Polar Biol (1998) 19: 264–271

ORIGINAL PAPER

P. Bustamante · Y. Cherel · F. Caurant · P. Miramand

Cadmium, copper and zinc in octopuses from Kerguelen Islands, Southern Indian Ocean

Received: 2 June 1997 / Accepted: 30 October 1997

Abstract Concentrations of cadmium, copper and zinc were measured in 34 octopuses over a large range of size and weight, caught in the Kerguelen shelf waters. Compared with levels normally encountered in European cephalopods, Cd concentrations in both species were very high: 30.7–47.1 and 27.3–54.4 μg/g dry weight in *Graneledone* sp. and *Benthoctopus thielei*, respectively; Cu concentrations were generally low while Zn concentrations exhibited similar levels. Distribution of Cd in tissues showed that the high levels of Cd in Kerguelen octopuses resulted from very high levels of the metal in the digestive gland (369 and 215 μg/g dry wt in *Graneledone* sp. and *Benthoctopus thielei*, respectively). The digestive gland accumulated about 90% of the total Cd in the whole animal. Due to the very high concentrations of Cd in the Kerguelen octopuses, we hypothesize that these species play an important role in the process of Cd transfer throughout the food chain to top vertebrate predators in this area.

Introduction

Recent studies have shown elevated concentrations of Cd in several marine invertebrates from Antarctic areas, mostly in crustaceans (Hennig et al. 1985; Mauri et al. 1990; Petri and Zauke 1993; Zauke and Petri 1993; Ahn et al. 1996; Bargagli et al. 1996). Data on Cd levels in molluscs from this area are few. Especially, there are no data available regarding cephalopods. Nevertheless, cephalopods occupy a predominant niche in the trophic chains (Rodhouse and Nigmatullin 1996), particularly in the Antarctic Polar Frontal Zone in the South Atlantic Ocean, where they, especially the ommastrephid *Martialia hyadesi*, occupy the ecological niche of epipelagic fish (Rodhouse and White 1995). Cephalopods are predominant in the trophic system because they are eaten by many oceanic animals, such as marine mammals (Clarke 1985; Clarke 1996) and seabirds (Croxall and Prince 1996; Cherel and Klages 1997). In the Southern Ocean, benthic octopuses have been found in the food of rockhopper and gentoo penguins (Brown and Klages 1987; Adams and Klages 1989), royal albatrosses (Imber 1991) and Weddell seals (Clarke and McLeod 1982). They have been also reported as minor but regular prey of southern elephant seals (Rodhouse et al. 1992) and albatrosses (Cherel and Klages 1997). In Kerguelen waters, octopuses are common food items of black-browed albatrosses during the chick-rearing period (Y. Cherel and H. Weimerskirch, unpublished data) and they have been found in the diet of gentoo penguins (Bost 1991). Moreover, some studies on elemental bioaccumulation show that cephalopods accumulate high levels of trace elements, particularly Cd and Cu (Ghiretti-Magaldi et al. 1958; Rocca 1969; Renzoni et al. 1973; Martin and Flegal 1975; Miramand and Guary 1980; Smith et al. 1984; Miramand and Bentley 1992). Thus cephalopods represent important species for studying the transfer of Cd into marine food webs in Antarctic and sub-Antarctic areas.

This paper describes the bioaccumulation and tissue distribution of Cd, Cu and Zn in two octopus species living in the Kerguelen shelf waters, *Graneledone* sp. and *Benthoctopus thielei*. The Kerguelen Islands constitute a small archipelago in the South Indian Ocean, at the Antarctic Polar Frontal Zone (Fig. 1), where release of heavy metals is presumably negligible or non-existent. Moreover, the Kerguelen Islands are of special interest because there is no information available on heavy metal levels in invertebrates from sub-Antarctic areas.

