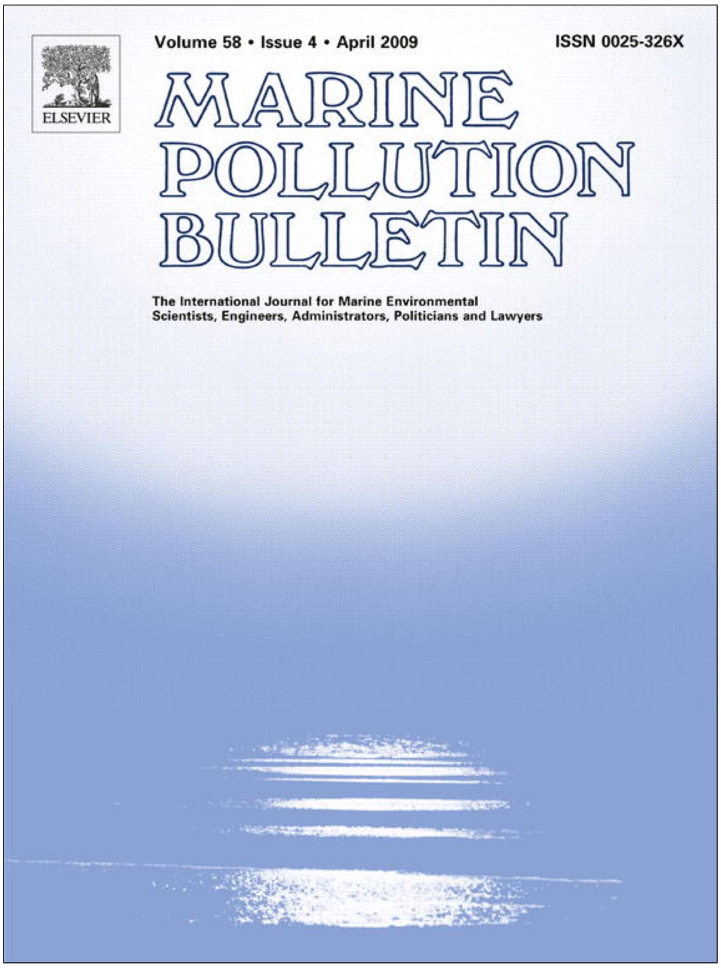
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Kyoto, Japan. Bulletin of Environmental Contamination and Toxicology 79, 427–431.

Senthil Kumar, K., Sajwan, K.S., Weber-Goeke, M.A., Weber-Snapp, S., Kelly, S., Sanya, S.C., Loganathan, B.G., 2007b. Organochlorine pesticides, PCBs and PBDEs in selected plant species from a Superfund Site at Brunswick, Georgia, USA. Organohalogen Compounds 69, 1341–1345.

Senthil Kumar, K., Peck, A., Whitney, P., Sajwan, K.S., 2008a. Clearance rate and mass loadings of triclosan and triclocarbon in four wastewater treatment plants in Savannah, Georgia, USA. Organohalogen Compounds 70, 233–236.

Senthil Kumar, K., Sajwan, K.S., Richardson, J., Kannan, K., 2008b. Contamination profiles of heavy metals, organochlorine pesticides, polycyclic aromatic hydrocarbons, and alkylphenols in sediment and oyster collected from marsh/estuarine Savannah, GA, USA. Marine Pollution Bulletin 56, 136–149.

Sinclair, E., Mayack, D.T., Roblee, K., Yamashita, N., Kannan, K., 2006. Occurrence of perfluoroalkyl surfactants in water, fish, and birds from New York State. Archives of Environmental Contamination and Toxicology 50, 398–410.

Sinclair, E., Kim, S.Y., Akinleye, H.B., Kannan, K., 2007. Quantitation of gas-phase perfluoroalkyl surfactants and fluorotelomer alcohols released from nonstick cookware and microwave popcorn bags. Environmental Science and Technology 41, 1180–1185.

Taniyasu, S., Kannan, K., Horii, Y., Hanari, N., Yamashita, N., 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds and humans from Japan. Environmental Science and Technology 37, 2634–2639.

Wendelaar Bonga, S.E., Lock, R.A.C., 1992. Toxicants and osmoregulation in fish. Netherlands Journal of Zoology 42, 478–493.

Zushi, Y., Masunaga, S., in press. Identifying the nonpoint source of perfluorinated compounds using a geographic information system based approach. Environmental Toxicology and Chemistry.

Zushi, Y., Takeda, T., Masunaga, S., 2008a. Existence of nonpoint source of perfluorinated compounds and their loads in the Tsurumi River basin, Japan. Chemosphere 71, 1566–1573.

0025-326X/$ - see front matter
doi:10.1016/j.marpolbul.2008.12.005

Essential (Se, Cu) and non-essential (Ag, Hg, Cd) elements: What are their relationships in liver of *Sotalia guianensis* (Cetacea, Delphinidae)?

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Cetaceans are very sensitive to environmental changes and have been considered good bioindicators of environmental contamination (Capelli et al., 2000). The analysis of tissues from different species of whales and dolphins has been used as a tool for the assessment of marine pollution by trace elements (Caurant et al., 1994; Woshner et al., 2001; Kunito et al., 2004; Seixas et al., 2007a). These organisms have high potential for accumulating some trace elements, such as selenium (Se), copper (Cu), silver (Ag) mercury (Hg) and cadmium (Cd), since they have relatively long life spans, and generally occupy a high trophic level in the marine food chain (Woshner et al., 2001; Kunito et al., 2004). They present high hepatic concentrations of these elements that are related to the role played by the liver in terms of pollutant bio-transformation, metabolizing nutrients and essential elements as well as removing some non-essential elements and toxins from the bloodstream (Frodello et al., 2000).

