, crushed, and sieved to <63 μm in the laboratory. These sediment samples, representing the crabs' habitats, were analyzed for total Zn and the labile Zn fraction (Zn F1), extracted using 0.11 M acetic acid (Table 1). At each location, a single sediment sample was collected in order to coincide precisely with the timing and locality of crab sampling. While we acknowledge that this limits the assessment of spatial variability in Zn concentrations, it is important to note that these sites have been thoroughly investigated in previous studies (Fig. 2).

2.3. Sample treatment and chemical analysis

Total digestion of sediment and crab samples was performed using Savillex® Teflon beakers on a hot plate using a multiple-step acid procedure with HNO_3, HCl, H_2O_2, and HF for sediment samples.

The labile fraction is defined here as the sediment fraction extracted using 0.11 M acetic acid. It is commonly attributed to represent the exchangeable/carbonate fraction according to the BCR (*Bureau Communautaire de Référence*) sequential extraction procedure. Here, we used the adapted protocol of Tonhá et al. (2020). Briefly, it evolves the addition of 0.11 M acetic acid (HAc) to 1g of dry sediment for 16 h

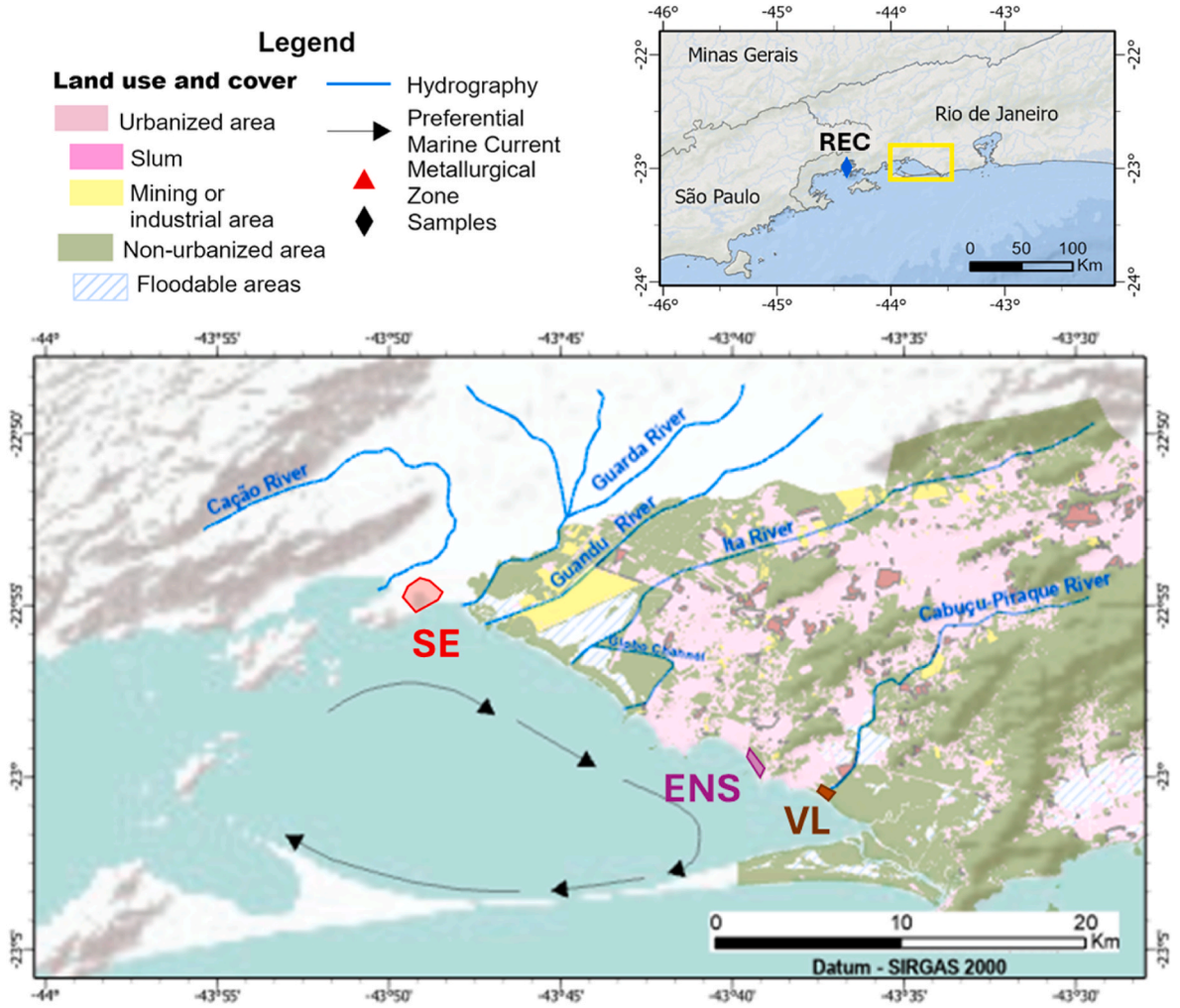

Fig. 1. – Location of the sampling sites. SE: Saco do Engenho (heavily contaminated by Zn); ENS: Enseada das Garças (contaminated by Zn); VL: Valão (contaminated by Zn); REC: Praia do Recife (pristine).

Table 1
– Burrowing crabs, sediments list and Zn elemental and isotope analytical results.

