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Cephalopods and cetaceans as indicators of offshore bioavailability of cadmium off Central South Brazil Bight

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Cd levels in ommastrephid squids from Brazil are the highest ever reported for cephalopods.

Abstract

Regarding Brazilian coast, industrial and urban developments are concentrated along Central South Brazil Bight. Samples from inshore and offshore species from the concerned area were analyzed, comprising 24 cetaceans (9 species) and 32 squids (2 species). Cadmium was determined by GFAAS and our results were in agreement with certified values (DOLT-2, NRCC). Mean cadmium concentration (in μg/g, wet weight) observed in the digestive gland of sexually mature Argentine short-finned squids (*Illex argentinus*) was 1002.9. To our knowledge this is the highest cadmium level ever reported for a cephalopod. Concerning cetaceans, our results include one of the highest renal cadmium concentrations described for striped dolphins (71.29 μg/g, wet weight). Anthropogenic action, upwelling and cannibalism of Argentine short-finned squid on the studied area are possible reasons for such remarkable cadmium concentrations.

Keywords: Cadmium; Southwest Atlantic Ocean; Brazil; Cephalopod; Cetacean

1. Introduction

Industrial and urban developments, at present, spread along the entire Brazilian coast; however, they are particularly concentrated along the region known as the Central South Brazil Bight (Fig. 1), which extends from Cabo Frio (23°S) to Cabo de Santa Marta (28°S), comprising the states of Rio de Janeiro, São Paulo, Paraná and Santa Catarina. This coast presents various protected estuaries and bays that have been receiving discharges of chemical contaminants from domestic, industrial and agricultural wastewaters.

Among these estuaries, Guanabara Bay (Fig. 1) may be mentioned as the most dramatic example of man-made degradation, since it is surrounded by four cities (including Rio de Janeiro metropolitan area) with a total population of about 11 million people, and is bordered by 6000 industries, with more than 6000 additional industries in its drainage basin (Kjerfve et al., 1997).

Studies on heavy metal contamination of Brazilian marine environment have been produced (for reviewing, see Pfeiffer

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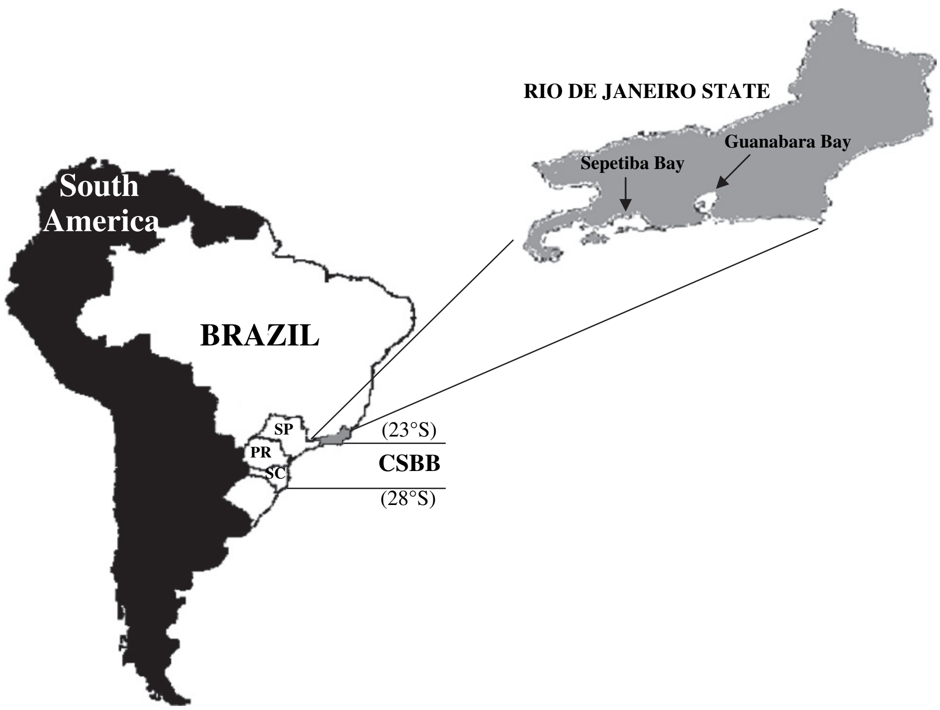

Fig. 1. South America map stressing Brazil, northern (Cabo Frio, 23°S) and southern (Cabo de Santa Marta, 28°S) limits of Central South Brazil Bight (CSBB) and the Brazilian states of Rio de Janeiro (gray), São Paulo (SP), Paraná (PR) and Santa Catarina (SC). The map of Rio de Janeiro state is amplified and shows Guanabara and Sepetiba Bays.

et al., 1988). However, these surveys were relatively isolated and confined to bays, estuaries and coastal lagoons.

Some researches on the geodynamics of heavy metals in Sepetiba Bay (Fig. 1) lead to the conclusion that part of the cadmium introduced into the bay may be exported to the coastal zone due to its great water solubility, bioavailability and little sedimentary flux (Barcellos, 1995; Lacerda et al., 1987; Lima et al., 1986). The data produced so far on the quoted bay draw attention to the possibility that a similar geodynamics of cadmium and hence, exportation of this metal, may also occur in less studied estuaries of the polluted Central South Brazil Bight.

Besides the anthropogenic input of cadmium, there is a possibility of a natural enrichment of this metal in the oceanic environment off Central South Brazil Bight, since cadmium is enriched in the surface waters of upwelling areas (Martin and Broenkow, 1975) and the region considered here is strongly influenced by this phenomenon (Borzone et al., 1999).

Considering all the mentioned above, it is of great interest to investigate the possibility of a man-made enrichment of cadmium in the adjacent neritic and oceanic waters. However, probably due to problems on cadmium determination in water, associated with difficulties related to the logistic of a representative sampling, this kind of research has not yet been accomplished in Brazil.

Considering that cephalopods are well known for their high cadmium bioaccumulation capacity (Bustamante et al., 1998a,b; Castillo et al., 1990; Caurant and Amiard-Triquet, 1995; Honda and Tatsukawa, 1983; Shiber, 1981) and that cadmium levels are higher in cetacean species that feed primarily on squid, compared with species that feed more on fish (Das et al., 2003a; Johnston et al., 1996; Law, 1996; O'Hara and O'Shea, 2001; Reijnders, 1996), cephalopods and squid-eating cetaceans were used in this study as source of information about cadmium contamination in oceanic waters off Central South Brazil Bight.

In this paper, we also examine the hypothesis that the phenomenon of cadmium bioaccumulation by cephalopods, and hence, the transfer of this metal to cetaceans presents global occurrence and therefore, it occurs in Brazilian waters as well.

2. Materials and methods

2.1. Sampling of digestive glands from squids and sample preparation

Slender inshore squids (*Loligo plei*, $n = 14$) and Argentine short-finned squids (*Illex argentinus*, $n = 18$) were caught by trawl in neritic and oceanic waters off Brazilian Coast between June and September 2004. The neritic region mentioned comprised an area that varied from 26°17′ to 26° 41′ S and from 47° 42′ to 48° 31′ W, in which the depths varied between 21 and 81 m, while the oceanic region quoted comprised an area that varied from 27° 18′ to 28° 04′ S and from 47° 03′ to 47° 10′ W, in which the depths varied between 355 and 403 m. Specimens were transported to the laboratory under ice, and sex and sexual maturity stage were determined for each individual, according to Andriguetto Filho (1989) for slender inshore squids and Brunetti et al. (1991) for Argentine short-finned squids. Total body weight and dorsal mantle length and weight were measured. The digestive gland was removed from the dissected individuals, weighed and kept frozen in individual polyethylene bags until analysis. In which concerns slender inshore squid, only part of the digestive gland was obtained as the quoted organ is easily destroyed while dissected.

2.2. Sampling of renal tissues from cetaceans and sample preparation

Kidney samples were obtained from 24 odontocetes stranded on beaches in Rio de Janeiro State from October 1995 to November 2003. After dissection, samples were stored in individual polyethylene bags and kept frozen until analysis. The 9 analyzed species were bottlenose dolphin (*Tursiops truncatus*), Atlantic spotted dolphin (*Stenella frontalis*), spinner dolphin (*S. longirostris*), pantropical spotted dolphin (*S. attenuata*), striped dolphin (*S. coeruleoalba*), rough-toothed dolphin (*Steno bredanensis*), long-beaked common dolphin (*Delphinus capensis*), marine tucuxi dolphin (*Sotalia guianensis*) and dwarf sperm whale (*Kogia sima*).

2.3. Analytical procedure

Two aliquots of approximately 200 mg of each organ were digested with 2 mL of 65% HNO_3 in a screw-capped vessel, during 24 h. The vessel was then heated to 60 °C for 120 min in a water bath. After cooling, the sample was made up to a known volume with high purity deionised water (18.2 MΩ cm) from a Milli-Q system. Blanks were carried through the procedure in the same way as the sample. Cadmium was determined by electrothermal atomic absorption spectrometry (ET AAS), using an Analytic Jena spectrometer ZEEnit 60 equipped with Zeeman-effect background correction. The mixture $Pd(NO_3)_2 + Mg(NO_3)_2$ was used as a matrix modifier. Reference material, dogfish liver DOLT-2 (NRCC), was treated and analyzed in the same way. Our analytical results (in μg/g ± S.D.) for the determination of cadmium in DOLT 2 (19.86 ± 0.9, $n = 4$) were in good agreement with certified value (20.8 ± 0.5). The detection limit of the method was 0.004 μg/g. The temperature program used and the operating conditions are shown in Tables 1 and 2 respectively.

2.4. Statistical analysis

Firstly, *Shapiro–Wilk's W* test was used in order to test for normality of the data. Since normal distributions were verified, *Pearson test* was used for evaluating the existence of correlation between cadmium concentrations and the biological parameters: mantle length, body weight, mantle weight and digestive gland weight. The differences in cadmium concentrations between sexes and between species were tested by the *Student's t-test*. The STATISTICA 6.0 Statistical Software System was used for statistical analyses.

3. Results

Cadmium concentrations (μg/g wet wt.) in the digestive gland from both slender inshore squid and Argentine short-finned squid, along with mantle length, sexual maturity stage, sex and, in the case of the Argentine short-finned squid, digestive gland weigh and cadmium burden, are presented in the Table 3. In our analysis, the Ommastrephidae Argentine short-finned squid exhibited significantly higher cadmium concentrations than the Loliginidae slender inshore squid ($p < 0.001$). The same statistical test showed the absence of significant differences ($p > 0.05$) in cadmium concentrations between sexes for both cephalopod species.

Table 1
Temperature Program used for cadmium determination in cephalopod and cetacean tissues

Drying 1	
Temperature (°C)	90
Ramp/Hold (s)	6/15
Drying 2	
Temperature (°C)	120
Ramp/Hold (s)	2/25
Pyrolysis	
Temperature (°C)	900
Ramp/Hold (s)	10/20
Atomize	
Temperature (°C)	1450
Ramp/Hold (s)	0.2/5
Cleanout	
Temperature (°C)	1950
Ramp/Hold (s)	0.5/7

Table 2
Operating conditions at the Analytic Jena spectrometer ZEEnit60

Wavelength (nm)	228.8
Slit (nm)	0.8
Lamp current (mA)	6.0
Integration mode	Peak area
Integration time (s)	5.0
Field mode	2-field
Fieldst (max.) (T)	0.8
Sample volume (μL)	16.00

Significant correlations were found between cadmium concentrations and mantle length in Argentine short-finned squid ($p < 0.01$). In which concerns all the other possible correlations tested, regarding both cephalopod species, no significant correlations were found ($p > 0.05$).

Renal cadmium concentrations (μg/g wet wt.) determined for the analyzed cetaceans, along with data concerning total length and number of specimens, are shown in Table 4.

The *Pearson test* showed the inexistence of correlation between renal cadmium concentrations and total length for the Atlantic spotted dolphins ($p > 0.05$), but this may be due to the small range of lengths among the specimens analyzed. The same evaluation has not been accomplished for the other analyzed cetaceans due to the low number of individuals of each species (Table 4).

4. Discussion

The remarkable cadmium concentrations observed in Argentine short-finned squid are possibly the highest ever reported for a cephalopod (Table 5). The reason for such a high level and the explanation for higher cadmium concentrations in an oceanic cephalopod (Argentine short-finned squid) than in a coastal squid (slender inshore squid) may be a result of both environmental and physiological aspects.

Cadmium is considered a nutrient-like element since it is incorporated into and released from marine biogenic detritus in direct proportion to the regeneration of phosphate and nitrate. Consequently, the surface layer of the ocean presents low levels of cadmium compared with deeper regions (Bewers et al., 1987). This information is relevant when it is considered that Argentine short-finned squids carry out vertical diel migrations, foraging throughout the water column (Moiseev, 1991).

Studies on Argentine short-finned squid life-cycle in southern Brazil raised the hypothesis that part of the spawners in the region would come from waters off northern Argentina and Uruguay (Santos and Haimovici, 1997a).

Table 3
Mean cadmium concentration (μg/g wet weight) and standard deviation (±S.D.) in the digestive gland of slender inshore squid (*Loligo plei*) and Argentine short-finned squid (*Illex argentinus*) mature and immature individuals, average mantle length (ML, in millimeters), number of specimens (*n*) and mean weight (g) and cadmium burden (mg) of the organ mentioned

Squid Species/Maturity	ML (mm)	*n*	Cd (μg/g)	Weight (g)	Burden (mg)
Loligo plei (mature)	140 ± 26	14	19.6 ± 9.00	N.A.	N.A.
Illex argentinus (Immature)	158 ± 28	03	18.5 ± 5.40	3.9 ± 1.4	0.06 ± 0.01
Illex argentinus (mature)	261 ± 25	15	1002.9 ± 566	9.9 ± 4.3	10.90 ± 7.60

Notation N.A. means that the information is not available.

Gerpe et al. (2000) determining cadmium concentrations in the digestive gland of Argentine short-finned squids from Argentinean waters (Table 5) observed high levels, however; the concentrations were lower than those verified in Brazil (this study).

Cannibalism would be a contributing factor for an increased exposure to cadmium in Brazilian waters. Concerning the ommastrephid Argentine short-finned squid, it was observed a higher cannibalism rate in southern Brazil (Santos and Haimovici, 1997b) than it had been previously reported in waters off Uruguay and Argentina (Ivanovic and Brunetti, 1994; Koronkiewicz, 1986). This seems to be a consequence of the fact that the overlapping in the spatial distributions between Argentine short-finned squids juveniles and subadults and larger specimens is intensified on Brazilian continental shelf (Haimovici and Perez, 1990), since it is narrower than the Argentinean one.

The occurrence of much higher cadmium concentrations in the digestive gland of the oceanic ommastrephid Argentine short-finned squid than in the coastal lolignid slender inshore squid may be related also to differences in the digestive physiology of both groups. In fact, the situation observed in this study corroborates data from literature, since levels observed in ommastrephids have been higher than those obtained in loliginids either in French (Bustamante et al., 1998a; Lahaye et al., 2005), Irish or Faroese waters (Bustamante et al., 1998a), as well as in North Pacific (Martin and Flegal, 1975).

It is plausible to believe that squids of the Ommastrephidae Family present a higher cadmium bioaccumulation capacity than those of the Loliginidae Family. The digestive gland cells of loliginid squids present some differences from those of other cephalopods. They do not have some structures called ''boules'', considered as heterolysosomes and heterophagosomes, and the lack of these structures in these cells might mean that the processes of particle capture and intracellular digestion do not occur widely in their digestive glands (Boucher-Rodoni and Boucaud-Camou, 1987). Such processes can be decisive for the remarkable cadmium absorption efficiency observed in cephalopods (Bustamante et al., 2002).

Considering that longer food chains may favour the occurrence of higher cadmium levels on nektonic predators (Dietz et al., 1998) and that oligotrophic oceanic environments are characterized by this feature, it can be concluded that the difference between cadmium concentrations observed in oceanic ommastrephids and in coastal loliginids may be also related to the habitat of these squids all over the world.

Concerning the analyzed cetaceans, the data raised by this study show that renal cadmium concentrations of cephalopod-eating delphinids from Brazil reflect oceanic or coastal habits of each species and hence their predation on oceanic ommastrephid squids or on coastal loliginid cephalopods. The highest concentration (3.29 μg/g wet wt.) observed among marine tucuxi dolphins, bottlenose dolphins and rough-toothed dolphins was lower than the lowest level (3.41 μg/g wet wt.) verified among individuals of the genus *Stenella* and the long-beaked common dolphin (*Delphinus capensis*). These data constitute interesting ecotoxicological features when the distribution of the quoted cetacean species is taking into account. Marine tucuxi dolphin is a small delphinid that is found in protected estuaries and bays along its distribution (da Silva and Best, 1996) and both bottlenose and rough-toothed dolphins are species commonly observed in Brazilian coastal waters (Moreno et al., 2005). On the other hand, with the only exception of the Atlantic spotted dolphin (*Stenella frontails*), species of the genus *Stenella* (Moreno et al., 2005) and common dolphins (genus *Delphinus*) are oceanic cetaceans (Jefferson et al., 1993).

The data raised by the present study concerning renal cadmium concentrations of Atlantic spotted dolphins suggest that the species may also have access to oceanic prey in Brazilian

Table 4
Mean renal cadmium concentrations (μg/g wet weight), with concentration range and standard deviation (±S.D.), number of individuals of each species (*n*) and average total length (TL, in centimeters), with range of length of the analyzed cetaceans

Cetacean species	Cd (μg/g) ± SD Range	*n*	TL (cm) Range
Marine tucuxi dolphin (*Sotalia guianensis*)	1.18 ± 1.10 0.04–3.29	5	189 185–194
Bottlenose dolphin (*Tursiops truncatus*)	1.10 ± 0.95 0.15–2.04	2	242 240.5–243.5
Rough-toothed dolphin (*Steno bredanensis*)	0.82 ± 1.10 0.04–2.37	3	215 194–256
Atlantic spotted dolphin (*Stenella frontalis*)	5.92 ± 2.13 3.41–10.57	8	189 173–203
Pantropical spotted dolphin (*Stenella attenuata*)	35.90	1	194
Spinner dolphin (*Stenella longirostris*)	10.11	1	213
Striped dolphin (*Stenella coeruleoalba*)	71.29	1	N.A.
Long-beaked common dolphin (*Delphinus capensis*)	8.79	1	216
Dwarf sperm whale (*Kogia sima*)	5.99 ± 2.45 3.54–8.43	2	226 220–232

Notation N.A. means that the information is not available.

Table 5
Cadmium concentrations (μg g^{-1}, dry weight, except while pointed) of the digestive gland of cephalopods from different areas

Area Species	[Cd] ± S.D. Range	*n*	Reference
Scotland (west coast)			
Loligo forbesi	4.77 1.32–15.86	17	Craig and Overnell (2003)
Northern Pacific Ocean			
Loligo opalescens	96.0 ± 55.5 22.6–265.5	43	Martin and Flegal (1975)
Ommastrephes bartrami	287.0 ± 202.0 71.0–694.0	14	Martin and Flegal (1975)
O. bartrami	211.0[a]	N.S.	Castillo and Maita (1991)
O. bartrami	826.5 ± 369.1 368.5–1405.6	10	Kurihara et al. (1993)
Stenoteuthis ovalaniensis	782 ± 255 427.0–1106.0	7	Martin and Flegal (1975)
Todarodes pacificus	31.1 ± 10.8[a] 20.3–41.8	3	Honda and Tatsukawa (1983)
Argentinean waters			
Illex argentinus	144.8 ± 65.0 88.6–298.2	10	Kurihara et al. (1993)
I. argentinus	485.01 ± 118.74	3	Gerpe et al. (2000)
Brazilian waters			
I. argentinus	1002.9 ± 566[a] 268.7–2 562.0	15	Present study
Mediterranean Sea			
Octopus vulgaris	50.0	54[b]	Miramand and Guary (1980)
Australian waters			
Nototodarus gouldi	50.0 ± 25.0 20.0–110.0	15	Smith et al. (1984)
N. gouldi	33.0 ± 30.0 11.0–88.0	6	Finger and Smith (1987)
English Channel			
Eledone cirrhosa	25.2	11[b]	Miramand and Bentley (1992)
Sepia officinalis	14.42	08[b]	Miramand and Bentley (1992)
Southern Indian Ocean			
Benthoctopus thielei	215.0	1	Bustamante et al. (1998b)
Graneledone sp.	369.0	1	Bustamante et al. (1998b)
New Caledonian waters			
Nautilus macromphalus	45.1 ± 13.2	4	Bustamante et al. (2000)
Portuguese coast			
Octopus vulgaris	19.56–761.47[c]	59	Raimundo et al. (2004)

When the original paper expressed separately mean cadmium concentrations of distinct groups of individuals, classified according to sex or different stocks, we opted just to show the mean concentration of the group presenting the highest cadmium level. Notation N.S. means that the information is not specified at the original article.
[a] Concentrations expressed in wet weight.
[b] Pooled sample.
[c] Concentrations originally expressed in nmol g^{-1} (dry weight).

waters. In fact, some recent investigations have already demonstrated the possibility of using cadmium as an auxiliary tool for understanding feeding ecology of marine mammals (Bustamante et al., 2004; Lahaye et al., 2005). This cadmium-related finding corroborates information obtained through sightings in Brazilian oceanic waters, since Atlantic spotted dolphins were also observed in deep water regions (Moreno et al., 2005).

Taking into account that the highest cadmium concentration was observed in a striped dolphin, one of the most studied cetacean species in regard to ecotoxicological investigations, the renal cadmium concentration of the analyzed striped dolphin was compared with information obtained in literature for the same species, around the world (Table 6). The concentration determined here figures among the highest reported, which is compatible with the biology described for the species from data produced in other parts of the world, since the striped dolphin is considered to be a squid-eating cetacean that inhabits oceanic waters (Jefferson et al., 1993). Although striped dolphin (*Stenella coeruleoalba*) is the least known species of the genus *Stenella* in the South West Atlantic, where it does not seem to be as abundant as in Mediterranean Sea and Pacific Ocean (Moreno et al., 2005), an individual stranded in

Table 6
Average renal cadmium concentrations of striped dolphins (*Stenella coeruleoalba*) all over the world

[Cd] ± S.D.	Range	*n*	Weight Basis	Area	Ref.
29.87	N.A.	25	ww	Northwest Pacific	1
44.80[a]	10.80–98.80	18	dw	Tyrrhenian coasts	2
136.0 ± 05.70	132–140	2	dw	French Atlantic coast	3
08.38[a] ± 06.57	N.A.	20	dw	Mediterranean coasts (Spain)	4
27.51[a] ± 31.29	N.A.	39	dw	Mediterranean coasts (Italy)	4
07.02 ± 04.08	1.83 –12.82	5	ww	Adriatic and Ionian coasts	5
91.00 ± 57.00	0.1–199	23	dw	North-east Atlantic	6
06.35 ± 04.29	0.25–15.68	10	ww	Mediterranean Sea	7
05.70 ± 04.34	1.51–12.59	6	ww	Mediterranean Sea	8
71.00 ± 10.40	<0.1–190	3	dw	French Channel coasts	9
150.0 ± 35.00	118–199	4	dw	Irish coasts	9
14.90 ± 11.12	3.60–30.00	5	ww	Mediterranean coast of Israel	10
71.29		1	ww	Brazilian coast	11

Whenever possible, calves and individuals smaller than 160 cm were excluded from this table. List of references (Ref.): 1 Honda and Tatsukawa (1983); 2 Leonzio et al. (1992); 3 Holsbeek et al. (1998); 4 Monaci et al. (1998); 5 Cardellicchio et al. (2000); 6 Das et al. (2000); 7 Cardellicchio et al. (2002); 8 Storelli and Marcotrigiano (2002); 9 Das et al. (2003b); 10 Roditi-Elasar et al. (2003); 11 Present study. Notation N.A. means that the information is not available.
[a] Median was used instead of mean values.

south-eastern Brazil provided valuable information. It contained remains of oceanic species in its stomach, suggesting that the species occurs in offshore deep waters also in South West Atlantic (Rosas et al., 2002). Regarding the essential role of the Argentine short-finned squid in the food web of southern Brazil (Santos and Haimovici, 2000), it is plausible to believe that the quoted cephalopod constitute an important prey for this cetacean.

The information obtained in literature, with regard to renal cadmium concentrations of squid-eating odontocetes from Brazilian waters, also points to the occurrence of higher concentrations in oceanic species, which probably feed on ommastrephids, than in coastal cetaceans that are well known to prey on loliginids. In Fraser's dolphins (*Lagenodelphis hosei*) stranded on Rio de Janeiro state, it was observed that renal cadmium concentrations (μg/g wet weight) reached 79.75 in this oceanic species (Lailson-Brito et al., 2000). On the opposite, patently lower concentrations have been observed in coastal cetaceans. Regarding marine tucuxi dolphin for example, besides the present study, Lailson-Brito et al. (2000) had already reported low cadmium levels (in μg/g wet weight) in individuals from Brazil. The latter study observed a concentration of 2.4 as the highest renal cadmium concentration verified among 14 marine tucuxi dolphins stranded on Rio de Janeiro state. Regarding franciscana (*Pontoporia blainvillei*), another coastal dolphin, the highest renal cadmium concentration verified among 17 individuals from Rio de Janeiro state was 1.2 μg/g ww (Lailson-Brito et al., 2002). Notwithstanding being primarily a squid-eating odontocete, in a research that analyzed the stomach content of 89 individuals, Loliginidae was the only cephalopod family found (Di Beneditto, 2000), which explains the low cadmium concentrations observed.

Cadmium concentrations observed in dwarf sperm whales are also noteworthy. The levels verified (Table 4) were not as high as expected for this species, since squids can constitute between 70 and 80% of its diet (Pauly et al., 1998). However, to our knowledge it is the first report of renal cadmium concentration of dwarf sperm whale, and although the species is well-known to rely on cephalopods, cadmium determination in the specific molluscs preyed by the species is needed before a high cadmium intake is assumed for this mammal.

5. Conclusions

Although quantification on the contribution of natural and anthropogenic phenomena to the cadmium concentration verified in the Argentine short-finned squid still remains to be evaluated, such exceptionally high cadmium levels are more likely to be due to the converging influence of both, physiological peculiarities of the species and environmental features. Among the latter, cadmium enrichment in waters of upwelling areas, the increased cannibalism rate in Brazilian waters and the possible contribution of the long oceanic food chains to an elevation of cadmium concentrations in nektonic predators constitute aspects to be highlighted.

The data produced so far, in regard to cadmium concentrations in cetaceans and their prey, show that not all cephalopods may be considered vectors for the transfer of cadmium to top marine predators in Southwest Atlantic, since the involvement of the loliginid slender inshore squid in this transfer was not verified. Albeit further research is still needed for better understanding of cadmium transfer in marine food chains, special attention should be given to the hypothesis that cephalopods of the family Loliginidae do not take part in this process around the world.

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