



Total tin (TSn) biomagnification: Evaluating organotin trophic flow and dispersion using hepatic TSn concentrations and stable isotope (C, N) data of nektonic organisms from Brazil

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ABSTRACT

A previous investigation of our research team has demonstrated the suitability of using hepatic total tin (ΣSn) concentrations for evaluating dolphin exposure to organotins (OTs). The present study develops the previous technique into three different approaches that comprise data: (1) on hepatic ΣSn concentrations of 121 Guiana dolphins (*Sotalia guianensis*) from five different coastal areas (CAs); (2) on ΣSn , $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for 40 dolphins from Rio de Janeiro state (RJ), including ten different delphinid species; as well as (3) on hepatic ΣSn concentrations and $\delta^{15}\text{N}$ values on 31 individuals from five different fish species from Sepetiba Bay (SB, Rio de Janeiro-RJ, Brazil). Hepatic ΣSn concentrations of Guiana dolphins from Guanabara Bay (GB, RJ) were significantly higher than those found in other four CAs from S and SE Brazilian regions. Significant positive correlations were found between ΣSn concentrations and $\delta^{13}\text{C}$ data in delphinid species, demonstrating a coast-ocean gradient in dolphin exposure to OTs in RJ state. Significant and positive correlations were observed between ΣSn concentrations and both $\delta^{15}\text{N}$ and Trophic Position (TP) values of fish, as well as high values were found for Trophic Magnification Factor (TMF = 3.03) and Trophic Magnification Slope (TMS = 0.14), demonstrating OT biomagnification in SB ichthyofauna.

1. Introduction

Thousands of new compounds are synthesized every year. This situation poses a challenge to environmental toxicologists, as the number of new chemicals released in the market surpasses by far their capacity of performing toxicological tests of environmental relevance on these new commercially available molecules (Muir and Howard, 2006). In addition, the appearance of new chemical threats to marine organisms is not a rare event (Alonso et al., 2012; Gago-Ferrero et al., 2013). The fast and abundant entrance in the environment of new molecules of

toxicological concern and a temporal decrease in organotin (OT) levels around developed countries (Arp et al., 2014) have apparently reduced the scientific interest on environmental exposure of top predators to OTs. The last affirmative is based on the fact that the most recent study on organotin levels in marine mammals from developed countries was published sixteen years ago (Ciesielski et al., 2004). The above-mentioned temporal decrease can be explained by the global ban on the use of tributyltin (TBT) and triphenyltin (TPhT) as antifouling agents in 2008 (Borges et al., 2013; de Castro et al., 2012).

Recent studies from different regions of the globe have demonstrated

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that pollution by OTs is still a matter of concern due to the high environmental persistence of these molecules (Anastasiou et al., 2016; Batista et al., 2016; Erdelez et al., 2017; Laranjeiro et al., 2018; Quintas et al., 2016). In Brazil, the environmental legislation presents some contradictory aspects when it comes to OTs. The use of TBT and TPhT on undersea surfaces for avoiding incrustation of molluscs and crustaceans is forbidden in Brazil; however, there is no prohibition for the production and commercialization of OTs in the country (Batista, 2016; Borges et al., 2013; de Castro et al., 2012). Considering the high OT concentrations found in Brazilian environments (Artifon et al., 2016; Fernandez et al., 2005; Maciel et al., 2018; Moreira et al., 2017), as well as aiming to use less expensive strategies for evaluating environmental contamination by OTs, some studies have been performed comprising the use of the imposex phenomenon. Therefore, the presence of penis and vas deferens in female gastropod molluscs (imposex) has been used for monitoring marine contamination by OTs (Artifon et al., 2016; Borges et al., 2013; Castro et al., 2012; da Costa et al., 2017; de Castro et al., 2012; Limaverde et al., 2007; Maciel et al., 2018). Although efficient, this approach does not allow evaluation of the exposure of species that feed on near-top positions of marine food webs, i.e., top consumers, including human beings.

In this context, the use of dolphins for this monitoring should be highlighted, due to their top position in the food web and their long-life span (Das et al., 2002; Lailson-Brito et al., 2008). In addition, differently from fish, cetaceans are air-breathing animals, which turns the food into the only significant via for pollutant uptake (Gray, 2002). This aspect should be stressed, as many species preyed by dolphins are commercially important fish, which allows the use of these mammals as sentinels not only of environmental but also of human health (Ross, 2000; Wells et al., 2004). The loss of integumentary structures (e.g. hair in mammals and feathers in birds) constitutes an elimination route for organometallic compounds (Guruge et al., 1996; Kim et al., 1996a), which increases the importance of analysing dolphin samples for measuring exposure to OTs, as cetaceans do not have hair. The absence of one elimination pathway for OTs in dolphins, associated to their apparent inferior capacity for metabolizing butyl and phenyltins (Tanabe, 1999), generates higher OT concentrations in their tissues in comparison to other mammals (Schilithz et al., 2013).

Regarding the delphinids that occur in Brazilian waters, the Guiana dolphin (*Sotalia guianensis*) is the species that raises the highest toxicological concern. This apprehension is a consequence of the fact that the species inhabits bays and estuaries whose drainage basins harbour dense human populations (Dorneles et al., 2016). In addition, it is well-known that Guiana dolphins do not perform long migrations (Espinoza-Rodríguez et al., 2019). The species exhibits habitat fidelity, with the same individuals being present all year round in relatively small coastal areas (Azevedo et al., 2004; Cremer et al., 2009) where the species occupy a top position in their food webs (Bisi et al., 2012). The ecotoxicological concern has been confirmed by investigations that have shown high concentrations of pollutants from different chemical classes in distinct Guiana dolphin populations along the distribution range of the species (e.g. Alonso et al., 2012; Koeman et al., 1972; Santos-Neto et al., 2014), i.e., from Santa Catarina state (SC), Southern Brazil, to La Mosquitia, Honduras (Cunha et al., 2005; Flores and Da Silva, 2009).

Aiming to assess the degree of organotin contamination of top predators in RJ waters, as well as to generate a simplified method for this assessment, our research team evaluated dolphin exposure to OTs through hepatic total tin (ΣSn) concentrations, in which constituted the first study to address OT contamination of marine mammals from the Southern Hemisphere (Dorneles et al., 2008a). The rationale that supported that approach was generated by landmark papers (Hai Le et al., 1999; Takahashi et al., 2000) that demonstrated organotin compounds to be the major contributors to the hepatic tin burden in marine mammals. The approach was also based on the fact that the percentage uptake of inorganic tin species through gastrointestinal mucosa is extremely low in mammals, as well as on the opposite scenario for OTs, i.

e., organotin compounds are efficiently absorbed through the same via (Schilithz et al., 2013). In addition, the evaluation of animal exposure to OTs through total tin determination has recently been adopted for fish as well (Zhang et al., 2016).

The aim of the present study was to evaluate dolphin exposure to organotins through hepatic ΣSn concentrations in a variation of the latter approach. The present and variant approach comprises three main objectives: (1) investigating possible differences in Guiana dolphin exposure to OTs among distinct bays/coastal areas of the Brazilian littoral; (2) evaluating the importance of the distance from the hotspot area for the cetacean exposure to OTs; and (3) investigating the possible occurrence of ΣSn biomagnification through a food web.