Selenium and copper are recognized as essential elements for the normal growth and metabolism of aquatic mammals (Eisler, 2000). Conversely, silver, cadmium and mercury are exogenous and harmful elements, which accumulate during growth (Feroci et al., 2005). Selenium is reported to have an antidotal action on the toxic effects of some heavy metals, e.g. mercury, cadmium, and copper. Although silver is not currently a major concern with regard to toxicity in mammals, it has been of some interest due to its interaction with selenium. The interaction of Ag with Se differs from other selenium–metal interactions in that silver can induce symptoms of selenium deficiency (Becker et al., 1995). Until now, most studies have focused on the contamination status of Se, Cu, Hg and Cd in liver of cetaceans (Caurant et al., 1994; Capelli et al., 2000; Gerpe et al., 2002; Kunito et al., 2004; Seixas et al., 2007a). However, few data are reported concerning the concentrations of silver in cetaceans (Becker et al., 1995; Woshner et al., 2001; Kunito et al., 2004; Dehn et al., 2006). Furthermore, extensive studies of Se, Cu, Hg, Cd and Ag concentrations in cetaceans have been carried out in the Northern Hemisphere (Caurant et al., 1994; Becker et al., 1995; Dietz et al., 1996; O'Shea, 1999; Woshner et al., 2001; Roditi-Elasar et al., 2003; Ikemoto et al., 2004; Dehn et al., 2006; Stockin et al., 2007) but relatively little is known about contaminant levels in Southern Hemisphere cetaceans (Gerpe et al., 2002; Bustamante et al., 2003; Kunito et al., 2004; Seixas et al., 2007a, 2008; Lavery et al., 2008).

The objectives of this study were to: (1) evaluate concentrations of essential (Se, Cu) and non-essential (Ag, Hg, Cd) elements in liver; (2) assess their hepatic inter-element relationships; and (3) determine whether these hepatic element concentrations differ with gender and body length in 19 individuals of *Sotalia guianensis* (estuarine dolphin) incidentally caught in fishing nets along the Northern Rio de Janeiro (Brazil) (~21°S to 22°S) between 1998 and 2005 (Fig. 1).

The biological characteristics of *S. guianensis* are presented in Table 1. The classification of *S. guianensis* individuals into three classes of age, calves, young and adults, was based on data concerning their body length (Table 1), as it was not possible to determine the age of all individuals in the basis of the growth layers of teeth. According to Di Beneditto and Ramos (2004), the average length at birth of these dolphin individuals occurs when they present a body length between 86.0 and 117.5 cm. However, estuarine dolphins from the northern Rio de Janeiro reach asymptotic length when they are approximately 6-years-old and 180 cm (males) or 6-years-old and 160 cm long (females) (Di Beneditto and Ramos, 2004). In this study, only three individuals were classified as calves as they presented body lengths up to 117.5 cm. Individuals of estuarine dolphins with a body length up to 160 cm (females) and 180 cm (males) were classified as young,

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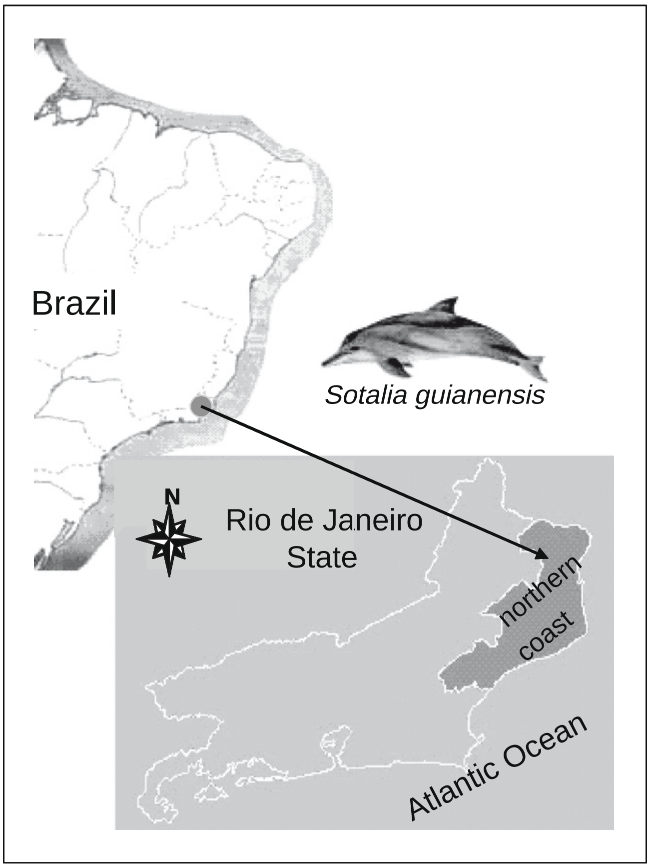

Fig. 1. Location of the Northern Rio de Janeiro (Brazil), where *Sotalia guianensis* individuals were collected.

while females longer than 160 cm and males longer than 180 cm were classified as adults.

