Regional Studies in Marine Science
December 2023, Volume 66, Pages 103105 (12p.)
https://doi.org/10.1016/j.rsma.2023.103105 https://archimer.ifremer.fr/doc/00847/95882/

Mercury biomagnification and trophic structure patterns in neotropical coastal estuaries impacted by a Chlor-alkali plant in northeast Brazil

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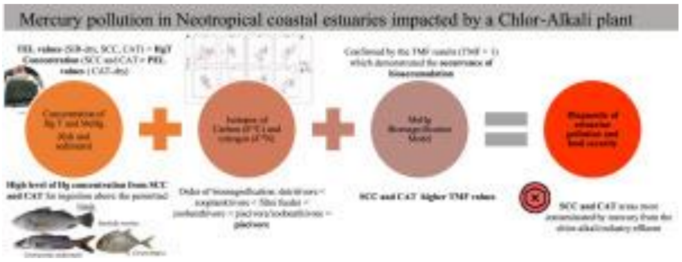
Abstract :

The present study reports the concentration of HgT and MeHg in sediments and food webs in estuarine and coastal areas of Northeast Brazil, which have been subject to different impacts, mainly by chlorine and alkali companies. The results showed that the HgT in the sediment varied from 1.7 to 1186 $ng.g^{-1}$ and from 3.3 to 2163 $ng.g^{-1}$ in the organisms. A strong positive relationship between the levels of Hg in the sediment and the organisms was detected. Methylmercury represented 42 to 99% in the muscles of fish and invertebrates. Biomagnification processes were identified for all study areas evaluated according the trophic magnification factor (TMF), which ranged from 3.1 to 12.3. We found significant negative correlations with $\delta^{13}C$ values and mercury concentrations and positive correlations between $\delta^{15}N$ values and mercury, typical of Hg trophodynamics. This suggests a direct impact of the level of site-specific contamination on local food web and the ecosystem, making continuous monitoring studies necessary to assess food security and the risks that the riverine community is exposed as a result of ingesting mercury contaminated fish.

Graphical abstract



Highlights

► Hg pollution and C and N stable isotopes were examined in four Brazilian estuaries. ► Increased concentrations of HgT between sediments and organisms were measured. ► Methylmercury represented 42 to 99% of HgT in the muscles of fish and invertebrates.

Keywords : Fish, Invertebrate, Sediment, Methylmercury, Biomagnification factor, Water contamination

2. Introduction

Bleach (sodium hypochlorite) and sodium hydroxide are consumer chemical products widely used. These products are industrially fabricated from sodium chloride solutions by different electrolytic processes, including those employing a mercury (Hg) cell (Crook and Mousavi, 2016; Mihaiescu et al., 2012), which is considered the oldest and the most polluting processes for the environment and are still being used. In Brazil, nine companies produce Chlor-alkali products and their subproducts. Among these companies, four of them employ the Hg cell process, accounting for 14% of the annual production, and are located in northeast Brazil (ABICLOR, 2012).

Brazil has one of the longest coastlines of the world and an enormous mangrove area (13.400 km^2). Due to their multiple uses and the ecosystem services they provide, coastal and marine resources are fundamental for the development of the country (Burke et al., 2001). The northeast is one of the most densely populated coastal regions of Brazil, with the Pernambuco State standing out as the epicenter of this concentration. Urbanization and degradation of coastal ecosystems have had multiple impacts, mainly due to domestic pollution, industrial activity, and habitat degradation and loss, all of which are most severe around the main urban zones (Mérigot et al., 2017).

Anthropogenic impacts related to elevated Hg levels in sediments of the drainage basin of the North coast of Pernambuco (Northeastern Brazil) have already been documented (Gondim, 2015; Lima et al., 2009; Lima, 2008). Early reports started in 1963, right after the installation of a chlor-alkali plant. In 1982, new regulations were imposed in Brazil (e.g. Decree 87.561/1982 and Law 9.976/2000) prohibiting the development of new installations and/or the expansion of already existing sites employing the Hg cell technique. Nevertheless, as already observed in other countries (Birkett et al., 2002; Fitzgerald and Lamborg, 2013; Levin, 2015), the contamination problem has persisted because Hg is highly stable in the environment and bioavailable through its biogeochemical cycle for several years and decades, even after the source of contamination has disappeared.

Worldwide studies on Hg contamination by Chlor-alkali plants evidence local impacts on coastal ecosystems (Adams and Paperno, 2012; Onsanit et al., 2012), with Hg leading to possible pathological alterations in the organisms through trophic pathways (Bravo et al., 2010; Soto et al., 2011). Since fish occupy a high trophic level and are consumed by the human population, the toxic organic form, methylmercury (MeHg), is likely to be transferred to humans (Condini et al., 2017; Hosseini et al., 2013; Wu et al., 2019). The degree of human dependency on coastal ecosystems is very high in northeast Brazil. The Pernambuco coast has 34 fishing communities with around 12 000 fishermen (Lessa et al., 2006), which are dependent on estuarine and marine resources for food supply and commercial trade (Lira et al., 2017; Viana et al., 2015). Understanding the concentration and speciation of Hg at different trophic levels from this region is essential to assess the risk of exposure of Hg for the local biota and humans.

The objectives of this study are to i) document total mercury (HgT) and MeHg concentrations in sediments, fish, and in the invertebrate community of four tropical estuarine coastal zones of Pernambuco, northeast Brazil; and (ii) compare and model Hg biomagnification and bioaccumulation in aquatic biota at each site using complementary carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) stable isotope data to diagnose Hg contamination in the study areas and its potential impact on food security of fish consumed by the riverside community.

3. Materials and methods

3.1. Study area and sample collection

Samples were collected in four estuarine and coastal areas of the Pernambuco state, northeast Brazil: 1) The Estuarine Complex of the Santa Cruz Channel - SCC (including the estuarine area and Itamaracá Island) and 2) the Catuama coastal zone– CAT, located in the northern zone of Pernambuco; 3) The Sirinhaém coastal zone - SIR and and 4) the estuary of Ipojuca River - SUAP (including the Suape Port area) both are located in the southern zone of Pernambuco (Fig. 1).

