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Abstract Total mercury (THg) and selenium (Se) concentrations were determined in hepatic, renal, and muscle tissues of seven specimens of Commerson's dolphins incidentally captured in artisanal fisheries of Tierra del Fuego, Argentina, by instrumental neutron activation analysis. Liver yielded the mean highest concentration of THg 9.40 (9.92) $\mu g g^{-1}$ dry weight (DW) (standard deviation of the average in parenthesis); kidney and muscle showed similar values, ranging from 2.34 to 3.63 $\mu g g^{-1}$ DW. Selenium concentrations were similar in hepatic and renal tissues, with values from 13.62 to 14.56 $\mu g g^{-1}$ DW; the lowest concentration was observed in muscle, 4.13 (2.05) $\mu g g^{-1}$ DW. Among the specimens analyzed, the maximum concentrations of THg and Se were observed in the single adult female studied. An increasing age trend is observed for THg concentrations in tissues analyzed. The molar ratio of Se/Hg in the hepatic, renal, and muscle tissues were 8.7 (9.6), 13.2 (9.5), and 9.0 (11.4), respectively, suggesting Se protection against Hg toxicity. Silver concentrations in the three tissues were included, and the Se/(Hg+0.5×Ag) molar ratio showed values closer to 1. Both Hg and Se concentrations in liver and kidney were comparable to those found in other small odontocetes from Argentine and Brazilian waters. This study constitutes the first joint description reported of Hg and Se concentrations in liver, kidney, and muscle of the Commerson's dolphin species.

Keywords Mercury · Selenium · Silver · Commerson's Dolphins · Southwestern South Atlantic Ocean

Introduction

Mercury (Hg) has long been considered a high-impact environmental pollutant which is derived from natural and

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anthropogenic sources around the world [1, 2]. Both inorganic and organic forms of Hg are toxic, particularly methylmercury (MeHg) which is a powerful neurotoxin affecting wildlife as well as humans through fish consumption [3–5]. Due to its long persistence and high mobility in the marine ecosystem, Hg accumulates during organisms' growth and biomagnifies throughout the food web, especially in the upper levels such as marine mammals [6–10]. For a given species, the total Hg content is also known to vary among different organs (e.g., liver, kidney, muscle, skin, brain, spleen, and bone); Hg is preferentially accumulated in the hepatic tissue in different compounds but, in organic forms, is mostly in the muscle tissues [8, 11, 12]. Selenium (Se), unlike Hg, is an essential element for metabolic activity, and as such, its concentration is physiologically regulated. It has long been observed that Se protects organisms from Hg toxicity [1, 5, 13]. Selenium is found naturally in marine food sources that are high in protein [14]. High positive association between Hg and Se is well documented, with an equimolar ratio in the liver of higher-trophic marine mammals [1, 15]. In this regard, one of the earliest reports for the Se/Hg molar ratio being 1 was by Koeman et al. [15, 16], who considered the interaction of Se to account for a protective effect against Hg toxicity [17–20]. Liver, one of the most important metabolic organs, participates in the transformation and synthesis of many substances. Some studies have described that the formation of an inert Hg–Se complex appears to be the last step of the Hg detoxification by Se, reducing the organic forms and blocking it in insoluble forms in the hepatic tissue [8, 14, 21, 22]. The liver of marine mammals may act as an organ for Hg demethylation and/or the sequestration of both organic and inorganic forms of mercury [19, 23], and Se is involved in these mechanisms [8, 14, 24]. In either case, the end result is the accumulation of the metal in chemical species innocuous to the organism [17, 20].

Cetaceans and pinnipeds incorporate potential contaminants principally by ingestion, which may vary according with the species consumed and with the habitat. Fish and shellfish preys are generally the main source of Se and Hg for odontocetes [9, 14, 16, 17]. In general, the variation in Hg levels between the different tissues and organs is discussed as regards storage, biotransformation, and elimination processes.

Mercury contamination is well documented for a variety of marine mammals worldwide [6, 25–27]. In South America, various studies have reported Hg concentrations in tissues of odontocetes such as the bottlenose dolphin (*Tursiops gephyreus*, usually cited as *Tursiops truncatus*), Franciscana dolphin (*Pontoporia blainvillei*), estuarine dolphin (*Sotalia guianensis*), tucuxi dolphin (*Sotalia fluviatilis*); Atlantic spotted dolphin (*Stenella frontalis*), common dolphin (*Delphinus capensis*), striped dolphin (*Stenella coeruleoalba*), pygmy sperm whale (*Kogia breviceps*) [28–38]. There are also reports on mysticetes from Antarctica, such as the minke whale (*Balaenoptera acutorostrata*) [39, 40]. However, only few recent works have focused on the relationship between Se and Hg [32, 34, 35, 38].

The Commerson's dolphin (*Cephalorhynchus c. commersonii*) is a small cetacean, endemic in the southwestern South Atlantic and Strait of Magellan from about 41°30′S to near Cape Horn 56°S [41]. Since the early 1980s, moderate to high levels of incidental by-catch in artisanal shore-set gillnets of Commerson's dolphins have been documented in northern Tierra del Fuego [41, 42]. The Commerson's dolphin is a coastal dolphin, which inhabits the shallow waters of the continental shelf with a foraging habitat near shoreshelf [43]. The diet studies indicated that it is a generalist feeder including alternative prey such as fishes, squids, and invertebrates [44].

The aim of this work is to study Hg and Se in the Commerson's dolphin, a mammal species accounting for scarce published research regarding heavy metal contents. The specific goals of our research on Commerson's dolphin specimens taken as incidental by-catch in the subantarctic waters of Tierra del Fuego are: (a) to study the concentrations of Hg and Se determined simultaneously in samples of liver, kidney, and muscle and (b) to present the Se/Hg molar ratio for each tissue in order to evaluate the potential protective effect of Se regarding Hg toxicity.

