



Trophic influence on selenium, cadmium, and manganese accumulation in fish from tropical estuary (Sepetiba Bay, Brazil)

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ABSTRACT

Estuarine regions are highly valuable ecosystems due to their high biological productivity and their role in providing food and habitats for numerous species. However, in the densely populated Southeast region of Brazil, these ecosystems face significant human-induced degradation and pollution. This study examined hepatic concentrations of selenium (Se), manganese (Mn), and cadmium (Cd) in five fish species from Sepetiba Bay (SB), Rio de Janeiro, Brazil, and explored their relationship with trophic position ($\delta^{15}\text{N}$). Our findings showed that Se concentrations increased significantly with trophic level when *Trichiurus lepturus* was excluded from the analysis ($r^2 = 0.45$, $p = 0.0002$), suggesting a potential for Se biomagnification in species sharing similar feeding zones. In contrast, Mn exhibited no correlation with trophic position, and the hypothesis that lower trophic level species would show higher Mn levels was not supported. Cd accumulation appeared to be species-specific, possibly linked to benthic invertebrate consumption and historical contamination in the bay. Additionally, *T. lepturus* showed a strong positive correlation between Se and Cd concentrations (Spearman $r = 0.86$, $p = 0.0107$), suggesting potential detoxification mechanisms, as well as evidence of biodilution, indicated by the negative correlation between Cd and body mass (Pearson $r = -0.83$, $p = 0.0116$). These results highlight the influence of trophic ecology on trace element dynamics in estuarine food webs. Given the ecological and economic importance of these fish, our findings contribute to environmental risk assessments and reinforce the need for continued monitoring in anthropogenically impacted tropical estuaries.

1. Introduction

Estuarine regions are widely acknowledged as ecosystems of significant importance due to their high biological productivity and capacity to provide sustenance and habitats for many species (Blaber et al., 2022). Moreover, estuaries hold both social and economic significance as they support coastal fishing communities (Blaber et al., 2022).

However, their geographical appeal and natural resources render them strategic environments for human habitation, leading to the establishment of ports, the concentration of industrial operations, and the advancement of coastal communities (Castelo et al., 2021). The South and Southeast regions of Brazil are characterized by high industrialization and urban development, thereby causing human-induced disturbances in coastal bays in these areas (Castelo et al., 2021; Dorneles

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et al., 2016). A noteworthy example is the semi-closed Sepetiba Bay (SB) located in the state of Rio de Janeiro, which faces critical environmental degradation due to human activities (Carvalho et al., 2021; Castelo et al., 2021). It holds a significant historical record of contamination linked to industrial activities, encompassing petrochemical and metallurgical sectors (Araújo et al., 2017; Carvalho et al., 2021; Castelo et al., 2021; de Lacerda et al., 1987; Molisani et al., 2004). SB has particularly notable historical cadmium (Cd) contamination, largely attributed to the industrial process of zinc refinement. Although the operations ceased in the 1990s, the Companhia Mercantil Industrial Ingá, which is located on Madeira Island, is responsible for processing and accumulating large quantities of zinc (Zn) - and cadmium (Cd)-contaminated waste. These contaminated waste materials were irresponsibly abandoned in open spaces, resulting in substantial environmental pollution from toxic metals across the vicinity (Barcellos and Lacerda, 1994; Gonçalves et al., 2020; Ribeiro et al., 2015). Furthermore, local sources such as agriculture, untreated domestic sewage, and harbor activities continue to introduce chemical elements into the bay (Araújo et al., 2017; Parqueti et al., 2004), leading to the ongoing accumulation of pollutants, including trace elements (Carvalho et al., 2021; Castelo et al., 2021; da Silva et al., 2022; Damasceno et al., 2024).

Recent studies indicate that the area is heavily polluted with various elements, including Cd and manganese (Mn) (Damasceno et al., 2024). Consequently, the presence of these elements, along with selenium (Se), poses risks to both aquatic organisms and human health (Peters et al., 2016; Yan and Allen, 2021). While Se and Mn are essential for maintaining organismal metabolism, excessive levels can be toxic (Jamwal et al., 2018; Manhães et al., 2021; Peters et al., 2016). In contrast, Cd is a non-essential element known for its harmful effects on most organisms (Le Croizier et al., 2019; Hashtjin et al., 2025). These toxic elements can negatively impact fish species, leading to physiological, reproductive, and immunological damage, neurodegeneration, teratogenic deformities, and even mortality (ATSDR, 2003; Hamilton, 2004; Hashtjin et al., 2025; Jamwal et al., 2018; Lall and Kaushik, 2021; Lemly, 1999; Liu et al., 2022; Uddin et al., 2024).

Considering that studies point to diet as one of the main routes of exposure to the elements mentioned above, the system where a certain population lives and obtains its food can lead to greater exposure to such pollutants, with the consumption of fish being a route of exposure to the human population as well (Borgå et al., 2012; Carvalho et al., 2021; Gray, 2002; Kurita and Pfeiffer, 1991). Although muscle tissue is important in terms of human exposure to contaminants through food, the liver exhibits higher concentrations of many contaminants than other fish tissues (Evans et al., 1993). Thus, hepatic concentrations can be used to assess exposure to contaminants, even when these contaminants are undetectable or present lower concentration in muscle tissue (Viana et al., 2005).

Notably, Se also plays a crucial protective role against the harmful effects of toxic metals. It acts as an antagonistic agent to elements such as Hg and Cd, contributing to detoxification mechanisms in aquatic organisms (Azevedo-Silva et al., 2016; Bisi et al., 2012; Lailson-Brito et al., 2012; Baptista et al., 2016; Hashtjin et al., 2025). Detoxification processes for Hg, Cd, and other elements have been reported in the liver of aquatic mammals and seabirds (Ikemoto et al., 2008; Lailson-Brito et al., 2012; Lino et al., 2018; Rodríguez-Gutiérrez et al., 2020). The association between Se and Cd was also observed in fish tissues (Hashtjin et al., 2025; Jamwal et al., 2018; Xie et al., 2016). Once Hg has biomagnification capacity, interaction related Hg detoxification processes may potentially lead to an elevation in Se concentrations in organisms as trophic levels increase (Kehrig et al., 2013; Molina-García et al., 2021).

Regarding Mn, it tends to bioconcentrate at lower trophic levels (e.g., plankton > aquatic plants > fish), indicating a low potential for biomagnification (Williams et al., 2012; Herman et al., 2021) similar to what is observed for Cd. However, research on Se biomagnification and trophic dynamics of trace-elements in bays and estuaries remains

limited, despite its potential to bioaccumulate and induce toxicity in aquatic food webs (ATSDR, 2003; Barwick and Maher, 2003; Córdoba-Tovar et al., 2021; Ikemoto et al., 2008).

Furthermore, stable-isotope tracers, particularly $\delta^{15}\text{N}$, provide a powerful ecological tool for clarifying trophic positions and gauging the likelihood that contaminants are biomagnified. Building on these data, the Trophic Magnification Slope (TMS) is calculated as the slope of a \log_{10} regression between contaminant concentration and $\delta^{15}\text{N}$, offering a quantitative measure of biomagnification capacity within food webs; a positive TMS indicates magnification, whereas a negative value signals biodilution. This approach has been widely applied to trace-element and organic contaminants alike (Asante et al., 2010; Bisi et al., 2012; Pestana et al., 2019).

Despite anthropogenic pressures on SB, fishing remains a significant economic activity, underscoring the importance of research aimed at identifying critical parameters for fish exposure to contaminants and their potential impacts on human health. This reinforces the need to investigate trace elements in Sepetiba Bay, an estuary that is ecologically important for several species (Guido et al., 2016; Pessanha and Araújo, 2003) and fishing activities (de Carvalho et al., 2021). To our knowledge, only da Silva Carneiro et al. (2011) have examined Se concentrations in fish muscles and organs of two fish species from SB, namely the whitemouth croaker (*Micropogonias furnieri*) and the acoupa weakfish (*Cynoscion acoupa*). This study revealed elevated concentrations of Cr, Zn, and Se in the analyzed samples, surpassing the maximum limits recommended by Brazilian legislation. Importantly, despite Se pollution being linked to a wide range of human activities, crucial sources of Se contamination in aquatic environments are often overlooked, as studies tend to focus on compounds or elements with greater toxicological potential (Lemly, 2004).

The environmental challenges observed in Sepetiba Bay mirror issues faced by estuarine and coastal regions globally, particularly those undergoing rapid industrialization. Understanding Se, Mn, and Cd behavior in tropical estuaries provides valuable insight for similar environments in developing countries experiencing intense anthropogenic pressure. This study offers a reference point for international comparisons regarding the biomagnification potential of trace elements in food webs of urbanized estuarine systems. As estuaries worldwide face increasing contamination, data from Sepetiba Bay contribute to the global database supporting environmental risk assessments and food safety regulations. Viana et al. (2005) reinforcing the call for coordinated monitoring efforts among countries, such as Brazil, Uruguay, and Argentina, to ensure the health safety of shared fishery resources. In this context, mullets, widely recognized as bioaccumulators of pollutants, emerge as sentinel species for contamination in estuarine environments (Viana et al., 2005).

Consequently, this study aims to investigate Se, Mn, and Cd concentrations in the livers of five fish species (*Micropogonias furnieri*, *Centropomus undecimalis*, *Aspistor luniscutis*, *Trichiurus lepturus*, and *Mugil curema*) from SB, Brazil. We assessed the bioaccumulation and biomagnification potential of these trace elements in the livers of ecologically and commercially important fish from Sepetiba Bay, and examined possible inter-element relationships arising from their interactions. Hepatic Se, Cd, and Mn concentrations were correlated with trophic relationships, as indicated by $\delta^{15}\text{N}$ values. Additionally, TMS values were calculated to analyze the behavior of trace elements in the SB ichthyofauna. Our hypotheses were: (1) Se will exhibit a significant positive correlation with trophic position due to its correlations with Hg, (2) Mn levels will be higher in fish species that occupy the trophic base, (3) Fish would present elevated Cd levels due to the historical anthropogenic contamination in SB.

2. Material and methods

2.1. Study area

Sepetiba is a semi-closed bay located in Rio de Janeiro state spanning between the latitudes 22° 54' and 23° 04' S and the longitudes 43° 34' and 44° 10' W (Fig. 1). In addition to the abandoned waste disposal sites, the SB region houses an industrial park encompassing the largest steel industry complex in Latin America (Araújo et al., 2017; Barcellos and Lacerda, 1994). Among various contributors to pollution, the SB area has three operational ports. The expansion of these ports necessitated dredging to deepen the channel, leading to the resuspension of sediment and associated contaminants. Another significant environmental alteration was the transposition of the Paraíba do Sul River to the Guandu. The waters from the Paraíba do Sul River traverse through the most industrialized region in the country before entering the Sepetiba Bay basin (de Lacerda and Malm, 2008; Molisani et al., 2007). The region surrounding the bay also houses the Rio Waste Treatment Center (CTR Rio), which receives waste from three cities, including Rio de Janeiro, a metropolis with a population of six million (Pereira, 2020). Additionally, there are small towns and villages along the coast that lack sewage treatment facilities (Copeland et al., 2003).

2.2. Sampling

In February and March 2009 (wet season), fish specimens were acquired in fishing landings within Sepetiba Bay, following the methodology previously outlined by Bisi et al. (2012). These specimens were obtained from local markets supplied by small-scale fishing boats that operate exclusively within the bay due to limited range and logistical capacity, ensuring that the fish reflect the environmental conditions of the region. The collection encompassed five fish species, which hold significant importance as both fishery resources and prey for Guiana dolphins (*Sotalia guianensis*), while also serving as a crucial commercial and sustenance resource for inhabitants (Bisi et al., 2012). The specimens comprised four carnivorous species: *Micropogonias furnieri* (whitemouth croaker, n = 24), *Centropomus undecimalis* (common snook, n = 10), *Aspistor luniscutis* (yellow catfish, n = 7) and *Trichiurus lepturus* (ribbonfish, n = 8). Additionally, a representative from the base of the food web was included: *Mugil curema* (white mullet, n = 10), an

iliophagous species.