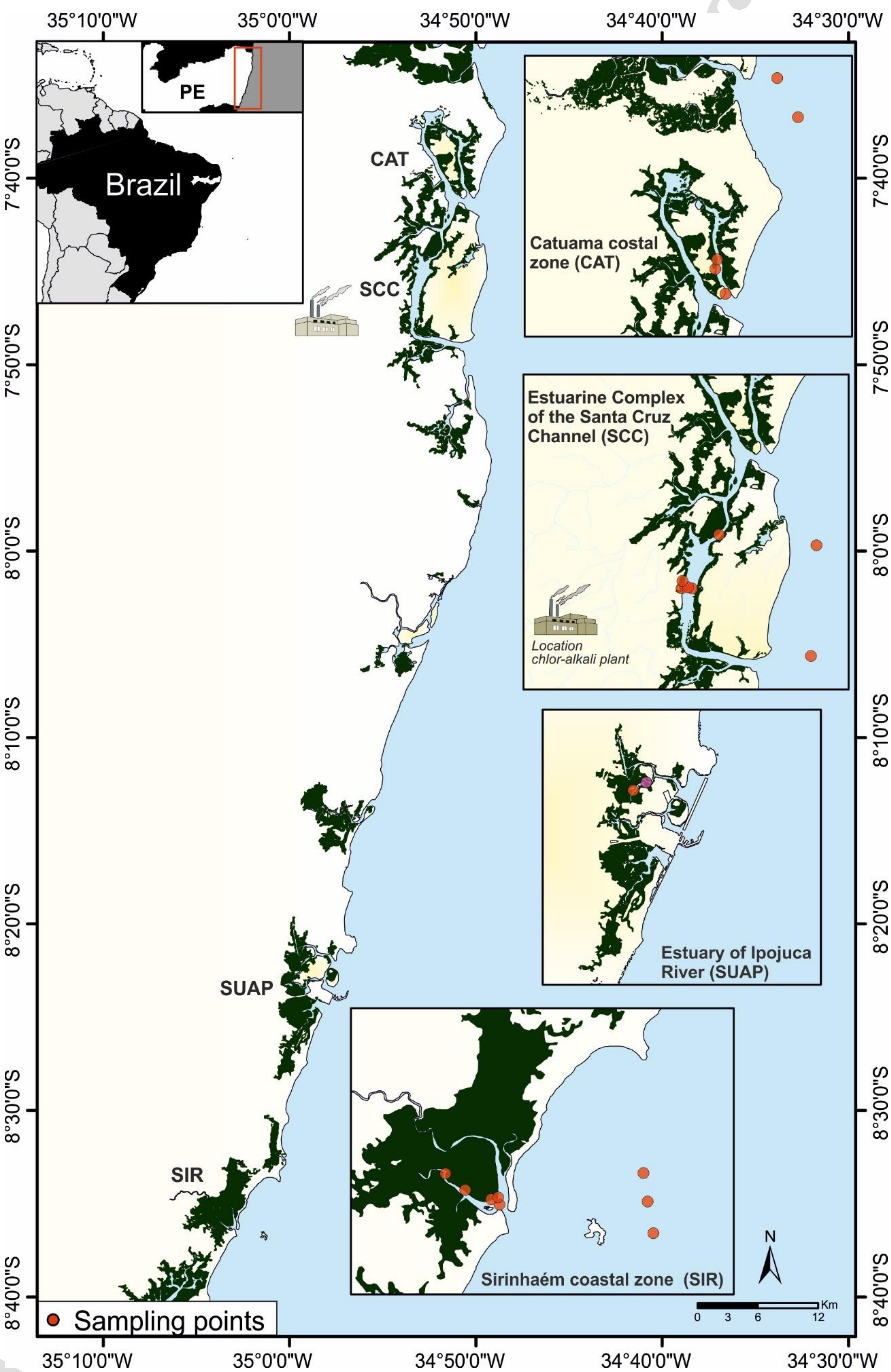


Figure 1 –Study sites in the coastal zone and the mangrove area (green surface) of Pernambuco, Brazil, chlor-alkali plant (represented by illustration in SCC), CAT-

Catuama coastal zone, SCC- Estuarine Complex of de Santa Cruz Channel, SUAP- Estuary of Ipojuca River, SIR - Sirinhaém coastal zone.

The Sirinhaém coastal zone (SIR) has 9.5 km long, 350 m wide, and 1.2–4.5 m in depth. It is located in the Marine Protected Area of Guadalupe, which covers 450 km^2, encompassing Atlantic Forest, rivers, estuaries, mangroves, and coral reefs. Sirinhaém is classified as a coastal plain estuary (Lira et al., 2010; Silva et al., 2011). The estuary of Ipojuca River (SUAP) has a hydrographic basin of 3,800 km^2 and an approximate range of 15 km. The mangrove suffered degradation following the construction of a large industrial port complex between 1973 and 1976, involving chemical, shipping, and logistics companies. The port resulted in a change in the tidal cycle, strong sedimentation and high deposition of suspended sediments, increasing water turbidity and turning the mouth of the estuary into a coastal lagoon; these effects led to a decrease in local depth that increased salinity (Neumann et al., 1998; Paiva and Araújo, 2010).

The estuarine complex of the Santa Cruz Channel (SCC) has a U-shape, is about 22 km long, and has variable width that can reach up to 1.5 km. Depth ranges from 4 to 8 m, with higher values (10–17 m) close to the ocean discharges, which consist of different rivers. The chlor-alkali plant was established in this complex in 1963 (Fig. 1). The SCC is considered the largest estuarine ecosystem of Pernambuco state, with irregular morphology where the tributaries run off to adjacent regions (Lira et al., 2017; Silva et al., 2011). The SCC is connected to the Catuama coastal zone (CAT), via a *ria*-type estuary (Silva et al., 2011). River discharge is the principal source of nutrients, followed by sediment resuspension, mangrove litter, waste input, terrestrial runoff, and atmospheric input (Medeiros et al., 2001).

The sediment, fish, and invertebrates were collected in the estuarine and an adjacent coastal region from January to April and August to September 2015, representing the dry and rainy seasons, respectively. As the estuaries and the coastal area show distinct dynamics, different sampling protocols were used (according to Lira et al., 2017; Mérigot et al., 2017; Silva et al., 2015). Block net and beach seines were adapted for each estuary to cover most of the studied areas: shallow coastal areas and sand/mud banks (beach seine), and flooded mangrove and channels (block net). The seine net was used in the Santa Cruz Channel and the beach seine in the Sirinhaém estuary. The two operations lasted no longer than 20 min and were repeated three times. Along the mangrove forest, channel block nets were set, measuring 70 and 90 m long, 2.5 m high, with a mesh size of 50 mm. At low tide, the net was anchored to the bottom. At slack high-water, the net was deployed and attached to stakes and pulled taut so that it was above the water, enclosing the mangrove area. Blocking was initiated at the end of high tide and continued throughout the entire ebb tide cycle (approximately 6 h). In the coastal environment, the gill net and the double trawler were used. Double trawler consisted of a network 10 m in length with a mouth of 6.10 m, with 30 mm and 25 mm mesh size in the net body and cod end, respectively. Data collection consisted of three hauls lasting two hours each. The gill net was 690 m long and had mesh sizes of 50, 70, and 80 mm.

In the laboratory, the biological specimens, consisting of fish and invertebrates, were identified following specific taxonomic keys (Allen, 1985; Carpenter, 2002; Figueiredo and Menezes 2000; Whitehead, 1985, Tavares 2002). A total of 16 species of fish of different trophic guilds and invertebrates were analyzed (Table S1).

The classification of the diet of each fish species was based on local studies of stomach content or, when not available, on the literature (Freitas et al., 2011; Leão et al., 2018; Lira et al., 2017, 2021; Mendoza-carranza, 2003; Monteiro et al., 2009; Vasconcelos Filho, 1979; Vasconcelos Filho et al., 2003). The trophic guild was classified according to Elliott et al. (2007) and Mourão et al. (2014): Filter feeder (FL);

Zooplanktivore (ZP); Detritivore (DV); Zoobenthivore (ZB); Omnivore (OV); Piscivore/Zoobenthivore (PVZB) and Piscivore (PV). Individuals were measured (total length for fish and shrimp, and carapace width for crab, in cm) and weighed (g). A minimum of two individuals of each species was analyzed for each season (dry and rainy), areas (CAT, SCC, SUAP, and SIR), and environment (coastal and estuary). For each specimen, the muscle of the dorsal region (fish), a cephalothorax (shrimp), or the cheliped muscle (crab) were removed, cleaned with distilled water, and dried at 60°C for 48 hours.