For the first objective, samples from different ecological populations of *Sotalia guianensis* were used, comprising a long (more than 2000 km) coastline extension. Guiana dolphins from five different bays/coastal areas were analysed, encompassing Grande Vitória region – GV, Espírito Santo (ES) state; Guanabara Bay – BG and Sepetiba Bay – SB, Rio de Janeiro (RJ) state; Paranaguá Bay – PB, Paraná (PR) state; and Babitonga Bay – BB, Santa Catarina (SC) state, comprising Southeast (RJ and ES) and South (SC and PR) Brazilian regions (Fig. 1). Regarding the second objective, data from two published studies from our research team were treated together in order to investigate the possible occurrence of an exposure gradient between a hotspot of environmental contamination by OTs, Guanabara Bay (GB, Rio de Janeiro state), and waters from the oceanic province. Therefore, for this second goal, data previously published by our research team on hepatic ΣSn concentrations (Dorneles et al., 2008a), as well as on stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) values (Bisi et al., 2013) were statistically treated together. Concerning the third objective, hepatic ΣSn concentrations were determined in five fish species from another impacted estuary from Rio de Janeiro state (RJ), Sepetiba Bay, for which our research team already possessed stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) data (Bisi et al., 2012). The stable isotope values allowed the trophic positions (TPs) of the fish species to be determined in the present study and treated in association with hepatic ΣSn concentrations for the calculation of the Trophic Magnification Factor (TMF). The Trophic Magnification Slope (TMS) was calculated as well.

2. Material and methods

2.1. Sampling and sample preparation

Regarding Guiana dolphins, liver samples were collected from 121 individuals accidentally captured or stranded on the beaches of Great Vitória (GV) coastal region, Espírito Santo state (ES, $n = 23$); Guanabara (GB, $n = 30$) and Sepetiba (SB, $n = 37$) bays, Rio de Janeiro state (RJ); Paranaguá Bay, Paraná state (PR, $n = 21$) and Babitonga Bay, Santa Catarina state (SC, $n = 10$), from 1994 to 2012 (Table 1; Fig. 1). Dissection, as well as sample drying and storage procedures can be found in published articles (Dorneles et al., 2007, 2008a). Concerning fish, 64 individuals of five different species, i.e., whitemouth croaker (*Micropogonias furnieri*, $n = 29$), common snook (*Centropomus* sp., $n = 10$), ribbonfish (*Trichiurus lepturus*, $n = 8$), yellow catfish (*Aspistor luniscutis*, $n = 7$) and white mullet (*Mugil curema*, $n = 10$) were sampled at Sepetiba Bay, comprising fish within the size range preyed by Guiana dolphins in the estuary (Araujo, 2012). Fish sampling was performed in austral summer 2009 (February and March – wet season) and the sampled individuals were directly acquired by the arrival of the fish on land, in Sepetiba Bay littoral.

2.2. Analytical procedure – stable isotope and total tin measurements

As mentioned, the stable isotope (SI) data treated herewith were generated by other investigations; therefore, the related analytical procedures can be found in those articles (Bisi et al., 2013, 2012). In Brief, SI measurements were performed on a V.G. Optima (Isoprime, UK)

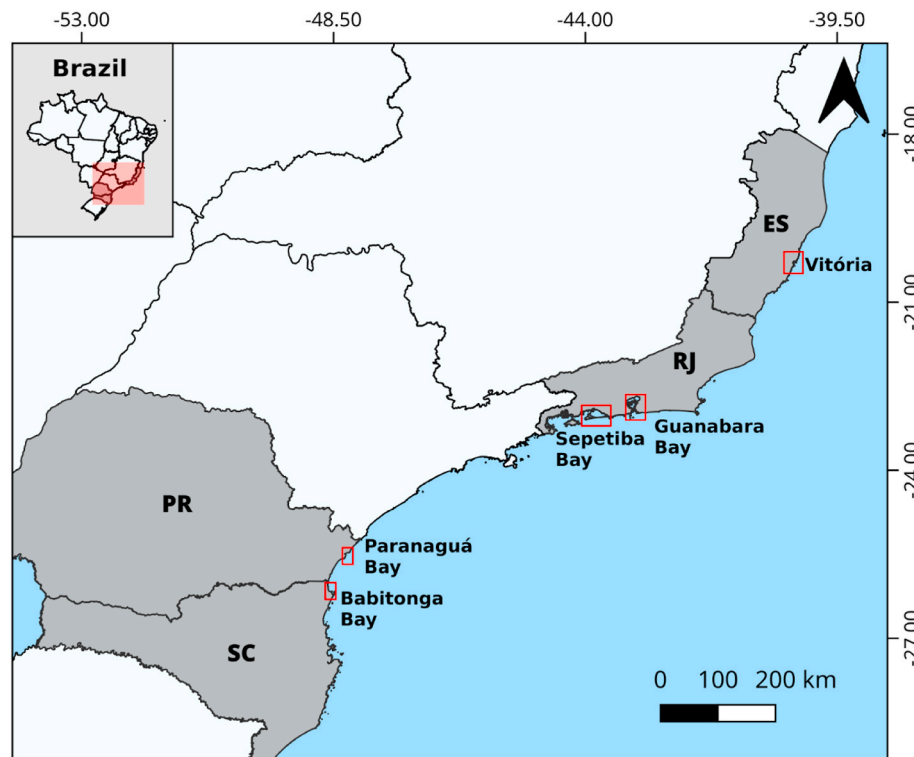


Fig. 1. Map of Brazil highlighting Espírito Santo (ES), Rio de Janeiro (RJ), Paraná (PR) and Santa Catarina (SC) states, complementarily stressing Vitória (ES) and Guanabara (RJ), Sepetiba (RJ), Paranaguá (PR) and Babitonga (SC) bays.

Table 1

Mean hepatic Σ Sn concentrations [in $\mu\text{g.g}^{-1}$, dry weight (dw)], as well as standard deviation (\pm SD), minimum and maximum levels, of juvenile and adult male and female Guiana dolphins from Great Vitória (GV), Espírito Santo state (ES), Guanabara Bay (GB) and Sepetiba Bay (SB), Rio de Janeiro state (RJ), Southeast Brazil (SE), Paranaguá Bay (PB), Paraná state (PR) and Babitonga Bay (BB), Santa Catarina state (SC), South Brazil (S), along with the number of samples analysed (n), and the number of samples that rendered values above the detection limit ($n > \text{DL}$).