P. Bustamante (✉) · F. Caurant · P. Miramand
Laboratoire de Biologie et Biochimie Marines, EA 1220,
Université de La Rochelle, rue de Vaux de Foletier,
17026 La Rochelle Cedex, France

Y. Cherel
Centre d'Etudes Biologiques de Chizé,
UPR 4701 du Centre National de la Recherche Scientifique,
F-79360 Villiers-en-Bois, France

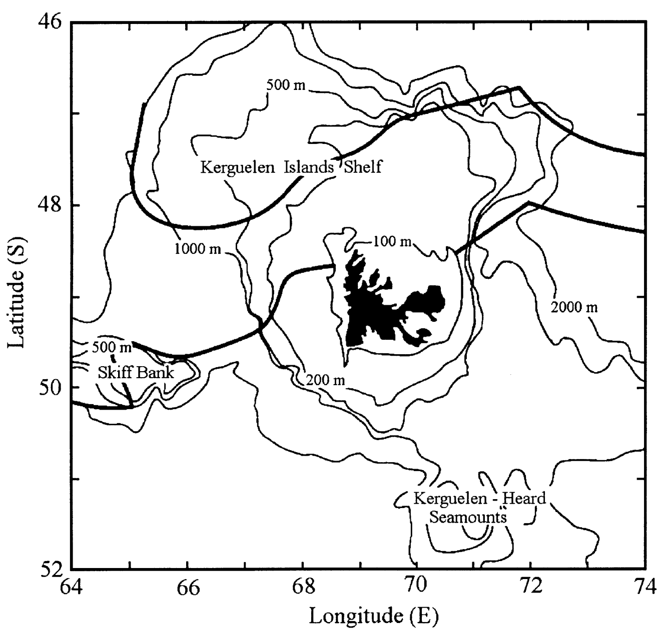

Fig. 1 Location of the Kerguelen Archipelago and the southern and northern limits of the Antarctic Polar Front, derived from joint French-Soviet oceanographic cruises in 1987 (Koubbi et al. 1991)

Materials and methods

Octopuses were collected from catches of a trawling fishery for Patagonian toothfish *Dissostichus eleginoides* in the upper slope (400–600 m) of the northern Kerguelen shelf, located between 47°00′ and 47°20′S, and 69°00′ and 69°20′E. They were immediately frozen aboard and kept at −20°C. Two groups of cephalopods were used: some were collected in February 1994, and the others in May/June 1995. In order to calculate allometric equations between body mass, body length, hood, and crest lengths of beaks (Y. Cherel, unpublished data), the first group was thawed once and refrozen before heavy metal analysis. Thus, due to possible metal diffusion during a thawing/freezing cycle (Martin and Flegal 1975), the distribution of heavy metals in various tissues was only measured in the latter group. The digestive gland, branchial hearts, gills, digestive tract, and genital tract were totally removed from the dissected individuals. In addition, pieces of mantle muscle and skin were sampled to determine metal concentrations. This implies that the remains of the animal were composed of arms, the rest of the mantle, muscle and skin. For all animals, stomach contents were removed before metal analysis. Our laboratory participates in European intercalibration exercises that allow us to quantify the internal analytical variability to about 12.5%.

For the nomenclature of the two octopus species commonly found in Kerguelen waters, i.e. *Benthoctopus thielei* and *Graneledone* sp. (a still undescribed species closely related to *G. antarctica*), we followed Nesis (1987). Seventeen individuals of each species were used: 11 females (mean wet wt = 123 ±89 g) and 6 males (mean wet wt = 121 ±75 g) of *Benthoctopus thielei* and 11 females (mean wet wt = 85 ±93 g) and 6 males (mean wet wt = 208 ± 98 g) of *Graneledone* sp. Each individual was weighted and measured (mantle length and total length).