For the intertidal zone and the coast, about 5 g of sediments were collected manually using a spatula during the low tide. For the main channel of the estuary, a core of 20 cm length and 10 cm diameter was taken. For each season, area, and environment, samples were collected in triplicate, using the three first mm of the surface layer, representing the SOM (sediment organic material). The sediment was then fractionated on meshes of 600 µm (coarse fraction) and 63 µm (fine fraction), to account for the effect of changes in sediment granulometry based on the contrasted hydrological/accumulation conditions present at the different sampling sites.

3.2. Total mercury (HgT) and methylmercury (MeHg) concentration analysis

The analysis of HgT in biological materials and sediments (ng $Hg.g^{-1}$, dry weight) was performed with a DMA-80 (Milestone, USA) and AMA-254 (Leco, Europe) for the sediments and the biological samples, respectively.

To investigate the robustness, accuracy, and precision of measurements, three biological and one sediment certified reference materials (CRM), with varying proportions of MeHg and HgT levels, were tested: TORT-3 (lobster hepatopancreas), IAEA-436 (tuna tissue), SRM2976 (mussel tissue) and Mess-3 (marine sediment). For each batch of ten samples, three blanks, and three CRMs were analyzed.

Methylmercury (MeHg) in biological samples were extracted and separated according to Masbou et al. (2013). The analysis of the final purified MeHg fractions was performed by cold vapor atomic fluorescence spectroscopy (CV-AFS). HgT concentrations in both sediment and biological samples were determined on dry material. HgT and MeHg concentrations for biological samples were converted to wet weight (wet ng.g^{-1}) with applying a moisture factor, previously determined for each sample (Table S1).

To assess the potential impact of Hg levels, HgT concentrations recorded in sediments were first compared to the Hg guidelines proposed by the "Canadian Sediment Quality Guidelines for the Protection of Aquatic Life" (CCME, 1995). These guidelines were developed to evaluate the degree of contamination and its likely impact on the environment, and consist of Threshold Effect Levels (TELs = 130 ng Hg.g^{-1}) and Probable Effect Levels (PELs = 700 ng Hg.g^{-1}): below the TEL- the minimal effect range within which adverse effects rarely occur; between the TEL and PEL - the possible effect range within which adverse effects occasionally occur; above the PEL - the probable effect range within which adverse effects frequently occur (Macdonald et al., 1996). Afterward, HgT and MeHg levels recorded in biological samples were compared to the World Health Organization (WHO) guidelines (Canady et al., 2001; World Health Organization, 1976; 1000 ng Hg.g^{-1} for predator and 500 ngHg.g^{-1} for the other fish).

3.3. Stable isotope analysis and trophic level position

To determine food web structure, carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) stable isotopes were determined for each sample. The isotopic measurements were performed by continuous flow Thermo Delta V+ mass spectrometer coupled via a Thermo ConFlo IV interface to a Thermo Flash 2000 Elementary Analyzer at the Pôle de Spectrométrie Océan (PSO, Plouzané, France). Standards used for $\delta^{13}C$ and $\delta^{15}N$ were Sigma-Peptone-Home STD, IVA- casein, IAEA-Sucrose, IAEA-N1, IAEA-N2, and IAEA-Caffeine. The home standard Thermo-Acetanilide was used for analytical precision of the analysis for every six samples, indicating the precision of ± 0.11‰ for carbon and ± 0.07‰ for nitrogen.

The trophic level (TL) of each species was estimated from $\delta^{15}N$ values using the oyster species *Crassostrea rhizophorae* as a baseline. Except, for *Mugil* spp. in SCC and CAT, where *G. stomatus* of near N value was considered as the most appropriate baseline. TL of one consumer was computed as:

$$TL_{consumer} = [(\delta^{15}N_{consumer} - \delta^{15}N_{baseline}) \times \Delta^{-1}] + TL_{baseline.}$$

with $TL_{baseline} = 2$ for both baselines, and $\Delta = 3.4‰$ as the isotopic discrimination factor for $\delta^{15}N$ (Post, 2002).

3.4. Methylmercury biomagnification model

To predict accumulation through the trophic web, we applied a biomagnification model based on trophic magnification factors (TMF) and nitrogen stable isotopes, according to Borgå et al. (2012) and McLeod et al. (2015). $\delta^{15}N$ values can be used to estimate relative trophic level, and TMF was estimated as the slope of the linear regression of log-transformed MeHg concentrations versus $\delta^{15}N$ values:

$$\log_{10}(MeHg) = b \cdot \delta^{15}N + a \quad \text{and} \quad TMF = 10^{b}$$

where the intercept a is the concentration of MeHg incorporated at the base of the food web and b is the slope from the linear regression. A TMF> 0 indicates that biomagnification has occurred (Lavoie et al., 2013).To investigate whether the slope *b* was significantly different from 0 (i.e., if there was disequilibrium), a Student's *t*-test was performed ($H_0 = 0$), with a confidence level of 95% (Zar, 2010). The differences between areas by environment were also compared with *t*-tests.

3.5. Data analysis and statistics

Differences in HgT and MeHg were tested for the sediment and the organisms in different areas (SIR, SUAP, SCC, and CAT), during both seasons (dry and rainy), two sediment fractions (63 and 600 µm) and environment (coastal and estuary). We used two-way ANOVA and Tukey's *post hoc* tests with data square-root transformed if required (Zar, 2010) or Kruskal-Wallis non-parametric tests including multiple comparisons Z scores. Pearson's correlation coefficient was used to test for correlations between HgT in sediments and organisms, and between HgT and the isotopes δ^{15}N and δ^{13}C, by season and area (Zar, 2010). All data were log-transformed.

A heat map visualization was performed to investigate the relationships between HgT concentrations in organisms about study area and seasonality. Data were square-root transformed and clustering was done using the Bray-Curtis dissimilarity and the hierarchical complete linkage method. The color scale mosaic represents the HgT concentration intensities (Wilkinson and Friendly, 2009).We used the *gplot* package from the R program (Warnes et al., 2015).

