



# Biomagnification of mercury through the food web of the Santos continental shelf, subtropical Brazil

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**ABSTRACT:** This study was conducted on the continental shelf surrounding a large metropolitan region on the coast of São Paulo State, Southeast Brazil. This region harbours a large industrial plant and the largest port in Latin America, both of which release pollutants into the Santos–São Vicente estuarine system. High levels of Hg have been reported in sediments and fish from the estuaries and Santos Bay; however, data for the biota in offshore waters are scarce, and the biomagnification of Hg across the food web here has never been assessed. In this study, the trophic structure of the Santos shelf was addressed through the carbon and nitrogen stable isotope compositions of different species across a trophic gradient. We determined the total Hg levels (THg, dry weight) of invertebrates and fish to estimate the rate of biomagnification of this metal in the benthic and pelagic food webs. The lowest mean THg levels were found in zooplankton ( $0.006 \mu\text{g g}^{-1}$ ) and surface-depositivore polychaetes ( $0.011 \mu\text{g g}^{-1}$ ); the highest THg levels were found in the largest fishes: Patagonian flounder ( $0.825 \mu\text{g g}^{-1}$ ), fat snook ( $0.714 \mu\text{g g}^{-1}$ ), and lesser guitarfish ( $0.639 \mu\text{g g}^{-1}$ ). Overall, the Hg concentration in fish was below the recommended limit for human consumption. The THg and  $\delta^{15}\text{N}$  were positively correlated in both food webs; however, the rate of biomagnification was higher and the basal Hg was lower in the pelagic food web. These differences may be related to the differing bioavailability of mercury in water and sediment, the higher diversity of prey and more complex feeding interactions in the benthic food web, and metabolic differences among different taxa.

**KEY WORDS:** Stable isotopes · Marine pollution · Trophodynamics · Southwest Atlantic

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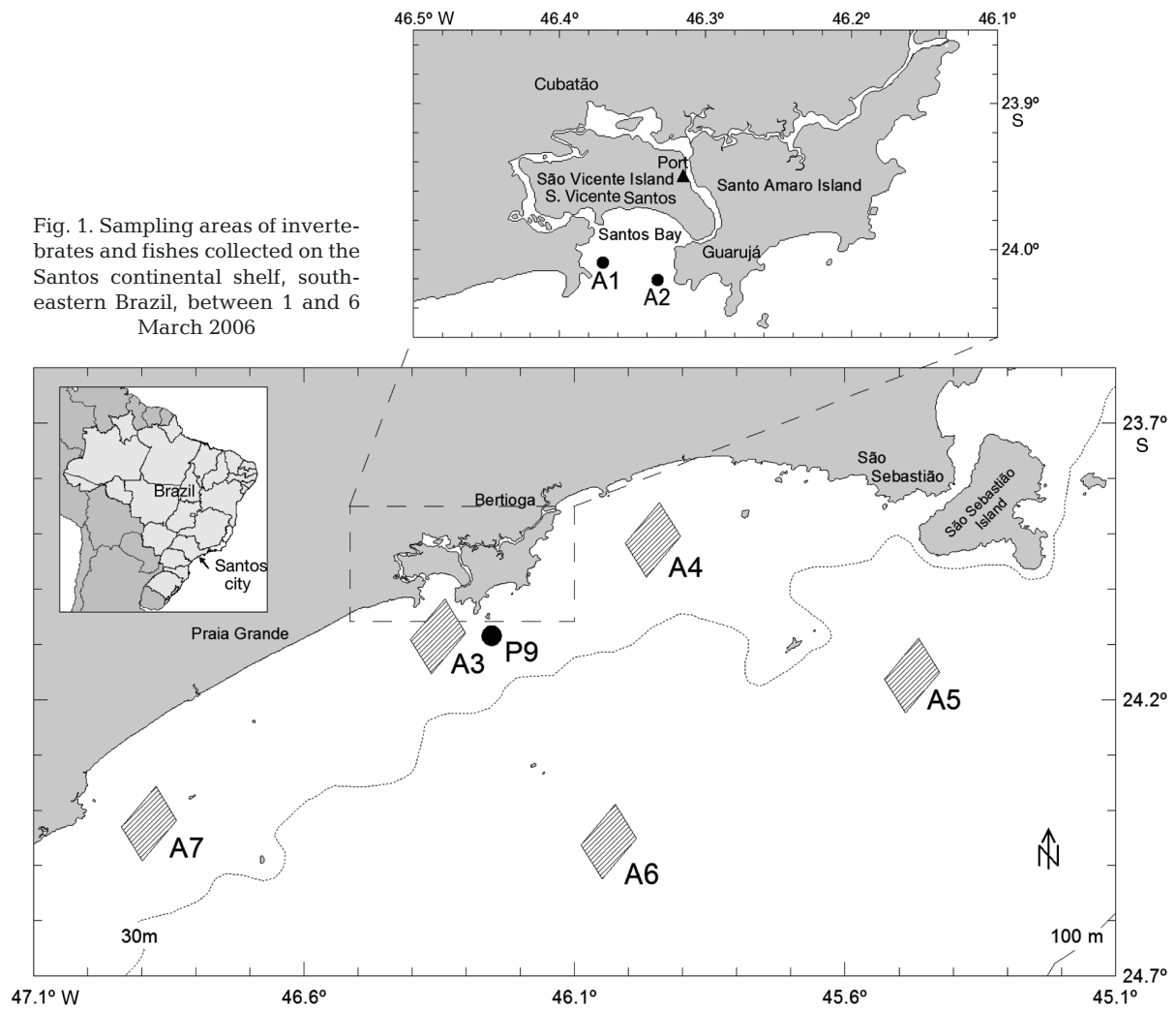
## INTRODUCTION

The Baixada Santista is a large (2402 km<sup>2</sup>), densely populated metropolitan region on the coast of São Paulo State (southeastern Brazil) that comprises 9 municipalities along 246 km of coastline (CETESB 2006). The large industrial complex of Cubatão and the port of Santos (Fig. 1), which is the largest port in Latin America, introduce intense anthropogenic pressure along the coastal area. Consequently, high concentrations of metals, PCBs, and PAHs have been found in sediments of the estuarine system of the re-

gion (Abessa et al. 2005, Bicego et al. 2006, Hortellani et al. 2008). The major potential sources of mercury (Hg) contamination in this area are paper mills, the chemical, fertiliser, petrochemical, and steel industries, and the disposal of domestic wastes and contaminated sediments (CETESB 2001, Abessa et al. 2005, Buruaem et al. 2012). Navigation in and around the port often promotes high sedimentation rates requiring periodic dredging to maintain safe conditions for ship navigation. The dredged sediment is severely contaminated with Hg and is disposed in a 3.24 km<sup>2</sup> area of open water (near Stns A3 and P9, see Fig. 1);

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Fig. 1. Sampling areas of invertebrates and fishes collected on the Santos continental shelf, south-eastern Brazil, between 1 and 6 March 2006



however, the toxicity of the sediment in the surrounding area is not significant because the contaminants disperse (Torres et al. 2009).

The continental shelf of Santos is an important fishery ground, accounting for 69.7% (16 607 t) of the fish landings in São Paulo State in 2005 (Ávila-da-Silva et al. 2007); therefore, understanding the dynamics of contaminants in the biological component of this system is of paramount importance. In Brazilian waters, high Hg levels have been reported in the bodies of top predators such as the swordfish *Xiphias gladius* and many shark species (Penedo de Pinho et al. 2002, Mársico et al. 2007, Dias et al. 2008). In the Santos–São Vicente estuary, sea catfish *Cathorops spixii* with Hg concentrations as high as  $0.447 \text{ mg kg}^{-1}$  wet weight have been found (Azevedo et al. 2012), while in Santos Bay, the Hg level can reach  $0.11 \text{ mg kg}^{-1}$  for this species (Azevedo et al. 2009).