Tissue samples (whole individual for 1994 samples and the different organs for 1995 samples) were dried for several days at 80°C to constant weight. Two aliquots of approximately 300 mg of each homogenized dry sample were digested with 4 ml 65% HNO_3 and 1 ml 70% $HClO_4$ for 24 h at 80°C. After evaporation, the residues were dissolved in nitric acid 0.3 N. Blanks were carried through the procedure in the same way as the sample. Cd, Cu and Zn were determined by flame atomic absorption spectrophotometry 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 material, Orchard-Leaves standard (NBS) and MA-A-2 fish-flesh standard (IAEA) were treated and analysed in the same way. The results for standards are shown in Table 1. All the results are given in micrograms of metal per gram of the dry weight tissue (μg/g dry wt). Detection limits were 0.05 μg/g for Cd, 2 μg/g for Cu and 3 μg/g for Zn. For each element, the mean ±standard deviation and the coefficient of variation are given. Distribution percentages of metals are given as percent of the total fresh weight of the individual.

Results

Our sampling included males and females and represented a large range of size and weight: between 14 and 279 g for *Benthoctopus thielei* and between 6 and 343 g for *Graneledone* sp. Metal concentrations (μg/g dry wt) in *Benthoctopus thielei* and *Graneledone* sp. from the Kerguelen Island waters are reported in Table 2. In both species, Cd, Cu and Zn were concentrated in similar amounts. Mean Cd concentrations were 39.1 ±5.3 μg/g in *Graneledone* sp. and 38.2 ± 7.6 μg/g in *Benthoctopus thielei*. Mean Cu concentrations were 68 ± 30 μg/g and 68 ± 29 μg/g and corresponding Zn concentrations 131 ± 19 μg/g in *Graneledone* sp. and 166 ± 39 μg/g in *Benthoctopus thielei*.

For both species, heavy metal concentrations were similar in small and large individuals. The analytical results for males and females were compared. An ANOVA test showed no significant differences among metal concentrations by sex ($P < 0.05$). For all elements, no correlations were found for *Graneledone* sp. while in *Benthoctopus thielei*, Cd and Zn were correlated positively ($P < 0.05$) and Cu and Zn were correlated nega-

Table 1 Concentrations (μg/g dry wt) of cadmium, copper and zinc in MA-A-2 fish flesh homogenate (mean ± standard deviation) and Orchard Leaves (mean ± 95% confidence interval)

Standards	Cd	Cu	Zn
Orchard Leaves			
Present study	0.13 ± 0.03	13 ± 1	25 ± 2
Certified value	0.11 ± 0.02	12 ± 1	25 ± 3
MA-A-2			
Present study	0.064 ± 0.001	4.0 ± 0.1	34 ± 2
Certified value	0.066 ± 0.004	4.0 ± 0.1	33 ± 1

Table 2 Metal concentrations (μg/g dry weight) in 17 whole *Benthoctopus thielei* and 17 whole *Graneledone* sp. caught in the Kerguelen shelf waters in February 1994 and May/June 1995. The standard deviation (*SD*) and coefficient of variation (*CV*) are given for each element

Species	Sample size (*n*)	Mantle length (mm)	Fresh weight (g)	Cd	Cu	Zn	Water content (%)
Graneledone sp.							
Males	6						
Mean		69	208	40.9	77	129	84
SD		10	97	4.2	46	10	1
CV (%)		14	47	10	59	8	1
Range		56–80	96–343	32.8–43.5	44–165	112–140	81–85
Females	11						
Mean		46	85	38.1	63	133	84
SD		19	93	5.8	17	22	1
CV (%)		42	110	15	28	17	1
Range		26–77	6–232	30.7–47.2	32–87	104–166	83–86
All specimens	17						
Mean		54	128	39.1	68	131	84
SD		20	110	5.3	30	19	1
CV (%)		36	86	14	44	14	1
Range		26–80	6–343	30.7–47.2	32–165	104–166	81–86
Benthoctopus thielei							
Males	6						
Mean		68	121	40.8	78	170	83
SD		18	75	9.3	36	26	2
CV (%)		26	62	23	46	16	2
Range		40–93	21–223	27.3–54.4	56–149	137–201	82–86
Females	11						
Mean		61	123	36.8	63	163	82
SD		21	89	6.5	26	45	4
CV (%)		34	72	18	41	28	5
Range		31–95	14–279	29.4–53.4	25–114	105–269	76–89
All specimens	17						
Mean		63	122	38.2	68	166	82
SD		20	82	7.6	29	39	3
CV (%)		31	67	20	43	23	4
Range		31–95	14–279	27.3–54.4	25–149	105–269	76–89