Brazilian region	Brazilian state	Coastal area	Σ Sn concentrations, $\mu\text{g.g}^{-1}$ dw, mean (\pm SD), min–max [n ($n > \text{DL}$)]		
			Juveniles	Adult Females	Adult Males
			{year of death}	{year of death}	{year of death}
SE	ES	GV	0.64 (\pm 0.83)	3.07 (\pm 2.40)	0.97 (\pm 0.70)
			0.12–2.40 [10 (4)]	0.67–8.25 [9 (9)]	0.23–1.92 [4 (3)]
	RJ	GB	7.29 (\pm 6.06)	12.6 (\pm 7.84)	16.0 (\pm 8.26)
			1.25–17.7 [14 (14)]*8*	4.91–22.9 [8 (8)]*6*	1.47–27.7 [8 (8)]*6*
S	RJ	SB	2.07 (\pm 3.45)	1.64 (\pm 0.78)	1.89 (\pm 2.62)
			0.29–14.1 [15 (14)]	0.47–3.09 [14 (14)]	0.27–8.30 [8 (7)]
	PR	PB	0.81 (\pm 0.53)	2.21 (\pm 1.98)	1.43 (\pm 0.44)
			0.26–1.58 [6 (5)]	0.49–5.15 [7 (7)]	0.62–1.94 [8 (8)]
SC	BB	6.81 (\pm 10.4)	2.27 (\pm 0.60)	5.05 (\pm 2.40)	
		0.63–24.8 [5 (5)]	1.80–2.95 [3 (3)]	3.35–6.75 [2 (2)]	
			0.63–24.8 [5 (5)]	1.80–2.95 [3 (3)]	3.35–6.75 [2 (2)]

Data on Σ Sn concentrations of 30 out of the 40 Guiana dolphins from Guanabara Bay were originally generated by Dorneles et al. (2008a) and the corresponding n within each age/sex class appears on the table between stars (e.g. *8*, demonstrating that data from eight juvenile Guiana dolphins had already been published in Dorneles et al., 2008a).

isotope ratio mass spectrometer coupled to an N–C–S elemental analyser (Carlo Erba). Similarly, detailed information on the determination of Sn concentrations can be found in a previous study (Dorneles et al., 2008a). Total tin concentrations were determined by electrothermal atomic absorption spectrometry (ET-AAS), using Analytic Jena spectrometers ZENit 60 (LREPF-UFRJ) ZENit 650P (MAQUA-UERJ) equipped with Zeeman-effect background correction. For quality assurance and quality control (QA/QC), the procedures included the use of the standard addition method. For this procedure, recoveries of Sn from spiked

extracts were 101%, 97%, 99% and 103% for 20-ng/mL, 30-ng/mL, 40-ng/mL and 60-ng/mL, respectively. For expressing the precision of the analytical procedure, samples were analysed in duplicates and the values were only considered to be valid when the coefficient of variation between the two concentrations was lower than 10%. For verifying the repeatability of the analyses, one liver sample (SEP#12) was digested eight times and the mean and standard deviation values were 608 ng/g (dry weight) and \pm 28 ng/g, respectively, generating a coefficient of variation of 4.6% for those total tin concentrations. The temperature

program used, and the operating conditions were shown in a previous investigation (Dorneles et al., 2008a). The number of individuals measured for $\delta^{15}\text{N}$ was sometimes lower than those analysed for ΣSn determination (Tables 2 and 3), with relevant differences only for fish. All the 64 fish mentioned in Subsection 2.1 (Sampling and sample preparation) had samples analysed for the determination of ΣSn concentrations; however, only 31 out of those 64 individuals had samples measured for $\delta^{15}\text{N}$ values, comprising 11 whitemouth croakers, 06 common snooks, 05 ribbonfishes, 04 yellow catfishes and 05 white mullets (Table 3).

2.3. Investigating a possible coast-ocean gradient in the exposure to OTs

The evaluation of the importance of the distance from the hotspot area, in this case Guanabara Bay (GB, Rio de Janeiro state – RJ), for the exposure of top marine predators to OTs was performed through an association between total tin and stable isotope measurements. This approach is based on the fact that changes in ratios of stable carbon isotopes ($^{13}\text{C}/^{12}\text{C}$) have been used to indicate the inshore vs. offshore contribution to food intake (Smith et al., 1996). For accomplishing this evaluation, data previously published by our research team have been treated herewith, encompassing hepatic ΣSn concentrations (Dorneles et al., 2008a) and $\delta^{13}\text{C}$ values (Bisi et al., 2013) of 40 dolphins stranded on the beaches of Rio de Janeiro state, from 1994 to 2006. The delphinid species and respective sampling numbers can be found in the footnote of Table 2. As data on stable nitrogen isotopes were also available for the same individuals (Bisi et al., 2013), the possible occurrence of significant correlations between hepatic ΣSn concentrations and $\delta^{15}\text{N}$ values were investigated as well.

2.4. Assessment of the trophic position of fish and total tin (TSn) biomagnification

Detailed procedures on this topic can be found in previous

Table 2

Mean, standard deviation ($\pm\text{SD}$), and minimum and maximum values of ΣSn concentrations [in $\mu\text{g}\cdot\text{g}^{-1}$, dry weight (dw)] in liver, as well as of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data (‰) in muscle, of delphinids from Rio de Janeiro state (RJ), Southeast Brazil (SE), along with the number of samples analysed (n), and the number of samples that rendered values above the detection limit ($n > \text{DL}$) for tin levels, comprising estuarine, continental shelf, SACW, shelf-slope and oceanic dolphins.

Habitat/area	Sn conc. mean ($\pm\text{SD}$) min–max [n (n above DL)]	$\delta^{13}\text{C}$ mean ($\pm\text{SD}$) min–max [n]	$\delta^{15}\text{N}$ mean ($\pm\text{SD}$) min–max [n]	Year of death
Estuarine	11.6 (± 8.08) 0.38–27.6 [24 (22)]	–13.5 (± 0.8) –15.1/–12.3 [17]	14.7 (± 0.8) 13.4/16.2 [17]	1994–2006
Cont. Shelf	4.03 (± 3.46) 0.32–8.37 [4 (3)]	–14.9 (± 0.5) –15.6/–14.4 [4]	14.3 (± 1.7) 11.6/15.9 [4]	1995–2001
SACW	4.04 (± 2.79) 1.61–8.46 [6 (6)]	–15.6 (± 0.4) –16.0/–15.0 [6]	13.6 (± 0.9) 12.2/15.2 [6]	1998–2001
Shelf-slope	0.86 (± 1.01) 0.21–3.06 [6 (3)]	–15.7 (± 0.4) –16.4/–15.4 [4]	11.5 (± 0.3) 11.1/12.0 [4]	1995–2003
Oceanic	0.11 (± 0.25) 0.04–0.95 [12 (1)]	–16.5 (± 0.2) –16.8/–16.0 [9]	12.8 (± 0.6) 11.8/13.8 [9]	1997–1999

Estuarine: *Sotalia guianensis* ($n = 20$) and *Steno bredanensis* ($n = 4$); Continental Shelf: *Tursiops truncatus* ($n = 3$) and *Pseudorca crassidens* ($n = 1$); SACW: *Stenella frontalis* ($n = 6$); Shelf-slope: *Delphinus sp.* ($n = 3$), *Stenella attenuata* ($n = 2$) and *Grampus griseus* ($n = 1$); Oceanic: *Stenella longirostris* ($n = 2$) and *Lagenodelphis hosei* ($n = 10$). Data on ΣSn concentrations and stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) values were originally generated by Dorneles et al. (2008a) and Bisi et al. (2013), respectively; however, they had never been statistically treated together. SACW stands for “under the influence of the South Atlantic Central Water”.