In aquatic ecosystems, Hg enters a complex cycle controlled by competing simultaneous methylation and demethylation reactions (Bisinoti & Jardim 2004, Rodríguez Martín-Doimeadios et al. 2004). Methylmercury (MeHg), the most toxic form of Hg, usually comprises more than 85% of the total mercury (THg) in fish (May et al. 1987, Andersen & Depledge 1997, Baeyens et al. 2003); therefore, human ingestion of fish is a significant pathway of Hg intake. Upon entering the food chain, MeHg can biomagnify effectively, increasing its concentration at each trophic level (Atwell et al. 1998, Kehrig et al. 2013).

A multidisciplinary project (ECOSAN) at the University of São Paulo was developed to evaluate the influence of the Santos–São Vicente estuarine system on the adjacent continental shelf. In the scope of this project, the trophodynamics of the demersal community were addressed using carbon and nitrogen stable isotopes (SI). Increasing knowledge of SI dynamics in

the environment and biological systems has allowed the application of this tool in several fields of ecology.  $\delta^{13}\text{C}$  is used in food web studies to identify different sources of organic matter (Fry & Sherr 1984, Peterson & Fry 1987), benthic vs. pelagic producers and consumers, and nearshore vs. offshore feeding areas (France 1995, Sherwood & Rose 2005, Chouvelon et al. 2012a). Because animals are usually 3–4‰ enriched in heavy nitrogen ( $^{15}\text{N}$ ) relative to their diets (Minagawa & Wada 1984, Peterson & Fry 1987), this isotope is useful for identifying the trophic positions of organisms and for tracing contaminants in food webs (Rolff et al. 1993, Atwell et al. 1998, Campbell et al. 2005). This approach was used in the present study to quantify the rate of biomagnification of Hg in the pelagic and benthic food webs of the Santos continental shelf. In addition, the THg in fish muscles was evaluated to verify whether the concentrations exceed the level for human safe consumption.

## MATERIALS AND METHODS

### Study area

The estuaries of Santos and São Vicente are the primary sources of nutrients, suspended material, and phytoplankton to Santos Bay (Fig. 1); transport of these materials occurs mainly during the rainy season (Moser et al. 2005). Sediment sampling conducted in 2007 showed that Hg concentrations increase from Santos Bay to the inner portions of the estuary (Buruaem et al. 2013). According to criteria established by the Canadian Council of Ministers of the Environment (1999) and adopted by the Environmental Agency of São Paulo State (CETESB), excessive Hg concentrations in sediments (probable effect level greater than  $0.70 \mu\text{g g}^{-1}$ ) occur in the inner part of the estuary. The sediment background of Hg for this estuarine system is  $0.12 \pm 0.04 \mu\text{g g}^{-1}$  (Luiz-Silva et al. 2006). In Santos Bay, values above the threshold effect level of  $0.13 \mu\text{g g}^{-1}$  occur near the submarine sewage outfall (Hortellani et al. 2005). No data are available for sediment, water, and biota in offshore waters of the Santos area.

The adjacent Santos continental shelf reaches 230 km in width and presents a slight declivity and shelf break at depths of 120 to 180 m. It is divided into 3 areas: the inner, middle (usually less than 100 m depth), and outer shelves (Zembruski 1979). The sediment of the inner and middle shelf is dominated by well-sorted fine and very fine sand (de Mahiques et al. 1999).

The high chlorophyll *a* concentrations recorded in the last 30 yr in the estuarine system and Santos Bay characterise those areas as eutrophic (Ancona 2007). The oceanographic conditions of the shelf adjacent to Santos Bay change seasonally and can be classified as oligotrophic in terms of nutrient availability and phytoplankton biomass (Carvalho 2009). Along the southeast Brazilian coast, the cold, nutrient-rich South Atlantic Central Water moves toward the coast over the ocean bottom during spring and summer. The episodic upwelling of this water mass promoted by east–northeast winds enhances the local primary production (Castro Filho et al. 1987, Aidar et al. 1993).

### Sample collection and preparation

All samples were collected during an oceanographic survey conducted during austral summer, from 1 to 6 March 2006. The sampling area included the Santos Bay and the adjacent continental shelf, both of which are under the influence of the Santos–São Vicente estuarine system (Fig. 1). The samples were taken from 2 sites located at the entrance of the Santos Bay (A1 and A2; depths of 8.9–11 m), 4 sites on the inner shelf (A3, A4, A7, and P9; depths of 19.8–26.5 m), and 2 sites on the middle shelf (A5 and A6; depths of 56–57 m; Fig. 1).

Zooplankton were sampled by oblique trawling using a Bongo net with a mesh size of 100  $\mu\text{m}$ , sieved to obtain 4 size fractions (100–300, 300–625, 625–1000, and 1000  $\mu\text{m}$ ), left for 6 h in seawater for gut cleaning, filtered in a glass-fibre filter (GFF), and frozen. Only the size fractions of 300–625 and 625–1000  $\mu\text{m}$  contained enough mass to perform Hg determination.

The benthic macrofauna (polychaetes and bivalves) were collected using a van Veen grab and a box corer. Sediments were washed and the invertebrates that were retained in 1 and 2 mm mesh sieves were kept alive in an aquarium with filtered and aerated water for 12–24 h for gut cleaning, and then frozen. The megabenthos (shrimp, crabs, sea stars, ophiuroids, octopi, and gastropods) and nekton (fish and squid) were caught using a bottom otter trawl with a 17 m net (60 mm stretch mesh in the body and sleeve and 25 mm in the cod end). Hauls of 15 and 30 min at a speed of 2 knots were executed in Santos Bay and on the continental shelf, respectively. After identification, invertebrates and fish were frozen on board at  $-20^\circ\text{C}$ .

Samples of fish dorsal muscles, squid and octopus mantle and arms, gastropod feet, shrimp abdomens,

and crab pereiopods were taken for SI ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and Hg measurements. Oral discs were used for echinoderms samples, while polychaetes, zooplankton, and unshelled bivalves were prepared whole. Polychaetes were grouped into carnivores (Eunicidae, Glyceridae, Lumbrineridae, Polyodontidae), surface depositivores (Terebellidae), and subsurface depositivores (Capitellidae). With few exceptions, each sample of invertebrates and fish is a composite of several individuals of similar size. To measure the  $\delta^{13}\text{C}$  content of zooplankton, ophiuroids, and sea stars, additional samples were treated with concentrated 12 M HCl fume in a desiccator to remove inorganic carbonates from carapaces (Harris et al. 2001). The samples were freeze-dried at  $-30^\circ\text{C}$  for 24 h (nekton) and 48 h (zooplankton, squid and benthic invertebrates) and powdered using a mortar and pestle.

### SI analysis

The  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of the samples were measured using a continuous-flow isotope mass spectrometer (Europa 20/20-IRMS) coupled with an elemental analyser (PDZ Europa ANCA-GSL) at the Stable Isotope Facility of the University of California, Davis (USA). The standard reference materials were Vienna-PeeDee Belemnite (V-PDB) and atmospheric nitrogen ( $\text{N}_2$ ) for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively. The analytical precision derived from replicate measurements of internal laboratory standards run every 12 samples was 0.04‰ for  $\delta^{13}\text{C}$  and 0.20‰ for  $\delta^{15}\text{N}$ . SI ratios are denoted as parts per thousand (‰) deviation from the standard, as follows:

$$\delta X (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}} - 1) \times 1000 \quad (1)$$

where  $X$  is  $^{13}\text{C}$  or  $^{15}\text{N}$  and the  $R$  ratio is  $^{13}\text{C}/^{12}\text{C}$  or  $^{15}\text{N}/^{14}\text{N}$ .