Liver samples from 19 individuals of estuarine dolphins were supplied by the Biological Specimen Banking from the Bioscience and Biotechnology Center (UENF). After dissection, samples were stored in identified individual polyethylene bags and kept frozen (−20 °C) until the freeze-drying process. They lost around 70% of their water content.

In homogenized dry samples Cu, Cd, Se, Ag and total mercury (Hg) were determined by atomic absorption spectrometry techniques. Aliquots of liver samples (~100 mg dry wt.) were acid mineralized (HNO_3) in a screw-capped Pirex® vessel at 60 °C in a water bath for 120 min, and Cu, Cd, Se and Ag determinations were made by graphite furnace atomic absorption spectrometry, using an Analytic Jena Model ZEEnit 60 spectrometer (Analytik Jena, Germany) with Zeeman Effect background correction equipped with MPE-52 auto sampler. Palladium nitrate was used as a chemical modifier only in Ag, Cd and Se determinations (Seixas et al., 2007b). Blanks were carried through the procedure in the same way as the sample. Hepatic samples were acid digested with H_2SO_4:HNO_3 (1:1 v/v) and H_2O_2 in an open system at 60 °C in water bath for 45 min. Hg concentrations in the acid digested solution were determined by cold vapor atomic absorption spectrometry with a Flow Injection Mercury System (FIMS) – FIAS 400 (Perkin Elmer, USA) equipped with an auto sampler AS90 (Perkin Elmer, USA) and using sodium borohydride as a reducing agent (Kehrig et al., 2008). Blanks were carried through the procedure in the same way as the sample. The accuracy and precision of the analytical methodologies for Hg, Ag, Cd, Cu and Se determinations were assessed by replicate analysis of certified material (CRM), DORM-2 (Dogfish muscle sample). Recovery of the trace elements in CRM varied between 85-107 % for mercury, 73-98 % for silver, 80-90 % for cadmium, 87-90 % for copper and 82-108 % for selenium.

Statistical analyses were performed using STATISTICA® 7.0 for Windows (StatSoft, Inc. 1984–2004, USA). Data were tested for normal distributions (Shapiro–Wilk's test) and non-parametric tests were then applied. The analysis of variance was performed by Kruskal–Wallis ANOVA followed by a post-hoc test (Mann–Whitney *U*-test) in order to define significant differences. Multiple regressions (R^2) were performed to determine the relationships between body length and the concentrations of trace elements in the liver and also inter-element relationships (on a molar basis). A *P* value of less than 0.05 was chosen to indicate statistical signifi-

Table 1
Biological data of the *Sotalia guianensis* individuals ($N = 19$); their classification in three groups of age; the mean concentrations of essential (Se, Cu) and non-essential (Hg, Ag, Cd) elements and their molar ratio (on a dry weight basis) in the liver of each specimen accidentally caught along the North coast of Rio de Janeiro State.

Code	Gender	Body length (cm)	Age	Concentration in $\mu g\ g^{-1}$ dry wt.					Ratio of molar concentration (dry wt. basis)		
				Se	Cu	Hg	Ag	Cd	Se:Hg	Se:Ag	Se:Cd
Sg01	Male	86	Calve	1.54	71.40	6.52	0.16	0.02	0.60	13.15	109.62
Sg02	Male	103	Calve	1.70	51.56	3.60	0.18	0.01	1.20	12.91	242.22
Sg03	Male	117	Calve	2.55	83.77	3.67	0.72	0.03	1.77	4.84	121.01
Sg04	Male	151	Young	3.72	18.40	5.89	0.14	0.38	1.60	36.30	13.94
Sg05	Male	176	Young	3.13	15.46	8.09	0.11	0.56	0.98	38.88	7.96
Sg06	Male	177	Young	16.63	16.44	26.51	0.34	0.13	1.59	66.80	182.06
Sg07	Male	179	Young	3.15	18.28	8.07	0.26	0.32	0.99	16.55	14.01
Sg08	Female	160	Adult	3.38	19.01	7.59	0.07	0.18	1.13	65.96	26.73
Sg09	Female	165	Adult	4.76	13.44	7.08	0.19	1.48	1.71	34.23	4.58
Sg10	Female	165	Adult	3.96	21.39	8.67	0.21	0.29	1.16	25.73	19.42
Sg11	Female	168	Adult	5.01	15.95	14.98	0.30	0.18	0.85	22.81	39.62
Sg12	Female	176	Adult	12.30	14.52	35.73	0.44	0.22	0.87	38.19	79.59
Sg13	Male	180	Adult	40.35	25.82	59.28	3.53	0.38	1.73	15.62	151.17
Sg14	Female	183	Adult	23.60	21.44	57.87	1.57	0.49	1.04	20.54	68.57
Sg15	Male	184	Adult	12.33	22.14	36.69	0.59	0.44	0.85	28.54	39.88
Sg16	Male	185	Adult	16.14	16.61	37.78	0.60	0.75	1.09	36.75	30.64
Sg17	Male	195	Adult	45.32	23.77	66.62	2.15	0.71	1.73	19.66	90.88
Sg18	Female	196	Adult	36.44	16.39	72.98	1.61	0.85	1.27	28.80	61.03
Sg19	Male	200	Adult	35.90	17.42	59.95	1.75	0.32	1.52	30.92	159.71
Mean	165.6			14.31	26.48	27.77	0.79	0.41	1.25	29.77	76.98
Median	176.0			5.01	18.40	14.98	0.34	0.32	1.16	28.54	51.35

Table 2
Regression coefficients (*R*) between hepatic trace elements concentration (in nmol g^{-1}) and the body length (*L*) of *Sotalia guianensis*.