Site	Type	Specie	Tissue	Sex	Number of animals in the composite	δ^{66}Zn JMC (‰)	2sd	n	Zn (mg/kg)	2sd	n
Praia do Recife (REC)	Crab	*Uca Rapax*	Muscle	Male	4	0.06	0.02	2	162	–	–
	Crab	*Uca Rapax*	Muscle	Male	4	−0.03	0.02	2	234	–	–
	Crab	*Panopeus lacustris*	Muscle	Female	4	−0.07	0.02	2	104	–	–
	Crab	*Aratus pisonii*	Muscle	Male	4	0.14	0.02	2	111	–	–
	Crab	*Aratus pisonii*	Muscle	Female	4	0.11	0.02	2	139	–	–
	Crab	*Aratus pisonii*	Hepatopancreas	Female	4	NA	NA	2	99	–	–
	Average hepatopancreas	–	–	–	–	–	–	–	99	–	1
	Average muscles	–	–	–	–	0.04	0.09	–	152	52	5
	Average considering both tissues	–	–	–	–	0.04	0.09	–	142	51	6
	Bulk sediment	–	–	–	–	0.20	0.02	–	68	–	–
	Sediment ZnF1	–	–	–	–	NA	–	–	9	–	–
Valão River (VL)	Crab	*Uca Rapax*	Muscle	Male	4	0.66	0.01	2	143	–	–
	Crab	*Aratus pisonii*	Muscle	Male	4	0.42	0.02	2	127	–	–
	Crab	*Aratus pisonii*	Hepatopancreas	Male	4	0.63	0.02	2	125	–	–
	Crab	*Panopeus lacustris*	Muscle	Male	4	0.28	0.02	2	309	–	–
	Average hepatopancreas	–	–	–	–	0.63	–	–	125	–	1
	Average muscles	–	–	–	–	0.45	0.19	–	193	101	3
	Average considering both tissues	–	–	–	–	0.50	0.18	–	176	89	4
	Bulk sediment	–	–	–	–	0.58	0.01	–	538	–	–
	Sediment ZnF1	–	–	–	–	0.87	0.02	–	260	–	–
Enseada das Garcas (ENS)	Crab	*Uca Rapax*	Muscle	Male	4	0.53	0.02	2	201	–	–
	Crab	*Uca Rapax*	Muscle	Female	4	0.53	0.01	2	107	–	–
	Crab	*Uca Rapax*	Hepatopancreas	Male	4	1.09	0.02	2	110	–	–
	Crab	*Panopeus lacustris*	Muscle	Male	4	0.39	0.01	2	198	–	–
	Crab	*Neohelice granulata*	Muscle	Male	4	0.57	0.04	2	222	–	–
	Crab	*Neohelice granulata*	Muscle	Female	4	0.43	0.02	2	261	–	–
	Crab	*Neohelice granulata*	Hepatopancreas	Male	4	0.74	0.02	2	103	–	–
	Average hepatopancreas	–	–	–	–	0.92	0.25	–	106	5	2
	Average muscles	–	–	–	–	0.49	0.08	–	198	57	5
	Average of both tissues	–	–	–	–	0.61	0.24	–	172	64	7
	Bulk sediment	–	–	–	–	0.60	0.03	–	504	–	–
	Sediment ZnF1	–	–	–	–	1.09	0.01	–	198	–	–
Saco do Engenho (SE)	Crab	*Uca Rapax*	Muscle	Male	4	0.58	0.02	2	308	–	–
	Crab	*Panopeus lacustris*	Muscle	Male	4	0.51	0.02	2	254	–	–
	Crab	*Panopeus lacustris*	Muscle	Female	4	0.42	0.01	2	266	–	–
	Crab	*Neohelice granulata*	Muscle	Female	4	0.57	0.01	2	143	–	–
	Crab	*Aratus pisonii*	Muscle	Male	4	0.58	0.02	2	274	–	–
	Crab	*Aratus pisonii*	Muscle	Female	4	0.49	0.02	2	138	–	–
	Crab	*Aratus pisonii*	Hepatopancreas	Male	4	0.52	0.02	2	480	–	–
	Crab	*Panopeus lacustris*	Hepatopancreas	Male	4	NA	NA	2	232	–	–
	Average hepatopancreas	–	–	–	–	0.52	–	–	356	176	2
	Average muscles	–	–	–	–	0.53	0.06	–	230	72	6
	Average considering both tissues	–	–	–	–	0.52	0.06	–	262	107	8
	Bulk sediment	–	–	–	–	0.82	0.02	–	4945.00	–	–
	Sediment ZnF1	–	–	–	–	1.08	0.03	–	1600.00	–	–

For each individual composite sample (n = 4 animals), the δ^{66}Zn values (‰, relative to JMC Lyon standard), zinc concentrations (mg/kg), and number of replicate analyses (n) are provided. "2sd" denotes the analytical uncertainty of Zn isotope measurements and twice the standard deviation of replicate measurements for Zn concentrations. Averages are presented separately for muscle and hepatopancreas tissues, as well as combined. Bulk sediment and ZnF1 fractions (acid labile Zn) are also reported for comparison. "NA" indicates data not available.

(Rauret et al., 1999).

Elemental concentrations were determined in the final extract solutions by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, iCAP Qc, Thermo Fisher Scientific) at the OSU OREME, University of Montpellier. Reference materials (RMs) of estuarine sediments (NIST-1646a) and animal tissues (oyster SRM 1566b-NIST®, dogfish liver DOLT 5) and procedural blanks were included in each sample batch for analytical control. The extraction yields for RMs were always within ±10 % of certified values.