### Mercury analysis

The THg concentrations of the organisms (dry weight,  $\mu\text{g g}^{-1}$ ) were measured by cold vapour generation using an Atomic Absorption Spectrophotometer Varian (model Spectr-AAS-220-FS) at 253.7 nm (using the flow injection analysis-cold vapour-atomic absorption spectrometry [FIA-CV-AAS] technique). The spectrophotometer was coupled to a typical FIA manifold, with a manual valve that injects 500  $\mu\text{l}$  of digested sample with a flow of Milli-Q water (10 ml  $\text{min}^{-1}$ ). The  $\text{Hg}^{2+}$  was reduced online by  $\text{SnCl}_2$  25% (m/v) in HCl 25% (v/v) at a flow rate of 1 ml  $\text{min}^{-1}$ .

Argon was used as carrier gas at a constant flow rate of 150 ml  $\text{min}^{-1}$  (Hortellani et al. 2005). The samples were digested in a 100 ml volumetric flask containing 2 ml of  $\text{H}_2\text{SO}_4$ , 1 ml of  $\text{HNO}_3$ , 1 ml of  $\text{HClO}_4$ , and 1 ml of water per 0.4–1.2 g of sample (Azevedo et al. 2012). The mixture was heated for 30 min at  $100^\circ\text{C}$  on a hot plate. After cooling, the sample was transferred into a 30 ml polypropylene flask, and the volume was increased to 20 g with high purity water obtained using the Milli-Q system of 18.2 M $\Omega$ -cm resistivity. Quality control was conducted through the analysis of CRM DORM2 (dogfish muscle) from the National Research Council, Ottawa, Canada, with a certified Hg content of  $4.64 \pm 0.26 \mu\text{g g}^{-1}$ . The measured value was  $4.71 \pm 0.16 \mu\text{g g}^{-1}$  ( $N = 3$ ), which is in agreement with the certified value. The average recovery was  $102 \pm 3.4 \%$ . The accuracy rate was 1.51% and the Z-score was calculated according to the National Institute of Metrology, Quality and Technology (INMETRO 2007) ( $|Z| = 0.27$ ). The detection limit (LD;  $0.6 \mu\text{g l}^{-1}$ ) was based on the mean value obtained from 7 blank preparations ( $\bar{X}$ ) plus 3 times the standard deviation ( $\text{LD} = \bar{X} + 3\text{SD}$ ). Each sample was run in duplicate, and coefficients of variation were less than 12%. Blanks and check standards were run every 8 to 10 samples. The technique used in this study (FIA-CV-AAS) had an expanded uncertainty of 12.5% for total Hg and is accredited by the Coordenação Geral de Acreditação do Inmetro (CGCRE/INMETRO 2013).

### Data analysis

The means ( $\pm\text{SD}$ ) of THg concentrations ( $\mu\text{g g}^{-1}$  dry weight) and the SI compositions (‰) were calculated for each taxonomic group. The major food categories for invertebrates and fishes were defined according to stomach content analyses of squid and fish collected during the project (Muto et al. 2008, 2014, Chalom et al. 2008, Coelho et al. 2010) and/or from the literature. Based on that information, the organisms were assigned to the pelagic or benthic food web. Putative pelagic taxa included zooplankton, squid, zooplanktivore fishes (4 species), and the piscivore fishes *Trichiurus lepturus* (largehead hairtail), *Merluccius hubbsi* (Brazilian hake), and *Percophis brasiliensis* (Brazilian flathead). Benthic invertebrates (bivalves, gastropods, octopi, sea stars, ophiuroids, polychaetes, shrimp, and crabs), benthivore fishes (13 species), and benthic piscivore fishes (*Paralichthys triocellatus*, *P. patagonicus*, and *Lophius gastrophysus*) comprised the benthic food web. The

mean  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of those groups were plotted in a diagram to depict the food web structure on the Santos continental shelf.

To determine the rate of Hg transfer between trophic levels, a simple linear regression was performed between the logarithm of THg ( $\mu\text{g g}^{-1}$  dry weight) and  $\delta^{15}\text{N}$  using data on individual samples of each taxon of invertebrates and fish. This analysis is analogous to the non-transformed equation of Rolff et al. (1993), where the parameter  $a$  of the regression depends on the initial concentration of the element at the base of the food chain, allowing comparisons among systems with different levels of contamination. The slope value indicates the biomagnification of the element when  $b > 0$ , i.e. the transfer of contaminants in each trophic level is more efficient than the transfer of biomass; conversely,  $b < 0$  denotes biodilution. The slope values were computed for the pelagic ( $N = 75$ ) and benthic ( $N = 188$ ) food webs as well for the full data set ( $N = 263$ ).

The food web biomagnification factor (FWMF), also referred as the trophic magnification factor (TMF), was obtained from the parameter  $b$  of the equation  $\log(\text{THg}) = a + (b \times \delta^{15}\text{N})$  as follows:  $\text{FWMF} = 10^b$  (Fisk et al. 2001). The original equation uses trophic levels instead of  $\delta^{15}\text{N}$ , but here we used  $\delta^{15}\text{N}$  to infer the trophic position because of prey diversity and the uncertainty in the proportion of each prey consumed by each predator.

The slope values of the relationship between THg and  $\delta^{15}\text{N}$  obtained from similar studies undertaken in other estuarine and marine regions of the world are summarised for comparison. For each study, we identified the primary producers or basal consumers sampled to classify the food web as pelagic (basal reference: particulate organic matter, phytoplankton, ice algae, seston, zooplankton) or benthic (basal reference: macroalgae, bivalves, amphipods, mysids), assuming that most of the top consumers are linked to the food chain derived from those food sources or their ecological equivalent. The food webs represented by both categories of basal organisms are denoted as 'pooled'.

### Statistical analyses

Data on THg were  $\log_{10}$ -transformed to fit the assumptions of normal distribution and homoscedasticity. The Hg concentrations of groups of species of the pelagic and benthic food webs were compared through 1-way ANOVA using GraphPad Prism. Tukey's multiple comparison test was performed when-

ever significant differences among samples were detected by ANOVA at  $p < 0.05$ . Gastropods, octopi, and sea stars were excluded from the analyses due to their small sample sizes.

The relationship between  $\log(\text{THg})$  and  $\delta^{15}\text{N}$  was tested using a simple linear regression for each food web and for the overall data. If the regressions were significant, the slope values (rates of biomagnification) of the pelagic and benthic food webs were compared by analysis of covariance (ANCOVA) using  $\delta^{15}\text{N}$  as the covariate. The general linear model routine of the statistical package Minitab 16 was used, and differences were considered to be statistically significant at  $p < 0.05$ .

## RESULTS

A total of 263 samples were used for determination of SIs ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and THg of the biota, most of them represented by fish ( $N = 174$ ).  $\delta^{13}\text{C}$  values of sea stars were omitted because the fumigation treatment failed to remove all carbonate from the samples ( $N = 4$ ). The details of the number of samples, dietary information, THg concentrations, SI signatures, food web assignments, size ranges of some organisms, and areas of sampling are presented in Table 1.

### Food web structure

The mean  $\delta^{13}\text{C}$  of the organisms ranged from  $-19.2\text{‰}$  for the zooplanktivore fish *Trachurus lathami* to  $-15.6\text{‰}$  for the shrimp *Xiphopenaeus kroyeri* (Table 1). Bivalves and zooplankton had similar values,  $-18.5 \pm 1.0$  and  $-18.2 \pm 1.0\text{‰}$ , respectively. For  $\delta^{15}\text{N}$ , the mean values ranged from 6.9 to 13.9‰ (Table 1). Bivalves (suspensivores), zooplankton (suspensivores), surface-depositivore polychaetes, and ophiuroids (depositivores) had the lowest mean  $\delta^{15}\text{N}$ , representing the lowest trophic positions in the food web (Fig. 2). Subsurface-depositivore polychaetes had a mean  $\delta^{15}\text{N}$  of 9.0‰, similar to that of shrimp (9.3–9.5‰), while carnivorous invertebrates displayed higher trophic positions ( $>10.0\text{‰}$ ). Zooplanktivorous fishes showed mean  $\delta^{15}\text{N}$  values from 12.0 to 12.7‰, piscivores from 11.4 to 13.9‰, and benthivores from 10.4 to 13.5‰ (Table 1).