Relationship	*R*	*P*
Se vs[a] *L*[b]	0.62	0.004
Cu vs[a] *L*[b]	−0.83	0.0001
Hg vs[a] *L*[b]	0.67	0.002
Ag vs[a] *L*[b]	0.43	0.060
Cd vs[a] *L*[b]	0.49	0.035

[a] vs = Versus.
[b] *L* = body length.

cance. Values are presented as mean ± standard deviation (SD) based on a dry weight basis.

Table 1 summarizes the hepatic concentrations of the essential (Se, Cu) and non-essential (Hg, Ag, Cd) elements according to gender and age classification of estuarine dolphin.

Se, Cu, Hg, Ag and Cd in female livers were not significantly different (Kruskal–Wallis ANOVA, $P > 0.05$) from those found in males. Normally, marine mammals present no gender differences in the accumulation of trace elements (O'Shea, 1999), as seen for estuarine dolphins from different Brazilian coastal areas (Monteiro-Neto et al., 2003; Kunito et al., 2004). However, the concentrations of trace elements in the liver of estuarine dolphins can vary with age; some elements, such as cadmium, beginning from zero at birth and increasing over the time; whilst copper concentrations are higher in neonates than in older animals in keeping with previous studies (Woshner et al., 2001; Lavery et al., 2008). In our study, the non-essential element silver did not present a significant difference ($P > 0.05$) in its concentrations between calves, young and adult individuals of estuarine dolphins. On the other hand, Ag concentration did not present a significant relationship with body length. However, Ag increased with increasing body length (*L*) of estuarine dolphins (see Table 2).

Age or growth-dependent increases of trace elements (such as Hg, Se, Ag and Cd) have often been found in livers of marine mammals (Caurant et al., 1994; Becker et al., 1995; Woshner et al., 2001; Gerpe et al., 2002; Monteiro-Neto et al., 2003; Kunito et al., 2004; Seixas et al., 2007a, 2008; Lavery et al., 2008). According to Kunito et al. (2004), the biological half life is rather long for trace elements with high affinity to the SH group in cysteine (Cd, Hg, Ag), leading to an age dependent increase in the concentration in marine mammals. According to Woshner et al. (2001), the decline of Cu accumulation in liver with the age of dolphins could be a consequence of the loss of this essential element over the