tively ($P < 0.05$). Figure 2 shows relationships between metal concentrations and mantle length by sex. Cu and Zn were correlated negatively with mantle length ($P < 0.05$) in females of *Graneledone* sp. and Cd and Zn were correlated negatively with mantle length ($P < 0.05$), in males and females of *Benthoctopus thielei*. The coefficients of variation (CV) were less than 25% for Cd and Zn, and near to 40% for Cu (Table 2).

The distribution of heavy metals in one individual of each species is reported in Table 3. Most of the Cd (91% and 89%, respectively in *Graneledone* sp. and *Benthoctopus thielei*) was accumulated in the digestive gland with concentrations as high as 369 and 245 μg/g in *Graneledone* sp. and *Benthoctopus thielei*, respectively. Zn concentration was higher in *Benthoctopus thielei* digestive gland (416 μg/g) and represented 53% of the total amount, whereas in *Graneledone* sp. it was close to the concentrations found in the other organs (102 μg/g), and represented only 16% of the total amount. In both species, the remains contained high percentages of Zn, with 67% for *Graneledone* sp. and 44% for *Benthoctopus thielei*.

Total Cu concentrations (165 μg/g for *Graneledone* sp. and 25 μg/g for *Benthoctopus thielei*), as well as distribution, were quite different between the two species. The digestive gland of *Graneledone* sp. had a high Cu concentration (1092 μg/g) and corresponded to the major site of Cu storage with 79% of the total body burden. In contrast, the digestive gland of *Benthoctopus thielei* contained only 25% of the total Cu body burden, having a very low concentration (42 μg/g).

Discussion

Metal levels

Despite the analysis of males and females over a large range of size and weight, the variability of the metal concentrations was relatively small. The most striking feature was the higher values for the coefficient of variation for Cu compared to that of Cd and Zn.

The homogeneity of metal concentrations found in the 34 individuals was particularly remarkable. We hypothesize that the concentrations measured in this study are a relatively good representation of the concentrations encountered in specimens subject to similar am-