The pattern of the SI signatures of suspended particulate organic matter (SPOM) sampled near the water surface and bottom (T. N. Corbisier pers. comm.) seemed to be followed by bivalves and zooplankton, especially for  $\delta^{13}\text{C}$  (Fig. 2). For the pelagic

Table 1. Mean ( $\pm$ SD) total mercury concentration (THg, dry weight) and stable isotope ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) signatures, and the main prey and food web assignment (P: pelagic; B: benthic) of invertebrates and fishes sampled in the Santos region, southeastern Brazil. Size ranges are specified for squid (mantle length; in mm), crabs (carapace width; in mm) and fish (total length; in mm [disc length for *Zapteryx brevirostris*]). For sampling areas, see Fig. 1. Am: amphipods; Biv: bivalves; Cop: copepods; Crust: crustaceans; Gast: gastropods; invert: invertebrates; Op: ophiuroids; Pol: polychaetes; Sh: shrimp; Zoop: zooplankton

Taxon	Scientific name	Food web	Main prey	THg ( $\mu\text{g g}^{-1}$ )	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	N	Size range (mm)	Sampling area
Zooplankton		P		$0.006 \pm 0.009$	$7.0 \pm 0.8$	$-18.2 \pm 1.0$			A2, A3, A7
Bivalves		B		$0.064 \pm 0.034$	$6.9 \pm 0.8$	$-18.5 \pm 1.0$			A3, A5–7
Gastropods	<i>Siratus tenuivaricosus</i>	B		$0.150 \pm 0.028$	$11.8 \pm 0.3$	$-16.6 \pm 0.1$			A6
Squid and octopi		P	<sup>2</sup> Crust, Fish	$0.115 \pm 0.016$	$12.5 \pm 0.1$	$-15.9 \pm 0.2$	4	30–50	A1, A2
Atlantic brief squid	<i>Lolliguncula brevis</i>	P	<sup>3</sup> Fish, Crust, Squid	$0.053 \pm 0.054$	$11.2 \pm 0.5$	$-16.7 \pm 0.3$	7	40–117	A7
Arrow squid	<i>Doryteuthis plei</i>	P	<sup>3</sup> Fish, Crust, Squid	$0.032 \pm 0.006$	$12.7 \pm 0.4$	$-18.4 \pm 1.2$	6	40–86	A5, A7
Sao Paulo squid	<i>Doryteuthis sanpaulensis</i>	P	<sup>4</sup> Biv, Gastr, Crust	$0.092 \pm 0.005$	$11.3 \pm 0.3$	$-17.9 \pm 0.4$	2		A5, A6
Common octopus	<i>Octopus vulgaris</i>	B							
Sea stars		B	<sup>5,6</sup> Biv, Op	$0.031 \pm 0.007$	$10.5 \pm 0.4$		3		A2
	<i>Luidia senegalensis</i>	B	<sup>6,7</sup> Sea stars, Sea urchin, Op	0.055	13.0		1		A6
	<i>Tethyaster vestitus</i>	B							
Ophiuroids		B		$0.048 \pm 0.023$	$8.3 \pm 0.5$	$-18.9 \pm 0.6$	5		A5, A6
Polychaetes		B		$0.045 \pm 0.028$	$10.5 \pm 1.2$	$-17.9 \pm 1.5$	4		P9, A2, A4, A6
<sup>1</sup> Carnivores	Eunicidae, Glyceridae, Lumbrinidae, Polyodontidae	B							
<sup>1</sup> Surface depositivores	Terebellidae	B		0.011	8.1	-17.9	1		A3
<sup>1</sup> Subsurface depositivores	Capitellidae	B		$0.037 \pm 0.005$	$9.0 \pm 0.2$	$-17.2 \pm 0.0$	2		P9
Shrimp		B							
Pinkspot shrimp	<i>Farfantepenaeus brasiliensis</i>	B	<sup>7</sup> Crust, Pol	$0.158 \pm 0.222$	$9.5 \pm 0.8$	$-15.9 \pm 0.4$	7		A2, A3, A6
Southern white shrimp	<i>Litopenaeus schmitti</i>	B	<sup>7</sup> Crust, Pol	$0.070 \pm 0.021$	$9.4 \pm 0.2$	$-17.2 \pm 1.1$	4		A1, A2
Atlantic seabob	<i>Xiphopenaeus kroyeri</i>	B	<sup>8</sup> Am, Crust, Pol	$0.276 \pm 0.380$	$9.3 \pm 0.5$	$-15.6 \pm 0.1$	3		A1
Small penaeids	Unidentified	B		$0.078 \pm 0.006$	$9.4 \pm 0.0$	$-16.5 \pm 0.1$	2		A3
Crabs		B							
Flekked box crab	<i>Hepatus pudibundus</i>	B	<sup>9</sup> Sh, Fish, Pol	$0.599 \pm 0.467$	$12.7 \pm 0.4$	$-15.8 \pm 0.3$	3	44–51	A3
True crab	<i>Leurocyclus turbeculosus</i>	B		$0.194 \pm 0.022$	$11.7 \pm 0.4$	$-17.4 \pm 0.1$	5		A5
Blue crab	<i>Callinectes ornatus</i>	B	<sup>9</sup> Sh, Pol, Biv, Crabs	$0.132 \pm 0.059$	$10.4 \pm 0.7$	$-15.8 \pm 0.4$	10	12–29	A1–3
Longspine swimming crab	<i>Achelous spinicarpus</i>	B		$0.139 \pm 0.099$	$10.2 \pm 0.5$	$-18.3 \pm 0.4$	6	15–31	A5, A6
Fish		B							
Zooplanktivores		P							
Longfinger anchovy	<i>Anchoa filifera</i>	P	<sup>10</sup> Pelagic Sh	$0.159 \pm 0.044$	$12.3 \pm 0.1$	$-17.5 \pm 0.2$	3	85–91	A1
Dogtooth herring	<i>Chirocentrodon bleekermanus</i>	P	<sup>11</sup> Cop, Pelagic Sh	$0.104 \pm 0.037$	$12.7 \pm 0.1$	$-17.2 \pm 0.2$	12	86–109	A3
American coastal pella	<i>Pellona harroweri</i>	P	<sup>11</sup> Cop, Pelagic Sh, Fish	$0.037 \pm 0.025$	$12.0 \pm 0.2$	$-16.4 \pm 0.2$	9	71–109	A1, A2
Rough scad	<i>Trachurus lathami</i>	P	<sup>10,12</sup> Am, Cop, Fish, Decapod larvae	$0.049 \pm 0.022$	$12.3 \pm 0.3$	$-19.2 \pm 0.1$	6	81–147	A5, A6
Piscivores		P							
Argentine hake	<i>Merluccius hubbsi</i>	P	<sup>10,13</sup> Fish, Zoop, Squids	$0.033 \pm 0.009$	$12.1 \pm 0.2$	$-18.6 \pm 0.1$	5	132–182	A5
Largehead hairtail	<i>Trichiurus lepturus</i>	P	<sup>10,14</sup> Fish, Squids, Zoop	$0.196 \pm 0.357$	$12.5 \pm 1.1$	$-16.3 \pm 0.4$	14	253–1070	A1–3, A7
Brazilian flathead	<i>Percophis brasiliensis</i>	P	<sup>10,15</sup> Fish, Squids	$0.458 \pm 0.633$	$13.1 \pm 0.4$	$-17.8 \pm 0.5$	3	370–578	A5

Table 1 (continued)