Table 3

Mean, standard deviation ($\pm\text{SD}$), and minimum and maximum values of ΣSn concentrations [in $\text{ng}\cdot\text{g}^{-1}$, dry weight (dw)] in liver, as well as of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data (‰) in muscle, of fish species from Sepetiba Bay (SB), Rio de Janeiro state (RJ), Southeast Brazil (SE), along with the number of samples analysed (n), and the number of samples that rendered values above the detection limit ($n > \text{DL}$) for tin levels.

Vulgar name scientific name	Sn ($\text{ng}\cdot\text{g}^{-1}$, dw) mean ($\pm\text{SD}$) min–max [n (n above DL)]	$\delta^{15}\text{N}$ (‰) mean ($\pm\text{SD}$) min–max [n]	TP mean ($\pm\text{SD}$) min–max [n]	TL (cm) mean ($\pm\text{SD}$) min–max [n]
Yellow catfish	257 (± 225)	14.4 (± 0.79)	2.7 (± 0.2)	27.0 (± 3.18)
<i>Aspistor luniscutis</i>	97.7–780 [7 (6)]	13.5/15.7 [4]	2.4/3.1 [4]	22.1/31.4 [7]
Ribbonfish	89.3 (± 39.9)	16.7 (± 0.29)	3.4 (± 0.1)	68.0 (± 23.0)
<i>Trichiurus lepturus</i>	53.9–159 [8 (5)]	16.2/17.1 [5]	3.2/3.5 [5]	21.4/94.6 [8]
Whitemouth croaker	159 (± 173)	14.3 (± 1.07)	2.7 (± 0.3)	40.7 (± 7.48)
<i>Micropogonias furnieri</i>	16.4–806 [29 (25)]	11.8/15.8 [11]	1.9/3.1 [11]	29.1/57.9 [29]
Common snook	137 (± 71.3)	15.1 (± 0.83)	2.9 (± 0.2)	27.9 (± 2.55)
<i>Centropomus sp.</i>	56.8–287 [10 (10)]	14.0/16.3 [6]	2.6/3.3 [6]	23.0/31.3 [10]
White mullet	6.76 (± 7.01)	10.0 (± 0.74)	1.4 (± 0.2)	26.9 (± 1.63)
<i>Mugil curema</i>	2.70–24.5 [10 (3)]	9.27/11.0 [5]	1.2/1.7 [5]	24.8/29.6 [10]

Data on stable nitrogen isotope ($\delta^{15}\text{N}$) values were originally generated by Bisi et al. (2012).

investigations of our research team (Bisi et al., 2012; Azevedo-Silva et al., 2016). Briefly, the trophic position (TP) of each individual was assessed by the formula: $\text{TP} = [(\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{source}})/3.4] + \lambda$ (Jepsen and Winemiller, 2002; Winemiller et al., 2007). The adopted denominator value (3.4) was extracted from studies on isotopic enrichment of ^{15}N (Minagawa and Wada, 1984; Post, 2002). The value “1” was used for λ , which references the source for the system (Jepsen and Winemiller, 2002; Vander Zanden et al., 1997). The latter statement is explained by the fact that the datum used was the mean $\delta^{15}\text{N}$ value (8.6‰) for the seston samples collected in the inner part, at low tide (8.9‰), as well as in the entrance, at high tide (8.3‰), of Sepetiba Bay, in the same period as the fish, i.e., austral summer 2009, as published in Bisi et al. (2012). The estimation of total tin (TSn) biomagnification was performed through the calculation of the Trophic Magnification Factor (TMF) and slope (b) of a log-linear regression between total tin (TSn) concentration and $\delta^{15}\text{N}$. TMF is the anti-log of the slope of a log-linear regression between contaminant level and TP. A TMF value higher than 1.0 would point out biomagnification, while a $\text{TMF} < 1.0$ would indicate pollutant trophic dilution (Borgå et al., 2012; Fisk et al., 2001; Jøger et al., 2009; Kelly et al., 2008). The used formula was $\text{TMF} = 10^b$, which is extracted from the equation $\text{Log}_{10}[\text{Sn}] = a + b(\text{TP})$, where a refers to the point of intersection to the axis of ordinates and b constitutes the slope of the regression. A significant and positive slope ($b > 0$) of a log-linear regression between the analyte concentration and $\delta^{15}\text{N}$ ($\text{Log}_{10}[\text{Pollutant}] = a + b(\delta^{15}\text{N})$) implies magnification in a food web (Lavoie et al., 2013). The slope (b) of regression, also known as Trophic Magnification Slope (TMS), have been used to estimate contaminant biomagnification in distinct environments (Campbell et al., 2005; Kidd et al., 2001; Lavoie et al., 2013; Poste et al., 2015), turning comparison among systems into an easier task.

2.5. Statistical treatment

Firstly, the appropriateness of employing non-parametric or parametric tests was assessed. Shapiro–Wilk’s W test was applied as data normality test, whereas the Brown–Forsythe one was used for evaluating the homogeneity of variance. The tests were used to separate data sets, i.e., Guiana dolphins from Guanabara Bay (the whole group, only males,

only females, etc). Based on the results of these tests, non-parametric [Kruskal–Wallis test, Mann–Whitney U test, Spearman's (R_s) correlation test] or parametric [ANOVA, Student's t -test, Pearson's (r) correlation test] tests were utilized. For statistical analysis, concentrations below DL were assigned a value equal to f^*DL , where f is the number of samples in which the compound was detected within the group concerned (e.g. male Guiana dolphins from ES state), divided by the total number of samples analysed (Das et al., 2017; Parente et al., 2018). The level of significance was set at $p \leq 0.05$ and the STATISTICA 8.0 Statistical Software System was employed for statistical treatment.

3. Results and discussion

3.1. Total tin levels of Guiana dolphins from distinct ecological populations

Due to some aspects of the biology of *S. guianensis*, comprising the fact that the species usually exhibits habitat fidelity, the Guiana dolphin presents various ecological populations through its occurrence area (Andrade et al., 2014; Azevedo et al., 2009; Lailson-Brito et al., 2010; Santos et al., 2019). An ecological population is understood herewith as the major ecological unit relatively to resource consumption. Since it constitutes a local concentration of individuals, the ecological population may not comprise a unit from the genetical point of view (Lewontin, 1974). This describes the situation of *S. guianensis*, since, for this species, a genetic unit may consist of a few ecological populations (Cunha et al., 2005; Cunha and Watts, 2007; Hollatz et al., 2011). Hepatic ΣSn concentrations of Guiana dolphins from five different coastal areas, comprising juveniles and adult males and females from two Brazilian regions (Southeast and South) and four states (Espírito Santo – ES, Rio de Janeiro – RJ, Paraná – PR and Santa Catarina – SC) are presented in Table 1. Male (M) and female (F) dolphins presenting total length (TL) values lower than 179 (M) and 177 cm (F) for individuals from the South region (Rosas et al., 2003), as well as 180 (M) and 160 cm (F) for Southeast Brazil (Beneditto and Ramos, 2004) were treated as juvenile dolphins.