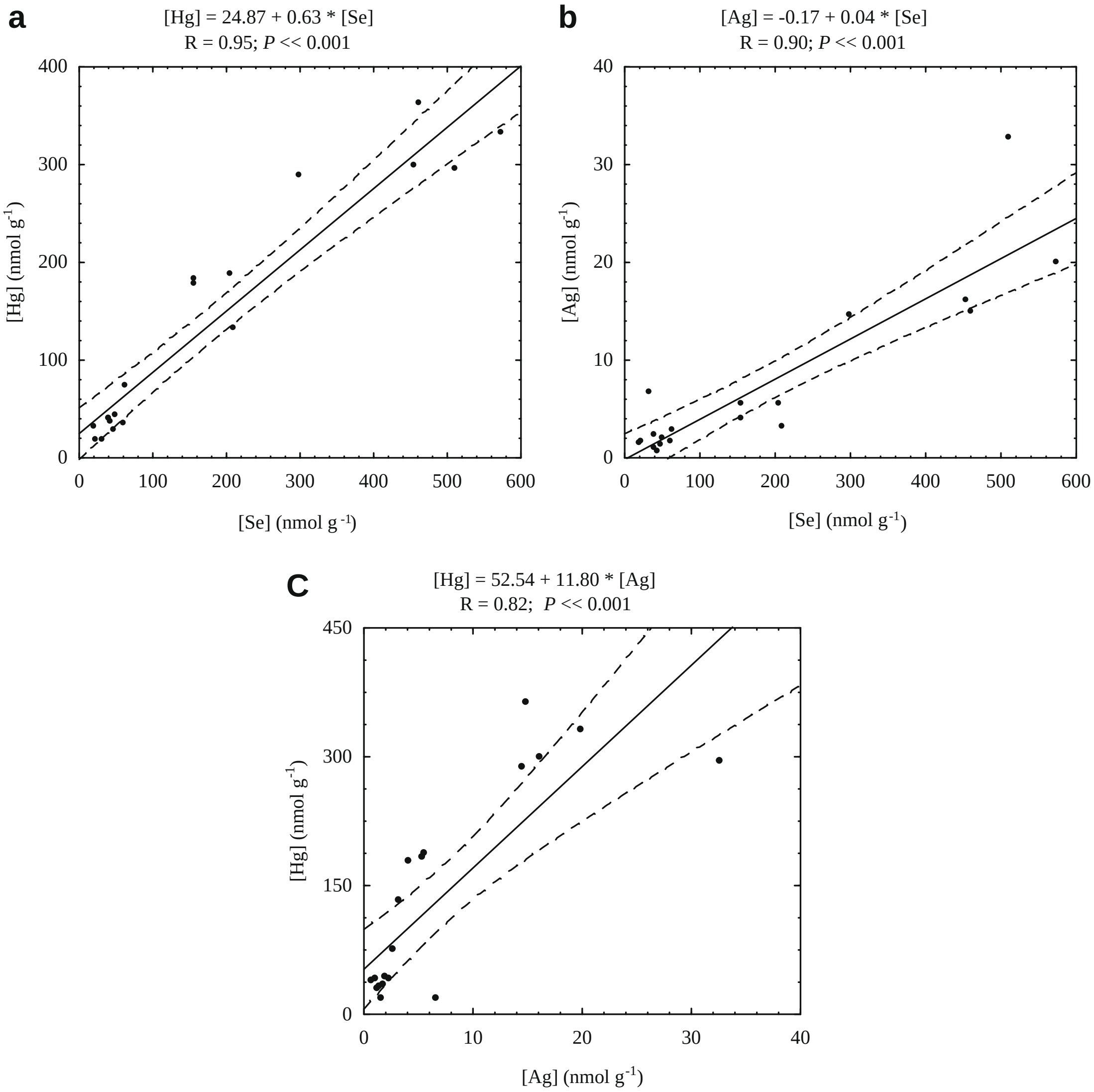

Fig. 2. Relationships between molar concentrations of trace elements in the liver of *Sotalia guianensis* from the Northern Rio de Janeiro (Brazil).

time, i.e. dilution of Cu levels by the increasing tissue mass with age or body length, or decreasing tissue level requirements for Cu (i.e. metabolic regulation). However, the diet of estuarine dolphins plays an important role in the pattern of trace element accumulation by the liver, due to calves feeding mostly on crustaceans species that are richer in copper, while fish (rich in Hg, Se, Ag) and squids (rich in Cd) are the main prey consumed by young and adults individuals (Di Beneditto and Ramos, 2004; Di Beneditto and Siciliano, 2007).

Correlations between elements (Se, Ag, Hg) were observed in the liver of estuarine dolphins (Fig. 2), whereas hepatic Cu and Cd were not associated with any trace element. Estuarine dolphins showed a positive and significant association between hepatic Hg and Se ($R = 0.95$, $P \ll 0.001$; see Fig. 2a), a relationship that has been previously recorded in marine mammals from the Brazilian coast: *S. guianensis* (Kehrig et al., 2004; Kunito et al., 2004) and *Pontoporia blainvillei* (Kunito et al., 2004; Seixas et al., 2007a, 2008). The ability of dolphins to withstand large concentrations of mercury is believed to be partly due to the protective pairing with selenium (O'Shea, 1999). This association between Hg and Se in the liver of marine mammals is in keeping with previous studies with cetaceans from the Southern Hemisphere (Bustamante et al., 2003; Lavery et al., 2008) and could be explained by the existence of a detoxification mechanism involving both elements (Arai et al., 2004). Selenium is also associated with silver ($R = 0.90$, $P \ll 0.001$; see Fig. 2b) in the present sample. However, no significant relationship was observed between hepatic molar selenium and cadmium ($R = 0.29$, $P = 0.23$) concentrations and also between hepatic molar selenium and copper ($R = -0.28$, $P = 0.24$) concentrations.

Previous studies have reported significant positive correlations between selenium and the transition metals, silver and cadmium, in the liver of marine mammals (Becker et al., 1995; Saeki et al., 2001; Woshner et al., 2001; Bustamante et al., 2003; Ikemoto et al., 2004; Seixas et al., 2007a; Lavery et al., 2008). Becker et al. (1995) stated that silver would be accumulated in the liver of marine mammals as a contaminant, as well as mercury and cadmium. This opinion may be acceptable because silver has not yet been recognized as an essential element for any organisms. However, the interaction of selenium with silver differs from other selenium–metal interactions in that silver can induce symptoms of selenium deficiency in vitamin E deficient animals by forming a silver–selenium complex that reduces the pool of available selenium used for normal cellular processes (Hammond and Beliles, 1980). Bustamante et al. (2003) stated that cadmium could be accumulated with extremely high hepatic concentrations in marine mammals as a contaminant, triggering cellular and physiological damage of the liver.

According to Woshner et al. (2001), while Se has been shown to ameliorate the toxic effects of Cd in laboratory animals, its association with cadmium in cetaceans could have resulted from coincidental accumulation of these elements with age, since in cetaceans, cadmium binds primarily to metallothioneins, an inducible small molecular weight metal-binding protein important for both homeostasis and detoxification of various metals, especially Cd, Zn and Cu (Das et al., 2000; Woshner et al., 2001).

Copper did not present a significant association with hepatic silver levels, contrary to previous findings of Woshner et al. (2001). In this study, the hepatic copper concentration in estuarine dolphins declined while the hepatic silver concentration increased. This finding, in conjunction with an age-related decline in hepatic Cu led Woshner et al. (2001) to suggest that aged cetaceans may become Cu deficient, as Ag may occupy sites vacated by Cu, as silver is chemically similar to copper in terms of its valence shell configuration (Woshner et al., 2001). Copper also did not present a significant association with hepatic selenium levels in estuarine dolphins. This pattern was also observed in previous studies with Odontocete species from the Southern Hemisphere (Bustamante et al., 2003; Lavery et al., 2008).

Estuarine dolphins also showed a positive and significant association between hepatic Hg and Ag ($R = 0.86$, $P \ll 0.001$; see Fig. 2c), a relationship that has been previously recorded in marine mammals from the North Atlantic Ocean (Becker et al., 1995) and Alaska (Mackey et al., 1996). However, this correlation does not necessarily indicate a direct relationship between silver and mercury, but might be due to independent factors such as accumulation of these metals with age (Becker et al., 1995).