Taxon	Scientific name	Food web	Main prey	THg ( $\mu\text{g g}^{-1}$ )	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	N	Size range (mm)	Sampling area
Blackfin goosefish	<i>Lophius gastrophysus</i>	B	<sup>10,16</sup> Fish	0.061 ± 0.032	13.2 ± 0.2	-17.8 ± 0.2	3	123–146	A5
Patagonian flounder	<i>Paralichthys patagonicus</i>	B	<sup>10,17</sup> Fish, Benthic invert	0.825	13.9	-16.6	1	560	A6
Large-tooth flounder	<i>Paralichthys triocellatus</i>	B	<sup>10</sup> Fish, Crabs	0.046 ± 0.009	11.4 ± 0.6	-18.9 ± 0.5	7	133–234	A5, A6
Benthivores									
Madamango sea catfish	<i>Cathorops spixii</i>	B	<sup>18</sup> Pol	0.229 ± 0.033	12.5 ± 0.5	-16.7 ± 0.2	6	180–236	A1
Fat snook	<i>Centropomus parallelus</i>	B	<sup>19,20</sup> Crabs, Fish	0.714 ± 0.017	13.2 ± 1.2	-16.9 ± 0.0	2	290–321	A3
Barbel drum	<i>Ctenosciaena gracilicirrhus</i>	B	<sup>10</sup> Pol, Crabs, Sh, Op	0.461 ± 0.175	13.5 ± 0.2	-17.5 ± 0.1	6	139–169	A6
Flying gurnard	<i>Dactylopterus volitans</i>	B	<sup>10</sup> Am, Crabs, Fish	0.104 ± 0.057	10.4 ± 2.0	-18.0 ± 0.7	12	85–239	A3, A6, A7
Large-tooth flounder	<i>Eitropus longimanus</i>	B	<sup>10</sup> Am, Crabs, Sh	0.083 ± 0.049	11.5 ± 0.7	-18.0 ± 0.7	6	71–127	A5
Silver mojarra	<i>Euclinostomus argenteus</i>	B	<sup>10</sup> Pol	0.228 ± 0.094	12.8 ± 0.8	-16.4 ± 0.5	6	107–179	P9
Southern kingcroaker	<i>Menticirrhus americanus</i>	B	<sup>10</sup> Am, Sh	0.141 ± 0.113	13.4 ± 0.6	-16.6 ± 0.3	14	82–264	A3, A4
Banded croaker	<i>Paralichthys brasiliensis</i>	B	<sup>10</sup> Pol, Crabs, Sh	0.120 ± 0.114	12.7 ± 1.2	-16.5 ± 0.3	14	117–227	A2, A3
Atlantic midshipman	<i>Porichthys porosissimus</i>	B	<sup>10</sup> Am, Sh, Fish	0.170 ± 0.121	11.5	-18.9 ± 0.5	12	87–245	A3, A5, A6
Red searobin	<i>Prionotus nudigula</i>	B	<sup>10</sup> Crabs, Fish	0.120 ± 0.117	12.0 ± 0.7	-18.7 ± 0.6	6	68–172	A6, A7
Banded cusk eel	<i>Raneya brasiliensis</i>	B	<sup>10</sup> Op	0.138 ± 0.040	11.3 ± 0.1	-17.4 ± 0.2	5	159–215	A6
Drum or croaker	<i>Stellifer brasiliensis</i>	B	<sup>10</sup> Sh	0.113 ± 0.019	13.1 ± 0.0	-16.0 ± 0.0	3	119–137	A2
Lesser guitarfish	<i>Zapteryx brevirostris</i>	B	<sup>10</sup> Pol, Crabs, Sh	0.639 ± 0.553	12.6 ± 0.5	-16.3 ± 0.4	19	268–531	P9, A3, A4,

References: <sup>1</sup>Fauchauld & Jumaris (1979), <sup>2</sup>Coelho et al. (2010), <sup>3</sup>Gasalla et al. (2010), <sup>4</sup>Smale & Buchan (1981), <sup>5</sup>Lima-Verde & Matthews (1969), <sup>6</sup>Bitter et al. (1980), <sup>7</sup>Tararam et al. (1993), <sup>8</sup>Branco & Moritz (2001), <sup>9</sup>Petti (1997), <sup>10</sup>Muto et al. (2008), <sup>11</sup>Muto et al. (2014), <sup>12</sup>Carvalho & Soares (2006), <sup>13</sup>Muto & Soares (2011), <sup>14</sup>Martins et al. (2005), <sup>15</sup>Milessi & Mari (2012), <sup>16</sup>Valentim et al. (2008), <sup>17</sup>Rossi-Wongtschowski et al. (1997), <sup>18</sup>Chalom et al. (2007), <sup>19</sup>Tonini et al. (2007), <sup>20</sup>Rabelo et al. (2009). References apply to all items in the row

food web, both isotopes increased from the surface SPOM to zooplankton to top predators (squid and fish) (Fig. 2). The mean  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of squid and zooplanktivorous and piscivorous fish were very similar to each other. For the benthic food web, increasing  $\delta^{15}\text{N}$  values were observed from near-bottom SPOM to suspensivorous/detritivorous invertebrates to carnivorous invertebrates to fish. This trend was not as clear for  $\delta^{13}\text{C}$ : the suspensivorous/detritivorous invertebrates (amphipods, bivalves, and ophiuroids) were more enriched than the bottom SPOM and had the lowest signatures among the sampled animals, while shrimp had the highest  $\delta^{13}\text{C}$  values. Other carnivorous invertebrates and fish had intermediate values.

## Mercury

The lowest mean THg occurred in zooplankton ( $0.006 \mu\text{g g}^{-1}$ ) and surface-depositivore polychaetes ( $0.011 \mu\text{g g}^{-1}$ ). The highest mean THg occurred in the Patagonian flounder ( $0.825 \mu\text{g g}^{-1}$ ), fat snook ( $0.714 \mu\text{g g}^{-1}$ ), lesser guitarfish ( $0.639 \mu\text{g g}^{-1}$ ), barbell drum ( $0.461 \mu\text{g g}^{-1}$ ), and Brazilian flathead ( $0.458 \mu\text{g g}^{-1}$ ). Those fishes, except for the barbell drum, were also the largest specimens sampled (Table 1). However, THg levels were highly variable within and among taxonomic groups of invertebrates and fish.

## Comparisons among invertebrates and fish groups

The Hg concentrations of groups of invertebrates and fishes differed significantly for the pelagic (ANOVA:  $F_{3,71} = 19.1$ ,  $p < 0.0001$ ) and benthic (ANOVA:  $F_{6,173} = 8.37$ ,  $p < 0.0001$ ) food webs (Fig. 3). For the pelagic food web, squid (Tukey's test:  $q = 8.11$ ,  $p < 0.001$ ), zooplanktivores ( $q = 9.58$ ,  $p < 0.001$ ), and piscivorous fishes ( $q = 10.50$ ,  $p < 0.001$ ) showed higher levels of THg than zooplankton but did not differ from each other. For the benthic food web, significant differences were found between benthivorous fishes and ophiuroids ( $q = 4.75$ ,  $p < 0.05$ ), polychaetes ( $q = 6.80$ ,  $p < 0.001$ ), and piscivorous fishes ( $q = 4.99$ ,  $p < 0.05$ ). Crabs also had higher levels of THg than polychaetes ( $q = 5.82$ ,  $p < 0.01$ ).