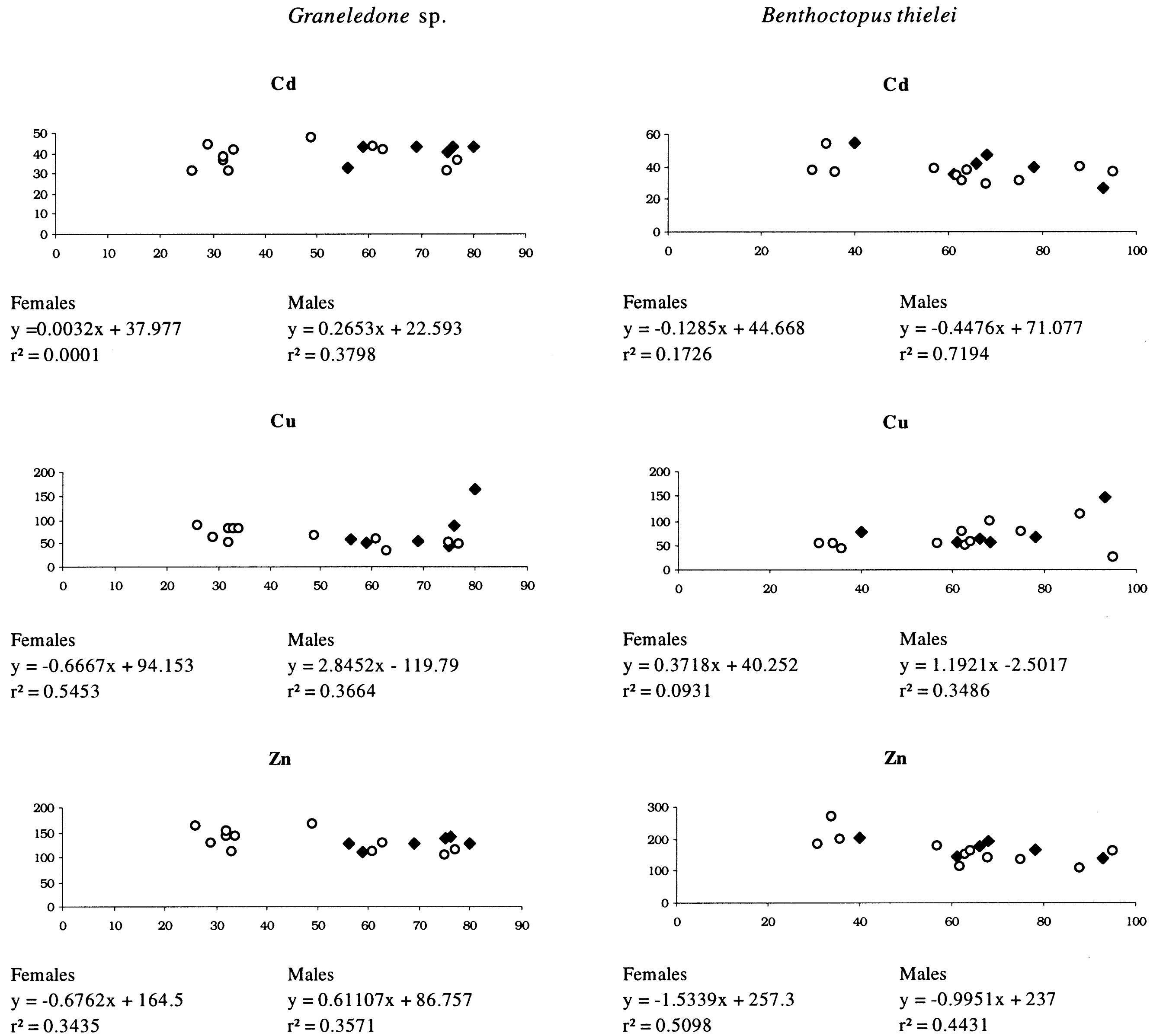

Fig. 2 Variations of metal concentrations (μg/g dry wt) in Kerguelen octopuses with mantle length (mm) by sex. ♦: males; ○: females

bient water composition and probably similar diets. Nevertheless, the coefficient of variation of Cu was particularly interesting. This coefficient was higher in both species sampled from the kerguelen waters than in other octopuses species: 27% in *Octopus vulgaris* (Miramand and Guary 1980) and 11% for *Eledone cirrhosa* (Miramand and Bentley 1992). Moreover, the Cu variability was higher than the Cd variability. This was surprising when one considers that Cu and Zn (unlike Cd) are essential elements, which implies that they are maintained at a fairly constant concentration. The high Cd concentration should disrupt Cu homeostasis. According to Zauke and Petri (1993), non-essential metals (e.g. Cd) may substitute for essential metals under deficient conditions. This may have occurred in Kerguelen octopuses: they showed a high Cd/Cu ratio (≈ 0.55) compared to Mediterranean octopus (≈ 0.005) or *Eledone cirrhosa* from the English Channel (≈ 0.04) (Miramand and Guary 1980; Miramand and Bentley 1992). In Kerguelen octopuses, this high ratio was due to elevated Cd concentrations but also to low Cu concentrations. Cu concentrations were lower than concentrations found in *Octopus vulgaris* or *Eledone cirrhosa* (Miramand and Guary 1980; Miramand and Bentley 1992). Martin and Flegal (1975) found similar ratios in the squids *Symplectoteuthis oualeniensis* and *Ommastrephes bartrami* from the Pacific Ocean. As in both Kerguelen octopuses, squids were highly contaminated with Cd. Cu in large amounts is known to be essential to marine molluscs. Generally in molluscs, Cd and Cu are known to bind to the same type of metalloproteins, e.g. metallothioneines, in the digestive gland. A competition