Materials and Methods

Specimens and Sample Conditioning

Liver, kidney, and muscle samples of seven specimens of Commerson's dolphin incidentally caught in artisanal fishing nets were studied. The specimens were recovered on the shores of Tierra del Fuego (S53°17′-W68°28′ to S54°25′-W66°33′) in the 2010–2011 summer campaigns (December to February) of the *Museo Acatushún de Aves y Mamíferos Marinos Australes*, Estancia Harberton, Tierra del Fuego (Fig. 1). During the campaigns, the coastline of the study area was regularly explored to search for beached and/or by-caught marine mammals. The necropsy of each specimen found was performed for the collection of biological material at the Museo Acatushún according to the protocol by Norris [45]. Whole liver, the kidneys, and approximately 150 g of epiaxial muscle were excised from each specimen using a surgical blade. The information recorded for each specimen included sex (determined by direct observation of the genital patch or genital organs), total length, and body weight. Four teeth were removed for age estimation (by counting growth layer groups (GLGs); Perrin and Myrick [46]) following the methodology used by Dellabianca et al. [47]. The organ samples were stored in individual polyethylene bags, refrigerated in field, and

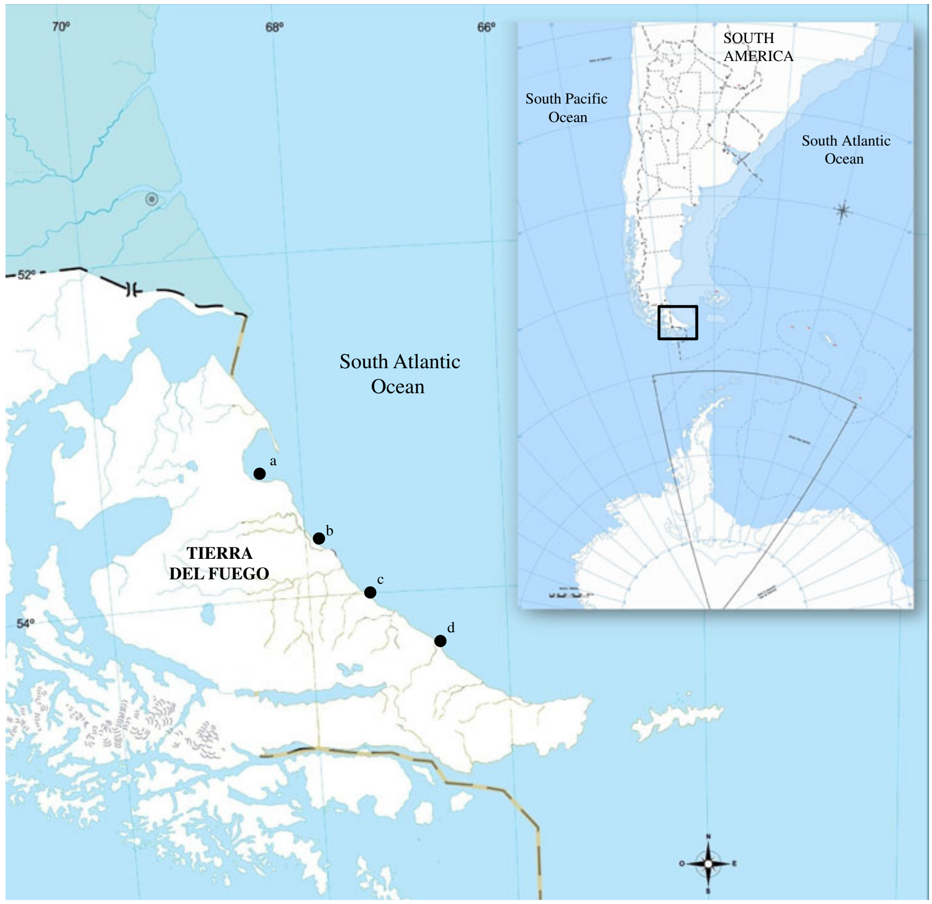

Fig. 1 Sampling points (*filled circle*) where the specimens of the Commerson's dolphin (*C. c. commersonii*) have been recovered on the coasts of Tierra del Fuego, Argentina. **a** Bahía San Sebastián; **b** Paso Cholgas; **c** Cabo Peñas; **d** Río Lainez

frozen at −20 °C before being airlifted to *Laboratorio de Análisis por Activación Neutrónica, Centro Atómico Bariloche, Comisión Nacional Energía Atómica* (CAB-CNEA), where they were stored at −20 °C until processing. After removal from the freezer, the tissue samples were lightly thawed, and the outer exposed tissue layer was cut away to exclude any potential contamination during necropsy and storage. The tissue samples were handled using polyethylene gloves without powder, and they were fractioned with titanium-bladed knives and Teflon® tools. All tools and devices for sample conditioning were previously washed in a 10 % nitric acid solution and double-rinsed with high-purity water (ASTM grade I). Liver samples were sectioned from the right lobe. About 30–40 renules from the central part of the right kidney (including both medulla and cortex) were included in kidney samples. Also, samples of epiaxial muscle were conditioned for the analysis. Samples from the central and posterior region muscles were also processed for four specimens. Tissues subsamples were prepared for Hg and Se determinations following the same procedure: of each tissue, 15–25 g was lyophilized for 5–8 days to constant weight. The dried samples were then ground to a fine powder. Aliquots ranging in mass from 100–150 mg were placed in Suprasil AN® quartz ampoules in a laminar flow hood and sealed for irradiation.

Mercury and Selenium Quantification

The concentration of total Hg ([Hg]) and Se ([Se]) in the samples was determined by instrumental neutron activation analysis (INAA). The samples were irradiated in the RA-6 nuclear reactor (MTR-type, 1 MW thermal power), CAB-CNEA. The irradiation was performed in the reactor core (thermal, epithermal, and fast neutron fluxes of 1×10^{13}, 5×10^{11}, and 2×10^{12}ncm^{-2}s^{-1}, respectively) for 20 h. Two gamma-ray spectra were collected after decay times of 7 and 20 days. The gamma-ray spectra were collected with coaxial HPGe detectors (12 and 30 % relative efficiency and 1.8 keV resolutions at 1.33 MeV) and 4,096-channel analyzers. The absolute parametric method was used to determine the elemental concentrations, using nuclear constants taken from current tables [48]. Thermal and epithermal neutron fluxes were determined by (n,γ) reactions of the pair Co–Au, using high-purity wires of pure Co and 0.112 % Au–Al alloy. Mercury was determined by evaluating two activation products: ^{197}Hg and ^{203}Hg. The activation product ^{75}Se was analyzed to determine Se concentrations. Corrections of analytical interferences were performed, particularly that of ^{75}Se on ^{203}Hg. The impurity content of the Suprasil NA quartz was evaluated previously, and no Hg or Se content was detected. The analytical quality control was performed by the analysis of the certified reference material NRCC TORT-2 (lobster hepatopancreas); the results showed good agreement with the certificate (Table 1).