4. Results and discussion

4.1. Mercury concentrations and distribution in estuarine sediments

Total mercury concentrations (HgT) in the sediment compartment ranged from 1.7 to 1186 $ng.g^{-1}$(Table 1), with a mean value of 288 ± 54 $ng.g^{-1}$. HgT concentrations in the fine sediment fraction (< 63 µm; Table 1) are significantly higher than that of the coarse fraction (> 63 µm and < 600 µm) at all sites and for the two seasons (Kruskal-Wallis $p < 0.001$), due to the strong affinity of Hg for small particles classes, with enhanced specific surface and organic matter contents (García-Rico et al., 2006). Overall, HgT concentrations in the North area (CAT and SCC) are 4-5 times higher than those found in the south coast (SIR and SUAP) (Kruskal-Wallis $p < 0.001$). When size fractions were considered, the fine fraction from CAT exhibited the highest concentrations during the dry season and was significantly different from SCC. During the rainy season, the coarse fraction from CAT had a lower concentration than SCC in the North area (two-way ANOVA, $p <0.05$, Table 1). HgT concentrations in southern areas (SIR and SUAP) were similar, except during the dry season, with lower HgT concentration in SUAP for both the fine and coarse fractions (two-way ANOVA, $p < 0.05$, Table 1). The lower HgT concentrations in SUAP may be associated with the similarity of an anthropic source with a low potential for mercury input in both areas, such as industrial and domestic waste with low mercury enrichment (CPRH, 2001). HgT concentrations in CAT (mesh 600 µm: 736 ± 158 and mesh 63µm: 1024 ± 58 $ng.g^{-1}$) and SCC (mesh 600µm: 547.5 ± 126.4 and mesh 63µm: 520.2 ± 154.4 $ng.g^{-1}$) were above the TEL (130 $ng.g^{-1}$) and PEL (700 $ng.g^{-1}$) guidelines, mainly during the dry season.

Table 1 – Total mercury concentrations (ng Hg.g^{-1}, dry weight) in sediments from the coastal zone of the Pernambuco region, Brazil. North zone: CAT- Catuama coastal zone and SCC – Estuarine Complex of the Santa Cruz Channel; South zone: SIR – Sirinhaém coastal zone and SUAP – Estuary of Ipojuca River; Mesh sizes: 600 and 63 µm; SE: Standard Error. Bold results correspond to locations where Hg concentrations exceed the threshold effect levels (TEL: 130 ng Hg.g^{-1}, dry weight) and probable effect levels (PEL: 700 ng Hg.g^{-1}, dry weight).

		63µm			600µm		
Area	**Season**	**Samples**	**Min-Max**	**Mean ±SE**	**Samples**	**Min-Max**	**Mean ±SE**
CAT	Dry	4	863 – 1138	**1.0248± 58.1**	4	511 – 1186	**735 ± 158**
	Rain	4	364 – 514	**456± 33.9**	4	74.8 – 229	**147 ± 36.6**
SCC	Dry	5	242 – 955.7	**547 ± 126**	7	1.7 – 794	**520 ± 154**
	Rain	4	403 – 525	**468 ± 29.4**	7	3.4 – 355	**293 ± 39.8**
SIR	Dry	6	103 – 306	**149± 31.5**	4	31.6 – 135	89.2 ± 21.9
	Rain	4	96.7 – 134	113* ± 7.8	4	54.1 – 109	85.3 ± 14.3
SUAP	Dry	5	74.1 – 109	83.7* ± 6.4	4	2.7 – 92.4	33.5 ± 20
	Rain	2	87.2 – 90	88.6* ± 1.4	2	30.9 – 56.8	43.8± 12.9

HgT values in the sediment exceeded the acceptable limit for maintenance of the biota according to the areas and season (Table 1) in CAT and SCC. Lima (2008) evaluated the evolution of the sediment contamination by comparing sediment cores over approximately 150 years (1851 to 2004) in the same area. This author observed that the concentration of Hg at the base of the core was close to 150 ng.g^{-1} (Table 2) and increased toward the top, exceeding 8 times the value established by PEL. The authors attributed this substantial increase to a single pollution source, which was the industrial production of chlor-alkali plant in the region. Studies conducted in the same region from 1981 showed no subsequent reduction in Hg contamination in the sediment, with values ranging between 110 and 3700 ng.g^{-1} (Table 2) (Gondim, 2015; Lima et al., 2009; Lima, 2008). Meyer et al. (1998) observed HgT between 300 and up to 20500 ng.g^{-1} in the grain size fraction < 63 µm (Table 2), and between 430 and 5560 ng.g^{-1} in the suspended matter.

The HgT concentrations observed in this study are considerably high and similar to other areas also impacted by chlor-alkali plants worldwide (Table 2). Specifically, in the Northern area (CAT and SCC), the concentration of Hg ranged from 147 to 1024 ng.g-

1, evidencing the persistent contamination by this trace metal in relation to previous studies. Hg adsorption occurs in both granulometries (63 and 600) fractions evaluated, but the higher clay and organic matter content of the smaller fraction (63) results in greater adsorption and metabolization of mercury into its organic species, and longer persistence in the environment. It is important to consider that the study area, located in the intertidal zone of the estuary, is a zone of high hydrological dynamics influencing the sedimentation of mercury. Moreover, the decrease in the concentration of Hg in the soil may be linked to the sedimentation rate of non-enriched geological material as reported by Albuquerque et al.(2019).

Gondim (2015) and Lima (2008) concluded that Hg transfer occurred from the site where the metal was discharged (via the river) into the estuary and Santa Cruz Channel (SCC), so the metal in the sediment was deposited into the river flow. In addition, Lima et al. (2009) showed that the deposition occurs mainly on the banks of the channel, because with the less interference of the currents occurs the greatest accumulation of fine particles, justifying an influence that is still measurable today.

Table 2- Total mercury concentrations (ng $Hg.g^{-1}$, dry weight) in the sediment of this study area and other coastal areas also contaminated by chlor-alkali industrial activities.

Location	THg ($ng.g^{-1}$)	Sampled year	Authors
Study area – Brazil			
Botafogo River	71–222 [a]	1851–1961 [b]	Lima (2008)
Botafogo River	398–5948 [a]	1963 [c] –2004	Lima (2008)
Botafogo River	110–3700	1981 [d]	Lima et al. (2009)
Santa Cruz Channel	300–20500	1993–1994	Meyer et al. (1998)
Botafogo River	130–240	2004–2006	Lima et al. (2009)
Botafogo River	480–6900	2011	Gondim (2015)
Botafogo River	130-10440	2017	Araújo et al (2019)
Botafogo River	100-14400	2015	Araújo et al. (2021)
Itapessoca River	40-1290[a]	2017	Albuquerque et al. (2019)
Santa Cruz Channel	**147–1024.3**	**2015**	**This Study**
Other regions - Brazil			
Guanabara Bay	42–7506	2005	Machado et al. (2008)
Portugal			

Estarreja	117–49233	1998	Inácio et al. (1998)
France			
Thur River basin	430–13000	2001–2002	Hissler and Probst (2006)
Spain			
Cinca River	15–400	2002	Raldúa et al. (2007)
Cuba			
Sagua River	160–9700	Before 2015	Bolaños-Álvarez et al. (2016)
USA			
Androscoggin River	33–2045	2010–2011	Buckman et al. (2015)

[a] Sediment core.
[b] Without contamination before the establishment of the chlorine industry.
[c] Establishment of the chlorine industry.
[d] First monitoring in the area by CETESB - Environmental Company of the State of São Paulo.