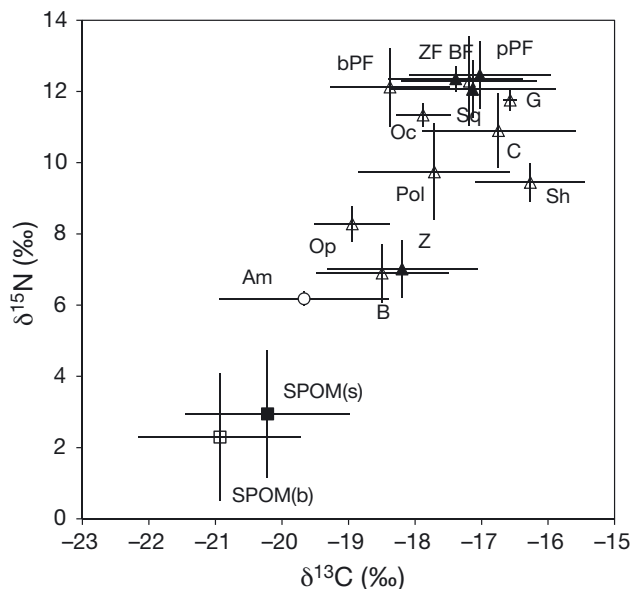


Fig. 2. Relationship between mean ( $\pm$ SD)  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of groups of organisms of the pelagic ( $\blacktriangle$ ) and benthic ( $\triangle$ ) food webs of the Santos continental shelf, during March 2006. Z: zooplankton; Sq: squid; ZF: zooplanktivore fish; pPF: pelagic piscivore fish; B: bivalves; Oc: octopi; G: gastropods; Op: ophiuroids; Pol: polychaetes; Sh: shrimp; C: crabs; BF: benthivore fish; bPF: benthic piscivore fish. Also shown are data on amphipods (O) and suspended particulate organic matter (SPOM,  $\blacksquare$ ,  $\square$ ) collected near the water surface (s,  $\blacksquare$ ) and bottom (b,  $\square$ ) during our sampling cruise (all sites,  $N = 24$ ) are from T. N. Corbisier (pers. comm.)

### Mercury transfer in the food web

The THg concentrations increased according to the  $\delta^{15}\text{N}$  values (trophic positions) of consumers, suggesting the biomagnification of this metal across the food web. The relationship between  $\log(\text{THg})$  and  $\delta^{15}\text{N}$  was significant for both pelagic ( $a = -4.23 \pm 0.29$ ,  $b = 0.25 \pm 0.02$ ,  $R^2 = 0.59$ , SE of the regression [ $s_{yx}$ ] = 0.337,  $F_{1,73} = 104$ ,  $p < 0.0001$ ) and benthic ( $a = -2.43 \pm 0.17$ ,  $b = 0.13 \pm 0.01$ ,  $R^2 = 0.31$ ,  $s_{yx} = 0.352$ ,  $F_{1,186} = 83.8$ ,  $p < 0.0001$ ) food webs, with a stronger relationship for the former (Figs. 3 & 4). The slope values of both regressions were statistically distinct (ANCOVA:  $F_{1,259} = 15.78$ ,  $p = 0.000$ ). The FWMF was higher in the pelagic (1.8) than in the benthic food web (1.4), although the basal THg was higher in the latter. When organisms from both food webs were pooled (i.e. the full data set), the FWMF was 1.4, as derived from the linear regression  $\log(\text{THg}) = 0.15 \delta^{15}\text{N} - 2.73$  ( $a = -2.73 \pm 0.17$ ,  $b = 0.15 \pm 0.01$ ,  $R^2 = 0.28$ ,  $s_{yx} = 0.411$ ,  $F_{1,261} = 102.0$ ,  $p < 0.0001$ ).

### Comparisons among food webs worldwide

The slope values of the total Hg concentrations versus  $\delta^{15}\text{N}$  found in 14 studies (27 food webs) conducted in estuarine and marine waters ranged from 0.04 to 0.32. The details of each study are presented in Table 2 to support the discussion.

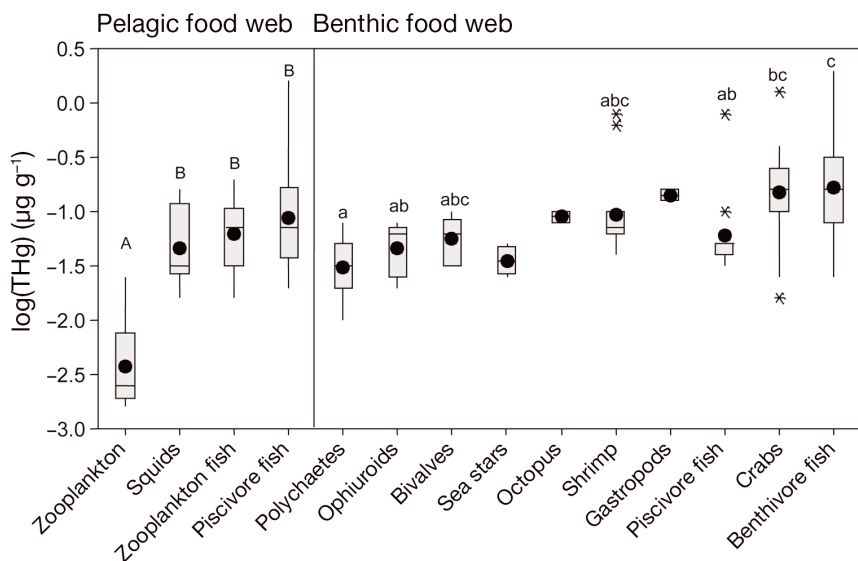


Fig. 3. Boxplot of log total mercury ( $\log(\text{THg})$ ; dry weight) as a function of groups of species of the pelagic and benthic food webs of the Santos continental shelf. Box length represents the interquartile range, bar length represents the range, horizontal lines are median values, closed circles are mean values, and the asterisks depict outliers. Groups sharing the same letter within the pelagic and benthic food webs are not significantly different

## DISCUSSION

### Food web structure

The trophic gradient in the food webs of the Santos continental shelf was depicted by the  $\delta^{15}\text{N}$  of the biota, representing at least 3 trophic levels. In the Gulf of St. Lawrence, benthic organisms were more enriched in  $\delta^{13}\text{C}$  than were benthopelagic and pelagic organisms (Lavoie et al. 2010); however, in our study,  $\delta^{13}\text{C}$  was not adequate to distinguish organisms from the pelagic and benthic food webs. Sediment collected at the same sites over the period of our sampling had  $\delta^{13}\text{C}$  signatures ( $-22.03 \pm 1.27\text{‰}$ ) less enriched compared with those found in SPOM sampled near



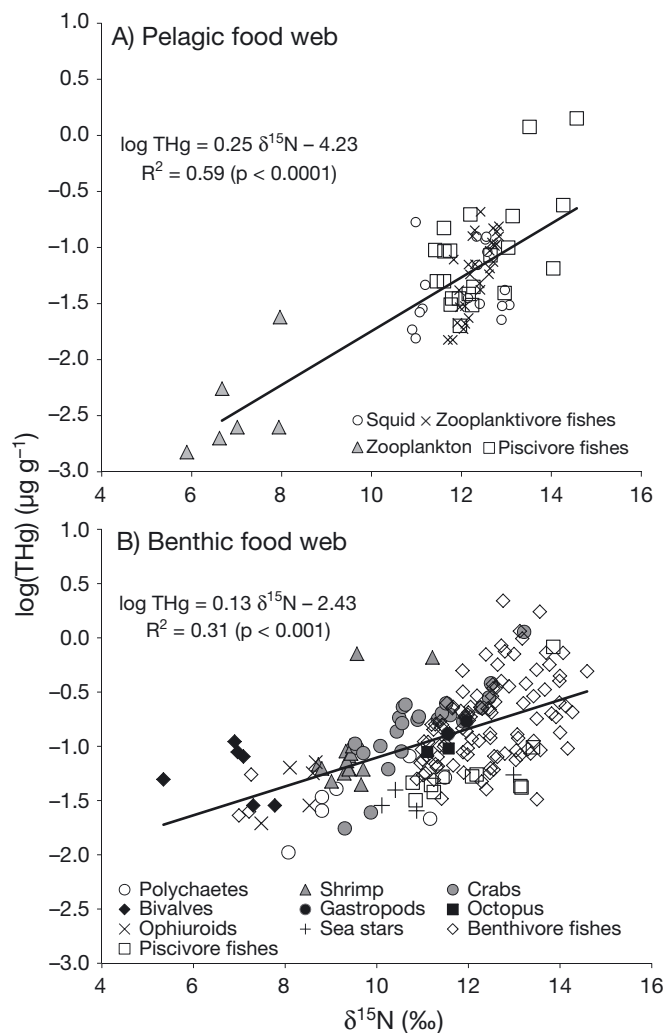


Fig. 4. Relationship between total mercury concentration ( $\log(\text{THg})$ ) and trophic position ( $\delta^{15}\text{N}$ ) of representative organisms of the (A) pelagic ( $N = 75$ ) and (B) benthic ( $N = 188$ ) food webs of the Santos shelf. Data points represent individual composite samples