According to Sasakura and Suzuki (1998), transition metals such as mercury, silver and cadmium interact with selenium in the body, and the toxicity of both transition metals and selenium is reduced by interaction through the formation of insoluble selenide compounds or simultaneous binding to the toxic metal and a high molecular weight protein in various marine mammals (Arai et al., 2004).

The molar ratios of transition metals (Hg, Ag and Cd) to selenium in the liver of estuarine dolphins are summarized in Table 1. A significant difference (Kruskal–Wallis ANOVA, $P < 0.05$) was found for the molar ratio of Se:Ag between calve, young and adult individuals of *S. guianensis*. The molar ratios of Se:Hg and Se:Cd did not present significant differences ($P > 0.05$) between the age classifications, i.e. calve, young and adult. It was observed that calf individuals presented values of molar ratios Se:Hg and Se:Cd close to the those found in the young and adult individuals, i.e. the values of Se:Hg and Se:Cd found in the liver of estuarine dolphins did not increase over time. The molar ratio of Se:Hg presented an asymptotic value close to 1 as Hg accumulates over time.

In liver of estuarine dolphins, the molar ratios of Se:Hg were not significantly different (U test, $P > 0.10$) for males and females. However, a difference between sexes was observed in *Globicephala melas* (Caurant et al., 1994).

The molar ratio of the three transition metals to selenium (Se:Hg, Se:Ag and Se:Cd) presented no significant differences ($P > 0.05$) between their hepatic ratios and the body length (L) of estuarine dolphins.

According to Sasakura and Suzuki (1998) the molar ratios of transition metals to selenium were 1:1 for Hg/Se and Cd/Se, but either 1:1 or 2:1 for Ag/Se. In this study, the molar ratios of transition metals (Hg, Ag and Cd) to selenium in the liver of estuarine dolphin presented averages of 1.25 for Se:Hg, 2.77 for Se:Ag and 76.8 for Se:Cd, respectively. The molar ratio of mercury to selenium found in the liver of estuarine dolphins was in accordance with that reported in earlier studies with this same species from different Brazilian areas (Kehrig et al., 2004; Kunito et al., 2004).

A previous study with *S. guianensis,* from the northern coast of Rio de Janeiro state, showed that the highest ratios of methylmercury (MeHg) to total mercury (28%) and the lowest ratios of mercuric selenide (HgSe) to total mercury (0%) occurred in the livers of individuals that presented total mercury concentration below 1.0 $\mu g\, g^{-1}$ dry wt. (Kehrig et al., 2008). In this previous study, all specimens of *S. guianensis*, which presented hepatic total mercury concentrations above 5.5 $\mu g\, g^{-1}$ dry wt. showed the highest amount of HgSe (ranging from 44% to 89%) and the lowest amount of MeHg (ranging 2% to 7%) in their livers (Kehrig et al., 2008). According to Kehrig et al. (2008), the relatively low fraction of methylmercury in the liver of all analysed species found (always $\leqslant$28%) and also, the increase of the fraction of mercuric selenide indicate that the liver may act as an organ for mercury demethylation and/or the sequestration of both organic and inorganic forms of this element from the body.

Mercury is stored in a permanent and continuous manner in the mammalian liver in the form of insoluble mercuric selenide (Frodello et al., 2000; Wagemann et al., 2000). In this study, concentrations of mercury, silver, selenium and cadmium found in the livers of estuarine dolphins were of the same order of magnitude as those

Table 3
Mean concentrations of selenium (Se), copper (Cu), total mercury (Hg), silver (Ag) and cadmium (Cd) (μg g^{-1} dry wt.) in the liver of *Sotalia guianensis* (estuarine dolphin) and other cetaceans species.

Cetacean species	Se	Cu	Hg	Ag	Cd	Location	Reference
Estuarine dolphin	14.31 ± 14.77	26.48 ± 19.89	27.77 ± 24.68	0.79 ± 0.92	0.41 ± 0.36	Southeast Brazil	This study
	38.00 ± 49.00	157.00 ± 436.00	77.00 ± 107.00	1.90 ± 1.30	0.65 ± 0.75	South Brazil	Kunito et al. (2004)
Common dolphins	30	27.7	23	0.82	2.55	South Brazil	Kunito et al. (2004)
	84.44 ± 39.49[a]	33.89 ± 11.13[a]	226.67 ± 95.39[a]	2.68 ± 1.22[a]	35.22 ± 30.81[a]	New Zealand	Stockin et al. (2007)
	47.13 ± 50.93[a]	37.83 ± 34.33[a]	104.03 ± 123.7[a]	–	3.73 ± 6.07[a]	South Australia	Lavery et al. (2008)
Beluga whale	60.94 ± 58.78[a]	–	92.38 ± 90.93[a]	86.44 ± 83.63[a]	–	Arctic Alaska	Becker et al. (1995)
	136.65 ± 85.57[a]	69.00 ± 78.41[a]	76.66 ± 85.57[a]	52.50 ± 33.66[a]	12.54 ± 0.20[a]	Arctic Alaska	Woshner et al. (2001)
	–	–	52.64 ± 50.06[a]	42.37 ± 29.30[a]	10.07 ± 5.02[a]	Arctic Alaska	Dehn et al. (2006)
Pilot whale	22.90 ± 31.86[a]	–	108.28 ± 127.03[a]	0.16 ± 0.11[a]	–	North Atlantic	Becker et al. (1995)