Fish specimens were measured, weighed, and dissected. Liver samples were individually stored in polyethylene bags and kept frozen at -20 °C. Before the analyses, the samples were dried in an oven at 60 °C for 3 days and macerated in an agate mortar for sample homogenization.

2.3. Analytical method and quality control

The method was adapted from Lailson-Brito et al. (2012). In summary, duplicates of 200 mg of hepatic tissue were solubilized with 2 ml of HNO₃ 65 % in a digester CEM's One Touch Technology MARS 6 microwave. Se, Cd, and Mn total liver concentrations were quantified using an Atomic Absorption Spectrometry with Electrothermal Atomization (ETAAS) ZEEnit 60 Spectrometer equipped with Zeeman effect background correction (Analytik Jena, Germany). Palladium nitrate (Pd (NO₃)₂) was used as an analyte modifier and argon (Ar) as a carrier gas. The quality control and method accuracy were verified with procedural blanks, sample replicates (coefficient of variation <15 %), certified reference material DOLT-4 (dogfish liver, from the National Research Council of Canada) for Se (8300 ± 1300 ng g⁻¹ with an average recovery of 94 ± 11 %, n = 5) and Cd (24300 ± 800 ng g⁻¹ with an average recovery of 95 ± 7 %, n = 5), and the reading of a 5 ppb standard solution for Mn (mean ± standard deviation, 4.9 ± 0.2 ng g⁻¹, n = 11). The detection limit was 3.68 µg.L⁻¹ for Se, 0.23 µg.L⁻¹ for Cd, and 0.26 µg.L⁻¹ for Mn.

2.4. Statistical treatment

The statistical analyses and data visualization were performed using GraphPad Prism 10 and RStudio. Data normality was assessed with the Shapiro-Wilk test. For evaluating potential interspecific variations, interspecific variations were evaluated using the Kruskal-Wallis (KW) test, as the data were non-normal. When significant differences were detected, post-hoc analysis was performed using Dunn's test with Bonferroni correction for multiple comparisons. To explore possible relationships between hepatic Se concentrations and biological parameters, the Pearson correlation coefficient or Spearman rank correlation was employed, based on the nature of the data. Inter-elements correlations were also examined, and when significant, regression analysis was applied. A significance level of 5 % (p < 0.05) was used for

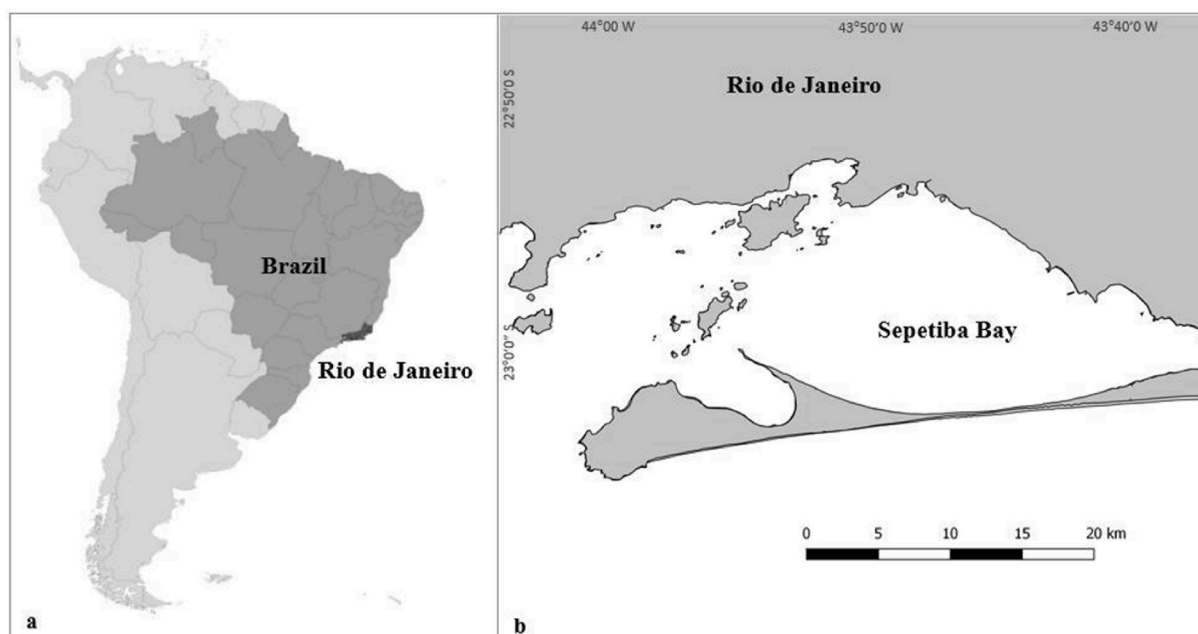


Fig. 1. Study area: a) South America continent with Brazil and Rio de Janeiro State contrasted; b) Sepetiba Bay, Rio de Janeiro State.

all tests.

2.5. Molar ratio Se:Cd

To investigate potential interactions and relative bioavailability between Se and Cd, we employed their molar ratio as an index in each fish sample. Cadmium and Se concentrations ($\mu\text{g}/\text{kg}$) in each individual fish sample were converted to molar concentrations ($\mu\text{mol}/\text{kg}$) using their respective atomic weights. The Se:Cd molar ratio was then calculated by dividing the molar concentration of Se by that of Cd for each sample as described in Kaneko and Ralston (2007) where a molar ratio greater than 1 indicates a molar excess of Se. The Se:Mn molar ratio was not calculated, as manganese is not expected to have the same type of association with Se. To estimate the molar excess of Se ("free Se"), the molar concentration of Cd was subtracted from the molar concentration of Se for each sample (Kaneko and Ralston, 2007).

2.6. Determination of biomagnification

To explore the potential for biomagnification, TMS values were computed by performing linear regressions between \log_{10} -transformed Cd, Mn, and Se concentrations and $\delta^{15}\text{N}$ values (Azevedo et al., 2021). $\delta^{15}\text{N}$ values used in the present study were obtained from a previous study by our research team (Bisi et al., 2012), which analyzed muscle tissue samples from the same specimens examined here.

3. Results

3.1. Interspecific differences and bioaccumulation

Fish biometric data, including body mass, length, and common names, are summarized in Supplementary Table S1. Briefly, *M. furnieri* exhibited the highest average body mass (640.4 ± 262 g) and length (32.4 ± 5.1 cm), while *T. lepturus* had notably greater length (68.03 ± 24.6 cm). The remaining species: *C. undecimalis*, *A. luniscutis*, and *M. curema* presented similar intermediate values for mass and length.

No significant correlations between Mn hepatic concentrations and body mass or standard length were observed for any of the studied species ($p > 0.05$). However, *M. furnieri* exhibited significant positive correlations between hepatic Cd concentrations and body mass (Spearman $r = 0.62$, $p = 0.0047$) as well as standard length (Spearman $r = 0.65$, $p = 0.0006$, Table S2). For *T. lepturus*, a significant but negative correlation was observed between total body mass and Se levels ($r = -0.78$, $p = 0.0233$, Table S2) and Cd levels (Pearson $r = -0.83$, $p = 0.0116$, Table S2).

In terms of interspecific differences, significantly higher hepatic Se concentrations were observed in *M. furnieri* compared to the other fish species ($p < 0.05$, Fig. 2 and Table S3). More specifically, hepatic Se concentrations were significantly higher in *M. furnieri* than in *T. lepturus* and *M. curema* (KW = 33.194, $df = 4$, $p < 0.0001$), which had the two

lowest Se concentrations (Fig. 2).

Mugil curema exhibited lower Cd hepatic concentrations than *C. undecimalis* (KW = 14.924, $df = 4$, $p = 0.005$). *T. lepturus* had the lowest observed Cd concentration (Fig. 2).

We observed no significant interspecific differences in Mn concentrations.

Furthermore, a positive relationship was observed between Se and Cd in *T. lepturus* (Fig. 3) with a strong linear correlation ($r = 0.89$, $r^2 = 0.79$; $p = 0.0029$). However, no significant correlations were found between the other elements or species ($p > 0.05$; Table S4). The corresponding Se:Cd molar ratios (mean \pm SD; Table 1) for each species were as follows: *M. furnieri* (93 ± 91), *C. undecimalis* (28 ± 41), *M. curema* (49 ± 71), *A. luniscutis* (121 ± 158), and *T. lepturus* (24.3 ± 10). Notably, 52 out of 53 individuals exhibited negative free selenium values (ranging from -417 to 31), indicating a molar excess of Se relative to Cd (Table 1).

3.2. Trace element concentrations in the trophic web

TMS including all fish species showed no significant correlation between $\delta^{15}\text{N}$ values and log-transformed hepatic concentrations of Se ($r^2 = 0.11$, $p = 0.07$), Mn ($r^2 = 0.06$, $p = 0.77$), and Cd ($r^2 = 0.01$, $p = 0.56$; Fig. 4). Taking into account the potential impact of *T. lepturus* on the bioaccumulation of Se, Mn and Cd, the TMS was also calculated without this species, as recommended by Bisi et al. (2012) in a comparable study on mercury bioaccumulation. By excluding *T. lepturus*, a statistically significant correlation between log-transformed hepatic Se concentrations and $\delta^{15}\text{N}$ values was observed ($r^2 = 0.45$, $p = 0.0002$; Fig. 5). The results of the new linear regression analysis showed that Se TMS values had increased significantly compared to Cd or Mn values. This indicates a trend of increasing element concentrations along the food web. The Se, Mn, and Cd concentrations and $\delta^{15}\text{N}$ data used in this analysis are summarized in Table S3, available in the supplementary material.

4. Discussion

To the best of our knowledge, this is the first study to present hepatic Se concentrations for the species *C. undecimalis*, *A. luniscutis*, *T. lepturus* and *M. curema* from Sepetiba Bay.

A positive regression observed in the present study between Se concentrations and $\delta^{15}\text{N}$ in four fish species emphasizes the importance of considering a trophic position as an influencing predictor for Se concentration in fish that share the same feeding zone. Moreover, a significant trophic level-dependent increase (with increasing $\delta^{15}\text{N}$ values) in Se concentrations has already been reported (Ikemoto et al., 2008). The issue of selenium biomagnification remains unresolved. Some studies have not observed relationships between Se concentrations and trophic positions (Arcagni et al., 2017; Ferraz et al., 2023; Ouedraogo et al., 2015) while others have suggested its magnification along the trophic web (Barwick and Maher, 2003; Økelsrud et al., 2016;

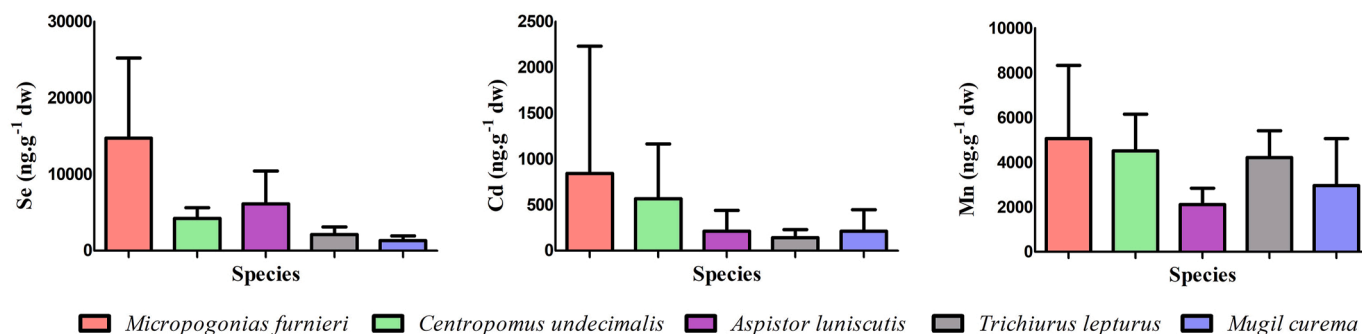


Fig. 2. Hepatic concentrations (mean \pm standard deviation $\text{ng}\cdot\text{g}^{-1}\text{ dw}$) of selenium (Se), cadmium (Cd) and manganese (Mn) in fish species from Sepetiba Bay, Rio de Janeiro State, Brazil.

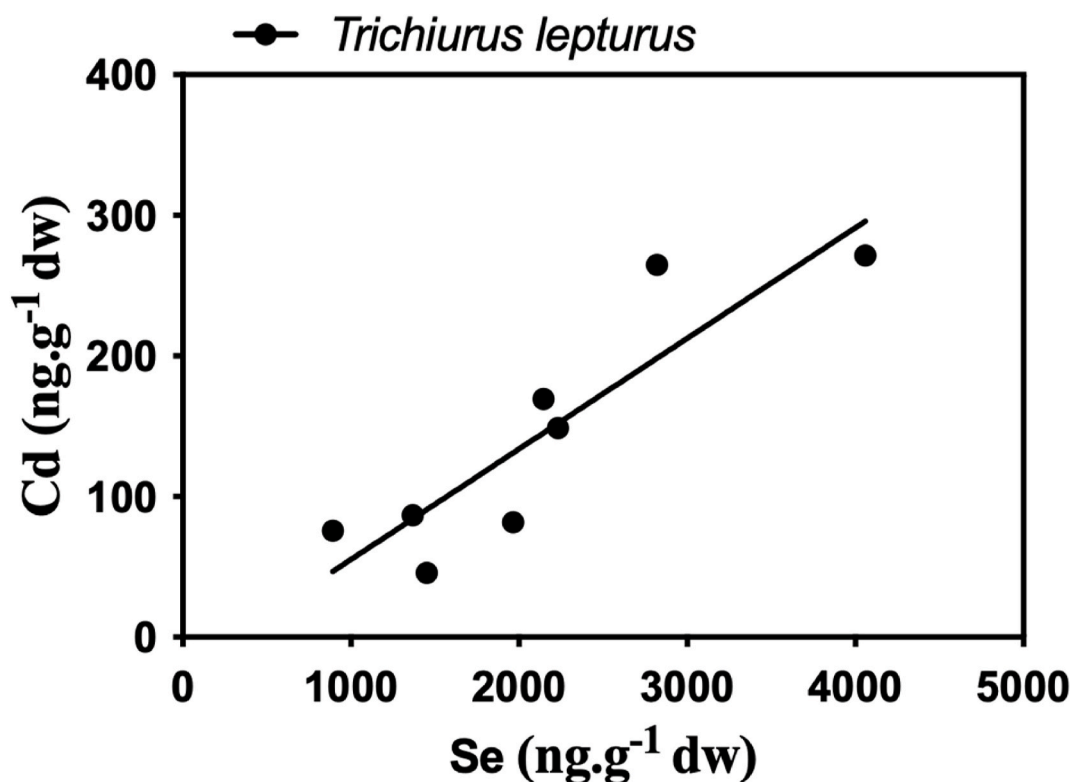


Fig. 3. Linear relationship between hepatic selenium (Se; ng.g⁻¹ dw) and cadmium (Cd; ng.g⁻¹ dw) concentrations in *Trichiurus lepturus* from Sepetiba Bay, Rio de Janeiro State, Brazil.

Table 1

Minimum (Min), maximum (Max), mean, and standard deviation (SD) of Selenium-to-Cadmium (Se:Cd) molar ratios and the mean molar excess of Se relative to Cd (Free Se) in the liver of fish species from Sepetiba Bay.

Spp	Ratio Se:Cd				Free Se
	Min	Max	Mean	SD	Mean
<i>Micropogonias furnieri</i>	0	317	93	91	-157
<i>Centropomus undecimalis</i>	3	134	28	41	-48
<i>Mugil curema</i>	3	173	49	71	-18
<i>Aspistor luniscutis</i>	10	436	121	158	-76
<i>Trichiurus lepturus</i>	15	45	24	10	-26

Molina-García et al., 2021; Pantoja-Echevarría et al., 2023). Arcagni et al. (2017) observed no biomagnification of Se or Hg, although they noted that fish with a more benthic diet had higher total Hg concentrations compared to those with more pelagic or mixed diets. Similarly, Pantoja-Echevarría et al. (2023) found evidence of Se biomagnification, but, like this study, Se concentrations did not consistently increase across trophic levels.

Borgå et al. (2012) have noted the potential impact of top-chain species on TMS values, and that the biomagnification can vary depending on the characteristics of the ecosystem and the species involved. For example, the bioavailability of metals can vary depending on their chemical form, water chemistry, and the presence of chelating agents in the sediment and water column (Borgå et al., 2012). Additionally, differences in metal uptake and accumulation among species can lead to variations in biomagnification patterns (Borgå et al., 2012). Therefore, the demersal-pelagic habits of *T. lepturus* and the unique characteristics of its trophic niche may influence Se concentrations in this species differently compared to others.

Mugil curema and *T. lepturus* displayed lower hepatic Se concentrations, while *M. curema*, a non-carnivorous fish species, serves as a foundation of the food web, *T. lepturus* is a demersal-pelagic species that

occupies the top of the food chain (Bisi et al., 2012). The interaction between Se and Hg, as well as the biomagnification capacity of the latter, might contribute to the lower concentrations in *M. curema* (Molina-García et al., 2021), although this does not fully explain the observed Se concentrations in *T. lepturus*. According to Molina-García et al. (2021), bivalve mollusk ingestion is a significant source of Se for higher trophic levels. The feeding habits of benthic invertebrate feeders, such as *C. undecimalis*, *A. luniscutis*, and *M. furnieri* (Bisi et al., 2012), could potentially elucidate the higher Se concentrations observed in these species. While habitat and feeding zones influence Se concentration in invertebrates, Se concentrations in fish are primarily influenced by feeding zones. Schneider et al. (2015) observed higher Se concentrations in fish that fed on benthos than in those that fed on organisms in the water column. Moreover, elevated Se concentrations in benthic invertebrates are often linked to their close interaction with sediment Schneider et al. (2015). Similarly, the elevated Se concentrations detected in carnivorous species in this study, particularly the higher levels detected in *M. furnieri* compared to *T. lepturus*, can likely be attributed to their benthic invertebrate feeding behavior. Thus, the feeding zone may exert a strong influence on Se concentrations in fish and should be explicitly considered and explored in future studies.

The complexity of trophic relationships among fish in Sepetiba Bay indicates diverse prey items from different taxa (Bisi et al., 2012). Such intricacy may also reflect a greater complexity of Se behavior in the Sepetiba Bay trophic web, as Bisi et al. (2012) observed for mercury. Azevedo et al. (2007) observed a peculiar habitat occupancy for some fish species in Sepetiba Bay, and *T. lepturus* was one of the fish species associated with the bay outer zone. Therefore, the lower selenium concentrations observed in *T. lepturus* from Sepetiba Bay compared to the other species studied here could be due to its participation in a different trophic web, as well as the lower bioavailability of selenium to this species. This latter statement is based on the fact that rivers would constitute one of the main sources of Se to Sepetiba Bay (Duan et al., 2010) and its concentrations could be higher in the inner zone of the

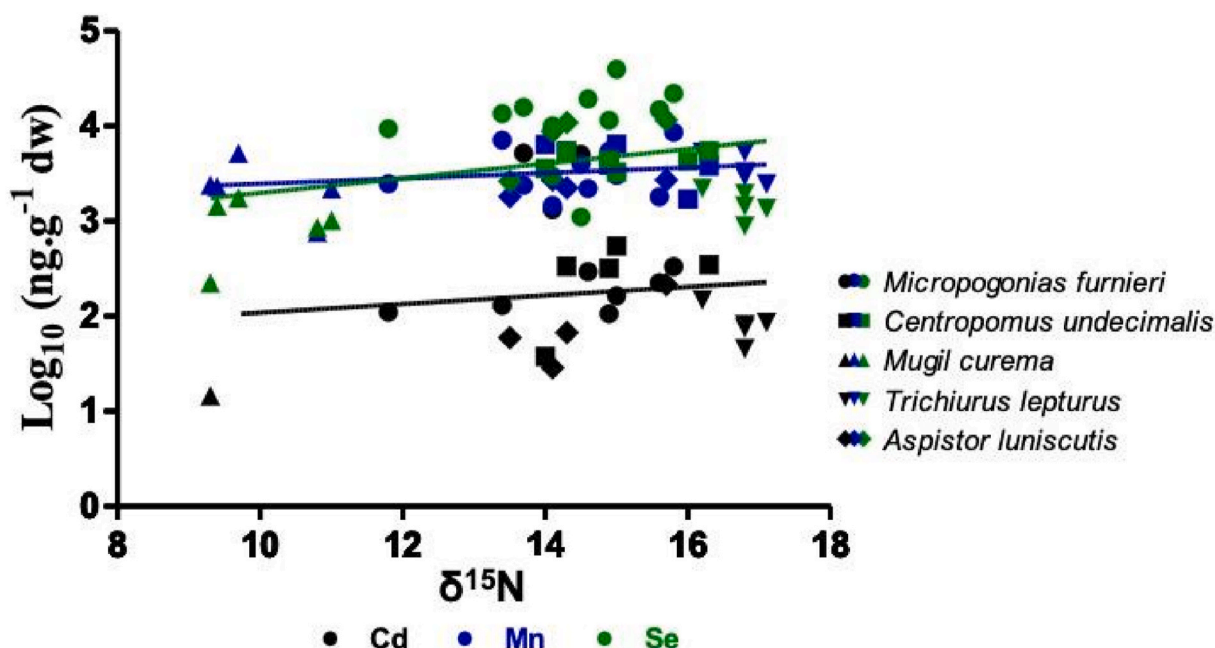


Fig. 4. Relationships between log-transformed hepatic Se, Cd, and Mn concentrations and $\delta^{15}\text{N}$ values in fish species from Sepetiba Bay, Rio de Janeiro State, Brazil.

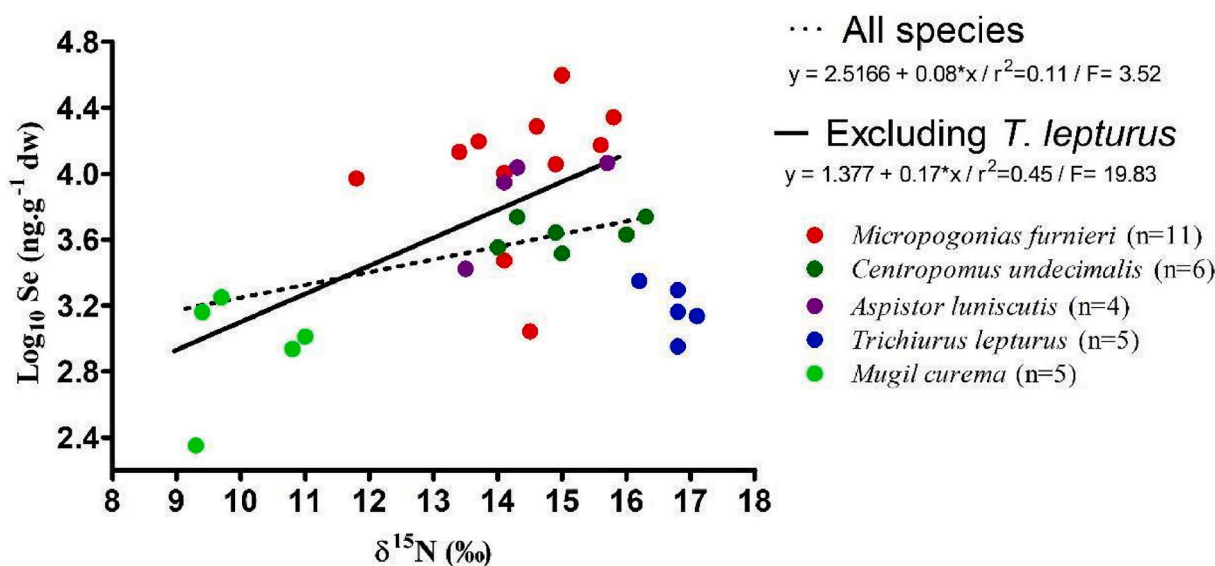


Fig. 5. Relationships between log-transformed hepatic Se concentrations and $\delta^{15}\text{N}$ values in fish species from Sepetiba Bay, Rio de Janeiro State, Brazil, with (all species) and excluding *T. lepturus*.

estuary, a continental drainage area.

The results of the linear regression analysis (Fig. 4) suggests that trophic position does not influence Mn concentrations. Although the studied species had similar Mn hepatic concentrations, *A. luniscutis* exhibited the lowest levels, followed by the concentrations observed in *M. curema*, whereas carnivorous species showed significantly higher concentrations. Generally, Mn tends to bioaccumulate more at lower trophic levels (Williams et al., 2012). Despite this, the hypothesis that Mn would be more concentrated at lower trophic levels was not corroborated. We detected no significant interspecific differences in Mn concentrations, and—contrary to expectations—the catfish *Aspistor luniscutis* exhibited particularly low Mn concentrations. This reduction cannot be attributed to biodilution, because Mn showed no correlation with specimen length or weight. Instead, *A. luniscutis*'s bottom-dwelling lifestyle (Guedes et al., 2015) could limit its exposure to bioavailable

Mn, resulting in comparatively lower accumulation.

Whereas manganese displayed no trophic dependence, Cd revealed an increasing trend in Cd TMS values (Fig. 4). These results suggest that trophic position may influence Cd concentrations in Sepetiba Bay, although other factors could also affect metal accumulation in these fish species. Once again, *T. lepturus* stood out by exhibiting the lowest Cd concentration among all species (Fig. 2). Furthermore, *T. lepturus* exhibited a significant negative correlation between total body mass and both Se levels and Cd levels (Table S2). According to the literature, *T. lepturus* maintains limited diet variation throughout its lifespan (Guedes et al., 2015). The divergence in Se and Cd bioaccumulation within this species might stem from its metabolism, wherein younger organisms could accumulate certain elements more effectively (Canli and Atli, 2003; Liang et al., 1999; Widianarko et al., 2000). Seixas et al. (2012) also observed a significant negative correlation between muscle

Se concentration and fish length for *T. lepturus* in two different coastal regions of Rio de Janeiro state (Guanabara Bay and Buzios coast). Similarly, Romèo et al. (1999) reported lower Cd concentrations in pelagic fish muscle, whereas species that consume fish and benthic invertebrates had higher hepatic Cd concentrations (Burger, 2008; Croteau et al., 2005).

Notably, the strong correlation between Se and Cd, along with the observed molar excess of Se relative to Cd, suggests a potential detoxification role of Se, as previously reported by other studies (De Carvalho et al., 2021; Seixas et al., 2014). Recent experimental data on the interaction of Se and Cd, shows that Se may reduce Cd accumulation and mitigate liver toxicity in fish (Hashtjin et al., 2025). Additionally, in our study, Se was consistently present in molar excess over Cd, resulting in negative free Se values reinforcing this suggestion. These findings suggest that *T. lepturus* has different absorption and excretion metabolic pathways for *T. lepturus* compared to the other species examined in this study.

In the present study, *M. furnieri* and *C. undecimalis* showed the highest hepatic Cd concentrations (range: 0.033 to 5.177 and 0.038–2.078 mg/kg dw, respectively). Marcovecchio (2004) observed a relationship between Cd accumulation and species-specific trophic and ecological habits, suggesting that Cd levels may reflect environmental exposure rather than biomagnification. De Lacerda et al. (1987) studied heavy metal concentrations in sediments of Sepetiba Bay and reported that the highest levels of trace-elements, including Cd, coincided with river deposition area, indicating also the Industrial Park as the main source of these elements to the bay with suggesting that these metals may be bioavailable to the local biota. Table 2 provides a comparative overview, juxtaposing the element concentrations measured in this study with values reported for muscle and liver tissues of *Micropogonia* spp. and *Mugil* spp. in other studies.

The hepatic Cd concentrations recorded for *Micropogonias* spp. in this study align most closely with the low levels reported by Tapia et al. (2012) for Chile's Lago Budi, representing the lowest values among the datasets reviewed. For *Mugil* spp., Fazio et al. (2020) documented even

lower Cd burdens in Bulgarian and Italian waters; however, those data were reported on a wet-weight basis, whereas our results are expressed as dry weight, partially accounting for the difference. Notably, *Mugil* spp. exhibited lower while *Micropogonias* spp. exhibited higher liver Se concentrations in Sepetiba Bay than those measured in a near and well-preserved estuary Ilha Grande Bay, Rio de Janeiro (Seixas et al., 2012). Although these findings point to a moderate present-day status for trace elements, Sepetiba Bay's legacy of industrial discharges, growing anthropogenic pressure, and the well-known toxicity of Cd make continued surveillance essential—especially of benthic invertebrates and their fish predators. In parallel, it is crucial to verify whether Cd concentrations in muscle comply with ANVISA (The Brazilian Health Regulatory Agency, responsible for establishing safety standards for food limits; see Table S5), because relationships between hepatic and muscular Cd burdens in fish remain poorly documented.

5. Conclusion

This study provides novel insights into the bioaccumulation and trophic dynamics of Se, Cd, and Mn in five fish species from Sepetiba Bay, a historically contaminated estuary in southeastern Brazil. The findings partially support the initial hypotheses: Se exhibited a significant trophic magnification trend when *T. lepturus* was excluded from the analysis, reinforcing its potential for biomagnification in species that share similar feeding zones. In contrast, no trophic pattern was observed for Mn, and the hypothesis that Mn would be more concentrated in lower trophic levels was not confirmed. Regarding Cd, although biomagnification was not evident, high concentrations in *M. furnieri* and *C. undecimalis* suggest species-specific accumulation linked to benthic invertebrate feeding and historical contamination in the bay.

In *T. lepturus*, the strong Se–Cd correlation along with the negative correlation of Se and Cd concentrations with body size, suggests ongoing detoxification processes and biodilution in this species. However, the relatively low Se:Cd molar ratio (mean = 24) indicates that the available Se may be insufficient to fully counteract Cd toxicity in this species.

Table 2

Comparison of data from the present study with other studies that analyzed the same elements in muscle and liver tissues of *Micropogonias* spp. and *Mugil* spp. The table presents the element analyzed, fish species, mean concentrations (\pm SD; mg/kg) in muscle and liver, sampling location, and the corresponding reference. ww = wet weight; dw = dry weight.

Element	Specie	Muscle	Liver	Local	Country	Study
Cd	<i>Micropogonias furnieri</i>	7.9 \pm 1.0 (dw)	25.4 \pm 5.5 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	28.9 \pm 8.9 (dw)	24.4 \pm 12.3 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	1.1 \pm 0.1	27.5 \pm 8.1 (dw)	Barra do Chuí estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	147.3 \pm 25.5 (dw)	37.3 \pm 1.6 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	5.3 \pm 2.8 (dw)	21.5 \pm 6.3 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	57.3 \pm 21.9 (dw)	19.5 \pm 4.8 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	14.0 \pm 4.5 (dw)	39.8 \pm 11.3 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	5.0 \pm 1.1 (dw)	25.4 \pm 5.3 (dw)	Barra do Chuí estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	46.0 \pm 19.6 (dw)	15.8 \pm 1.3 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	25.3 \pm 4.5 (dw)	20.4 \pm 2.1 (dw)	Lagoa dos Patos estuary	Brazil	Marques et al., (2019)
Cd	<i>Micropogonias furnieri</i>	–	3.13 \pm 1.04 (ww)	Samborombon Bay	Argentina	Marcovecchio (2004)
Cd	<i>Micropogonias manni</i>	0.05 (dw)	0.20 (dw)	Budi lake	Chile	Tapia et al. (2012)
Cd	<i>Micropogonias furnieri</i>	–	0.797 \pm 1.551 (dw)	Sepetiba Bay	Brazil	This study
Cd	<i>Mugil cephalus</i>	0.0008 \pm 0.0010 (ww)	0.0351 \pm 0.0217 (ww)	Ionian Sea	Italy	Fazio et al. (2020)
Cd	<i>Mugil cephalus</i>	0.0391 \pm 0.0043 (ww)	0.2391 \pm 0.0034 (ww)	Black Sea	Bulgaria	Fazio et al. (2020)
Cd	<i>Mugil cephalus</i>	0.15 \pm 0.00 (dw)	15.15 \pm 9.72 (dw)	Callao Bay	Peru	Alvariano et al. (2024)
Cd	<i>Mugil liza</i>	0.34 \pm 0.05 (ww)	9.15 \pm 1.25 (ww)	Samborombon Bay	Argentina	Marcovecchio (2004)
Cd	<i>Mugil curema</i>	–	2.83 \pm 2.95 (dw)	Sepetiba Bay	Brazil	This study
Mn	<i>Micropogonias manni</i>	1.76 (dw)	2.99 (dw)	Budi lake	Chile	Tapia et al. (2012)
Mn	<i>Micropogonias furnieri</i>	–	5.416 \pm 3.016 (dw)	Sepetiba Bay	Brazil	This study
Mn	<i>Mugil cephalus</i>	0.3040 \pm 0.0484 (ww)	1.5350 \pm 0.2455 (ww)	Ionian Sea	Italy	Fazio et al. (2020)
Mn	<i>Mugil cephalus</i>	0.1376 \pm 0.0183 (ww)	1.6710 \pm 0.0204 (ww)	Black Sea	Bulgaria	Fazio et al. (2020)
Mn	<i>Mugil cephalus</i>	0.96 \pm 0.41 (dw)	4.23 \pm 1.07 (dw)	Callao Bay	Peru	Alvariano et al. (2024)
Mn	<i>Mugil curema</i>	–	2.972 \pm 2.101 (dw)	Sepetiba Bay	Brazil	This study
Se	<i>Micropogonias furnieri</i>	1.632 \pm 0.451 (dw)	5.965 \pm 2.999 (dw)	Ilha Grande Bay	Brazil	Seixas et al. (2014)
Se	<i>Micropogonias furnieri</i>	–	16.726 \pm 10.244 (dw)	Sepetiba Bay	Brazil	This study
Se	<i>Mugil liza</i>	1.388 \pm 0.736 (dw)	14.543 \pm 9.691 (dw)	Ilha Grande Bay	Brazil	Seixas et al. (2014)
Se	<i>Mugil cephalus</i>	1.71 \pm 1.11 (dw)	9.00 \pm 5.00 (dw)	Callao Bay	Peru	Alvariano et al. (2024)
Se	<i>Mugil curema</i>	–	1.316 \pm 0.613 (dw)	Sepetiba Bay	Brazil	This study

These results underscore the complexity of trace element dynamics in estuarine food webs and highlight the influence of species-specific ecological traits, such as habitat use and diet, on contaminant accumulation.

Our hypothesis, that historical industrial inputs would still translate into elevated hepatic Cd, was not corroborated. Although these findings point to a moderate current status for trace elements, given the ecological and economic importance of these fish, and their role in the diet of top predators such as *S. guianensis*, continued monitoring of trace element contamination in Sepetiba Bay is essential. Understanding the behavior and possible increase in trace element concentrations within the trophic web is essential for the management and conservation of aquatic ecosystems. This study contributes with data to support environmental risk assessment and management strategies in impacted coastal ecosystems. This aspect should not be neglected, particularly given the high degree of environmental impact in Sepetiba Bay.

CRediT authorship contribution statement

T.C. Paiva: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **J. Souza-Kasprzyk:** Writing – original draft, Visualization, Methodology, Investigation, Data curation. **J.A.G. Padilha:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **K. Das:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Formal analysis. **T.L. Bisi:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **C.E. Azevedo-Silva:** Writing – review & editing, Supervision, Investigation. **A.F. Azevedo:** Writing – review & editing, Investigation, Funding acquisition, Conceptualization. **J. Lailson-Brito:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Data curation, Conceptualization. **O. Malm:** Writing – review & editing, Resources, Investigation, Funding acquisition. **P.R. Dorneles:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marenvres.2025.107425>.

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Data availability

Data will be made available on request.

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