the bottom ( $-20.93 \pm 1.22\%$ ) and surface ( $-20.22 \pm 1.24\%$ ) (T. N. Corbisier pers. comm.). Although these small differences can be observed in lower-trophic-level consumers, they become diluted farther up the food chain, most likely because carnivores have a wider food niche, especially in the benthic food web. Additionally, those values suggest that pelagic production may contribute to the benthos, as is expected in offshore waters where phytoplankton are the main primary producers. Indeed, the continental shelf of northern São Paulo State is dominated by pelagic production during the summer; however, the contribution of detritus is very significant, especially during the winter (Rocha et al. 2003, 2007). The high similarity between bivalve and zooplankton  $\delta^{13}\text{C}$  val-

ues also suggests some degree of pelagic–benthic coupling, as observed in the Barents Sea (Tame-lander et al. 2006).

The SI compositions of squid and planktivores and pelagic piscivorous fishes were very similar, most likely because they share similar prey at particular stages of their life cycles. Ontogenetic dietary shifts are common features in fish and squid; thus, changes in the trophic position with growth are expected. For instance, *Trichiurus lepturus* shift their diet from small crustaceans (copepods, mysids) to euphausiids, shrimp, squid, and fish as they grow (Martins et al. 2005). Adult *Merluccius hubsi* feed mainly on fish but small hakes also feed on euphausiids and amphipods (Muto & Soares 2011). Although squid are voracious predators, the incidence of crustaceans in the stomach of small squid is higher than that in larger ones (Coelho et al. 2010, Gasalla et al. 2010). In contrast, small fish and squid can also be preyed on by larger individuals of *Pellona harroweri* and *Chirocentron bleekermanus*, respectively (Muto et al. 2008). Several benthivorous fish also undergo ontogenetic dietary changes, feeding on peracarid crustaceans and more sedentary invertebrates before changing their diets to decapods (mainly crabs) and fish (Muto 2004, Chalom et al. 2008, Marion et al. 2011). In the food web of Santos, low  $\delta^{15}\text{N}$  signature of amphipods (6.0–6.3‰) (T. N. Corbisier pers. comm.) was reflected in their predators, especially in fish (see Table 1). In summary, the average SI signatures tend to overlook the feeding variability in fish, unless the sample is composed of similarly sized individuals.

### Mercury in organisms

As a whole, the biota of the Santos shelf had low Hg concentrations, comparable with values reported for the same species from the Rio de Janeiro coast (Bisi et al. 2012, Di Benedetto et al. 2012, Kehrig et al. 2013) and with species from others regions of the world (Prudente et al. 1997, Bargagli et al. 1998, Anan et al. 2005, Rigét et al. 2007, Ikemoto et al. 2008, Lavoie et al. 2010). Based on the assumption that marine fish are made up of 60–80% water (Ciancio et al. 2007, Eder & Lewis 2005, Ikemoto et al. 2008) and the fact that our data are based on dry weight, the Hg concentrations of the 23 species analysed were under the set limit of  $0.5 \mu\text{g g}^{-1}$  wet weight (approximately  $1.67 \mu\text{g g}^{-1}$  dry weight, assuming 70% water) for safe fish consumption (WHO 1976, ANVISA 1998). Only 2 individual samples of the guitarfish had THg levels (1.74 and

Table 2. Slope values of the linear regressions of logTHg vs.  $\delta^{15}\text{N}$  and food web biomagnification factors (FWMF) from several studies performed in estuarine and marine waters around the world. POM: particulate organic matter; WW: wet weight; DW: dry weight

Region	Food web	Basal–top predator	Slope (b)	FWMF ( $10^b$ )	Unity	Reference
Baffin Bay, Arctic	Pelagic	Ice algae–Mammals	0.20	1.57	WW	Campbell et al. (2005)
Chukchi Sea, Arctic	Benthic	Bivalves–Fish	0.10	1.26	DW	Fox et al. (2014)
Lancaster Sound, Arctic	Pooled	POM–Mammals	0.20	1.58	DW	Atwell et al. (1998)
West Greenland	Pooled	Zooplankton–Mammals	0.18	1.52	DW	Rigét et al. (2007)
Baltic Sea	Pelagic	Plankton–Fish	0.18	1.50	WW	Nfon et al. (2009)
Gulf of St. Lawrence, Canada	Pooled		0.13	1.36	DW	Lavoie et al. (2010)
	Pelagic	POM–Seabirds	0.22	1.65	WW	Lavoie et al. (2010)
	Benthopelagic	Bivalves–Seabirds	0.19	1.56	WW	Lavoie et al. (2010)
	Benthic	Amphipods–Seabirds	0.11	1.29	WW	Lavoie et al. (2010)
Nain Bay, Canada	Benthic	Algae–Fish	0.11	1.29	DW	van der Velden et al. (2013)
Okak Bay, Canada	Benthic	Algae–Fish	0.11	1.29	DW	van der Velden et al. (2013)
Saglek Bay, Canada	Benthic	Algae–Fish	0.06	1.15	DW	van der Velden et al. (2013)
Dry Bay, Canada	Benthic	Algae–Fish	0.06	1.15	DW	van der Velden et al. (2013)
Iqaluit, Canada	Benthic	Algae, Plankton–Fish	0.13	1.35	DW	van der Velden et al. (2013)
Pound Inlet, Canada	Benthic	Algae–Fish	0.13	1.35	DW	van der Velden et al. (2013)
Gulf of the Farallones, USA	Pelagic	Zooplankton–Mammals	0.32 <sup>a</sup>	2.09	DW	Jarman et al. (1996)
Ria de Aveiro coastal lagoon, Portugal	Benthic	Algae–Fish	0.04	1.10	DW	Coelho et al. (2013)
Mekong Delta, South Vietnam	Pooled	Phytoplankton–Fish	0.10	1.26	DW	Ikemoto et al. (2008)
Guanabara bay, Rio de Janeiro, Brazil	Pooled	Seston–Mammals	0.18	1.51	WW	Bisi et al. (2012)
Sepetiba bay, Rio de Janeiro, Brazil	Pooled	Seston–Mammals	0.07 <sup>b</sup>	1.17	WW	Bisi et al. (2012)
Ilha Grande Bay, Rio de Janeiro, Brazil	Pooled	Seston–Mammals	0.22	1.66	WW	Bisi et al. (2012)
Rio de Janeiro coast, Brazil	Pooled	Phytoplankton–Fish	0.25	1.76	DW	Di Benedetto et al. (2012)
Rio de Janeiro coast, Brazil	Pooled	Mesoplankton–Mammals	0.21	1.62	DW	Kehrig et al. (2013)
Santos shelf, São Paulo, Brazil	Pooled		0.15	1.41	DW	Present study
	Pelagic	Zooplankton–Fish	0.26	1.82	DW	Present study
	Benthic	Bivalves–Fish	0.13	1.35	DW	Present study

<sup>a</sup>Original data =  $\ln 0.74$ ; <sup>b</sup>Linear regression ( $p = 0.06$ )

2.20  $\mu\text{g g}^{-1}$ ) higher than this limit. However, a recent review on the effect of dietary MeHg on fish indicated adverse effects on reproduction as well as histological, biochemical, and genetic effects at concentrations below 0.2  $\mu\text{g g}^{-1}$  wet weight (Depew et al. 2012). Some samples composed of large individuals of guitarfish, fat snout, largehead hairtail, Patagonian flounder, and barbel drum from the Santos region had Hg concentrations of that magnitude; however, the health impact on these species at the population level is difficult to assess.