Table 3 Metal concentrations (μg/g dry wt) and percentage distribution (wet wt) in the organs of one male *Graneledone* sp. (fresh weight = 343 g) and one female *Benthoctopus thielei* (fresh weight = 279 g) caught in the Kerguelen shelf waters in May/June 1995. Skin and muscles are included in remainder

Organs	Cd	%	Cu	%	Zn	%	Water content (%)
Graneledone sp.							
Digestive gland	369	91.2	1092	79.9	102	15.8	68
Branchial hearts	24.6	0.11	465	0.61	126	0.35	84
Gills	22.6	0.52	530	3.59	98	1.41	84
Digestive tract	90.5	1.96	354	2.27	92	1.25	85
Genital tract	5.57	0.41	31	0.68	306	1.4	84
Remainder	6.64	5.76	50	12.9	121	67.0	86
Skin	1.94	–	67	–	121	–	90
Muscles	0.37	–	15	–	113	–	87
Whole individual	43.5	100	165	100	128	100	85
Benthoctopus thielei							
Digestive gland	215	88.6	42	24.8	416	52.6	69
Branchial hearts	31.5	0.15	306	3.46	172	0.26	85
Gills	49.1	0.89	168	7.07	147	0.82	84
Digestive tract	85.1	1.30	35	1.24	202	0.95	86
Genital tract	10.3	0.47	34	3.59	101	1.41	84
Remainder	7.06	8.54	22	59.8	118	43.9	85
Skin	0.81	–	18	–	95	–	90
Muscles	0.21	–	3	–	138	–	82
Whole individual	36.2	100	25	100	159	100	84

or a substitution between Cd and Cu may have occurred in Kerguelen octopuses.

In order to compare the concentration of trace elements with other cephalopod species, Table 4 shows Cd, Cu and Zn concentrations in the digestive gland and in whole individuals of cephalopods from European waters where industrial releases of pollutants occur. In both species from Kerguelen waters, Zn concentrations were in the same range as those found in other species (Table 4).

In contrast, Cd and Cu concentrations found in octopuses caught from Kerguelen waters were noteworthy. Cu concentrations were low except for one individual of *Graneledone* sp. (165 μg/g) and two individuals of *Benthoctopus thielei* (114 and 149 μg/g) (Tables 2, 4). Cd concentrations in both species were very high (Table 2). These concentrations in Kerguelen Islands octopuses were 1 order of magnitude greater than those found in other cephalopods (Table 4).

Such high Cd concentrations were unexpected for molluscs coming from a presumed unpolluted area far from any anthropogenic source of contaminants. Recently, Bargagli et al. (1996) measured Cd concentrations in various organisms caught in Terra Nova Bay (Antarctica). All organisms collected in this area showed relatively elevated Cd concentrations, but in most groups concentrations were lower than 10 μg/g dry wt or close to 15 μg/g dry wt. Only some samples of the sponge *Porifera* exhibited higher Cd concentrations (i.e. 10–80 μg/g dry wt). In Antarctic areas, such high Cd concentrations only occurred in the scallop *Adamussium colbecki* (Berkman and Nigro 1992), and in some zooplanktonic crustaceans, particularly the hyperiid amphipod *Themisto gaudichaudii*. These species accumulated Cd to levels similar or greater than Kerguelen octopuses (Hennig et al. 1985). Compared with Cd concentrations in other mollusc species, these concentrations were also remarkable. Thus, most of the mollusc species (bivalves and gastropods) caught in unpolluted areas contained Cd concentrations lower than 5 μg/g dry wt (Eisler 1981; Bryan 1984). Only some Pectinidae species, which are well known for their ability to accumulate Cd, exhibited concentrations nearer to those found in the Kerguelen octopuses (Bryan 1973; Berkman and Nigro 1992; Francesconi *et al*. 1993). For comparison, Cd concentrations similar to those found in whole Kerguelen octopuses (excluding Pectinidae) have only been encountered in filter-feeders caught in Cd-polluted areas (Boutier and Chiffoleau 1986).