The concentrations are presented in dry weight (DW) basis. As [Hg] is reported frequently in wet weight (WW) basis, the conversion factor from dry to wet weight was determined for each tissue analyzed to allow the comparison with all data reported in the literature. The dry to wet weight conversion factors averaged for each tissue are 0.294 (0.015), 0.254 (0.018), and 0.286 (0.007) for hepatic, renal, and muscle tissue, respectively.

Selenium to Mercury Molar Ratio

The molar ratio of Se to Hg was calculated as:

$$\mathrm{Se}:\mathrm{Hg}=\frac{[\mathrm{Se}]/78.96}{[\mathrm{Hg}]/200.59}$$

where 200.59 and 78.96 $\mathrm{g\,mol^{-1}}$ are the atomic weights of Hg and Se, respectively.

Data Analysis

Descriptive statistics analysis was used to present [Hg] and [Se] in the three tissues analyzed; the concentrations are presented as mean, standard deviation (in parenthesis), and median. Linear correlations (Pearson coefficient, *r*) were performed to evaluate individual relationship for [Hg] and [Se] within different tissues (liver, kidney, and muscle). The level of statistical significance was set at $P<0.05$. Data analyses were conducted using InfoStat (2011) and Origin-Pro Version 8 (2007).

Results and Discussion

Total Hg and Se concentrations in the specimens of Commerson's dolphin studied are presented in Table 2, together with age, sex, and total body length. As regards to the age of each specimen, the examination of tooth sections (one GLG corresponding to 1 year in toothed-whales, according to Lockyer et al. [49, 50] and Dellabianca et al. [47]) allowed us to estimate that three of them were calves (less than 1 year of age), two were yearlings, one, a 2-year-old juvenile, and a single specimen was 7 years old. According to age and body length, we classified the individuals following the categories of adults and non-adults established by Lockyer et al. [50]. Therefore, only one female probably was a mature adult (RNP 2670 in Table 2). This female specimen was found beached together with a calf less than 1 year old (RNP 2671 in Table 2).

Table 1 Analytical quality control: results of the analysis of the certified reference material NRCC TORT-2 (lobster hepatopancreas) by instrumental neutron activation analysis (INAA)

	Measurement by INAA		Concentration certified
	Replicate 1	Replicate 2	
Hg ($\mu g\ g^{-1}$)	0.249±0.058	0.257±0.053	0.27±0.06
Se ($\mu g\ g^{-1}$)	6.54±0.48	6.35±0.48	5.63±0.67

Concentrations in dry weight basis. The analytical uncertainty is reported after the plus minus sign

Concentrations of Hg and Se in the Commerson's Dolphin Tissues

Mercury concentrations in Commerson's dolphin ranged from 1.30 to 30.4 $\mu g\,g^{-1}$ DW in liver, from 1.64 to 7.10 $\mu g\,g^{-1}$ DW in kidney, and from 0.63 to 4.99 $\mu g\,g^{-1}$ DW in muscle tissue. The lowest concentrations corresponded to a female specimen less than 1 year old, whereas the highest were from the 7-year-old adult (Table 2). Both [Hg] and [Se] showed high variability among the specimens in the tissues analyzed, leading to a high standard deviation of the average. Total Hg concentrations between liver and kidney showed significant linear correlation (R^2=0.91; P= 0.0019) (Fig. 2a), indicating a proportional accumulation of Hg in these two organs. [Hg] as well showed significant linear correlation (R^2=0.93; P=0.0024) between liver and muscle (Fig. 2b) (the average value is considered when there are two determinations in muscle tissues of the same specimen), with similar slope and intercept in both cases. Ratios of [Hg] in tissues were 4.1 for liver/muscle, 2.4 for liver/kidney, and 1.7 for kidney/muscle.

The hepatic tissue of the Commerson's dolphins showed the highest [Hg]. In this sense, it is well known that the liver of marine mammals appears to be the preferential organ for Hg accumulation, due to the differential distribution of certain proteins, transport of Hg on a differential basis to particular organs, or transportation through cellular barriers, leading to buildup in specific organs [51]. Hepatic Hg accumulation is related to its demethylation role [12, 19, 21, 26], or even by induction of metallothioneins that is believed to occur within this organ [14, 27].

Also, high [Hg] have been reported in renal tissue, although the higher values are lower than those observed in liver [6, 18]. This is due to the fact that the kidney stores a significant fraction of the metal, although this organ is also involved in the process of elimination. Because of its ability to reabsorb and accumulate metals, the kidney is another organ of heavy metal accumulation. Muscle tissue generally presents moderate concentrations of Hg respect to organ tissues such as liver or kidneys, due to the significantly high mass proportion of this tissue with respect to the total body mass [26]. Mercury and other elements such as Cd, with

Table 2 Mercury and selenium in liver, kidney, and muscle of Commerson's dolphin (*C. c. commersonii*) by-caught on the shores of Tierra del Fuego, Argentina