Hg contamination was higher in sediments during the dry season than during the rainy season (Table 1). In tropical latitudes, one of the main factors influencing the concentration or dilution of Hg is the volume of river discharge (Costa, et al., 2009; Barletta et al., 2012; Di Beneditto et al., 2013).. In areas adjacent to those of the present study, Costa et al. (2009) and Lima (2008) showed that when the rainfall increases during the rainy season, river drainage dilutes Hg.

These results indicate that the Hg concentrations in the sediments at the four investigated sites are a function of: (i) the distance of the source of Hg pollution (chlór-alkali plant), e.g., SCC and CAT are close to important sources of Hg and presented high Hg values whereas in SUAP and SIR, away from strong mercury sources, the concentration is low; and (ii) the hydrological control of the estuarine system between wet and dry seasons.

4.2. Mercury concentrations, speciation, and distribution in the estuarine food webs

Similar to what was observed for sediments, the HgT concentrations in estuarine organisms of CAT and SCC were significantly higher than those reported in SIR and

SUAP (Kruskal-Wallis, $p < 0.001$) (Table S2 to S5 in supplementary material). When the areas were compared between the coastal and estuarine environments, no significant differences were found for CAT and SCC (Kruskal-Wallis, $p>0.05$). However, significant differences were found between seasons, with higher concentrations observed in the dry season for all areas (Kruskal-Wallis, $p<0.05$). This may be linked to a reduction of river discharge due to lower freshwater input from natural sources, such as rainfall. In contrast, the increased river discharge during the rainy season causes the dilution of contaminants and/or their displacement within the estuary. A strong relationship was observed between the HgT concentrations in sediments and the corresponding Hg levels in organisms for CAT and SCC (north area) (Pearson, $r= 0.82$, $p < 0.05$) suggesting direct site-specific contamination of the local food webs and the close ecosystem. In contrast, SIR and SUAP (south area) did not exhibited a significant relationship between HgT concentrations in the sediment and the corresponding Hg levels in organisms (Pearson, $r= 0.70$, $p >0.05$).

The total mercury concentration observed in organisms ranged from 3 to 2163 $ng.g^{-1}$(wet weight) (Table S2 to S5). We recorded high concentrations above WHO guidelines (Fig.2) for some species, such as *Centropomus undecimalis* and *Bardiella ronchus* for CAT as well as *Bardiella ronchus* and *Caranx hippos* for SCC.

Considering that some fish species are more generalists than others, the contamination by Hg can occur indirectly via consumption of different resident invertebrates and fishes that have fed on other contaminated sources; this can lead to the greater the intake of Hg. However, further studies focused on prey and predators need to be developed to investigate this issue. The increase in the mercury concentration can also be influenced by the variability in the consumption of small fish by larger fish (Hosseini et al., 2013), such as *Caranx hippos*. Methylmercury represented 42 to 92% of HgT concentrations in invertebrates and 56 to 99% in fish (Tables S2 to S5). This means that the coastal area of Pernambuco offers favourable conditions for the methylation of inorganic mercury and the bioavailability of *in situ* produced MeHg to these organisms. Piscivore and piscivore/zoobenthivore fish showed higher MeHg concentrations than invertebrates, with methylmercury accounting for 70 to 90% of HgT.

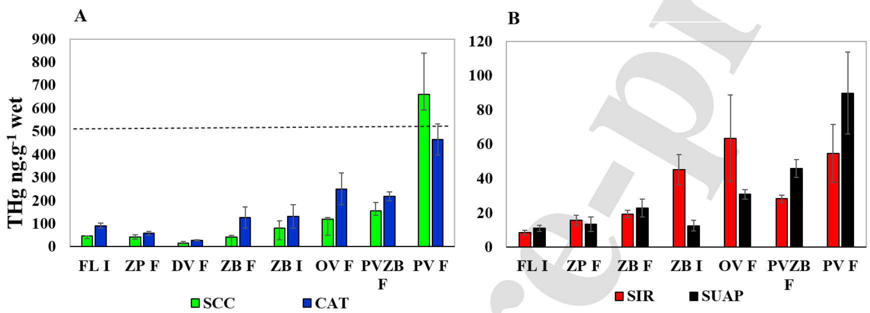


Figure 2 –Total mercury for organisms by area and trophic guild. A) CAT – Catuama coastal zone and SCC – estuarine complex of Santa Cruz Channel; B) SIR – Sirinhaém coastal zone and SUAP – estuary of Ipojuca River. Filter feeder (FL); Zooplanktivore (ZP); Detritivore (DV); Zoobenthivore (ZB); Omnivore (OV); Piscivore/Zoobenthivore (PVZB); Piscivore (PV); I – Invertebrate and F – Fish. The horizontal dashed line at 500 $ng.g^{-1}$ indicates the limit recommended by the WHO for non-piscivores.

Two groups were observed considering the distribution of the organisms according to the relationship between trophic guild and HgT: (i) one representing the area contaminated by anthropogenic mercury (northern zone) and (ii) the area reflecting more natural Hg inputs (southern zone) (Table1, Fig. 3). The dendrogram also showed the formation of two groups segregated by trophic position, and the formation of four subgroups differentiated by accumulated Hg concentrations.

The first group was represented by organisms that occupy lower levels compartments of the food web and present lower HgT concentrations, such as zooplanktivores (ZP), zoobenthivores (ZB), and detritivores (DV). The second group of organisms is formed by the carnivorous generalist and specialist, such as omnivores (OV), piscivores/ zoobentivores (PVZB), and piscivores (PV), with higher Hg concentrations

(Fig. 3). The mean HgT concentrations by trophic guild revealed that, piscivores had higher Hg concentrations compared to the other trophic guilds (Fig. 2) (Kruskal-Wallis, p<0.001) for all areas, except to SIR where omnivorous Hg concentrations were higher.