The particularly large accumulation of Cd in octopuses from Kerguelen, an area without anthropogenic inputs of this metal, is difficult to explain. The Kerguelen Islands are located at the Antarctic Polar Frontal Zone (Fig. 1), and Cd enrichment in surface waters may be due to upwelling of deep nutrient-rich waters (Plancke 1977). Unfortunately, we lack measurements of dissolved Cd in Kerguelen seawater and this hypothesis cannot be tested. Nevertheless, metal analyses of the stomach contents of some Kerguelen octopuses showed elevated Cd concentrations, greater than 30 μg/g dry wt (unpublished data). This suggests elevated Cd concentrations in octopus prey, which could be an indicator of a Cd enrichment in Kerguelen waters or bottom fauna. In this context, food could be an important pathway of Cd uptake for Kerguelen Octopodidae. Octopuses eat many prey species, mainly crustaceans, molluscs and fishes (Boyle 1990; McQuaid 1994; Laidig et al. 1995), but it has been impossible to clearly determine the diets of Kerguelen octopuses from stomach contents, and no fish otoliths was found. The carnivorous diet of octo-

Table 4 Cd, Cu and Zn concentrations (μg/g dry wt) in digestive gland and in whole animals of European cephalopods and Kerguelen octopuses. Values are means ± standard deviation

Species	Sample size (n)	Fresh weight (g)	Digestive gland	Whole animal	Origin	Source
Cd						
Graneledone sp.	17	128 ± 110	369	39 ± 5	Southern Indian Ocean	Present study
Benthoctopus thielei	17	122 ± 82	215	38 ± 8	Southern Indian Ocean	Present study
Eledone cirrhosa	15	494 ± 108	24 ± 2	5 ± 1	English Channel	Miramand and Bentley (1992)
Octopus vulgaris	54	640	50 ± 10	1.2 ± 0.1	Mediterranean Sea	Miramand and Guary (1980)
Alloteuthis subulata	–	–	–	1.4	English Channel	Bryan (1976)
Sepia officinalis	15	518 ± 74	14 ± 1	1.34 ± 0.03	English Channel	Miramand and Bentley (1992)
Cu						
Graneledone sp.	17	128 ± 110	1092	68 ± 30	Southern Indian Ocean	Present study
Benthoctopus thielei	17	122 ± 82	42	68 ± 29	Southern Indian Ocean	Present study
Eledone cirrhosa	15	494 ± 108	456 ± 11	122 ± 11	English Channel	Miramand and Bentley (1992)
Octopus vulgaris	54	640	2500 ± 700	260 ± 70	Mediterranean Sea	Miramand and Guary (1980)
Alloteuthis subulata	–	–	–	146	English Channel	Bryan (1976)
Sepia officinalis	15	518 ± 74	315 ± 3	59 ± 1	English Channel	Miramand and Bentley (1992)
Zn						
Graneledone sp.	17	128 ± 110	102	131 ± 19	Southern Indian Ocean	Present study
Benthoctopus thielei	17	122 ± 82	416	166 ± 39	Southern Indian Ocean	Present study
Eledone cirrhosa	15	494 ± 108	646 ± 86	234 ± 20	English Channel	Miramand and Bentley (1992)
Octopus vulgaris	54	640	1450 ± 400	150 ± 50	Mediterranean Sea	Miramand and Guary (1980)
Alloteuthis subulata	–	–	–	83	English Channel	Bryan (1976)
Sepia officinalis	15	518 ± 74	571 ± 47	134 ± 6	English Channel	Miramand and Bentley (1992)

puses strengthen on the hypothesis of a low supply of Cd by the soluble phase, unlike filter-feeder species which filter important volumes to feed on micro-organisms. Moreover, the gills in cephalopods shown low Cd concentrations and have less than 1% of the total Cd body burden (Table 3, Miramand and Bentley 1992).