Specimen collection number	Age	Sex	Body Length (cm)	Liver			Kidney			Muscle		
				Hg	Se	Se/Hg	Hg	Se	Se/Hg	Hg	Se	Se/Hg
RNP 2671[a]	<1	Male	109	3.89±0.23	9.14±0.69	5.97	3.03±0.18	12.66±0.97	10.61	2.19±0.13	6.57±0.48	7.62
RNP 2701	<1	Male	117.4	2.80±0.17	10.58±0.81	9.60	1.79±0.11	13.5±1.1	19.16	1.489±0.089	3.41±0.27	5.82
										1.297±0.078	3.02±0.23	5.92
RNP 2727	<1	Female	99.3	1.302±0.078	15.2±1.2	29.66	1.64±0.098	19.1±1.5	29.59	0.584±0.053	8.62±0.67	37.50
										0.677±0.061	6.48±0.48	24.30
				2.7 (1.3) [b]	11.6 (3.2) [b]	15.1 (12.8) [b]	2.1 (0.8) [b]	15.1 (3.5) [b]	19.8 (9.5) [b]	1.2 (0.7) [b]	5.6 (2.4) [b]	16 (14) [b]
RNP 2628	1	Male	118.9	8.85±0.53	12.8±1.0	3.68				3.07±0.18	3.81±0.29	3.15
										3.06±0.18	2.89±0.22	2.40
RNP 2728	1.5	Male	116.6	7.06±0.42	20.3±1.6	7.30	3.68±0.22	13.0±1.0	8.97	1.85±0.11	2.57±0.19	3.53
										1.73±0.10	2.73±0.21	4.01
RNP 2669	2	Male	121	11.51±0.69	13.4±1.0	2.96	4.52±0.27	12.55±0.85	7.05	2.29±0.14	3.2±0.24	3.55
				9.1 (2.2) [b]	15.5 (4.2) [b]	4.6 (2.3) [b]	4.1 (0.6) [b]	12.8 (0.3) [b]	8.0 (1.4) [b]	2.4 (0.6) [b]	3.0 (0.5) [b]	3.3 (0.6) [b]
RNP 2670[a]	7	Female	139	30.4±1.8	20.5±1.6	1.71	7.1±0.43	10.89±0.79	3.90	4.99±0.30	2.36±0.19	1.20
Average (SD)				9.4 (9.9)	14.6 (4.4)	8.7 (9.6)	3.6 (2.0)	13.6 (2.8)	13.2 (9.5)	2.1 (1.3)	4.2 (2.1)	9.0 (11.4)
Median				7.1	13.4	6.0	3.4	12.8	9.8	1.9	3.2	4.0

Total mercury and selenium concentrations are expressed in micrograms per gram dry weight; the analytical uncertainty is reported after the plus minus sign. The molar ratio Se/Hg is also reported

[a] A mother–calf pair found dead together on the beach

[b] Average for the age group; standard deviation in parenthesis

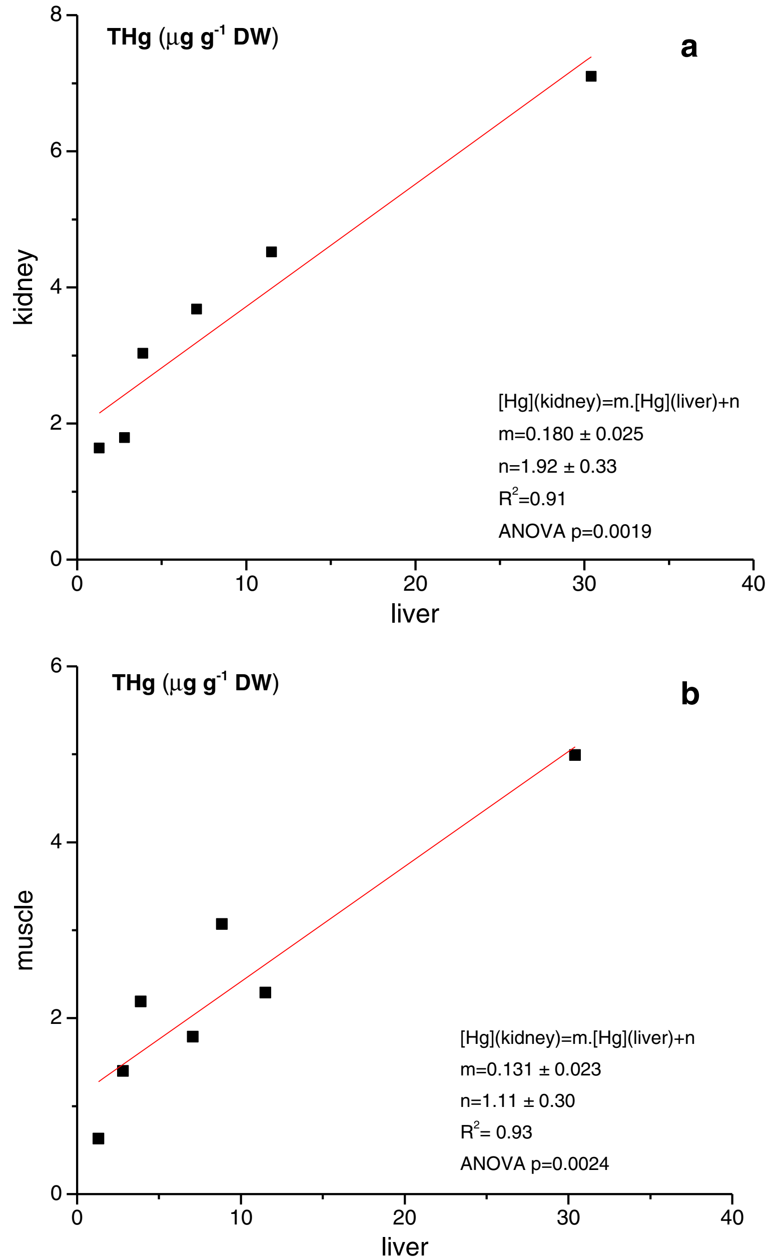

Fig. 2 Correlation of THg concentration in Commerson's dolphin **a** liver and kidney, and **b** liver and muscle tissues

significant inter-tissue correlation, are classified into soft acids or chalcophile elements that have high affinity to the SH group in cysteine, showing high accumulation in tissues [24, 52, 53].

Selenium concentrations ranged in liver from 9.1 to 20.5 $\mu g g^{-1}$ DW and in renal tissue from 10.9 to 19.1 $\mu g\, g^{-1}$ DW, with lower values for the muscle tissue (2.36 to 7.55 $\mu g g^{-1}$ DW) (Table 2). As Hg, the liver of Commerson's dolphins also showed the highest [Se]. Studies have been reported that hepatic [Se] is usually more elevated in stranded and emaciated specimens than those observed in subsistence-harvested animals [54]. Ketone body metabolism requires Se, and it is possible that during starvation [Se] is elevated to increase turnover of lipids and ketone bodies [54, 55]. There was no evidence of starvation in the specimens studied. No significant correlation for Se was found among tissues. Other studies have reported significant relationships between tissues (e.g., liver, kidney, and muscle) for [Hg] in cetaceans and pinnipeds from others regions worldwide [53, 56, 57], whereas no significant correlations were observed for [Se] between liver and kidney for some of these species [33, 53]. This is mostly due to the homeostatic control upon essential element concentration in tissues, the mechanism inactive for non-essential or potentially toxic elements [53].

Grouping the specimens studied by age in three classes, the younger than 1 year, those between 1 and 2 years old, and the only adult (7 years old), the [Hg] averaged per class increases with age in all tissues, although the limited number of specimens analyzed conditioned any conclusion. Selenium concentration averaged per age class show slight increase with age in the liver, decreasing in renal and muscle tissue. The growth stage seems to influence Se accumulation in the Commerson's dolphin specimens collected in our study; this is consistent with other studies of Franciscana dolphins [32, 34]. Even though the data set comprises few specimens, there is a consistent increase of [Hg] with age that could be associated with a stable intake, higher than elimination, leading to increasing concentrations with age in all the tissues studied. The highest incorporation rate was observed in hepatic tissues, with average [Hg] of 2.66 $\mu g g^{-1}$ DW in calves (age <1 year) and 9.14 $\mu g g^{-1}$ DW in juvenile specimens (1–2 years), and for the adult female, the [Hg] was 30.4 $\mu g g^{-1}$ DW. In renal tissues, the average THg concentrations were 2.15, 4.10, and 7.1 $\mu g g^{-1}$ DW per age class, respectively, and in muscle tissues were 1.25, 2.40, and 4.99 $\mu g g^{-1}$ DW. As we mentioned above, Se denotes an increase with age in the liver but decreases in kidney and muscle. This could be linked to the formation of mercury selenide (HgSe, also called tiemannite) and storage in the liver while, in other tissues, Se concentrations are regulated by homeostatic control, having primarily biological function. Furthermore, the highest rate of Hg incorporation was in liver, which may also be due to storage as HgSe.

To emphasize, kidney sub-sampling included portions of both cortex and medullar tissue that could have different accumulation rates due to their different physiological role. The [Hg] and [Se] reported correspond to kidney organ levels, not aiming tissue discrimination.

Age- and even growth-dependent increase of [Hg] (and [Se] as well) are often found in the liver of odontocetes [8, 17, 58, 59], related to the capacity of these species to bioaccumulate this element throughout life [12, 17, 51]. This likely results from the continuous uptake of Hg via diet combined with slow elimination and storage in stable forms (e.g., HgSe), bringing on a relatively long half-life of hepatic Hg of about 10 years [23]. Nevertheless, the biological half-life of Hg in the organism is closely dependent on many variables interacting in the processes of storage at cell level and on inter-organ transfers [25]. Particularly, Hg has strong affinity with the SH group as mentioned above; therefore, its biological half-life is rather long in animals, leading to age-dependent increase in concentration [32, 53]. Hence, the age-dependent increase in hepatic [Se] was most likely due to the interactions of Hg and Se within this organ [23, 53]. A similar pattern was detected for Hg accumulation in kidney and muscle as well, though to a lesser extent, which implies that demethylation is not exclusively performed in the liver but also in other tissues [17], or suggests that Hg compounds produced after MeHg degradation are transported and stored in other tissues [60].

In marine mammals, there normally are no sex-related variations regarding trace element concentrations [12, 61]. Nevertheless, it has been reported that Hg concentration is low at birth and increases with age in both sexes but with a higher rate in females [62]. As suggested by Caurant et al. [7], sex- and age-related variations could be associated with differences in metabolic pathways linked to hormone cycles. The small data set of the Commerson's dolphin specimens studied (five males and two females; Table 2) does not allow the analysis of correlations between sexes.

Selenium-to-Mercury Relationship

The Se/Hg molar ratio determines the ability of protective action of Se to Hg toxicity by forming HgSe, a stable compound with no relevant biological impact. Although Se can be combined with other elements forming different compounds, ratios$>$1 suggest Se molar excess in the tissue, implying potential Se protection against Hg toxicity whereas ratios$<$1 indicate limited Se protection against the Hg toxicity [3, 5]. Additionally, a molar ratio of 1 or lower would indicate that all available Se is bound to Hg, leaving animals, in particular, diving marine mammals, vulnerable to oxidative stress [54]). Selenium integrates selenoproteins that are involved in hormone homeostasis and anti-oxidant enzyme systems (e.g., glutathione peroxidase) by preventing lipid peroxidation in tissues [10, 58, 63]. At low concentrations, Se is beneficial; however, it becomes toxic at high levels, and the range between deficiency, essentiality, and toxicity is very narrow. A diet containing less than 1 μg g^{-1} of Se can result in deficiency, but amounts higher than 5 $\mu g g^{-1}$ may cause toxic effects [64, 65]. Selenium's protective effect had been attributed to sequestration of Hg by Se. Even though Hg toxicity in this case is not associated to direct oxidative damage; otherwise, the oxidative damage occurs as a result of the inhibition of the activities of Se-dependent enzymes that normally detoxify free radicals formed during normal cell metabolism [63]. Regarding Hg toxicity specifically, the limit of tolerance in mammalian hepatic tissue seems to be within the range 100–400 μg g^{-1} WW [66], far above the [Hg] (0.38 to 8.94 $\mu g g^{-1}$ WW) determined in the liver samples of Commerson's dolphin studied.

In the Commerson's dolphin, molar ratios of Se/Hg in liver, kidney, and muscle presented average values of 8.7 (9.6), 13.2 (9.5), and 9.0 (11.4), respectively (Table 2). These ratios exceed those reported for different marine mammals, particularly those with a relatively high [Hg] in liver [10, 15, 17, 19, 23]. The molar ratio of Se/Hg close to 1 was only found in the adult female specimen with the highest hepatic [Hg] and [Se] (30.4 and 20.5 $\mu g g^{-1}$ DW, respectively), also with a molar ratio of 1.2 in muscle tissue. The other specimens showed ratios ranging from 2.96 to 29.66 in liver and 2.40 to 37.50 in muscle (Table 2). The [Se] varied within the range reported for other cetaceans [56, 58, 67]. As we have seen, the Se/Hg ratio decreases with age in all tissues analyzed, related to the higher increase in [Hg] than [Se]. This could be explained in that HgSe is formed and accumulates, and at the same time, the physiological level of Se is kept at similar levels, thus the fraction of Hg and Se in the form of HgSe increases with respect to other compounds. As a result, both concentrations increase but approaching to 1 with the age of the specimen. The variability of the Se/Hg ratio between specimens suggests that these elements might occur in a consistent proportion only when a physiologic threshold has been surpassed, or that adherence to this ratio is not a physiologic necessity, as suggested for ringed seals (*Phoca hispida*) and polar bears (*Ursus maritimus*) of Arctic Alaska [68]. Palmisano et al. [8] stated that a threshold seems to exist for Hg above which a significant correlation between Se and Hg is found, and Wagemann et al. [23] established that only marine mammals with exceedingly high concentrations of Hg show a molar ratio of 1. In agreement with Ikemoto et al. [53], the Se/Hg molar ratio is close to 1 in those marine mammals with hepatic [Hg] higher than 200 $\mu g g^{-1}$ DW. The [Hg] determined in the Commerson's dolphin liver samples were lower (from 1.3 to 30.4 $\mu g g^{-1}$ DW; Table 2) than this limit, although the Se/Hg molar ratio approaches 1 for higher THg concentrations with an exponential behavior (ANOVA p= 0.00053; Fig. 3). The exponential variation of the Se/Hg molar ratio with [Hg] is in agreement with the findings already mentioned, implying Se/Hg ratios close to 1 after a certain [Hg], which corresponds to the oldest specimen (7 years old) in this study. The $y0$ parameter of the exponential fitting (Fig. 3) that expresses the Se/Hg for large [Hg] should be 1, according to the hypothesis stated; the value obtained (3.9±1.0; Fig. 3) is higher, overestimated probably due to the lack of determinations for higher [Hg]. This behavior is similar to that reported by other authors, who find different thresholds in [Hg] for the Se/Hg to be 1, ranging in 20–30 $\mu g g^{-1}$ DW in Dall's porpoises (*Phocoenoides dalli*) [20] and approximately 100 $\mu g g^{-1}$ WW in striped dolphins (*S. coeruleoalba*) [8], which is much higher than the former. Yang et al. [20] suggest that the ability of Dall's porpoise to detoxify further Hg via formation of HgSe seems to be low, and this species might be more sensitive to Hg than striped dolphins.

Previous studies on the Franciscana dolphins from southern Brazilian coasts reported Se/Hg molar ratios over 1 in liver and kidney (4 and 16, respectively; Seixas et al. [33]). Also, a higher value was found in an earlier study analyzing hepatic tissue (8; Kunito et al. [32]), whereas the Se/Hg molar ratio in hepatic tissue from other species such as the estuarine dolphin was close to one (1.2; Kunito et al. [32]). The differences have been attributed to metabolism and foraging habit variations of the cetacean species influencing the accumulation of Hg and Se, reflected hence in the Se/Hg molar ratios [32, 33], although the ratio can vary depending on the geographical location, on the diet, and on the age of individuals. Kunito et al. [32] differentiated between eight mature specimens ([Se] 14 (7) $\mu g g^{-1}$ DW, and [Hg] 5.7 (2.0) $\mu g g^{-1}$ DW) and 15 immature specimens ([Se] 6.6 (1.3) $\mu g g^{-1}$ DW and [Hg] 2.4 (0.9) $\mu g g^{-1}$ DW) and mentioned that [Se] was much higher than that of [Hg] on a molar base in liver of Franciscanas. In the specimens of the Commerson's dolphin studied, the Se/Hg molar ratio approached 1 with both age and [Hg], which is consistent with the Hg and Se accumulation in

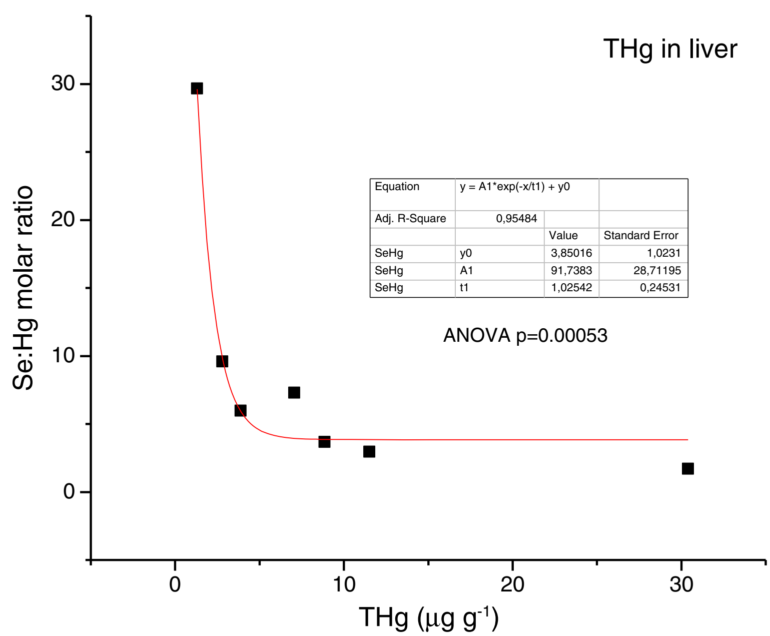

Fig. 3 Selenium to mercury (Se/Hg) molar ratio and total Hg concentration in the liver of the Commerson's dolphin bycaught on the shores of Tierra del Fuego, Argentina

the HgSe form with age. Regarding diet habits, the Franciscana dolphins eat more cephalopods and less fish than the estuarine dolphin [32]. Feeding habits of the Commerson's dolphin include, as main items, three types of small demersal fishes (20.4 %), squids (14.1 %), crustaceans (22.5 %), benthic invertebrates (about 4.2 % sessile and 10 % free-living species), algal (10 %), and miscellaneous (19.7 %) [44]. Among odontocetes, those species which predominantly feed on fish rather than cephalopods generally accumulate higher [Hg] in the liver [9, 25, 39, 54], an observation consistent with the comparatively low [Hg] observed in Commerson's dolphin liver, considering that the contribution of fish to the diet may be only 20 %.