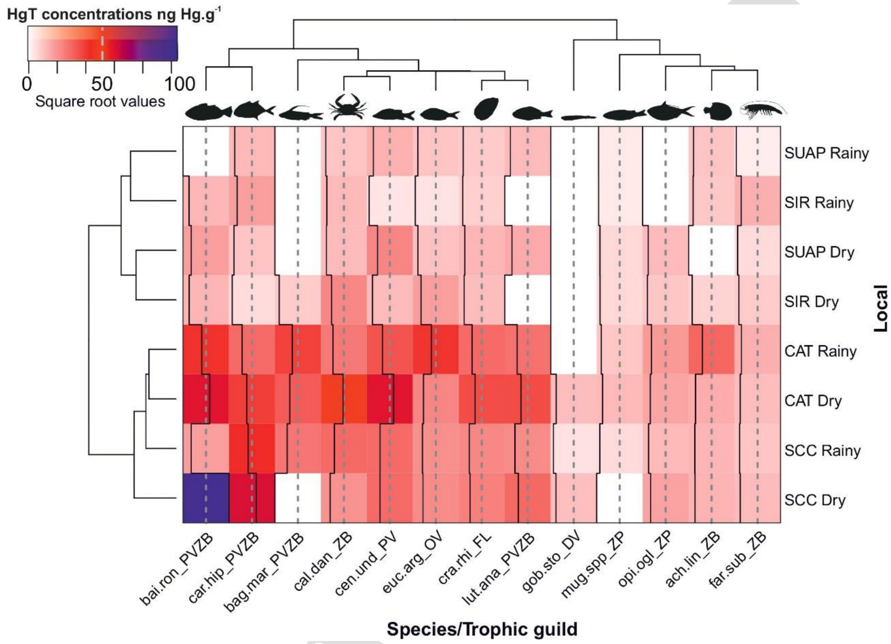


Figure 3 – Cluster heatmap of total mercury concentrations in organisms from study areas using a color scale ranging from light pink (low concentration) to purple (high concentration). CAT – Catuama coastal zone and SCC – estuarine complex of Santa Cruz Channel; SIR – Sirinhaém coastal zone and SUAP – estuary of Ipojuca River. Filter feeder (FL); Zooplanktivore (ZP); Detritivore (DV); Zoobenthivore (ZB); Omnivore (OV); Piscivore/Zoobenthivore (PVZB); Piscivore (PV); ach.lin – *A. lineatus*; opi.ogl – *O. oglium*; far.sub – *F. subtilis*; gob.sto – *G. stomatus*; mug.spp - *Mugil spp.*; cal.dan – *C. danae*; cen.und – *C. undecimalis*; euc.arg – *E. argenteus*; bag.mar – *B. marinus*; cra.rhi – *C. rhizophorae*; lut.ana – *L. analis*; bai.ron – *B. ronchus*; car.hip – *C. hippos*.

Among the species at the base of the food web (first group), the zooplanktivore *O. oglium* and the zoobenthivore fish *A. lineatus* presented the highest mercury concentrations during the rainy season, mainly in CAT coastal areas. On the other hand, the detritivore *G. stomatus* and zooplanktivore *Mugil spp.* showed the highest Hg concentrations during the dry season (Fig. 3, Tables S2 to S5). In the second group, the piscivore/zoobenthivore *B. marinus* and the omnivore *E. argenteus* showed the highest Hg concentrations during the rainy season, while the other species showed enriched Hg concentrations during the dry season. The predators *B. ronchus* and *C. hippos* displayed the highest HgT levels relative to all other organisms and therefore they were grouped as similar in the dendrogram, mainly in SCC and CAT, in dry season (Fig. 3, Tables S2 to S5). High Hg concentrations were also reported for the filter feeder *C. rhizophorae* and the zoobenthivore *C. danae* of SCC, displaying similar Hg concentrations to organisms of higher trophic levels (Fig.3, Tables S2 to S5).

Our results demonstrate the occurrence of biomagnification along the trophic chain, in the order of detritivore < zooplanktivore < filter feeder < zoobenthivore < piscivore/zoobenthivore < piscivore, increasing from the lower trophic position, represented by invertebrates and primary consumers up to the fish predators. It is well documented that mercury, mainly in the form of methylmercury, is more concentrated at higher trophic levels, where predators feed on contaminated prey (Di Beneditto et al., 2013; Hosseini et al., 2013; Scudder Eikenberry et al., 2015).

4.3. Mercury biomagnification trends in the estuarine food webs of the Pernambuco region

For CAT and SCC areas, correlations between HgT and MeHg with $\delta^{13}C$ were negative and significant: the more enriched the samples in ^{13}C, the lower their HgT concentration (Fig. 4, Table S2-S3, Pearson = Dry: -0.69 (CAT), -0.78 (SCC), $p < 0.05$ and Rainy: -0.62, $p < 0.05$ and -0.52, $p>0.05$, respectively CAT and SCC). Enriched carbon values (-17.05 to -13.27) were found in the low trophic guilds' species, such as *Mugil spp.*, *O. oglium*, *G. stomatus*, *E. argenteus*, *C. danae*, *F. subtilis*, and juveniles of

C. hippos. However, in SIR and SUAP areas (south zone), the results showed weaker correlations for both seasons, but tended to be negative in the dry season and slightly positive during the rainy season (Fig. 4, for SIR Pearson = Dry: -0.08, $p>0.05$; Rainy: 0.47, $p > 0.05$; for SUAP Pearson= Dry: -0.28; Rainy: 0.43, $p>0.05$).

Correlations between HgT and MeHg with $\delta^{15}N$ were higher during the dry season than the rainy season, in both areas (Fig.5). In CAT, the Pearson correlation for the dry season was 0.80 for HgT and 0.77 for MeHg and, in the rainy season, 0.73 for HgT and 0.78 for MeHg ($p<0.05$, Fig. 4-5). Finally in SCC, the correlation between HgT and MeHg with $\delta^{15}N$ were 0.80 and 0.90 respectively. This result indicates that Hg levels increase with trophic level (Fig. 5).

The negative correlation between HgT and $\delta^{13}C$ observed in the northern zone can be related to feeding behaviour (trophic guild), considering the nutritional source used by the species. Studies show that primary consumers can assimilate nutrients derived from detritus, macroalgae, microalgae, and seagrass that are the source of carbon and energy at the base of the food web in estuaries (Adams and Paperno, 2012; Claudino et al., 2015). Several authors reported that consumers with lower $\delta^{13}C$ values combined with reduced $\delta^{15}N$ values, have benthic-based prey as their consumption preference (Adams and Paperno, 2012; Fry et al., 2008; Peterson et al., 1985). This corroborates with the increase in exposure and greater accumulation of Hg into biota because most of the Hg contamination is concentrated in the sediment. In an estuary of northeast Brazil, Claudino et al. (2015) discussed that the higher $\delta^{13}C$ values found in fishes probably were a result of the values of this $\delta^{13}C$ in the seagrass and macroalgae which were incorporated by the fishes directly or indirectly via consumption of invertebrates that feed upon mangrove detritus.