Comparison among the five Guiana dolphin ecological populations studied herewith for ΣSn concentrations was performed in three different age and sex groups, i.e., considering only juveniles (J), only adult females (AF) and only adult males (AM). Significant differences were found in these three age and sex groups [Kruskal–Wallis test: H (4, $N = 50$) = 22.89, $p = 0.0001$, for J (Fig. 2A); H (4, $N = 41$) = 18.85, $p = 0.0008$, for AF (Fig. 2B); and H (4, $N = 30$) = 17.80, $p = 0.0014$, for AM (Fig. 2C)] and the highest tin levels were found in Guanabara Bay (GB). Considering only juvenile dolphins, significantly higher ΣSn concentrations were found in GB than in Great Vitória – GV ($U = 7$; $p = 0.0002$), Sepetiba Bay – SB ($U = 29$; $p = 0.0009$) and Paranaguá Bay – PB ($U = 4$; $p = 0.002$). Regarding adult females, significantly higher ΣSn concentrations were found in GB than in GV ($U = 6$; $p = 0.004$), SB ($U = 0$; $p = 0.0001$), PB ($U = 2$; $p = 0.003$) and BB ($U = 0$; $p = 0.01$). For adult males, significantly higher ΣSn concentrations were found in GB than in GV ($U = 1$; $p = 0.01$), SB ($U = 1$; $p = 0.01$) and PB ($U = 4$; $p = 0.003$). The highest concentrations were expected to be found in GB, as extremely high concentrations of other persistent bioaccumulative toxicants (PBTs) have been found in the small (~40 individuals) Guiana dolphin population (Azevedo et al., 2017) that inhabits this estuary (Dorneles et al., 2010, 2007; Lailson-Brito et al., 2012), including investigations in which the expression “high accumulation” appears in the title (Dorneles et al., 2008b, 2013; Lailson-Brito et al., 2010). In fact, Guanabara Bay is considered the most disturbed system along the area of *S. guianensis* occurrence (Lailson-Brito et al., 2000). The estuary has been suffering for decades with the increase of human population and industrialization in its surroundings (Fistarol et al., 2015). Guanabara Bay receives effluents from 15 municipalities that harbour approximately 12 million people (IBGE, 2018), and it is surrounded by more than 16,000 industries, several shipyards, many marinas, two commercial ports, two

naval bases, as well as by oil and gas terminals (Coelho, 2007; Fonseca et al., 2009). Concerning ΣSn levels, a previous study of ours (Dorneles et al., 2008a) observed that the concentrations found in Guiana dolphins from GB were among the highest ever reported for marine mammals. In addition, extremely high concentrations of butyltin (BT) species had been found in environmental samples from the estuary, reaching ΣBT values higher than 915 ng g^{-1} (dry weight, as Sn) in sediment (Fernandez et al., 2005).

Regarding our results involving comparison between coastal areas other than GB, significantly higher ΣSn concentrations were found in Babitonga Bay (BB, Santa Catarina state) than in Great Vitória (GV) in two different age and sex groups, i.e., for juveniles ($U = 8$; $p = 0.037$) and for adult males ($U = 0$; $p = 0.037$). In addition, significantly higher ΣSn concentrations were found in Sepetiba Bay (SB) than in GV ($U = 34$; $p = 0.023$). Our results from Babitonga Bay corroborate those from an investigation that analysed sediment samples from Santa Catarina state collected between July 2008 and October 2007, since those authors verified intense inputs of antifouling paints to the environment in the region (de Oliveira et al., 2010). Although less impacted than GB, Sepetiba Bay (SB) has suffered an abrupt increase in anthropogenic disturbance in the last decades. Taking into account the two municipalities that drain exclusively to SB as an example, Itaguaí and Mangaratiba, it is possible to observe increases of 141 and 66% in the infrastructure coverage from 1985 to 2015, respectively. The exact notion on how sudden the urbanization process in those two municipalities occurred can be achieved when it is considered that an expressively smaller increase (12%) was verified for the same variable and period of time in the capital and largest city of the state, Rio de Janeiro city (MapBiomias, 2019). Moreover, a decrease of approximately 26% in Sepetiba Bay mangrove area was verified between 1987 and 2015 (Araújo et al., 2017) and metallurgical, petrochemical and pyrometallurgical smelters have been established on the drainage basin of the bay since the beginning of the 1970s (Molisani et al., 2004).

In order to investigate an interference of a possible temporal variation in the exposure of Guiana dolphins, the relation between ΣSn concentrations and the year of death was investigated on juvenile dolphins. A significant negative correlation was found between the two variables when all juvenile Guiana dolphins were included in the statistical test ($p = 0.006$, $R_s = -0.38$); however, this correlation ceases to exist ($p = 0.4$) when the individuals from GB are excluded from the statistical test. In addition, evaluating Guiana dolphins from each ecological population separately, a significant negative correlation between ΣSn concentrations and the year of death was found only for Guanabara Bay ($p = 0.002$, $R_s = -0.75$). This estuary was the area whose samples presented the widest range for the year of death, as it ranged from 1994 to 2009. For the other four study areas, the year of death varied from 2005 to 2012. Therefore, the possibility of occurrence of correlation between ΣSn concentrations and year of death was investigated for juvenile Guiana dolphins from all five areas, comprising individuals who died between 2005 and 2012 and there was no correlation in this scenario as well ($p = 0.99$). Considering all the results mentioned in this paragraph, the investigation of possible geographical differences was performed restricted to juvenile Guiana dolphins that died from 2005 to 2012 in order to minimize the possible interference of a temporal variation. Significant differences in ΣSn concentrations were found in this new scenario [Kruskal–Wallis test: H (4, $N = 42$) = 12.05, $p = 0.017$] and the highest tin levels were found in Guanabara Bay (GB). Still in this scenario, significantly higher ΣSn concentrations were found in GB than in Great Vitória – GV ($U = 7$; $p = 0.01$), as well as than in Paranaguá Bay – PB ($U = 4$; $p = 0.02$).

Possible gender-related dissimilarities were investigated both within each Guiana dolphin ecological population and considering all individuals; however, no significant differences in hepatic ΣSn concentrations were found between adult males and females. These results corroborate those from our previous study on total tin concentrations (Dorneles et al., 2008a), as well as data from investigations comprising