Other elements than Hg can form different compounds with Se, particularly Ag, may compete with Hg for binding sites on Se, as was noted in striped dolphins (*S. coeruleoalba*), belugas (*Delphinapterus leucas*), and pilot whales (*Globicephala melas*), thus limiting the Se/Hg molar ratio to evaluate the potential protective effect of Se. Selenium could also form a Ag stable compound, Ag_2Se, also detoxifying Ag [24, 32, 58, 59]. Consequently, the molar ratio should be computed considering Ag contents in the proportion of the stable Se compound: the molar ratio between Se and (Hg+0.5 silver (Ag)). Silver concentrations were determined by INAA simultaneously with Se and Hg in the same samples and reported in a previous work, with mean values of 5.4 (5.0) $\mu g g^{-1}$ DW in liver, 1.2 (2.7) $\mu g g^{-1}$ DW in kidney, and 0.017 (0.005) $\mu g g^{-1}$ DW in muscle [69]. The highest concentration of Ag reached in liver was 15.42 $\mu g\ g^{-1}$ DW. The database for Ag in marine mammals is limited, although it appears that the range of concentrations in hepatic tissue may be relatively wide (<1 to>10 $\mu g g^{-1}$ WW), as well as the ranges for Hg [58]. The molar ratio Se/(Hg+0.5Ag) in the Commerson's dolphin ranged between 1.53 and 7.31 in liver, 3.34 and 28.63 in kidney, and 1.19 and 23.85 in muscle tissue. A decrease in molar ratios (together with Ag) was observed, possibly limiting the protective effect of Se. This result might suggest the influence of Ag on the relationship between Hg and Se. In this sense, the essential role of Se besides its detoxification function against Hg and Ag in the liver might occur. The biological interaction between transition metals (e.g., Ag and Hg) and Se has been reported, and evidence has been described for Se acting as an antioxidant through the formation of metal–selenide complexes, in particular, for Ag and Hg [58, 70, 71].

Comparison with Other Species from South America

Mercury and Se concentrations in ten species of cetaceans inhabiting marine areas of South America were reported in the literature (Table 3). The direct comparison of this data is difficult, since there are many variables to consider such as sampling methods and analytical techniques applied, or age and sex. However, it is clear that the maximum [Hg] were found in the liver of certain odontocetes, with the highest values of 290 $\mu g g^{-1}$ DW in striped dolphins (*S. coeruleoalba*) and 86.0 (7.3) $\mu g g^{-1}$ WW in bottlenose dolphins (*T. gephyreus* or cited as *T. truncatus*) (Table 3). Information on Se concentrations for these species is limited and available for the liver mostly, with the highest value corresponding to the same specimen of striped dolphin mentioned above, ([Se]=190 $\mu g g^{-1}$ DW) and in Atlantic spotted dolphins (*S. frontalis*) ranging in 27–130 $\mu g\ g^{-1}$ DW [32]. Mercury concentrations in liver of Commerson's dolphins were lower than those reported for other populations from Patagonia, Argentina, but higher in the renal tissues and similar in muscle tissues (Se was not analyzed; Gil et al. [72]).

The reports on small coastal odontocetes with similar characteristics to the Commerson's dolphins, such as the Franciscana dolphins, show Hg concentrations in the ranges 3.8–8.79 $\mu g g^{-1}$ WW for liver, 1.73–1.9 $\mu g g^{-1}$ WW for kidney, and 2.0–3.0 $\mu g g^{-1}$ WW for muscle tissue (Se was not analyzed), in specimens collected in Argentine waters [28, 29]. A more extensive study in Brazilian waters presented regional differences in hepatic [Hg] and [Se] between mature and immature specimens of Franciscana dolphins [34]. In the southeast area, the mean hepatic [Hg] was 1.54 and 4.38 $\mu g g^{-1}$ DW, respectively, whereas in the south was 2.89 and 31.13 $\mu g g^{-1}$ DW, respectively. In both cases, [Hg] increased with age, results that are consistent with our [Hg] determinations in Commerson's dolphins (Table 2), which are similar to the concentrations determined in the southern region of Brazilian waters in dolphins. The mean [Se] in liver for immature specimens was 2.48 $\mu g g^{-1}$ DW and in mature 4.90 $\mu g g^{-1}$ DW, whereas for the southern region was 4.75 and 19.38 $\mu g g^{-1}$ DW, respectively. Such regional variation in the accumulation of Hg and Se has been attributed to differences in demographic and genetic aspects of the populations, involving different nutritional, developmental, and reproductive characteristics [34]. Also, our [Se] determinations in Commerson's dolphins (Table 2) are closer to those in Franciscana dolphins from the southern region of Brazilian waters. In kidney tissues of Franciscana dolphins, [Hg] and [Se] were similar in both areas of Brazil [34]. These findings were consistent with the results reported in other studies in Brazil on the same dolphin species [32, 33, 73].

Regarding other odontocete species from the South Atlantic Ocean, [Hg] in liver of Commerson's dolphins ranged among the lower values (Table 3). In renal tissues, [Hg] in Commerson's dolphins was similar to the determinations in tucuxi dolphins but much lower than those in bottlenose dolphin and in the pygmy sperm whale (Table 3). For muscle tissue, no determination of [Se] was found, and Hg

Table 3 Mercury and selenium concentrations in the liver, kidney, and muscle of cetaceans from the South America region