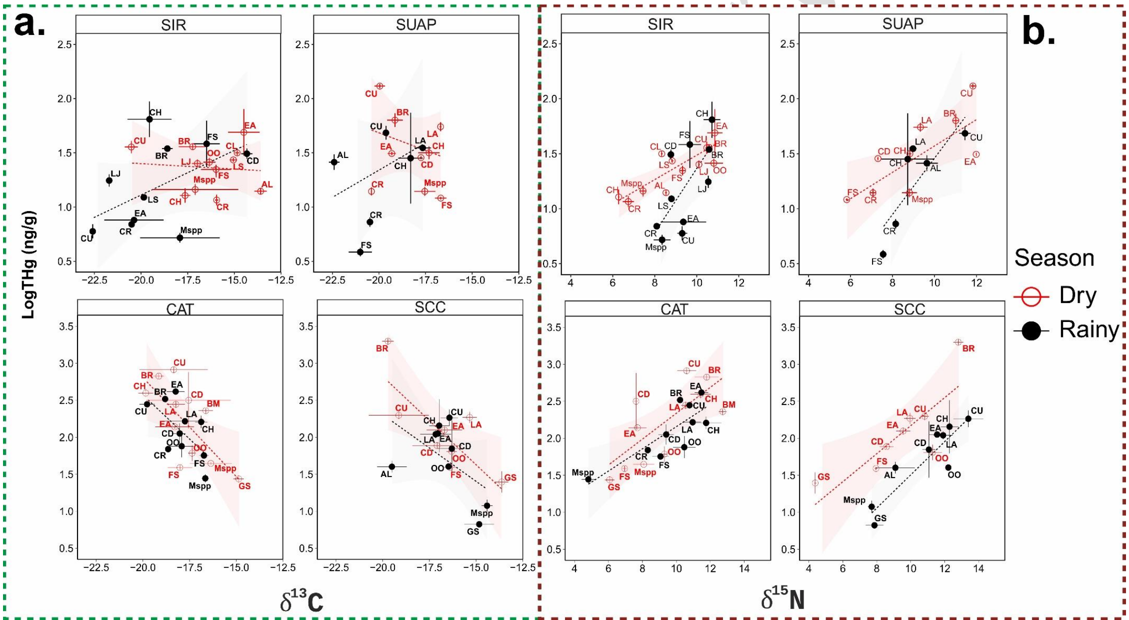


Figure 4 - Scatterplots between nitrogen isotope ($\delta^{15}N$), carbon ($\delta^{13}C$), and the logarithm of total mercury (Log HgT) for the costal of Pernambuco, Brazil. CAT – Catuama coastal zone and SCC – estuarine complex of Santa Cruz Channel; SIR – Sirinhaém coastal zone and SUAP – estuary of Ipojuca River (statistics on table S6 in supplementary material) Species code: AL: *Achirus lineatus;* BM: *Bagre marinus;* BR: *Bardiella ronchus;* CD: *Callinectes danae;* CH: *Caranx hippos;* CL: *Caranx latus;* CU: *Centropomus undecimalis;* CR: *Crassostrea rhizophorae*, EA: *Eucinostomus argenteus*, FS: *Farfantepenaeus subtilis; GS: Gobionellus stomatus;* LA*: Lutjanus analis;*LJ: *Lutjanus jocu;*LS: *Lujanus synagris;* Mspp: *Mugil spp.;* OO: *Opistonema oglium*).

The proportion of HgT as methylmercury with HgT concentrations varied from the mean value of 41± 3% (*F. subtilis*) to 92 ± 5% (*C. danae*) for invertebrates, and from 56 ± 3% (*L. analis*) to 99 ± 19% (*B. ronchus*) for fish, with higher proportions observed in the coastal area of SCC and the estuarine area of SUAP (Tables S3 and S5). There were no significant differences in the proportion of HgT as methylmercury between the dry and rainy seasons when all areas were gathered (two-way ANOVA, $p > 0.05$). The biplot between %MeHg and $\delta^{15}N$ showed a positive correlation, with the top predator presenting a higher accumulation MeHg than those at the base of the trophic chain (Fig. 5).

For all studied areas, these results were confirmed by the methylmercury biomagnification model. All TMFs were higher than 1 ($b \neq 1$, t-test: $p < 0.05$) (Table 3) and there were significant differences in slope in different zones of the same environment (t-test: $p < 0.05$), ranging between 3.1 and 12.3 in SUAP estuary and SCC coastal area respectively, except for SIR and SUAP which were similar. The HgT and, in particular MeHg concentration are magnified up to 12 times for each unit of increase in trophic level as found in SCC. Other documented environments with TMF values higher than 4, such as the Gulf of St. Lawrence in Canada and the northern coast of Rio de Janeiro, are also known to be highly influenced by anthropogenic processes and mercury discharges into the water (Di Beneditto et al., 2012; Lavoie et al., 2010).

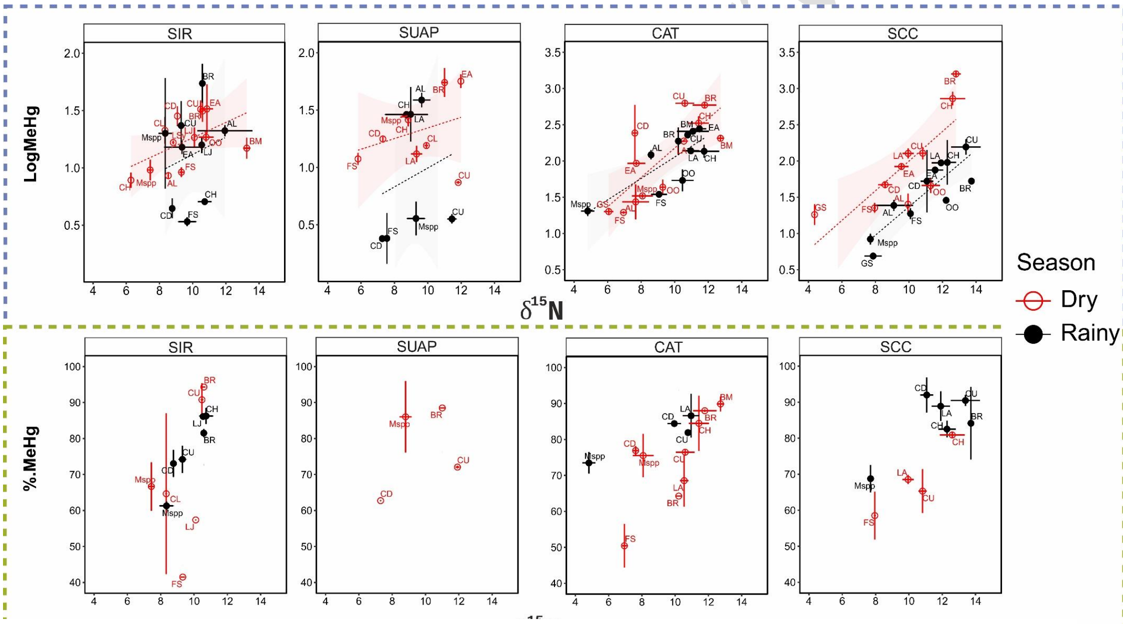


Figure 5- Scatterplots between nitrogen isotope ($\delta^{15}N$), logarithm methylmercury (Log MeHg), and %MeHg for the costal of Pernambuco, Brazil. CAT – Catuama coastal zone and SCC – estuarine complex of Santa Cruz Channel; SIR – Sirinhaém coastal zone and SUAP – estuary of Ipojuca River (statistics on table S7 in supplementary material). Species code: AL: *Achirus lineatus;* BM: *Bagre marinus;* BR: *Bardiella ronchus;* CD: *Callinectes danae;* CH: *Caranx hippos;* CL: *Caranx latus;* CU: *Centropomus undecimalis;* CR: *Crassostrea rhizophorae*, EA: *Eucinostomus argenteus,* FS: *Farfantepenaeus subtilis; GS: Gobionellus stomatus;* LA*: Lutjanus analis;*LJ: *Lutjanus jocu;*LS: *Lujanus synagris;* Mspp: *Mugil spp.;* OO: *Opistonema oglium*).

Table 3- Methylmercury biomagnification model for the coastal zone of Pernambuco, Brazil. N – Number of individuals; S – Number of Species evaluated; *b* = slope of the regression curve; *a* = intercept of the concentration of MeHg in the baseline; CI – Confidence interval; R^2 = Coefficient of Pearson *r*-squared; TL – Trophic level (Min – minimum and Max – maximum); TMFs - Trophic magnification factors.