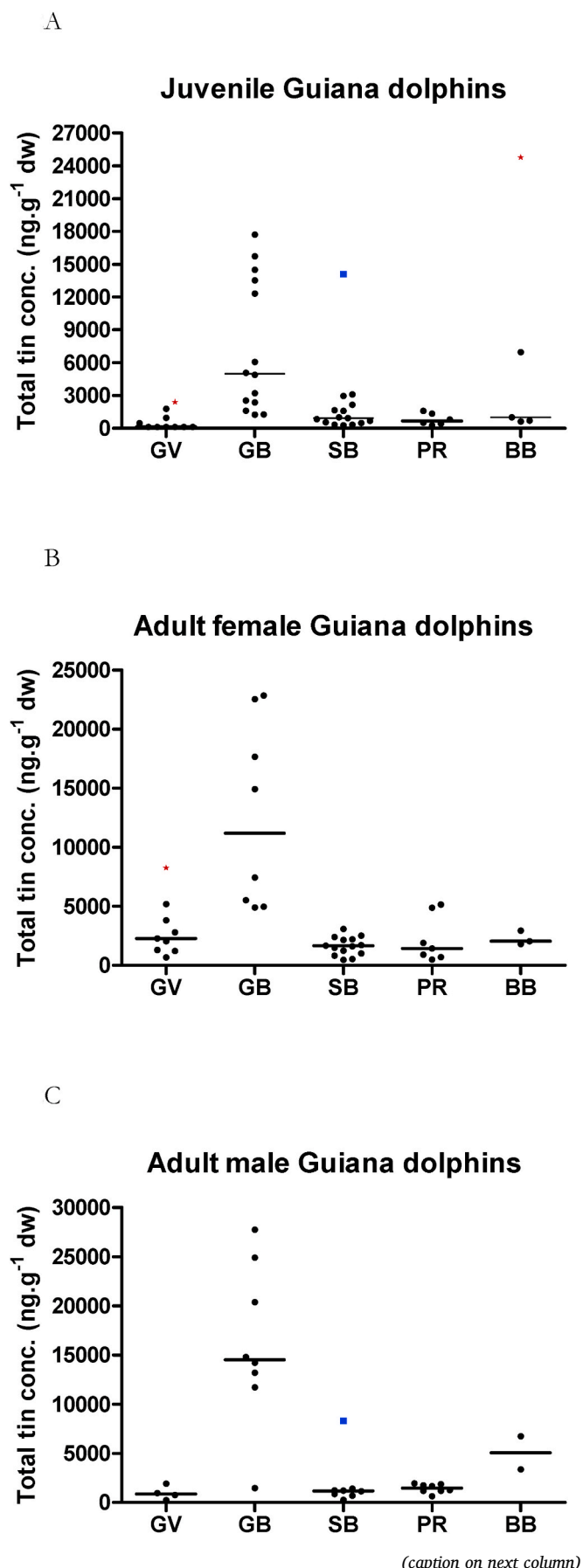


Fig. 2. Scatter dot plots of hepatic Σ Sn concentrations [in $\text{ng}\cdot\text{g}^{-1}$, dry weight (dw)] of juvenile (A) and adult female (B) and male (C) Guiana dolphins from Great Vitória (GV), Guanabara Bay (GB), Sepetiba Bay (SB), Paraná state (PR) and Babitonga Bay (BB). The red stars and the blue squares indicate outlier and extreme values, respectively, while the horizontal line designate the median. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

butyltin levels in cetaceans, since either no significant gender-related differences (Ciesielski et al., 2004; Kannan and Falandysz, 1997; Kim et al., 1996b; Madhusree et al., 1997; Strand and Jacobsen, 2005; Takahashi et al., 2000) or slightly higher concentrations in males than in females (Focardi et al., 2000) have been found. Although the mother-to-calf transfer of OTs occurs (Dorneles et al., 2008a; Focardi et al., 2000; Kannan and Falandysz, 1997; St-Louis et al., 2000; Tanabe et al., 1998; Yang et al., 2007; Yang and Miyazaki, 2006), it does not seem to be enough for generating significant lower concentrations in females than in males, as it is a common finding for organohalogen compounds in cetaceans (Das et al., 2017; Dorneles et al., 2015).

Regarding the possibility of bioaccumulation of OTs by mammals, an important characteristic to be considered is that total length is not a perfect proxy for age in this vertebrate class, as the aging process continues for years after the growing has ceased (Harrison et al., 1988). However, length could be a good proxy for age, as long as the growth of the animal is still occurring. Therefore, the possibility of Σ Sn bioaccumulation was investigated for juvenile dolphins. Evaluating each ecological population of Guiana dolphins separately, a significant positive correlation between Σ Sn concentrations and total length was only found for Grande Vitoria region ($p = 0.0009$, $R_s = 0.87$). Nevertheless, a significant positive correlation between tin levels and TL was also verified when data on juvenile Guiana dolphins from the five ecological populations investigated were treated together ($p = 0.038$, $R_s = 0.3$). These findings corroborate those from previous studies on OTs in marine mammals, as they observed a concentration increase with length until maturity and then a tendency for the levels to remain constant (Ciesielski et al., 2004; Kannan et al., 1997; Kim et al., 1996b; Madhusree et al., 1997; Strand and Jacobsen, 2005; Takahashi et al., 2000).

3.2. A coast-ocean gradient in dolphin exposure to organotins (OTs)

For evaluating the importance of the distance from the hotspot area for cetacean exposure to OTs, data from two published studies from our research team were treated together for the first time, as they provided hepatic Σ Sn concentrations (Dorneles et al., 2008a) and stable isotope (N and C) ratios (Bisi et al., 2013) from delphinids species/populations that inhabited from Guanabara Bay (GB, Rio de Janeiro state) to oceanic waters. This allowed an investigation on a possible coast-ocean gradient in dolphin exposure to these organometallic compounds. The data on hepatic Σ Sn concentrations and stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) values in muscle of marine mammals from Rio de Janeiro state (RJ), Southeast Brazil (SE), were summarized on Table 2. The sampling set comprised estuarine, continental shelf, shelf-slope and oceanic dolphins, as well as delphinids that live under the influence of the South Atlantic Central Water (SACW). The main finding is shown on Fig. 3A, i.e., a significant positive correlation was found between hepatic Σ Sn concentrations and $\delta^{13}\text{C}$ values ($p = 2.2\text{E-}11$, $R_s = 0.84$; Fig. 3A), demonstrating the coast-ocean gradient in the exposure of delphinids from Rio de Janeiro state to organotin compounds. Estuaries are the hotspots for environmental contamination by antifouling agents not only because they present the highest number of vessels per Km^2 among the marine systems, but also since they constitute the areas where maintenance of ships and oil platforms takes place. Within bays, ship and boat hulls containing residues of old antifouling agents are sandblasted and new coats of antifouling paints are applied on those surfaces (Fent, 1996). Concerning carbon, the most important isotopic fractionation is produced during the fixation of this element by photosynthesizing organisms (Kelly,