[a] Wet weight basis concentration was converted to dry weight basis concentration assuming that moisture content was 69.7% (Yang and Miyazaki, 2003).

reported in an earlier study with the same dolphin species (Table 3), but hepatic copper concentrations were lower than those found in samples from the southern coast of Brazil (Kunito et al, 2004; Table 3). Metals and selenium in the livers of common dolphins, a coastal dolphin species that feeds on squids and fishes, from South Australia (Lavery et al., 2008) presented higher concentrations than those found in the livers of estuarine dolphins from the northern coast of Rio de Janeiro (Brazil). Hepatic trace elements of estuarine dolphins were generally lower than those found in the liver of two Odontocete species from different regions in the Northern Hemisphere (Becker et al., 1995; Woshner et al., 2001; Dehn et al, 2006; Table 3) and from the South Pacific (Southern Hemisphere) (Bustamante et al., 2003). However, it is difficult to compare data for trace elements in species with different feeding habits, life span, and from various locations worldwide. In this case, it is better to compare the trace element concentrations between individuals of the same species that present a similar life span. Life span seems to be a significant factor influencing trace element accumulation in internal organs of cetacean species.

The present research adds new insight to and complements the existing studies on trace element concentrations in the liver of a small dolphin species from the southwestern Atlantic. This cetacean, which inhabits Brazilian coastal and estuarine waters, has been affected by gill-net fisheries and contamination from anthropogenic inputs of chemical contaminants from untreated domestic and industrial sewage and also agricultural wastewaters. Relatively low concentrations of trace elements were found in the livers of estuarine dolphins when compared with other marine mammal species worldwide, mainly those from the Northern Hemisphere. Silver and mercury concentrations were positively correlated with selenium in estuarine dolphins. One possible explanation for this correlation is that these trace elements are sequestered within a selenium complex, as has been observed in laboratory animals. However, further studies should be devoted to the understanding of the relationships of trace elements with the complex systems involved in trace element metabolism.

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References

Arai, T., Ikemoto, T., Hokura, A., Terada, Y., Kunito, T., Tanabe, S., Nakai, I., 2004. Chemical forms of mercury and cadmium accumulated in marine mammals and seabirds as determined by XAFS analysis. Environmental Science Technology 38, 6468–6474.

Becker, P.R., Mackey, E.A., Demiralp, R., Suydams, R., Early, G., Koster, B.J., Wise, S.A., 1995. Relationship of silver and selenium and mercury in the liver of two species of toothed whales (Odontocetes). Marine Pollution Bulletin 30 (4), 262–271.

Bustamante, P., Garrigue, C., Breau, L., Caurant, F., Dabin, W., Greaves, J., Dodemont, R., 2003. Trace elements in two Odontocete species (*Kogia breviceps* and *Globicephala macrorhyncus*) stranded in New Caledonia (South Pacific). Environmental Pollution 124, 263–271.

Capelli, R., Drava, G., De Pellegrini, R., Minganti, V., Poggi, R., 2000. Study of trace elements in organs and tissues of striped dolphins (*Stenella coeruleoalba*) found dead along the Ligurian coasts (Italy). Advances in Environmental Research 4, 31–43.

Caurant, F., Amiard, J.C., Amiard-Triquet, C., Sariau, P., 1994. Ecological and biological factors controlling the concentrations of trace elements (As, Cd, Cu, Hg, Se, Zn) in delphinids *Globicephalas melas* from the North Atlantic Ocean. Marine Ecology Progress Series 103, 207–219.

Das, K., Debacker, V., Bouquegneau, J.M., 2000. Metallothionein in marine mammals. Cellular and Molecular Biology 46, 283–294.

Dehn, L., Follmann, E.H., Thomas, D.L., Sheffield, G.G., Rosa, C., Duffy, L.K., O'Hara, T.M., 2006. Trophic relationships in an Arctic food web and implications for trace metal transfer. Science of the Total Environment 362, 103–123.

Di Beneditto, A.P.M., Ramos, R.M.A., 2004. Biology of the marine tucuxi dolphin (*Sotalia fluviatilis*) in south-eastern Brazil. Journal of the Marine Biology Association of the United Kingdom 84, 1245–1250.

Di Beneditto, A.P.M., Siciliano, S., 2007. Stomach contents of the marine tucuxi dolphin (*Sotalia guianensis*) from Rio de Janeiro, south-eastern Brazil. Journal of the Marine Biology Association of the United Kingdom 87, 253–254.

Dietz, R., Riget, F., Johansen, P., 1996. Lead, cadmium, mercury and selenium in Greenland marine animals. Science of the Total Environment 186, 67–93.

Eisler, R., 2000. Selenium hazards to fish, wildlife and invertebrates: a synoptic review. US Fish and Wildlife Service Biological Report 85, v. 1.5, 57p.

Feroci, G., Badiello, R., Fini, A., 2005. Interactions between different selenium compounds and zinc, cadmium and mercury. Journal of Trace Elements in Medicine and Biology 18, 227–234.

Frodello, J.P., Romeo, M., Viale, D., 2000. Distribution of mercury in the organs and tissues of five toothed-whale species of the Mediterranean. Environmental Pollution 108, 447–452.

Gerpe, M.S., Rodriguez, D.H., Moreno, V.J., Bastida, R.O., Moreno, J.A.E., 2002. Accumulation of heavy metals in the Franciscana (*Pontoporia blainvillei*) from Buenos Aires Province, Argentina. Latin American Journal of Aquatic Mammals 1 (1), 95–106.