The Hg content in the biota of Santos differed among different types of invertebrates and fish; however, significant differences were detected only

between some groups. This result may be linked to the high variability within species and among species of a particular group. In fact, the Hg concentration in demersal crustaceans increases with increasing trophic level (Asante et al. 2008) and is size-related in crabs, MeHg being the major form of Hg accumulated in muscle (Andersen & Depledge 1997). The crabs of the Santos shelf showed the same pattern: larger species had higher  $\delta^{15}\text{N}$  values and were more contaminated than were smaller species. In cephalopods, Hg mostly accumulates in muscle; the degree of contamination is related to the size and sex of Loliginidae squid (Bustamante et al. 2006). Because benthic species were more contaminated

than pelagic species, those authors suggested that diet is not the main route for Hg uptake, as would be expected from the piscivore diet of the latter. Conversely, the high Hg concentration in the digestive glands (as well as muscles) of *Octopus vulgaris* supports a dietary source of Hg (Seixas et al. 2005). For polychaetes, feeding modes and depth position in sediment are stronger predictors of Hg contamination than trophic position; burrowing deposit-feeding polychaetes bioaccumulate more MeHg than carnivores do (Sizmur et al. 2013). On the Santos shelf, tissue Hg in polychaetes was higher in carnivores; however, subsurface depositivores had higher levels of Hg than did surface depositivores.

Food is the main source of MeHg exposure in wild fish (Hall et al. 1997) and high-trophic-level species tend to be more contaminated. As a whole, Hg levels are positively correlated to age, longevity, size, and weight, as a result of bioaccumulation over time (Andersen & Depledge 1997, Adams et al. 2004, Anan et al. 2005, Lavoie et al. 2010, Payne & Taylor 2010). Growth rate also affects the Hg content in fish: faster-growing fish have lower Hg concentration because of somatic dilution during rapid growth (Simoneau et al. 2005). In general, the most contaminated species of Santos shelf were the larger ones associated with high  $\delta^{15}\text{N}$  values.

### **Biomagnification of mercury across the food web**

On the Santos continental shelf, Hg concentrations in biota were related to  $\delta^{15}\text{N}$  (trophic position); however, the stronger relationship found for the pelagic food web may be related to the small number of species analysed and/or to the narrower food niche in pelagic organisms. FWMF values greater than 1 indicate that Hg was transferred up the food web, though this occurs at different rates in the pelagic and benthic food webs.

In the estuaries of the Gulf of Maine, higher MeHg concentrations in the pelagic-feeding fauna suggest that feeding in or on sediments is less efficient for MeHg transfer than feeding on SPOM (Chen et al. 2009). Many studies comparing pelagic- and benthic-feeding fishes show a similar pattern. For instance, in a lacustrine system of Canada and in Manila Bay, fishes linked to the benthic food chain were less contaminated than those connected to the pelagic food chain (Prudente et al. 1997, Power et al. 2002). A comparison between 2 flatfish showed that species feeding on fish, squid, and macrocrustaceans had higher Hg concentrations than did species feeding on

amphipods and polychaetes (Payne & Taylor 2010). In contrast, and similar to our findings, an analysis of organisms across a wide depth range in the Bay of Biscay (30–600 m) showed that the pelagic fauna were less contaminated than the benthic and benthopelagic fauna (Chouvelon et al. 2012b). Demersal fish of the Antarctic inner shelf were more contaminated than epipelagic fish (Bargagli et al. 1998). The differences observed among those studies may be related to biological features of the analysed organisms or to the differential bioavailability of Hg in water and sediments in different systems. As a whole, benthic organisms of the Santos region were more contaminated than pelagic organisms, especially those at low trophic levels, suggesting the higher bioavailability of Hg in sediment than in water.

In the Gulf of St. Lawrence, the rates of Hg biomagnification decrease from pelagic (0.22) to benthopelagic (0.19) to benthic (0.11) food webs and Hg concentrations at the base of the food chain were higher for the benthic system. This trend was attributed to the greater bioavailability of Hg to low-trophic-level organisms feeding in deep waters and a more efficient transfer in the pelagic and benthopelagic chains. We found similar patterns in our study, and the differences observed between the 2 food webs on the Santos shelf may also be related to the higher complexity of the benthic–trophic interactions derived from the high diversity of potential prey with different feeding habits and the different metabolisms of benthic and pelagic organisms. The higher basal THg in the benthic food web of Santos is most likely associated with the higher bioavailability of Hg in the bottom sediments than in water; however, this hypothesis must be tested. Although we have addressed the biomagnification of Hg according to the main feeding habits of the biota, the pelagic and benthic domains are coupled, with several organisms (both prey and predators) displaying trophic vertical migration through the water column, such as zooplankton (Ashjian et al. 1998, Hays 2003), squid (Santos & Haimovici 1998, Gasalla et al. 2010), and fish (Prenski & Angelescu 1993, Martins et al. 2005). However, a separate examination of the pelagic and benthic food webs may help us to understand the trophodynamics of contaminants in different compartments of the system and should be considered in comparisons among food webs across latitudes.

To identify the main variables (physical, chemical, and biological) that affect Hg biomagnification in aquatic systems, a meta-analysis was performed on a large number of studies conducted in freshwater and

marine regions worldwide (Lavoie et al. 2013). For marine sites, the average slope value was  $0.20 \pm 0.10$  (mean  $\pm$  SD), with no significant difference between THg and MeHg, coastal and offshore sites, or food web composition (inclusion of fish or proportion of endotherms). Polar and temperate sites had higher slope values than tropical sites, which is explained by slower excretion rates of Hg at cold temperatures and the dilution of tissue Hg due to enhanced growth rates in warmer waters. However, somatic growth dilution of an element is only effective when rapid growth is associated with a low efflux rate (excretion) (Karimi et al. 2010). Other studies have not found latitudinal differences in the biomagnification rates of Hg in marine and freshwater environments (Campbell et al. 2005, van der Velden et al. 2013)

The slope values for the pooled ( $b = 0.15$ ), benthic ( $b = 0.13$ ), and pelagic ( $b = 0.25$ ) food webs of the Santos shelf were within the range (0.04 to 0.32) of those observed in similar studies performed in estuarine and marine waters of a broad latitude range (Table 2). Those studies varied in the type of organisms sampled at the base and top of the food webs, metric (wet or dry weight), latitude, and feeding habitat (pelagic, benthopelagic, benthic, and pooled). Although we have not observed a trend in relation to the 3 first variables, the highest slope values occurred in the pelagic and pooled food webs, and most of the values for the benthic food webs were smaller than 0.013. Although Loseto et al. (2008) found similar values for benthic and pelagic food webs (0.23–0.26) in the Arctic, the beluga was the top predator in all food webs, and the details of the diet of this cetacean are still uncertain.

In conclusion, Hg is transferred across the pelagic and benthic food webs of the Santos continental shelf at different rates, being higher in the pelagic food web. Low-trophic-level benthic invertebrates were more prone to Hg accumulation than pelagic species, which is most likely associated with the higher availability of this metal in sediments than in water. Although the degree of contamination of fishes was below the set limit for safe human consumption, the monitoring of large specimens is advisable. Because low levels of Hg induce sublethal effects on fish, toxicological tests with different endpoints may improve our knowledge on the impact of Hg on the health and survival of the fish populations of Santos shelf. Finally, considering the many sources of anthropogenic pollution on the Santos coast, sediment, water, and biota should be monitored to detect long-term trends, especially for those contaminants that biomagnify in the food web.

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