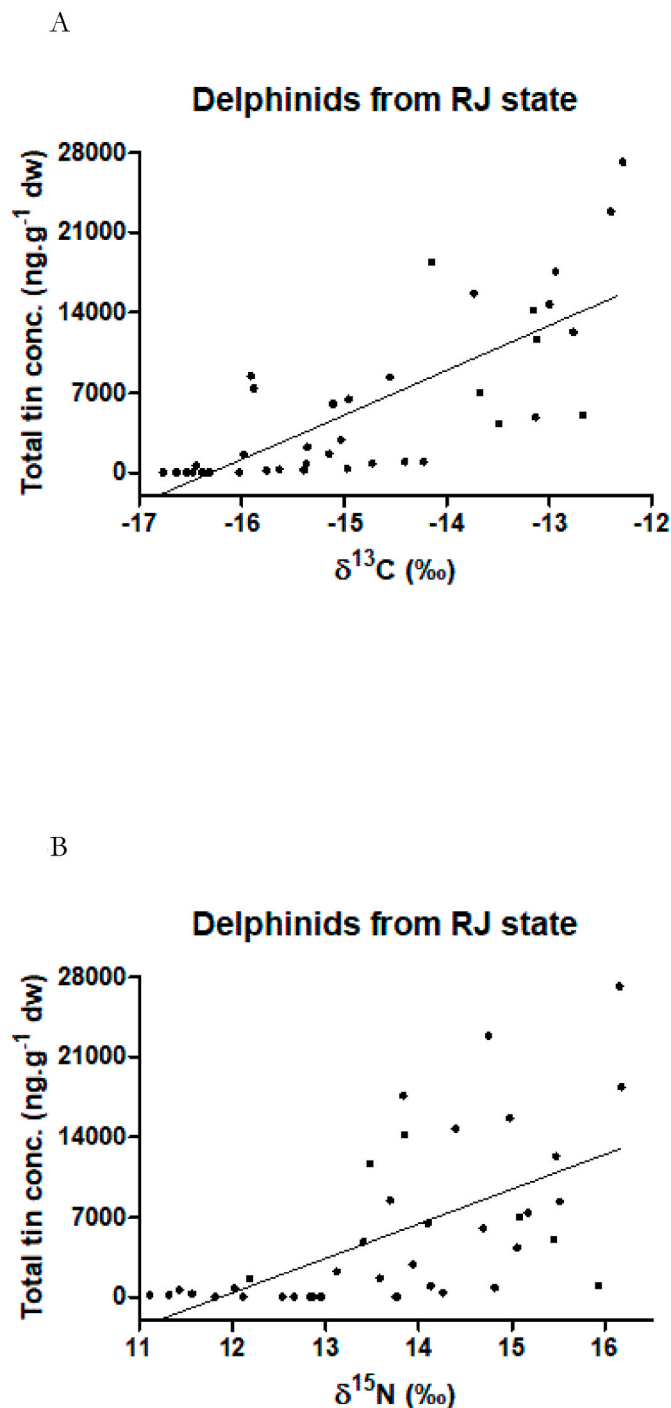


Fig. 3. Significant positive correlations between hepatic total tin (Σ Sn) concentrations ($\text{ng}\cdot\text{g}^{-1}$, dry weight) and $\delta^{13}\text{C}$ (‰) values ($p = 2.2\text{E-}11$, $R_s = 0.84$; Fig. 3A), as well as $\delta^{15}\text{N}$ (‰) values ($p = 0.000002$, $R_s = 0.67$; B) of estuarine, continental shelf, SACW, shelf-slope and oceanic delphinids from Rio de Janeiro state. Estuarine: *Sotalia guianensis* ($n = 14$) and *Steno bredanensis* ($n = 3$); Continental Shelf: *Tursiops truncatus* ($n = 3$) and *Pseudorca crassidens* ($n = 1$); SACW: *Stenella frontalis* ($n = 6$); Shelf-slope: *Delphinus* sp. ($n = 1$), *Stenella attenuata* ($n = 2$) and *Grampus griseus* ($n = 1$); Oceanic: *Stenella longirostris* ($n = 1$) and *Lagenodelphis hosei* ($n = 8$). Data on Σ Sn concentrations and stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) values were originally generated by Dorneles et al. (2008a) and Bisi et al. (2013), respectively; however, they had never been statistically treated together. SACW stands for “under the influence of the South Atlantic Central Water”.

2000). The carbon isotope ratio of these organisms will result from a combination of factors that includes which enzymes would be involved in this fixation and the molecule (CO_2 , HCO_3^-) source (Fry, 2006). The phytoplankton from the oceanic province is ^{13}C depleted in comparison to the photosynthesizing organisms that contributes to the energy flow within estuaries. The higher is the contribution of oceanic phytoplankton to the energy that is obtained by a sea animal, the lower is the $\delta^{13}\text{C}$ value of this component of the marine fauna. Therefore, the $\delta^{13}\text{C}$ value ends up being a continuous variable that indicates how distant from the continent a marine animal feeds (Glew et al., 2019; MacKenzie et al., 2014). Thus, the significant positive correlation found between hepatic Σ Sn concentrations and $\delta^{13}\text{C}$ values corroborates those from several studies on marine mammals in which stable carbon isotopes ($^{13}\text{C}/^{12}\text{C}$) have been used to investigate the relationship between contaminant uptake and distance from their habitats to sources of pollution (Das et al., 2004, 2003; 2000; Fontaine et al., 2007; Van de Vijver et al., 2003).

Similarly, a significant positive correlation was found between hepatic Σ Sn concentrations and $\delta^{15}\text{N}$ values ($p = 0.000002$, $R_s = 0.67$; Fig. 3B) as well. Although the ratio between stable nitrogen isotopes has been used for evaluating trophic position, this positive correlation may not result only from the OT biomagnification process. Different regions and consequently food webs are being considered here and it is well-known that variations in $\delta^{15}\text{N}$ values of organisms on the base of the food webs may occur among distinct environments (Cabana and Rasmussen, 1996; Pinela et al., 2010). It is relevant to draw attention to the fact that cyanobacteria constitute key producer organisms in oceanic provinces and the low $\delta^{15}\text{N}$ values commonly found in the oceanic biota have been linked to the N fixation by those microorganisms (Carpenter et al., 1999, 1997; McClelland et al., 2003). In that oligotrophic region, nitrate constitutes a fundamental N source and this molecule in general presents extremely low $\delta^{15}\text{N}$ values (Liu and Kaplan, 1989; Sigman et al., 2009). The correlation between Sn levels and $\delta^{15}\text{N}$ values seems to be a consequence of an enhancement of the contribution of the cyanobacteria to the energy flow of the food web with an augmentation of the distance from the continent, which is supported by another finding, i.e., a significant positive correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values ($p = 0.000001$, $R_s = 0.68$).

3.3. Investigation of Σ Sn trophic flow through a food web

Hepatic Σ Sn concentrations of fish from Sepetiba Bay, comprising five different species, together with total length and trophic position values are presented on Table 3. Although the $\delta^{15}\text{N}$ values of these fish have already been published (Bisi et al., 2012), they were summarized in Table 3 as well. Concerning the feeding habits of these species: the whitemouth croaker is a carnivore fish, with preference for benthic organisms (Denadai et al., 2015); the common snook is essentially piscivorous, since an investigation on its diet demonstrated that fishes made up 71% of the prey by number and 90% by weight (Blewett et al., 2006); the ribbonfish feeds on fish, squids and shrimps (Bittar et al., 2012); the yellow catfish has a specialised diet of teleost scales, but it also exerts predation on crustaceans (Guedes et al., 2015); as well as the white mullet is a planktivorous fish that feeds near the surface (Mai et al., 2018; Rueda, 2002). A positive linear relationship between log-transformed hepatic Σ Sn concentrations ($\text{ng}\cdot\text{g}^{-1}$, dry weight) and $\delta^{15}\text{N}$ values (‰) was found (linear regression, $p < 0.006$; Fig. 4A) and the Trophic Magnification Slope (TMS) value was 0.14. In addition, a positive linear relationship between Trophic Position (TP) values and hepatic Σ Sn concentrations was found (linear regression, $p < 0.006$; Fig. 4B), generating the Trophic Magnification Factor (TMF) value of 3.03. Therefore, the TMF was higher than 2.0, the value suggested by Borgå et al. (2012) for enhancing the consistency of the TMF results. Consequently, Σ Sn biomagnification was verified in the ichthyofauna of Sepetiba Bay by both methods adopted for calculating the rate of such trophic magnification process, i.e., TMF and TMS. A similar