Hammond, P.B., Beliles, R.P., 1980. Metals. In: Doull, J., Klaassen, C.D., Amdur, M.O. (Eds.), Casareet and Doull's Toxicology: The Basic Science of Poisons, second ed. Macmillan, New York, pp. 409–467.

Ikemoto, T., Kunito, T., Watanabe, I., Yasunaga, G., Baba, N., Miyazaki, N., Petrov, E.A., Tanabe, S., 2004. Comparison of trace element accumulation in Baikal seals (*Pusa sibirica*), Caspian seals (*Pusa caspica*) and northern fur seals (*Callorhinus ursinus*). Environmental Pollution 127, 83–97.

Kehrig, H.A., Seixas, T.G., Baêta, A.P., Lailson-Brito Jr., J., Moreira, I., Malm, O., 2004. Total mercury, methylmercury and selenium in the livers and muscle of different fishes and a marine mammal from a tropical estuary – Brazil. RMZ-Materials and Geoenvironment 51 (1), 1111–1114.

Kehrig, H.A., Seixas, T.G., Palermo, E.A., Di Beneditto, A.P.M., Souza, C.M.M., Malm, O., 2008. Different species of mercury in the livers of tropical dolphins. Analytical Letters 41, 1690–1698.

Kunito, T., Nakamura, S., Ikemoto, T., Anan, Y., Kubota, R., Tanabe, S., Rosas, F.C.W., Fillmann, G., Readman, J.W., 2004. Concentration and subcellular distribution of trace elements in liver of small cetaceans incidentally caught along the Brazilian coast. Marine Pollution Bulletin 49, 574–587.

Lavery, T.J., Butterfield, N., Kemper, C.M., Reid, R.J., Sanderson, K., 2008. Metals and selenium in the liver and bone of three dolphin species from South Australia, 1988–2004. Science of the Total Environment 390, 77–85.

Mackey, E.A., Becker, P.R., Demiralp, R., Greenberg, R.R., Koster, B.J., Wise, S.A., 1996. Bioaccumulation of vanadium and other trace metals in livers of Alaskan cetaceans and pinnipeds. Archives of Environmental Contamination and Toxicology 30, 503–512.

Monteiro-Neto, C., Itavo, R.V., Moraes, L.E.S., 2003. Concentrations of heavy metals in *Sotalia fluviatilis* (Cetacea: Delphinidae) of the coast of Ceará, Northeast Brazil. Environmental Pollution 123, 319–324.

O'Shea, T.J., 1999. Environmental contaminants and marine mammals. In: Reynolds, J.E., III, Rommel, S.A. (Eds.), Biology of Marine Mammals. Smithsonian Institution Press, Washington, pp. 485–563.

Roditi-Elasar, M., Kerem, D., Hornung, H., Kress, N., Shoham-Frider, E., Goffman, O., Spanier, E., 2003. Heavy metal levels in bottlenose and striped dolphins off the Mediterranean coast of Israel. Marine Pollution Bulletin 46, 503–512.

Saeki, K., Nakajima, M., Loughlin, T.R., Calkins, D.C., Baba, N., Kiyota, M., Tatsukawa, R., 2001. Accumulation of silver in the liver of three species of pinnipeds. Environmental Pollution 112, 19–25.

Sasakura, S., Suzuki, K.T., 1998. Biological interaction between transition metals (Ag, Cd and Hg), selenide/sulphide and selenoprotein P. Journal of Inorganic Biochemistry 71, 159–162.

Seixas, T.G., Kehrig, H.A., Fillmann, G., Di Beneditto, A.P.M., Souza, C.M.M., Secchi, E.R., Moreira, I., Malm, O., 2007a. Ecological and biological determinants of trace elements accumulation in liver and kidney of *Pontoporia blainvillei*. Science of the Total Environment 385, 208–220.

Seixas, T.G., Kehrig, H.A., Moreira, I., Malm, O., 2007b. Distribuição de Selênio em organismos marinhos da Baía de Guanabara/R.J.. Química Nova 30 (3), 554–559.

Seixas, T.G., Kehrig, H.A., Costa, M., Fillmann, G., Di Beneditto, A.P.M., Secchi, E.R., Souza, C.M.M., Malm, O., Moreira, I., 2008. Total mercury, organic mercury and selenium in liver and kidney of a South American coastal dolphin. Environmental Pollution 154, 98–106.

Stockin, K.A., Law, R.J., Duignan, P.J., Jones, G.W., Porter, L., Mirimin, L., Meynier, L., Orams, M.B., 2007. Trace elements, PCBs and organochlorine pesticides in New Zealand common dolphins (*Delphinus* sp.). Science of the Total Environment 387, 333–345.

Yang, J., Miyazaki, N., 2003. Moisture content in Dall's porpoise (*Phocoenoides dalli*) tissues: a reference base for conversion factors between dry and wet weight trace element concentrations in cetaceans. Environmental Pollution 121, 345–347.

Wagemann, R., Trebacs, E., Boila, G., Lockhart, W.L., 2000. Mercury species in the liver of ringed seals. Science of the Total Environment 261, 21–32.

Woshner, V.M., O'Hara, T.M., Bratton, G.R., Suydam, R.S., Beasley, V.R., 2001. Concentrations and interactions of selected essential and non-essential elements in bowhead and beluga wales of Arctic Alaska. Journal of Wildlife Diseases 37 (4), 693–710.

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