Species	N	Location	Hg			Se			Concentration basis	Reference
			Liver	Kidney	Muscle	Liver	Kidney	Muscle		
C. commersonii Commerson's dolphin	7	Tierra del Fuego (Arg.)	9.4 (9.9)	3.6 (2.0)	2.1 (1.3)	14.6 (4.4)	13.6 (2.8)	4.2 (2.1)	$\mu g\,g^{-1}$ DW	This study
	2	Patagonia (Arg.)	13.0	0.22	0.40				$\mu g\,g^{-1}$ WW[a]	[72]
P. blainvillei Franciscana dolphin	2	South-east Buenos Aires (Arg.)	3.8 (1.6)	1.9 (0.7)	3.0 (1.2)				$\mu g\,g^{-1}$ WW	[28]
	18	North Buenos Aires (Arg.)	8.79	1.73	1.73 2.0				$\mu g\,g^{-1}$ WW[a]	[29]
	17	North Rio de Janeiro (Brazil)	0.90–47	0.42–4.1					$\mu g\,g^{-1}$ WW[b]	[30]
	23	São Paulo-Parana State (Brazil)	3.5 (2.1); 1.1–8.6			9.10 (5.50); 3.5–30			$\mu g\,g^{-1}$ DW[b]	[32]
	13 and 18	Rio Grande do Sul and Rio de Janeiro (Brazil)	10.7; 2.6	1.7; 1.4		11.1; 3.2	8.8; 7.0		$\mu g\,g^{-1}$ DW[a]	[33]
	7	Rio de Janeiro (Brazil)	1.13; 0.30–2.70		0.17; 0.06-0.27				$\mu g\,g^{-1}$ WW[a,b]	[36]
	18	North Rio de Janeiro (Brazil)				3.24 (2.0) 0.84–9.05			$\mu g\,g^{-1}$ DW[b]	[73]
S. guianensis estuarine dolphin	20	São Paulo-Parana State (Brazil)	77.0 (107.0); 1.4-380			38.0 (49.0); 3.0–170			$\mu g\,g^{-1}$ DW[b]	[32]
	29	North Rio de Janeiro (Brazil)	0.84–87.92						$\mu g\,g^{-1}$ DW[b]	[37]
	6	Rio de Janeiro (Brazil)	9.98; 1.10–21.7		0.73; 0.34-1.42				$\mu g\,g^{-1}$ WW[a,b]	[36]
	19	North Rio de Janeiro (Brazil)	27.77 (24.68); 3.60–72.98			14.31 (14.77); 1.54–45.32			$\mu g\,g^{-1}$ DW[b]	[35]
	21	North Rio de Janeiro (Brazil)				20.7 (32.22); 1.38–115.32			$\mu g\,g^{-1}$ DW[b]	[72]
	20	Rio de Janeiro (Brazil)			1.07 (0.35); 0.2-1.66				$\mu g\,g^{-1}$ WW[b]	[74]
	12, 42 and 9	Guanabara, Sepetiba, and Ihla Grande Rio de Janeiro (Brazil)			0.920 (0.656); 0.269 (0.332); 0.688 (0.221)				$\mu g\,g^{-1}$ WW	[75]
	19	Rio de Janeiro (Brazil)	0.53–132			0.17–74.8			$\mu g\,g^{-1}$ WW[b]	[38]
S. frontalis Atlantic spotted dolphin	2	São Paulo−Parana State (Brazil)	39; 230			27; 130			$\mu g\,g^{-1}$ DW	[32]
	4	Northern Rio de Janeiro (Brazil)				15.92 (12.45); 4.58–30.41			$\mu g\,g^{-1}$ DW[b]	[73]
S. fluviatilis tucuxi dolphin	11	Ceará (Brazil)	0.10–29.51	0.06–5.63					$\mu g\,g^{-1}$ WW[b]	[31]
S. coeruleoalba striped dolphin	1	São Paulo-Parana State (Brazil)	290			190			$\mu g\,g^{-1}$ DW	[32]
D. capensis common dolphin	1	São Paulo-Parana State (Brazil)	23			30			$\mu g\,g^{-1}$ DW	[32]
	1	South-east Buenos Aires (Arg.)	86.0 (7.3)	13.4 (2.5)	5.5 (0.8)				$\mu g\,g^{-1}$ WW	[28]

Table 3 (continued)

Species	N	Location	Hg Liver	Hg Kidney	Hg Muscle	Se Liver	Se Kidney	Se Muscle	Concentration basis	Reference
T. gephyreus (*T. truncatus*) bottlenose dolphin										
K. breviceps pygmy sperm whale	1	South-east Buenos Aires (Arg.)	11.7	10.5	1.6				$\mu g g^{-1}$ WW	[28]
B. acutorostrata minke whale	135	Antarctica	0.189 (0.076) m; 0.207 (0.076) f						$\mu g g^{-1}$ DW	[39]
	19	Antarctica	0.238 (0.083) m; 0.111; 0.410 f			18.1 (8.9) m; 8.40; 18.9 f			$\mu g g^{-1}$ DW	[40]

Mean and standard deviation of the average in parenthesis (SD)

N number of specimens, *f* female, *m* male, *DW* dry weight, *WW* wet weight

[a] Averages

[b] Range

Conversion factor (dry to wet weight) for liver=0.294(0.015), kidney=0.254(0.018), and muscle=773 0.286(0.007) in this study

seems to be similar to other dolphins [74, 75]. The difference between species could be associated to the metabolism but also to different exposure levels.

With regard to mysticetes, [Hg] in liver of Commerson's dolphins were higher than those observed for the minke whales from sites around Antarctica with mean concentrations of 0.189 (0.077) $\mu g g^{-1}$ DW for males and 0.207 (0.077) $\mu g g^{-1}$ DW for females [39]. Also, another study of southern minke whales with low hepatic accumulation of Hg (0.111–0.414 $\mu g g^{-1}$ DW) showed relatively high [Se] in the liver (6.08−32.9 $\mu g g^{-1}$ DW) (Table 3) and in skin tissue (10.0–70.05 $\mu g g^{-1}$ DW) [40]. The lower [Hg] in minke whales reflect the contents in its prey, Antarctic krill, associated with the low Hg levels in seawater and with the short food chain in the Antarctic marine ecosystem [39, 76]. The differences in Hg dietary intake, habitat, and position on the food web suggest that [Hg] in toothed cetaceans should be relatively higher than in baleen whales [26, 38, 66]. Differences in the levels of [Hg] among species might be caused not only by their prey items but also for other factors such as feeding and growth rate, size, and lifespan [17, 40].

Conclusions

The present study reports new information on Hg, and particularly so, as this is the first time Se has been measured in liver, kidney, and muscle tissues of Commerson's dolphins, which contributes to the existing studies of heavy metals in the southwestern South Atlantic Ocean. Furthermore, the information from this study is relevant to increase the knowledge of odontocete population's health and conservation in view of the anthropogenic impact in the marine ecosystem. As in other marine mammals, the liver as an organ of active dietary metabolism appears to be the preferential organ for Hg accumulation. Mercury concentrations found in the liver and kidney of the Commerson's dolphin were within the range to those observed in other small dolphins from the Argentine and Brazilian coastal waters. The variation in [Hg] observed in relation to other groups of cetaceans is likely to reflect interspecific dietary differences, age-accumulation trends, and even exposure levels. The molar Se/Hg ratio showed high variability, with average values in liver, kidney, and muscle in 8.7 (9.6), 13.2 (9.5), and 9.0 (11.4), respectively, with the ratios closer to 1 in the only adult female specimen studied. Values of the Se/(Hg+0.5Ag) molar ratios were close to 1, possibly limiting the protective effect of Se. To our knowledge, no previous information about Se concentrations and its relation to Hg and Ag for this species was reported.

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