Area: Environment	N	S	a	95%CI a	b	95% CI b	R^2	TLMin-Max	TMFs
Catuama coastal zone									
Coastal	26	5	-0.361	(-0.986) - (0.263)	0.81	(0.596) - (1.022)	0.72	2-3.81	6.45
Estuary	43	7	-0.184	(-0.837) - (0.468)	0.89	(0.613) - (1.157)	0.51	2-3.34	7.76
Estuarine complex of the Santa Cruz Channel									
Coastal	19	5	-1.346	(-2.823) - (0.130)	1.09	(0.594) - (1.593)	0.54	2-4.59	12.30
Estuary	41	7	-0.635	(-1.305) - (0.035)	0.90	(0.655) - (1.154)	0.58	2-3.95	7.94
Sirinhaém coastal zone									
Coastal	22	6	-1.157	(-2.052) - (0.262)	0.88	(0.560) - (1.198)	0.62	2-3.95	7.58
Estuary	34	6	-0.128	(-0.593) - (0.337)	0.51	(0.330) - (0.686)	0.51	2-3.55	3.23
Suape Port									
Estuary	33	5	0.194	(-0.267) - (0.657)	0.49	(0.312) - (0.669)	0.53	2-3.6	3.10

The regression slopes (*b*) were used to evaluate the biomagnification power of MeHg for the estuaries in the present study (Table 3). Smaller values of *b* indicate low TMF, and higher values, the opposite. The results clearly showed values much higher than those observed worldwide (CAT: 0.89, SCC: 0.90, SIR: 0.51, SUAP: 0.49), showing that the anthropic inputs transferred to the food webs are higher in the north than in the south zones. This suggests that the Chlor Alkali plant has a direct impact from the site-specific contamination level in SCC and CAT, because of the concentration of mercury in food webs and sediments. In temperate marine ecosystems, *b* fluctuates between 0.235 and 0.260; in tropical waters between 0.140 and 0.833; in polar marine areas from 0.210 to 0.941 and tropical freshwater from 0.08 to 0.430 (Di Beneditto et al., 2012; Lavoie et al., 2013, 2010; Poste et al., 2015; Pouilly et al., 2013; Ruus et al., 2015).

The other parameter of the mercury biomagnification model, the intercept (*a*), can be considered as an estimate of the Hg incorporation at the base of the food web (Borgå et al., 2012). Initially, it is possible to observe an association between the trophic interception and amplification. The lower the value of *a* in SCC (-1.34) the higher the TMF (12.30), and the higher value of *a* in SUAP (+0.19), presented the lowest TMF (3.10). The trophic level may also influence the intercept value as it was possible to observe in the present study since the values of the intercept on the coast were lower than those obtained in the estuary for all areas, consequently, the coastal environments reached the highest maximum trophic level. Thus, through this parameter, it was observed that a SUAP baseline was the least impacted and SCC the one with the greatest impact among the studied areas, pointing out that regardless of local contamination, the range of variation of trophic levels in the area, trophic guild is one of the main factors that interfere in the increase of biomagnification of mercury in the environment. Studies developed by Di Benedito et al. (2012) in Rio de Janeiro corroborate our study about the rate of biomagnification. Lavoie et al. (2013) explained that, in warmer regions, the trophic transfer efficiency of Hg and, therefore, biomagnification would be reduced at each trophic step, which is the opposite of what was observed in this study. Furthermore, these authors and Al-Reasi et al. (2007) observed that high diversity of species, characterized by a complex food web, could potentially reduce the efficiency of trophic Hg transfer. The results of the present study, that high diversity was not associated with reduced biomagnification, also contradict this hypothesis.

High diversity of species found in these regions can mean a longer food web, which typically increases relative bioaccumulation at the top (Post, 2002). Doi et al. (2009) suggested that resource availability and ecosystem size can predict the food-chain length. The two characteristics are present in the estuaries and coastal region of Pernambuco: a heterogeneous resource availability and a highly complex system (Gonzalez et al., 2019; Lira et al., 2017, 2021; Mérigot et al., 2017; Silva-Júnior et al., 2017, Ferreira, 2019). However, from the diversity of species evaluated in the region was not associated with reduced biomagnification.

The significant correlation between HgT and $\delta^{15}N$ ($R^2 > 0.50$) showed the importance of mercury transfer through the food web, confirmed by the TMF results (TMF > 1) which demonstrated the occurrence of bioaccumulation. The use of $\delta^{15}N$ verified the accuracy of the trophic position of species (Lavoie et al., 2010; Scudder Eikenberry et al., 2015). This could explain why, in the northern zone, the organisms of higher trophic levels showed a higher concentration of mercury. The TMF assumes that the main source of the exposure of organisms to contaminants in the diet and, this absorption and transfer occurs faster than elimination, resulting in an accumulation that increases with increasing TL (Borgå et al., 2012).

5. Conclusions

This study is the first to use stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) associated with Hg and MeHg to evaluate the biomagnification and contamination by mercury in food webs in estuarine/coastal zones of Northeast Brazil. The industrial Hg contamination occurring in the Northern Coast of Pernambuco is attributed to a chlór-alkali company installed in 1963, which after about 29 years of direct discharge of mercury-enriched effluents into the estuary, still presents high Hg levels in the sediment, above the acceptable limit for biota in the two areas influenced by this industry (CAT and SCC). The increased concentrations of HgT between sediments and organisms in CAT and SCC areas relative to SIR and SUAP is clear evidence that basal levels of Hg are the main route of Hg concentration transfer along the food web to the upper trophic levels. Among the sources of mercury, the most relevant is the chlór-alkali plant, influencing the biomagnification process that took place in all study areas.

Our results also demonstrate the occurrence of Hg biomagnification along the trophic chain was confirmed by a methylmercury biomagnification model. We found a significant correlation of HgT and MeHg with carbon and nitrogen stable isotope ratios for the four areas, indicating that there is an enrichment of the nitrogen isotope with the increase of trophic level but that the opposite occurs for the carbon isotope, with a negative correlation related to the food sources used by these species.

The biomagnification of mercury, mainly in the form of methylmercury, in areas where the chlor-alkali industry operates is a reality, so it is necessary to improve existing legislation and mainly to provide the continuous monitoring of the areas already impacted, by obligating a complete change of the existing Hg process, by other less polluting technologies. This work reveals that even if the Hg inputs from the chlór alkali industry are over, Hg is highly stable and accumulated in the sediment compartment leading to legacy contamination of the entire nearby ecosystems for decades and likely centuries.

Acknowledgments

This research was supported by the Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE), (Brazilian National Council for Scientific and Technological Developmen (CNPq) and Ciências sem Fronteiras Program (207122/2014-8) and CAPES-COFECUB Program (88881.142689/2017-01). The CNPq financed a productivity research grant Flávia Lucena-Frédou (308554/2019-1). In addition, the present study could not have been done without the work of all the participants in the BIOIMPACT Laboratory and the French cooperation with the GET and LEMAR laboratories.

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6. Supplementary material

Highlight

- Hg pollution and C and N stable isotopes were examined in four Brazilian estuaries.
- Increased concentrations of HgT between sediments and organisms were measured.
- Methylmercury represented 42 to 99% of HgT in the muscles of fish and invertebrates.

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: