Cephalopods as a key of the transfer of cadmium to top marine predators

Paco Bustamante, Florence Caurant, Scott W. Fowler, Pierre Miramand

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P. Bustamante, F. Caurant, S. W. Fowler, P. Miramand

Laboratoire de Biologie et Biochimie Marines, EA 1220, Université de La Rochelle, rue de Vaux de Foletier, 17026 La Rochelle Cedex, France

ABSTRACT: Cephalopods of 11 species differing in their geographic distribution (French , Irish and faroese waters) and feeding habitats, were analysed for their cadmium contents. When comparing the cadmium levels of these cephalopods, it show that the squid *Todarodes sagittatus* and the octopus *Eledone cirrhosa* coming from the Faroe Islands contain respectively 17 and 18 times more than the animals from the French Atlantic coast. High cadmium levels in cephalopods from sub-polar areas were related with high cadmium concentrations in the tissues of top predators in these areas. Weekly doses of cadmium were estimated for the Faroese pilot whales and the Adélie Penguins and were compared to the "Provisional Tolerable Weekly Intake" defined by the World Health Organisation for humans. Our results show that cephalopods constitute an important source of cadmium for cephalopods predators.

KEY WORDS: Cephalopods. Sub-Arctic. Heavy metals. Cadmium. Transfer. Top predators. Seabirds. Marine mammals. Dose

Cadmium, like other heavy metals, is well known to accumulate in a great number of marine invertebrates, especially molluks, bivalves and gastropods (Bryan 1984), but concentrations of these metals in cephalopods, one of the essential links in marine trophic chains (Amaratunga 1983, Rodhouse 1989, Rodhouse & White 1995), have rarely been documented. The studies have mostly concerned essential elements (Ghiretti-Magaldi et al 1958, Rocca 1969, Nardi et al. 1971, Martin & Flegal 1975, Schipp & Hevert 1978, Miramand & Guary 1980, Smith et al. 1984, Finger & Smith 1987, Miramand & Bentley 1992, Bustamante et al. in press) and reports of levels of toxic metals such as cadmium are few (Renzoni et al. 1973, Martin & Flegal 1975, Ueda and al. 1979, Miramand & Guary 1980, Smith et al. 1984, Finger & Smith 1987, Miramand & Bentley 1992, Yamada et al. 1997, Bustamante et al. in press). The studies addressing cadmium levels in cephalopods have shown varied results with high values often present in tissues (Miramand & Guary 1980, Smith et al. 1984, Finger & Smith 1987, Miramand & Bentley 1992) and very high concentrations in certain cases is remarkable (Martin & Flegal 1975, Bustamante et al. in press). All of these studies have shown the cephalopod ability to concentrate cadmium in the digestive gland.

In this paper, we hypothesise that cephalopods may be a significant source of cadmium, one of the most toxic metals in the marine environment, to their predators which in some areas exhibit high levels of this metal in liver and kidney. Indeed, a large number of top predators regularly include cephalopods in their diets, or at least opportunistically. Cephalopods are eaten by many oceanic animals, such as marine mammals (Clarke 1996, Klages 1996), seabirds (Croxall & Prince 1996) and fish (Smale 1996). Over 80 % of odontocete species and two baleen whales species regularly include cephalopods in their diets (Clarke 1996). In 28 odontocetes, cephalopods comprise the main food with the Ziphiidae and Physeteridae being the principal consumers. Nevertheless, cephalopods are an important part of the diets of all the other odontocetes species (Monodontidae, Phocaenidae, Delphinidae, Stenidae). Among the various cephalopods groups, the Ommastrephidae are the most common cephalopod family in the diets of odontocetes in oceanic waters, and Loliginidae are the main family in neritic waters (Clarke 1996). For 31 of the 33 existing species of pinnipeds, it is either known or suspected that cephalopods are a primary food source in their diets (Klages 1996). Altough, data are few, the Ommastrephidae, Loliginidae, Onychoteuthidae, Gonatidae and Octopodidae are the most common cephalopods families recorded in the diet of seals. In the same way, a great number of seabirds species, like penguins, procellariforms, pelecaniforms and alcids, are known to feed on cephalopods, mainly squid (Croxall & Prince 1996). Numerous seabirds species prey up on cephalopods which are only as important as fish or crustaceans for some albatrosses and petrel species (Croxall & Prince 1996). Penguins, auks and terns also eat significant quantities of squid during certain seasons. Squid are generally the most common items for seabirds, and the Ommastrephidae, Onychoteuthidae, Histioteuthidae and Gonatidae families probably represent the greatest fraction (Croxall & Prince 1996).

To estimate the intake of cadmium for cephalopod consumers, cadmium concentrations in cephalopods originating from French, Irish and Faroe Island waters were determined and compared. Then, the weekly intake of cadmium in predators due to ingestion of cephalopods is estimated and compared with the “Provisional Tolerable Weekly Dose” (PTWI) recommended by the World Health Organisation.

MATERIALS AND METHODS

A large sampling of several species of cephalopods, caught by trawl between 1992 to 1997 in Bay of Biscay, English Channel, Atlantic Irish coast and Faroe Islands waters have been used in the analysis. Each individual has been weighted and measured (mantle length, total length), and the sex determined. The origin, sampling date, number of individuals, mantle length and body weight for each species of cephalopods are given in Table 1. Digestive gland was totally removed from the dissected individuals and treated separately from the remains of the animals. Cadmium concentrations in the whole animals were calculated from remains and digestive gland concentrations.

Tissue samples were dried for several days at 80°C to constant weight. Two aliquots of approximately 300 mg of each homogenized dried sample were digested with 4 ml of 65 % HNO_3 and 1 ml of 70 % $HClO_4$ during 24 hours at 80°C. After evaporation, the residues were dissolved in 0.3 N nitric acid. Blanks were carried through the procedure in the same way as the sample. Cd was determined by flame atomic absorption spectrophotometry (AAS) for the digestive gland and by graphite furnace for the remaining tissues using a Varian spectrophotometer Vectra 250 Plus with Deuterium background correction.

All glassware and plastic was cleaned with HNO_3 / HCl 1N and rinsed with deionized water. Reference materials, dogfish liver DOLT-2 and MA-A-2 fish-flesh standard (IAEA), were treated and analyzed in the same way. The results for standards were in good agreement with certified values. All the results are given in micrograms of metal per gram of the wet weight tissue (µg/g w wt). The detection limits for Cd were 0.05 µg/g by flame AAS and **XXXX** by flameless AAS.

Results

Our sampling includes most of the species commonly encountered in French near shore waters and some other species from the Irish and Faroe Island waters. It represents males and females over a large range of size and weight. Cd concentrations (µg/g wet wt) in these whole cephalopods are reported in Table 2 along with other values from the literature. In our analysis, the octopus *Eledone cirrhosa* from the Faroe Islands exhibited the highest Cd concentrations, 9.06 ± 3.38 µg/g, while the lowest were encountered in the Loliginidae squid, *Alloteuthis subulata*, *Loligo forbesi* and *L. vulgaris*, from European waters with values around 0.10 µg/g w wt.

Indeed, there is a great variability in tissue concentrations in a same area and between different areas for the same species. Cadmium concentrations in the cuttlefish *Sepia elegans* and the octopuses *E. cirrhosa* and *Octopus vulgaris* from the Bay of Biscay, were 5 to 9 times higher than those found in the squid *A. subulata* and *L. vulgaris* (Table 2). Likewise, the octopus *E. cirrhosa* from the Faroe Islands exhibits cadmium concentrations 18 times higher than the same species from the Bay of Biscay (Table 2).

According to the World Health Organisation, the limit of cadmium intake is 1µg/kg/day for humans, i.e. 7 µg/kg/week. The minimum weight of cephalopods necessary to reach these limits has been calculated for each species (in g/kg) and is called "weekly dose" (Table 2). For the Ommastrephidae squid *Todarodes sagittatus* from Irish waters and the octopus *E. cirrhosa* from the Faroe Islands, the weekly dose was reached with less than one gram of cephalopod. The total cadmium content in cephalopods was calculated using means of fresh weight and cadmium concentrations (Table 2). Cadmium contents of cephalopods were very high with more than 22 mg for a single *T. sagittatus* from Irish waters and more than 4 mg for an *E. cirrhosa* from Faroe Islands (Table 2).

DISCUSSION

Cadmium concentrations show high variability in cephalopods with respect to the families, geographical origin and feeding habits (benthic or pelagic). For example, in cephalopods from the Bay of Biscay, the lowest concentrations are encountered in Loliginidae while the highest are found in Octopodidae (Table 2). It is possible to classify the cephalopods families based solely on cadmium concentration: Loliginidae < Ommastrephidae < Sepiidae ≤ Octopodidae with mean concentrations according to families of approximately 0.13 µg/g, 0.25 µg/g, 0.50 µg/g and 0.52 µg/g respectively. These differences be diet related: benthic cephalopods (octopuses and cuttlefish) feed mainly on bottom invertebrates (mostly crustaceans, bivalves and polychetes; Boyle 1990, McQuaid 1994) while neritic and pelagic cephalopods (mostly squid) prey mainly on fish and cephalopods (Rocha et al. 1993, Pierce et al. 1993, Collins & Pierce 1996). From a same area, fish exhibit lower cadmium concentrations than benthic invertebrates (Cossa & Lassus 1988), thus diets of the benthic cephalopods should be more rich in cadmium than these based on fish.

In addition, cephalopods show large differences of cadmium concentrations according to their origin. For example, the Ommastrephidae squid *Todarodes sagittatus* from the Faroe Islands contains very high cadmium concentrations (about 3.5 µg/g) while the cadmium levels in the same species of similar sizes from the Bay of Biscay are 17 times lower (Table 2). The same species from Irish waters exhibit very high values (i.e. 8.4 µg/g, Table 2) perhaps because they are very large individuals. Likewise, cadmium concentrations in the octopus *Eledone cirrhosa* are very different according to their origin; the lowest levels were encountered in individuals coming from the Bay of Biscay (0.5 µg/g) with more elevated concentrations in individuals from English Channel (1.2 µ/g) and Faroe Islands (9.1 µg/g) (Table 2). Furthermore, with respect tothe large differences in cadmium concentrations in cephalopods, species from sub-Arctic and sub-Antarctic areas contain very high cadmium concentrations (Table 2). According to the data in Table 2, both of the sub-polar areas appear to be regions where there is a cadmium enrichment in the food web. Thus, top predators from polar and sub-polar areas which ingest cephalopods should exhibit high cadmium concentrations in their tissues, particularly in the liver and kidney, the target organs for this metal. Such differences in temperate areas are confirmed when concentrations in the tissues of marine mammals (Table 3) and seabirds (Table 4) are considered. For example, the beluga *Delphinapterus leucas* exhibit cadmium concentrations in kidney ranging from 10 to 22 µg/g in arctic area whereas in the same species from the estuary of Saint Lawrence, cadmium concentrations in this tissue are about 1.5 µg/g wet wt (Table 3). Likewise, cadmium concentrations in the liver of the harbor porpoise *Phocoena phocoena* from the Atlantic waters vary from less than 0.07 to 0.5 µg/g whereas some individuals from Greenland have levels as high as 11.9 µg/g in the liver and 72.5 µg/g wet wt in the kidney (Table 3). In French waters, stranded dolphins have been used to investigate heavy metal concentration. Cadmium concentrations recorded in the liver and kidney of *Stenella coeruleoalba* and *Delphinus delphis* are, respectively, 17 and 6, and 42 and 18 times lower than concentrations found in Faroe Island pilot whales (Table 3). *Stenella coeruleoalba* and *Delphinus delphis* are known to eat neritic squid, particularly Loliginidae, however fish comprise the main portion of their diet. Cadmium transfer from squid is not negligible, and the lowest cadmium concentrations recorded in neritic squid from French waters (i.e. Loliginidae and Ommastrephidae) may explain these low values.

In older individuals of the species from the Arctic and sub-Arctic areas (i.e. pilot whales, beluga, narwhal), the cadmium concentrations in kidney are close to or higher than critical values established for humans (Table 3). Values as high as 500 to 900 µg/g wet wt have been measured in some pilot whales from the Faroe Islands (Caurant 1994). These critical values are about 200 µg/g wet wt in the renal cortex (Lauwerys 1990). Such cadmium concentrations could lead to severe toxic effects which are nevertheless difficult to show in wild animals. Despite these high concentrations, there is no evidence of a decrease of these populations in these areas, an observation which suggests physiological adaptations in cadmium metabolism. Indeed, during over time, consumers of cephalopod have been submitted to high doses of cadmium, and they probably evolved to withstand cadmium toxicity with efficient detoxification processes.

If we consider all existing data on cadmium concentrations in cephalopods, the range of these concentrations varies over 1 to 2 orders of magnitude between the lowest levels found in the French waters (i.e. Loliginidae with about 0.10 µg/g wet wt) and the highest in the Pacific Ocean (i.e. the Ommastrephidae *Symplectoteuthis oualaniensis* with about 13.71µg/g wet wt) (Table 2). Nevertheless, regardless of the origin of the cephalopods, we propose that cephalopods constitute an important source of cadmium for many oceanic top predators. We have estimated the weight of cephalopods necessary to reach the Provisional Tolerable Weekly Dose determined by World Health Organisation for humans which is relatively low (1µg Cd/ kg human/day). The highest weight estimated is about 70 g of cephalopod with Loliginidae squids from French waters and the lowest is about 1 g for several species (Table 2). This induces a high exposure to cadmium for marine predators which include cephalopods in their diets and could explain the high cadmium concentrations found in their target organs. In the case of pilot whales whose diets have been well studied (Desportes 1985, Desportes & Mouritsen 1993, Gannon et al. 1997ab), there is strong evidence for a large cadmium contribution from cephalopods for cadmium intake in these species. For example, very high values of cadmium have been recorded in the liver (63 µg/g) and kidney (78 µg/g) in the pilot whales from Faroe Islands (Caurant et al. 1994). Caurant et al. (1994) have estimated the total intake of cadmium from diet studies of the pilot whales from Faroe Islands which show a mean of 18.3 cephalopods per stomach with exceptional values as high as 380 cephalopod remains in one stomach (Desportes 1985, Desportes & Mouritsen 1993). Our estimations with the cadmium concentrations found in the squid *Todarodes sagittatus*, the most common prey in the diet of the Faroe Island pilot whales (Desportes & Mouritsen 1993), are about 765 µg of cadmium per cephalopod (Table 2). We have calculated a minimum weekly intake of 98 mg of cadmium per week. The maximum value was estimated to be about 2037 mg of cadmium. With the mean weight for pilot whales of 690 kg, the total weekly intake is from 142 to 2952 µg/kg/week. This is much higher than values calculated by Caurant & Amiard-Triquet (1995) using another squid species, *Loligo forbesi*; their values ranged from 25.2 to 516.6 µg/kg/week. All these dosages are much higher than values reported by Nogawa (1984) as limits beyond which metabolic disorders appear in human beings. This author has shown in Japanese exposed to cadmium by rice consumption that an increase of metabolic disorders was evident for a weekly intake of 1.41 to 2.03 mg of cadmium for people older than fifty years. For a mean weight of 70 kg, the weekly intake for humans is from 20.3 to 28.7 µg/kg/week.

It is more difficult to calculate such values for pinnipeds, but on the 33 pinniped species, only two species, Baikal Seal and Caspian Seal, exclude cephalopods in their diets because they inhabit freshwater where cephalopods do not occur. Watanabe et al. (1996) have recorded very low cadmium concentrations in both liver and kidney of Baikal Seal, *Phoca sibirica*, with mean values respectively of 0.28 ± 0.45 and 2.0 ± 1.1 µg/g wet wt, compared to levels in the marine species which include cephalopods in their diet (Table 3). These authors suggest that the low levels of cadmium are due to low concentrations in their fish prey.

Concerning seabirds, most of the species whose diets have been studied have only been investigated at one site and usually only during their chick-rearing period (Croxall & Prince 1996). Nevertheless, energy requirements have been calculated for seabirds and translated into food requirements, assuming an energetic value of 4.5 kJ per gram fresh weight food (Franeker 1992). Such energy contents is approximately the value for krill whereas fish usually has higher and squids lower energy contents (Brown 1988, Croxall et al. 1985, Jackson 1986). For example, the Adélie penguin needs about 870 g of food per day. Estimate of squid occurrence in the diets of Adélie penguins from Weddell Sea and Adélie Land were 54 % (Ridoux & Offredo 1989) and 3 % (Ainley et al. 1992) corresponding to a minimum of 26 and 470 g of squid by day, i.e. 182 and 3290 g per week, respectively. We lack cadmium concentrations in the squid species included in the diet of Adélie penguin (i.e. *Psychroteuthis glacialis* and *Kondakovia longimana*, Ridoux & Offredo 1989, Ainley et al. 1992). Nevertheless, taking the lowest cadmium concentration in squid from our study (e.g. 0.10 µg/g, Table 2), ingested cadmium by Adélie penguins would be about 18.2 µg in Weddell Sea and 3290 per week µg in Adélie Land. Assuming a mean body weight of 4.4 kg for an adult Adélie penguin, the doses estimated are 4.1 and 748 µg/kg/week, respectively. These dosages obtained with minimum values (e.g. energetic value for squid, lowest cadmium concentrations) are close to and much higher, to the Provisional Tolerable Weekly Dose of 7 µg/kg/week for humans. Thus, high cadmium concentrations such as 35.0 ± 17.6 µg/g wet wt found in the kidney of Adélie penguins from the Weddell Sea (Schneider et al. 1985, Table 4) are not surprising and can be explained by regular cephalopod consumption in this area.

CONCLUSION

Cadmium levels in top vertebrate predators can be very high in sub-polar areas remote from industrial sites (e.g. Faeroe Islands, Gough Islands, Kerguelen Islands). In contrast, in the shelf waters of industrial countries (e.g. French Atlantic coast), top predators regularly exhibit cadmium concentrations lower than those in similar species from sub-polar areas (Table 3). This apparent natural accumulation of cadmium in marine mammals and seabirds can be explained by the contribution obtained from consuming cephalopods. The high variability of cadmium concentrations in cephalopods due to their geographical origin and their ecological behaviour may explain why top predators bioaccumulate cadmium in sub-polar areas remote from industrial inputs as opposed to the case in the shelf waters of industrial countries, where the same animals contain far lower cadmium concentrations in their tissues. Altough, in our study we have measured cadmium levels in 5 families of cephalopods including 11 different species, we still lack information about most of the important cephalopod families eaten by whales, pinnipeds and seabirds (i.e. Cranchidae, Gonatidae, Histioteuthidae, Onychoteuthidae, Octopoteuthidae). Future works focused on these families should further light on the transfer of cadmium to top predators in marine food chains.

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Table 1. Compilation of cadmium concentrations (µg/g wet wt) and cadmium content (µg) in whole cephalopods from different geographical locations in the Northeast Atlantic Ocean. The weekly dose is the cephalopod weight ingested necessary to reach the WHO 'Provisional Tolerable Weekly Intake' limit for humans of 7 µg Cd/kg/week. In most all cases values are Mean ± 1 SD.

Origin	Species	Sample size	Fresh weight (g)	Water content (%)	Cd concentration (µg/g wet wt)	Weekly dose (g/kg)	µg Cd per individual	Reference
Faroe Islands								
	Loliginidae							
	Loligo forbesi	21	123 ± 61	78 ± 1	0.46 ± 0.30	16.3	57 ± 46	This study
	Ommastrephidae							
	Todarodes sagittatus	17	221 ± 125	75 ± 2	3.46 ± 1.49	2.0	765 ± 544	This study
	Octopodidae							
	Eledone cirrhosa	4	448 ± 85	81 ± 1	9.06 ± 3.38	0.8	4059 ± 1699	This study
West Irish shelf								
	Loliginidae							
	Loligo forbesi	18	91 ± 37	78 ± 1	0.11 ± 0.03	63.6	10 ± 5	This study
	Ommastrephidae							
	Todarodes sagittatus	5	2692 ± 460	76 ± 3	8.41 ± 5.99	0.8	22640 ± 16583	This study
	Octopodidae							
	Benthoctopus ergasticus	1	1512	87	3.65	1.9	5519	This study
	Opisthoteuthidae							
	Opisthoteuthis sp.	1	1206	94	0.70	10.0	844	This study
English Channel								
	Loliginidae							
	Alloteuthis subulata		-	78	0.31	-	-	Bryan (1976)
	Alloteuthis subulata	56	3.5 ± 2.0	78 ± 3	0.37 ± 0.17	18.9	1 ± 1	This study
	Loligo forbesi	9	1195 ± 585	78 ± 1	0.10 ± 0.04	70.0	120 ± 76	This study
	Loligo vulgaris	8	56 ± 49	75 ± 1	0.10 ± 0.03	70.0	6 ± 5	This study
	Octopodidae							
	Eledone cirrhosa	15	494 ± 108	78	1.19 ± 0.24	5.9	588 ± 175	Miramand & Bentley (1992)
	Sepiidae							
	Sepia officinalis	15	518 ± 74	76	0.33 ± 0.01	21.2	171 ± 25	Miramand & Bentley (1992)
Bay of Biscay								
	Loliginidae							
	Alloteuthis subulata	92	8.4 ± 1.1	78 ± 2	0.10 ± 0.02	70.0	0.8 ± 0.2	This study
	Loligo vulgaris	21	118 ± 73	78 ± 3	0.14 ± 0.06	46.7	17 ± 12	This study
	Ommastrephidae							
	Illex coïndetii	22	165 ± 191	79 ± 2	0.29 ± 0.09	25.0	48 ± 30	This study
	Todarodes sagittatus	5	93 ± 113	83 ± 4	0.21 ± 0.02	33.3	20 ± 24	This study
	Octopodidae							
	Eledone cirrhosa	6	214 ± 146	81 ± 1	0.49 ± 0.10	14.3	105 ± 75	This study
	Octopus vulgaris	13	1486 ± 581	82 ± 1	0.54 ± 0.24	13.0	802 ± 475	This study
	Sepiidae							
	Sepia elegans	14	28 ± 11	75 ± 2	0.90 ± 0.43	7.8	25 ± 16	This study
	Sepia officinalis	22	112 ± 85	77 ± 1	0.20 ± 0.06	28.0	22 ± 18	This study
	Sepia orbignyana	15	57 ± 24	76 ± 2	0.41 ± 0.28	17.9	23 ± 19	This study

Table 2. Cadmium concentrations in whole fish from different locations in the North Atlantic and the Arctic Oceans. The weekly dose is the fish weight ingested necessary to reach the WHO 'Provisional Tolerable Weekly Intake' limit for humans of 7 µg Cd/kg/week. All values were converted from dry weight to wet weight concentrations, assuming a wet/dry weight ratio of 4.0.

Origin	Species	Sample	Cd concentration (µg/g wet wt)	Weekly dose (g/kg)	Reference
North American Arctic					
	Arctic cod (*Boreogadus saida*)	50	0.10 (0.05-0.19)	70 (37-133)	Macdonald & Sprague (1988)
English Channel					
	Trisopterus luscus	-	0.004-0.011	636-1750	Miramand, unpublished data)
	Potamoschistus minutus	10	0.013 ± 0.008 (0.004-0.028)	538 (250-1750)	Miramand et al. (1997)
	Platichtys flesus	40	0.005 ± 0.002	1400	Miramand et al. in press
	Dicentrarchus labrax	20	0.006 ± 0.002	1167	Miramand et al. in press
French Atlantic coast					
	Potamoschistus minutus	-	0.002	3500	Amiard-Triquet et al. (1983)
	Platichtys flesus		0.003	2333	Amiard-Triquet et al. (1983)
	Calionymus lyra	-	0.009	778	Amiard-Triquet et al. (1983)
	Merlangius merlangius	-	0.005	1400	Amiard-Triquet et al. (1983)
	Pollachius pollachius	-	0.008	875	Amiard-Triquet et al. (1983)