The isotope ratios of Zn were measured using MC-ICP-MS (Neptune, Thermo Scientific, Germany) at OSU OREME, University of Montpellier. Before the isotope analysis, samples consisting of 2–4 μg of Zn were purified by anion exchange chromatography using a Bio-Rad PolyPrep column filled with the anion exchange resin AG-MP1, 100–200 mesh (Araújo et al., 2017b). The chromatography yields and interferent removals were close to 100 %, and the procedure blanks were below 1 % of

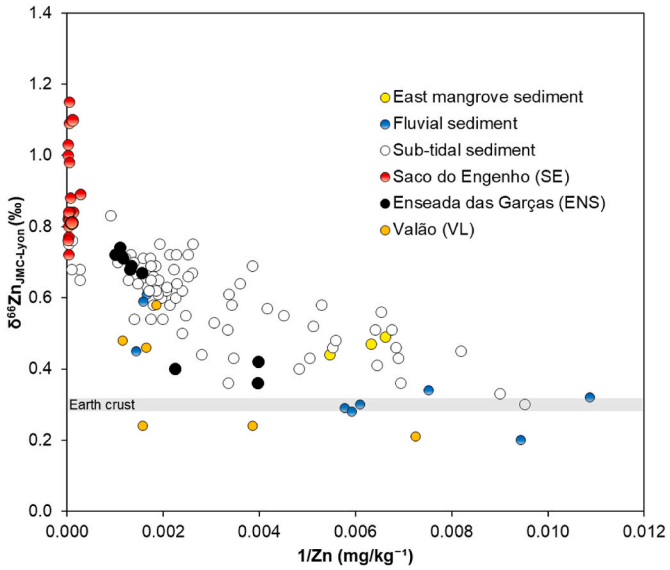

Fig. 2. Scatterplot of $\delta^{66}Zn_{\text{JMC-Lyon}}$ x 1/Zn (kg/mg) in sediments (surface and cores up to 85 cm; Araújo et al., 2017a) from the Sepetiba Bay. East mangrove sediment: Araújo et al. (2018); Fluvial sediment: Tonhá et al. (2020; 2021); Sub-tidal sediment: Araújo et al. (2017a), Tonhá et al. (2020), Cunha et al. (2022); Saco do Engenho (SE) sediment: Araújo et al. (2017b; 2018), Tonhá et al. (2020); Enseada das Garças (ENS): Araújo et al. (2017a); Valão River (VL): Tonhá et al. (2020), Garnier et al. (2024); Earth crust: Zhang et al. (2020).

the analyte mass. The samples were introduced into MC-ICP-MS in a diluted nitric medium using a Stable Introduction System (SIS: cyclonic spray chamber) coupled with a low-flow PFA nebulizer (50 μL min-1). The purified Zn samples were doped with Cu NIST-SRM 976 (Zn:Cu 1:1, m/m), and the standard bracketing method, combined with exponential law, was used to correct the instrumental fractionation. The final isotope composition is expressed as a $\delta^{66}Zn$ value in reference to the "JMC-Lyon" (Johnson Matthey Company 3-0749-L):

$$\delta^{66}Zn_{\text{JMC-Lyon}}\ (‰) = \left(\frac{R\left(\frac{^{66}Zn}{^{64}Zn}\right)_{\text{sample}}}{R\left(\frac{^{66}Zn}{^{64}Zn}\right)_{\text{Zn-UnB}}} - 1 \right) \text{x } 1000$$

To assess the method accuracy, reference material JMC IRMM 3702 (0.32 ± 0.02, 2s, n = 6) was measured for $\delta^{66}Zn$ along the session analysis. Our results aligned with the reported data from several laboratories compiled by Moynier et al. (2017). MESS-4.

Long-term monitoring of $\delta^{66}Zn$ values using identical methods confirmed the accuracy of measurements based on certified biotic reference materials (SRM 1566b Oyster Tissue and ERM-CE278k Mussel Tissue) and abiotic reference material (MESS-3 marine sediment), showing agreement with literature values (e.g., Jeong et al., 2021).

The long-term average $\delta^{66}Zn$ values obtained for SRM 1566b and ERM-CE278k were 0.70 ± 0.05 ‰ and 0.41 ± 0.05 ‰ (2s), respectively. The average external reproducibility across all unknown samples and reference materials was 0.06 ‰ (2s). For each sample, the uncertainty reported in Table 1 corresponds to the standard deviation of replicate measurements.

3. Results and discussion

3.1. Trace metal (Cu, Zn, Pb and Cd) concentrations within burrowing crabs

Fig. 2 illustrates a scatterplot of $\delta^{66}Zn$ versus reciprocal Zn concentrations in SE, ENS, and VL sediments. The SE hotspot consistently exhibits elevated Zn concentrations, high $\delta^{66}Zn$ (up to 0.98 ‰ compared to 0.32 ‰ in natural local soil), and a significant proportion of labile Zn (up to 45 %) (Araújo et al., 2017b; Tonhá et al., 2020). ENS and VL display moderate to high Zn contamination, with $\delta^{66}Zn$ spanning the range between natural sources and anthropogenic inputs (Araújo et al., 2017b; Tonhá et al., 2020).

The sediment samples from this study show a gradient of Zn contamination across the sampling stations: SE (4945 mg/kg) > VL (538 mg/kg) > ENS (508 mg/kg) > REC (68 mg/kg) (Table 1). Crabs from the SE station exhibited the highest Zn levels among the studied sites, with 356 ± 176 mg/kg in the hepatopancreas and 230 ± 72 mg/kg in muscle tissues. These concentrations exceeded those observed in crabs from the pristine REC mangrove (99 mg/kg in the hepatopancreas and 152 ± 52 mg/kg in muscles). The VL and ENS areas show Zn concentrations (average of 113 ± 11 mg/kg in the hepatopancreas, 193 ± 61 mg/kg in the muscles; Table 1 and Fig. 3) slightly higher than the crabs from the pristine mangrove REC.

The critical concentration of metabolically available Zn in crustaceans is estimated as 150 μg/g (Rainbow et a., 2011), and studies on other crab species, such as *Carcinus maenas*, have reported a lower body concentration threshold of 83 ± 19 mg/kg (Rainbow, 1985), below values found in the present study. This suggests that trace metal uptake is occurring beyond the metabolic needs of these animals in the contaminated areas of Sepetiba Bay, especially in the SE region. This interpretation warrants further investigation.

The SE station is the only one where the average Zn concentration in the hepatopancreas is higher than in the muscles. Moreover, its maximum Zn concentration in the hepatopancreas is 480 mg/kg, around five times higher than those from moderately contaminated areas, ENS and VL (average 112 ± 11 mg/kg), and the background area, REC (99 mg/kg) (Fig. 3). Despite pronounced differences in both total and labile Zn concentrations in sediments across the studied areas (e.g., labile Zn ranging from 8.9 mg/kg at REC to 1600 mg/kg at SE), Zn concentrations in crab muscles showed no significant variation among sites (ANOVA, p = 0.06).

When a metal enters the body of a crustacean, whether via dissolved or particulate phase, it is initially metabolically available, such as for the muscles (Rainbow, 2002). However, any accumulation beyond metabolic needs necessitates subsequent excretion or detoxification processes, primarily involving the hepatopancreas, the major organ responsible for this function in aquatic invertebrates (Ahearn et al., 2004). The varying concentrations in the hepatopancreas of crabs, alongside the uniformity of concentrations in the muscles from different areas, underscore the role of the former in regulating trace metal levels. The consistent muscle concentrations across sites suggest that the hepatopancreas may serve as a more sensitive indicator of environmental metal exposure in crabs. It also indicates a strong regulation capacity of trace metals by burrowing crabs, as observed in *Palaemon elegans* and other decapod crustaceans (Bryan, 1968; Rainbow, 1998).

Although Zn concentrations in the hepatopancreas appeared to follow the general trend *Aratus pisonii* (235 ± 213 mg/kg) > *Panopeus lacustris* (232 mg/kg) > *Uca rapax* (109 mg/kg) > *Neohelice granulata* (103 mg/kg), and in muscle tissues *Panopeus lacustris* (226 ± 78 mg/kg; n = 5) > *Neohelice granulata* (224 ± 59 mg/kg; n = 3) > *Uca rapax* (189 ± 62 mg/kg; n = 8) > *Aratus pisonii* (123 ± 16 mg/kg; n = 6), these interspecific comparisons should be interpreted with caution. Species were not uniformly distributed across the sampling sites, which limits the validity of direct ranking. However, the comparison between *Uca rapax* and *Panopeus lacustris* is more robust, as they were the only species consistently collected at all sites.

Interestingly, *Aratus pisonii* exhibited relatively low Zn concentrations in muscle despite elevated levels in the hepatopancreas, which may reflect species-specific differences in Zn allocation and regulation. Further investigation is needed to confirm this hypothesis (Table 1).

Sex-based comparisons of Zn concentrations in muscle tissue were limited by sample size. For species where both male and female

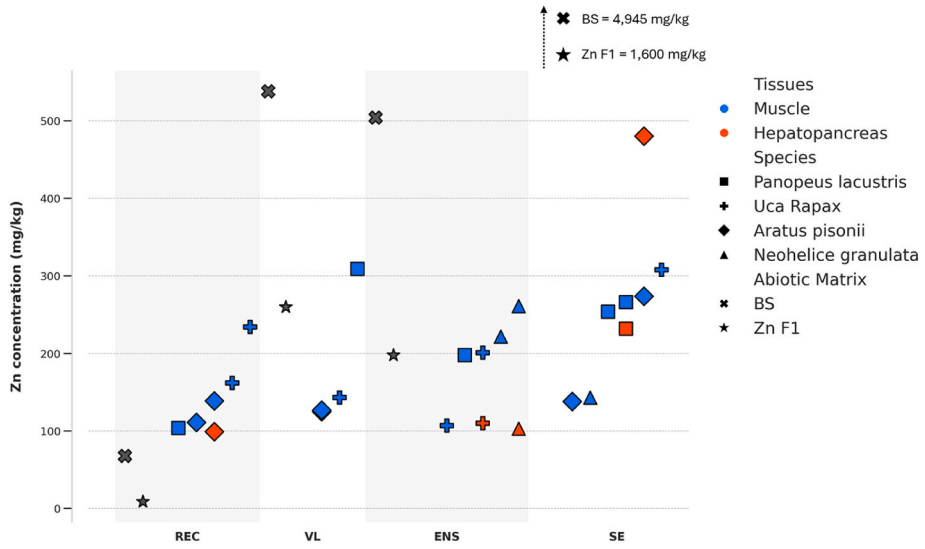

Fig. 3. – Zn concentration in different tissues from burrowing crab samples from the Sepetiba Bay and Praia do Recife. BS: bulk sediment; Zn F1: labile Zn fraction (ZnF1), extracted using 0.11 M acetic acid. REC (Praia do Recife) is the pristine reference area, while SE (Saco do Engenho) is the hotspot of Zn contamination in the Sepetiba Bay. VL and ENS are moderately contaminated areas from the Sepetiba Bay. Hepatopancreas and muscles from the same samples are vertically aligned. Zn concentrations are in ascending order for muscles from each sapling area. BS and Zn F1 from SE are outside the range of the y axis to highlight relevant distinctions from 0 to 600 mg/kg, which is the range encompassing all the remaining the data points.

individuals were available (e.g., *Panopeus lacustris* and *Aratus pisonii*), statistical tests cannot reliably detect statistical separation because a greater number of replicates is needed to compare adequately the distribution.

3.2. Zn isotope systematics in burrowing crabs: assessing controlling factors

3.2.1. Zn sources to crabs inferred from Zn stable isotope ratios

The δ^{66}Zn in crab tissues (including hepatopancreas and muscle) varies from 0.-0.07 ‰ to 0.1.09 ‰ (Table 1), displaying significant spatial variability (ANOVA, $p = 5.6 \times 10^{-5}$ considering both muscles and hepatopancreas between sampling sites). The δ^{66}Zn in crab tissues (including hepatopancreas and muscle) from the contaminated sites (VL: 0.40 ± 0.24 ‰, n = 5; ENS: 0.54 ± 0.28 ‰, n = 8; SE: 0.52 ± 0.06 ‰, n = 7) are significantly higher compared to those found in crab tissues from the background area (REC: 0.04 ± 0.08 ‰, n = 5) (Fig. 4). This trend aligns with the isotope signatures of sediments and suspended particulate matter (SPM) impacted by electroplating waste, indicating the incorporation of anthropogenic Zn into the biological systems of crabs (Fig. 2; Araújo et al., 2024; Tonhá et al., 2020). While sediment and SPM samples were collected at different periods - from 2017 to 2024 - and locations of the Sepetiba Bay, Fig. 2 demonstrates the persistence and widespread character of legacy contamination fingerprints that are

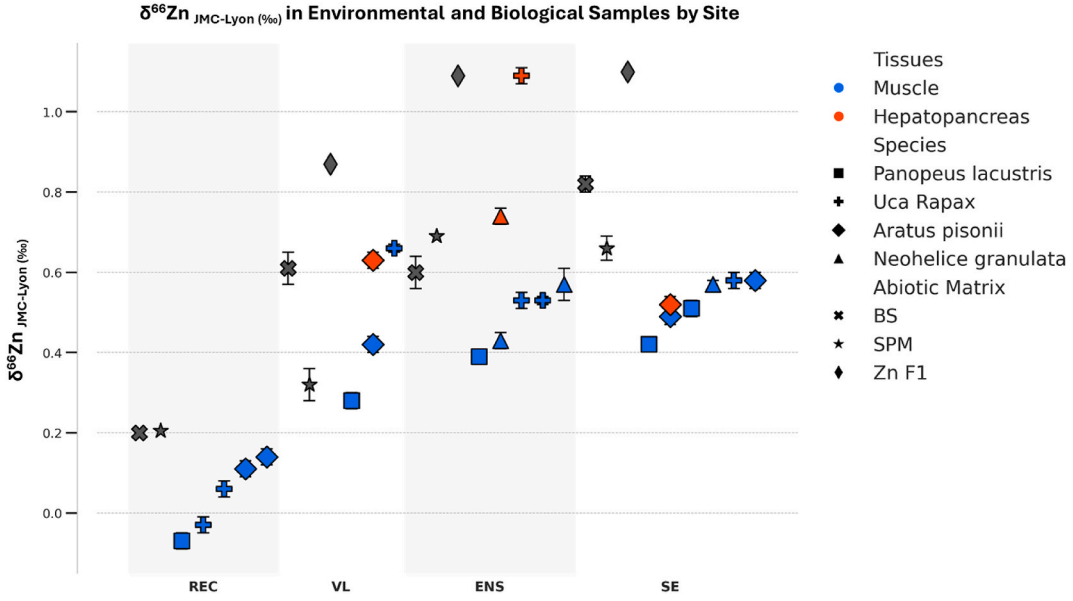

Fig. 4. – $\delta^{66}Zn_{JMC\text{-}Lyon}$ in different tissues from burrowing crab samples from the Sepetiba Bay and Praia do Recife. Error bars are not presented when the analytical uncertainty of the analysis is smaller than the size of the symbols. Error bars refer to the analytical uncertainty of the isotope measurements. BS: bulk sediment; SPM: suspended particulate matter; Zn F1: labile Zn fraction (ZnF1), extracted using 0.11 M acetic acid. REC (Praia do Recife) is the pristine reference area, while SE (Saco do Engenho) is the hotspot of Zn contamination in the Sepetiba Bay. VL and ENS are moderately contaminated areas from the Sepetiba Bay. Hepatopancreas and muscles from the same samples are vertically aligned. $\delta^{66}Zn_{JMC\text{-}Lyon}$ are in ascending order for muscles from each sapling area.

partially reflected in the biological tissues from this study.

These findings underscore the utility of Zn isotopes as tools to trace anthropogenic Zn bioaccumulation in mangrove burrowing crabs. This is in line with recent studies, such as those on brown crabs from fjord ecosystems affected by mine tailings, where Zn isotopes were used to identify contamination sources (Bank et al., 2024), and in crab muscles incorporating other element isotopic signatures, such as rare earth from sediments contaminated by fertilizers (Bosco-Santos et al., 2018). However, it is important to note that δ^{66}Zn in biological tissues are not solely a reflection of the source material. Isotope compositions may also vary due to fractionation processes occurring during uptake, transport, and tissue-specific assimilation.

For instance, the δ^{66}Zn of crab tissues were consistently lower than those of the labile sediment fraction (Zn F1 in Fig. 4) in contaminated areas and generally lower or equal to bulk sediment isotope signatures. This observation suggests that the anthropogenic Zn pool undergoes additional isotope fractionation as it is transferred from sediments to crabs.

While our observation supports the occurrence of trophic isotope fractionation, relying solely on the acid-soluble fraction (exchangeable + carbonate-bound) as a proxy for bioavailable Zn may oversimplify the complexity of Zn speciation in sediments. Recent studies (e.g., Nitzsche et al., 2024; Little et al., 2016) have demonstrated that Zn associated with organic matter—typically recovered in the oxidizable fraction—can also exhibit low δ^{66}Zn values, particularly in organic-rich sediments. Despite this, our focus on the acid-soluble fraction was motivated by its operational definition as a relatively labile and potentially bioavailable pool, as well as its strong correlation with total Zn in contaminated mangrove sediments ($r^2 = 0.97$), as previously reported for Sepetiba Bay (Tonhá et al., 2020). Nonetheless, a more detailed investigation of the oxidizable fraction would enhance our understanding of the Zn sources contributing to bioaccumulation in crab tissues from this region.

It is also important to consider that trace metals associated with operationally defined non-labile sediment fractions—such as the reducible and oxidizable phases—can become bioavailable under certain environmental or biological conditions. For example, metals bound to organic matter (oxidizable fraction), which are often depleted in heavy Zn isotopes (Nitzsche et al., 2024), may be released through microbial degradation or solubilized within the acidic environment of the crab digestive tract (Fig. 5). Additionally, bioturbation (Araújo Júnior et al., 2016) and resuspension-redeposition events (Monte et al., 2015) may enhance the remobilization of these metals. Given the organic-rich nature of sediments in the study area (up to 7 %; da Silva et al., 2022), the oxidizable fraction likely constitutes a relevant source of Zn to crabs.

These processes could partially account for the observed differences in δ^{66}Zn between leached sediments and crab tissues, but other factors—such as species-specific feeding behavior, uptake mechanisms, and physiological regulation—may also contribute to this observed isotopic fractionation.

Regarding species, δ^{66}Zn (including both hepatopancreas and muscle) follow this decreasing order: *Neohelice granulata* (0.57 ± 0.13 ‰; n = 4) > *Aratus pisonii* (0.41 ± 0.21 ‰; n = 7) > *Uca rapax* (0.39 ± 0.39 ‰; n = 9) > *Panopeus lacustris* (0.35 ± 0.22 ‰; n = 5). However, as with concentration data, these interspecific comparisons should be interpreted with caution due to the uneven distribution of species across sampling sites. For example, the elevated isotope values observed in *Neohelice granulata* likely reflect environmental contamination, as this species was just collected at contaminated sites, rather than only intrinsic species-specific traits. Further studies with balanced sampling designs are needed to statistically assess interspecific differences and evaluate the robustness of these preliminary observations.

In the context of dietary sources, mangrove green leaves in Sepetiba

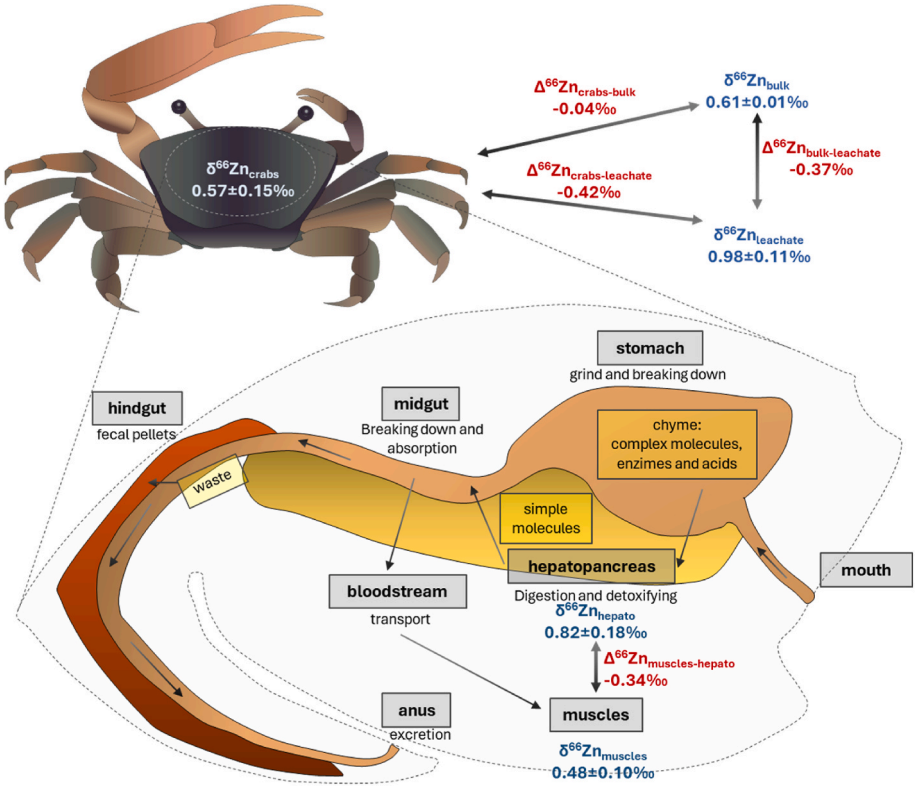

Fig. 5. Biologically driven zinc isotope fractionation within burrowing crabs from contaminated sites in Sepetiba Bay (ENS and VL). The schematic illustrates Zn isotope variations ($\delta^{66}Zn_{JMC\text{-}Lyon}$) across key digestive and transport compartments — from sediment sources (bulk and leachate) through the digestive system (stomach, midgut, hepatopancreas) and into the muscles. Isotopic offsets (Δ^{66}Zn) highlight fractionation between compartments. Morphological structure and digestive/transport processes are based on McGaw and Curtis (2013) and Vogt (2021).

Bay (*Laguncularia racemosa*) exhibit a notably low δ^{66}Zn average of 0.06 ± 0.04 ‰ compared to the higher δ^{66}Zn values found in contaminated sediments (~0.8 ‰; Araújo et al., 2018). Since crabs play a significant role in mangrove detritus cycling—removing approximately 28 % of annual litterfall in low to mid-intertidal zones and up to 70 % in high intertidal zones (Robertson, 1986; Robertson and Daniel, 1989)—their feeding on litter-fall-derived organic matter might influence their δ^{66}Zn values. This dietary input could theoretically lead to lower δ^{66}Zn values in crab tissues compared to the sediment, as observed in the present study, since crabs consume organic material with a lighter δ^{66}Zn. Additionally, plankton—also characterized by relatively light δ^{66}Zn values due to preferential uptake of lighter isotopes (Vance et al., 2006; John et al., 2007)—may contribute to the detrital pool or be consumed directly by some species, further influencing the isotopic composition of Zn in crab tissues.

No significant differences in δ^{66}Zn were observed between the predominantly herbivorous *Aratus pisonii* and the other detritivore species analyzed (Kruskal-Wallis Test, $p > 0.05$). This suggests that diet type may not exert a dominant influence on Zn isotope systematics in these crabs, or alternatively, that the detritus consumed is largely plant-derived, leading to homogenized δ^{66}Zn across species with differing feeding strategies. Nonetheless, these interspecific comparisons should be interpreted with caution due to the limited and uneven distribution of species across sampling sites, underscoring the need for further targeted studies.

3.2.2. Zn bioaccumulation routes

In sediments and water column, trace metals exist in both dissolved and particulate phases. These sedimentary and biological phases—including organic matter (Jouvin et al., 2009), sulfides (Fujii et al., 2011), aluminum silicates (Guinoiseau et al., 2016), carbonates (Mavromatis et al., 2019), and Fe/Mn oxides (Juillot et al., 2008; Veeramani et al., 2015)—often display distinct δ^{66}Zn. Crustaceans accumulate trace metals not only through diet, but also via their permeable ectodermal surfaces, allowing for uptake directly from the solution (Rainbow and Phillips, 1993; Rainbow, 2002). This dual pathway suggests that Zn speciation and associated isotope fractionation in the crabs' surrounding environment might influence the isotope offset observed between sediments and crab tissues.

In the SE mangrove of Sepetiba Bay, labile Zn concentrations (Zn F1 = 1600 mg/kg) and fractions (32 %) are high and exhibit heavier isotope signatures (Table 1; Fig. 4). Interestingly, the δ^{66}Zn in crab tissues from this region are not significantly heavier than those from other contaminated sampling points (VL and ENS; Fig. 4). Contrasting observations were reported for oysters in the SE mangrove, which showed lower δ^{66}Zn (0.49 ± 0.06 ‰, n = 3) compared to nearby stations (0.85 ± 0.06 ‰, n = 12) (Araújo et al., 2018). In SE, dissolved Zn concentrations exceed 3000 μg/L, a level at which adsorption sites on particles and ligands may begin to saturate, potentially reducing the extent of isotope fractionation. Nevertheless, previous studies have shown that even under relatively high Zn concentrations, lighter isotopes tend to be retained in the dissolved phase. This is due to the preferential adsorption of heavier isotopes onto suspended solids and mineral surfaces (Bryan et al., 2015; Szynkiewicz and Borrok, 2016), as well as onto chloride ligands in seawater (Fujii et al., 2011). Therefore, although the magnitude of isotope fractionation during sorption processes may be attenuated at elevated concentrations, it can still contribute to the isotopically lighter δ^{66}Zn values observed in crab tissues relative to heavier, adsorbed or particulate-bound Zn phases.

To confirm this hypothesis, further studies are needed to address the gap on the δ^{66}Zn of porewater and seawater from the Sepetiba Bay. Although dissolved Zn δ^{66}Zn values were not directly measured in this study, if we assume endmember values δ^{66}Zn ≈ 0.3 ‰ for dissolved Zn (as supported by Bermin et al., 2006) and δ^{66}Zn ≈ 0.9 ‰ for particulate Zn (Zn F1), then a 50:50 uptake from both reservoirs would result in an intermediate tissue δ^{66}Zn of ~0.6 ‰ — which aligns with the measured values in crab tissues from SE.

Selective uptake of lighter Zn isotopes has been documented in various biological systems, including plankton (Vance et al., 2006; John et al., 2007) and during dietary Zn assimilation in freshwater fish (Nitzsche et al., 2020). Similar patterns are observed in Zn transport and translocation within plants (Weiss et al., 2005; Viers et al., 2007; Caldelas and Weiss, 2017; Araújo et al., 2018). However, crab tissues (muscle and hepatopancreas) showed higher δ^{66}Zn than their habitat sediments in fjord ecosystems (Bank et al., 2024). Indeed, macroinvertebrates likely exhibit more complex Zn biological isotope dynamics compared to, e.g., the lighter isotope membrane transportation mechanisms documented in unicellular organisms like phytoplankton.

3.2.3. Zn internal regulation factor

In the case of SE, muscle and hepatopancreas δ^{66}Zn are nearly identical (Fig. 4). However, crabs from ENS and VL sites display a notable isotope offset between these tissues of $\Delta^{66}Zn_{muscle\text{-}hepatopancreas} = -0.34$ ‰ (Fig. 5). This suggests that Zn trafficking within crab tissues may involve significant isotope fractionation processes, particularly in moderately contaminated environments.

Zn absorption begins in the mid-gut and associated structures, where digested matter is processed. Trace metals are then transported to the hemolymph, distributing nutrients to peripheral tissues like muscles (Fig. 5; Vogt, 2021; McGaw and Curtis, 2013; Negro and Collins, 2017). The hepatopancreas synthesizes digestive enzymes, stores nutrients and metals, detoxifies, and facilitates metal excretion when concentrations exceed metabolic demands (Ahearn et al., 2004).

The Zn isotope partitioning within crabs' tissues is possibly associated with detoxification mechanisms that regulate Zn levels. If kinetic isotope effects dominate during digestion and translocation, muscle tissues would become isotopically lighter than the hepatopancreas. This is because lighter isotopes would preferentially be processed and transported for metabolic needs, leaving the storage pool (hepatopancreas) enriched in heavier isotopes.

However, equilibrium isotope effects driven by ligand-binding preferences may also contribute to observed Zn fractionation patterns. In organisms, the metabolic pool is generally associated with proteins containing oxygen- and nitrogen-donor ligands, while detoxification processes often involve the sequestration and excretion of Zn into insoluble granules enriched in phosphate and sulfur-donor ligands (Rainbow, 2002). Empirical evidence from Truchet et al. (2020) shows that Zn preferentially accumulates in the hepatopancreas of *Neohelice granulata*, where cysteine-rich proteins play a key role in metal binding and detoxification through interactions with sulfur-donor ligands.