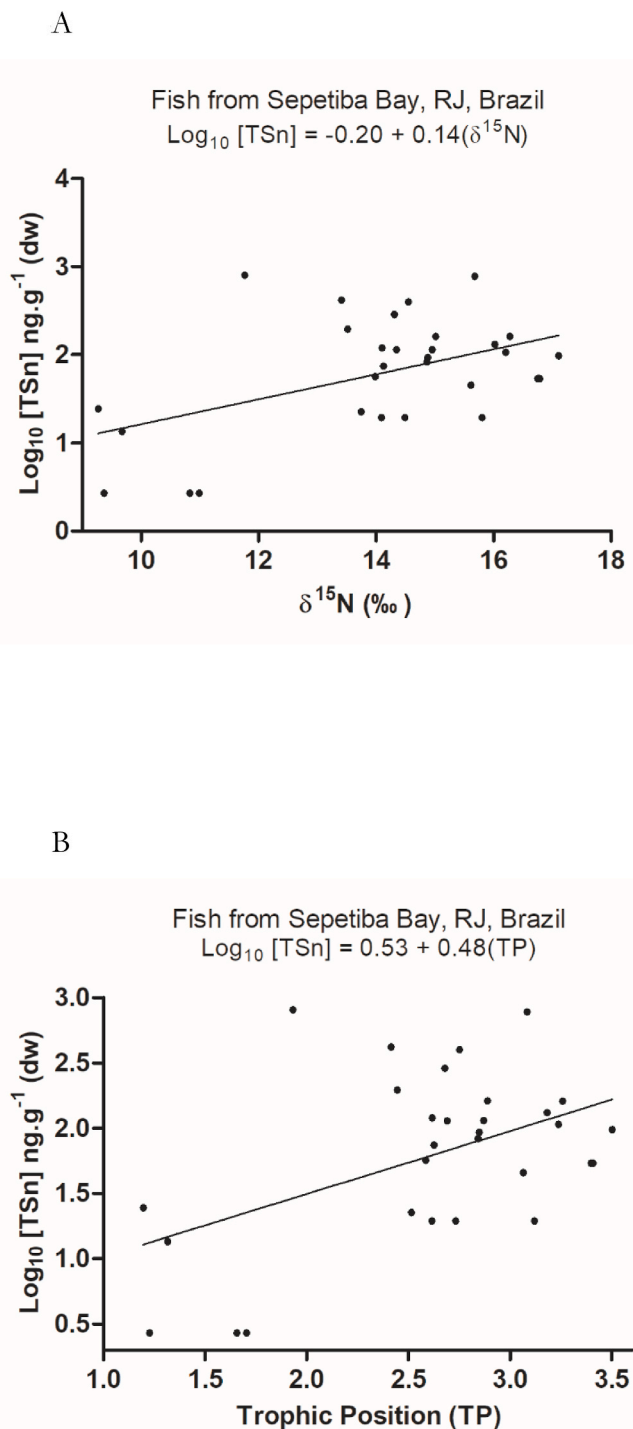


Fig. 4. Positive linear relationships between log-transformed hepatic ΣSn concentrations (ng.g^{-1} , dry weight) and $\delta^{15}\text{N}$ (‰) values (linear regression, $p < 0.006$; TMS = 0.14; A), as well as Trophic Position (TP) values (linear regression, $p < 0.006$; TMF = 3.03; B) of fish from Sepetiba Bay, comprising 31 individuals, from five different species (yellow catfish, *Aspistor luniscutis*, $n = 4$; ribbonfish, *Trichiurus lepturus*, $n = 5$; whitemouth croaker, *Micropogonias furnieri*, $n = 11$; common snook, *Centropomus* sp., $n = 6$; white mullet, *Mugil curema*, $n = 5$). TMS and TMF stand for Trophic Magnification Slope and Trophic Magnification Factor, respectively.

biomagnification scenario was found for TBT, dibutyltin (DBT, a TBT metabolite) and the sum of butyltins [ΣBT , which is the sum of TBT, DBT and monobutyltin (MBT)], since the TMF values of 3.98, 4.62 and 3.88 were found for TBT, DBT and ΣBT , respectively, in a Northern Adriatic food web (Fortibuoni et al., 2013). Other investigations that adopted the same approach as the latter and the present studies, i.e., which used $\delta^{15}\text{N}$ data for evaluating trophic magnification, have found biomagnification for TPhT but not for TBT (Hu et al., 2006; Murai et al., 2008). Some studies have shown higher concentrations of TPhT than that of TBT in marine environments with lower input of TPhT in comparison to TBT and an explanation for those findings seemed to be provided by the hypothesis that TPhT would biomagnify, but not TBT (Borghi and Porte, 2002; Hu et al., 2006). Since both organotin compounds, TBT and TPhT, can contribute to ΣSn concentrations and both have been used as anti-fouling agents in Brazil, it is not possible to know which OT is providing the most significant contribution to the ΣSn biomagnification found in the present study. Since all studies that investigated the trophic flow of butyltin and phenyltin using $\delta^{15}\text{N}$ data have shown TPhT biomagnification, it is important to draw attention to the fact that the latter OT has been used in Brazil, not only as antifouling agent, but also as a fungicide in agriculture (Antes et al., 2011).

It is interesting to perform comparison to mercury, not only as it is a metal that consistently biomagnifies, but also because Hg undergoes this trophic magnification due to its presence in an organic molecule, methylmercury (Gray, 2002). Therefore, it is worth drawing attention to the fact that lower TMS values than those found in the present study have been verified for ΣHg (0.13) in tropical marine environments (Lavoie et al., 2013). In this context, it is worth mentioning that using samples that included the same individuals analysed in the present study, Bisi et al. (2012) have found a lower (0.07) slope than that verified in the present study (0.17). However, it is important to highlight that more fish species, as well as a squid and a crustacean were included in the sample set analysed by Bisi et al. (2012).

4. Conclusions

The evaluation of exposure of top estuarine predators from South and Southeast Brazil to Organotins (OTs) through hepatic ΣSn concentrations, using the same species (Guiana dolphin) and restricting the comparison to the same sex/age class, reaffirmed Guanabara Bay as an important hotspot area for environmental contamination by OTs. There was an increasing delphinid exposure to OTs, in marine waters of Rio de Janeiro state, from the oceanic province to the estuarine environments. As for total Hg, whose biomagnification occurs as a result of methylmercury flow through the food webs, the trophic magnification of organotin compounds results in the biomagnification of total tin. Therefore, hepatic ΣSn concentrations in fish can be used for investigating the biomagnification of OTs.

Declaration of competing interest

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

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Paulo R. Dorneles: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition. **Priscila F. Schilithz:** Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. **Thais de C. Paiva:** Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. **Leonardo Flach:** Methodology, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Lupercio A. Barbosa:** Methodology, Investigation, Resources, Project

administration, Funding acquisition. **Camila Domit:** Methodology, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Marta J. Cremer:** Methodology, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Claudio E. Azevedo-Silva:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. **Alexandre F. Azevedo:** Methodology, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Olaf Malm:** Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Gilles Lepoint:** Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Tatiana L. Bisi:** Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **Krishna Das:** Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition. **José Lailson-Brito:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing, Project administration, Funding acquisition.

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