Heavy Zn isotopes tend to bind more strongly to oxygen and nitrogen ligands, whereas lighter isotopes are preferentially associated with sulfur ligands (Balter et al., 2013; Moynier et al., 2013). This leads to the theoretical enrichment of lighter isotopes in detoxified pools, potentially counteracting the kinetic fractionation effects described earlier. Theoretical modeling by Fujii et al. (2011) further supports this mechanism, showing that Zn complexes with sulfur-containing ligands such as glutathione and cysteine—common in metallothioneins—exhibit lower δ^{66}Zn values than those bound to oxygen- or nitrogen-based ligands. Thus, both equilibrium (ligand-driven) and kinetic (transport-related) isotope effects may act in opposing directions, jointly shaping the Zn isotope patterns observed in crab tissues.

Adding an extra layer of complexity, the final δ^{66}Zn can be further influenced by whether lighter or heavier isotopes are preferentially eliminated or retained. For example, lighter isotopes may be excreted from the detoxified pool, leaving heavier isotopes behind, as observed in bivalve mollusks (Barreira et al., 2024). Conversely, the retention of lighter isotopes would drive isotope values in the hepatopancreas toward lighter compositions.

In sum, both the translocation, internal chemical speciation, and excretion mechanisms can cause isotope effects within the tissues of aquatic invertebrates. The relative importance of each factor can stem

from diverse physiological aspects of the animals under examination, such as metabolic rates and detoxification mechanisms, warranting further investigation. For instance, differently from the present study, Bank et al. (2024) found heavier δ^{66}Zn in muscles from fjord brown crabs compared to hepatopancreas.

In SE crabs, where Zn concentrations in sediments are substantially higher (Table 1), muscle and hepatopancreas display nearly identical isotope values. This could indicate an overwhelming of effects from physiological processes by larger influences of the heavy Zn isotope uptake from the hot spot source or disruption of internal Zn regulation, either through non-selective elimination of lighter isotopes or saturation of the system by isotopically light Zn from the environment. This means that Zn isotope systematics in crabs are not only species or tissue-dependent but can also be affected by environmental stress triggered by high Zn exposure.

4. Conclusion

This study explored the Zn isotope systematics in mangrove crabs from contaminated environments, discussing how Zn sources, bioaccumulation routes, and homeostasis influence crab tissue isotope compositions.

The δ^{66}Zn in these organisms are connected to Zn sources, and they distinguish between contaminated and pristine sites. Isotopically heavier burrowing crab tissues resemble those of contaminated sediments and suspended particulate matter (SPM) from Sepetiba Bay. However, this application has its limitations. It is effective in comparing pristine environments with contaminated ones to discern anthropogenic influences but not enough sensitive to discern between different levels of contamination.

The δ^{66}Zn of crab tissues are consistently lighter than those of both bulk and labile sediment fractions. This offset may reflect contributions from dietary sources, as mangrove-derived leaves in Sepetiba Bay (Araújo et al., 2018) and detrital phytoplankton (Vance et al., 2006; John et al., 2007) are known to incorporate lighter Zn isotopes. These sources likely contribute to an isotopically light Zn pool transferred through the food web. In parallel, aqueous Zn has been shown to display lighter δ^{66}Zn values than particulate-bound forms in other estuarine systems (e.g., Borrok et al., 2007; Vance et al., 2006), although δ^{66}Zn of dissolved Zn was not directly measured in this study. Importantly, the δ^{66}Zn of organic matter in sediments—particularly within the oxidizable fraction—remains poorly characterized in mangrove and estuarine environments. Targeted research on δ^{66}Zn in organic-rich material is needed to better constrain its role in trophic transfer and sediment-biota isotopic offsets.

Finally, internal regulatory processes—including translocation, intracellular binding, and excretion—may further shape δ^{66}Zn in crab tissues, as supported by tissue-specific differences observed across sites. Our results show biologically driven isotope fractionations, particularly the lower δ^{66}Zn values observed in crab muscles compared to the hepatopancreas. We propose that this reflects preferential translocation of lighter isotopes to the muscles, with heavier isotopes accumulating in the hepatopancreas. The extent and specific mechanisms behind this fractionation are likely influenced by the physiology and ecological context of the crustaceans.

To better understand the underlying processes, further research is needed to examine how these variations are influenced by environmental factors, dietary habits, and species-specific physiological traits. To advance the application of Zn isotopes in environmental monitoring, controlled experiments with pre-determined isotope signatures in end members and regular isotope analyses of biological tissues and environmental media over time are crucial. These studies will provide greater precision in identifying the sources and mechanisms behind biologically driven isotope fractionation. Future studies should consider the isotopic variation across age classes to investigate whether the δ^{66}Zn evolves throughout the ontogenetic development of crabs. This approach could help determine whether metabolic shifts from juvenile to adult stages influence bioaccumulation processes and isotopic fractionation.

Overall, our study shows that mangrove crabs can be effectively utilized alongside isotope tools to provide insights into environmental conditions, as well as the bioavailability and transfer of metals to other trophic levels. Further studies are needed to develop this tool to complement interpretations purely based on elemental concentrations.

CRediT authorship contribution statement

João Barreira: Writing – review & editing, Writing – original draft, Visualization, Validation. **Jeremie Garnier:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. **Bruno Cunha:** Methodology, Investigation. **Myller Souza Tonhá:** Methodology, Investigation, Formal analysis. **Elton Dantas:** Supervision, Resources, Project administration. **Remi Freydier:** Methodology, Investigation, Formal analysis. **Wilson Machado:** Supervision, Methodology, Investigation. **Marly Babinski:** Supervision, Resources, Project administration, Funding acquisition. **Rafael de Araujo:** Formal analysis. **Daniel F. Araújo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Methodology, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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