Distribution of metals and implication in detoxification process

The dissection of a single individual of *Graneledone* sp. and one individual of *Benthoctopus thielei* (Table 3) indicates that these Kerguelen octopuses exhibit a Cd distribution in tissue similar to that found in octopuses from the Mediterranean Sea (Miramand and Guary 1980), or the English Channel (Miramand and Bentley 1992), with about 90% of the metal contained in the digestive gland. The digestive glands of Kerguelen octopuses contained very high Cd concentrations (Table 3). In contrast, muscle concentrations of Cd are close to, or slightly greater than, those encountered in other octopus species (0.1–0.5 μg/g dry wt) (Miramand and Guary 1980; Miramand and Bentley 1992; Barghigiani et al. 1993). Thus, the high concentrations measured in whole Kerguelen octopuses were due to the high concentrations in the digestive gland.

The high Cd concentrations in the digestive gland were greater than those usually found in other cephalopods (Table 4). Only two species caught in the Pacific Ocean exhibited similar or higher concentrations: Martin and Flegal (1975) found 287 μg/g dry wt in the liver of *Ommastrephes bartrami* and 782 μg/g dry wt in the liver of *Symplectoteuthis oualaniensis*. High concentrations of Cd in the digestive gland of cephalopods suggested that most of the detoxification processes occurred in this organ. However, studies on these mechanisms are scarce and concern only two squid species. Tanaka et al. (1983) and Finger and Smith (1987) have shown an association of Cd with high molecular weight material in the digestive gland of the squids *Todarodes pacificus* and *Nototodarus gouldi*. Nevertheless the Cd detoxification processes in octopuses are not known and more studies are needed to clarify this mechanism. In this context, Kerguelen octopuses appear to be good species for future investigations.

Branchial hearts of octopuses, which have polyhedral cells containing granules with brown pigments (adenochromes) rich in iron (Fox and Updegraff 1943; Ghiretti-Magaldi et al. 1958; Nardi and Steinberg 1974; Schipp and Hevert 1978), are certainly also involved in storage and detoxification processes for some trace elements such as cobalt, copper, vanadium (Nakahara et al. 1979; Ueda et al. 1979; Miramand and Guary 1980) or transuranic elements (Guary et al. 1981; Miramand & Guary 1981; Guary and Fowler 1982). However, in European octopuses with relatively low Cd concentrations in whole tissues, branchial hearts (concentrations < 0.3 ± 0.1 μg/g) do not seem to be implicated in Cd detoxification processes (Miramand and Guary 1980; Miramand and Bentley 1992). In octopuses from Kerguelen, branchial hearts exhibited high Cd concentrations (Table 3). A possible hypothesis could be a threshold effect, that is, beyond a certain Cd concentration the digestive gland would not be sufficient for the entire detoxification process and branchial hearts would then be used.

The ink sac of cephalopods contains melanin, a macromolecule with the ability to act as a cation-exchange resin (Larsson and Tjalve 1978). It is known that tissues containing melanin pigments are often rich in some trace elements such as manganese, copper and zinc. The binding affinity of melanin towards certain metal ions has been investigated in some detail (Aime et al. 1989). The interaction is essentially electrostatic and its strength is therefore expected to be dependent on the charge to mass ratio of the metal ion. However, Sarzanini et al. (1992) found in *Sepia officinalis* that the ability to concentrate metals by melanin is significantly lower than that observed for melanin sampled from other marine organisms, such as bivalves (Simkiss et al. 1982). The ink could be an excretion pathway for Cd in many cephalopods but the lack of ink sac in Kerguelen octopuses exclude Cd excretion by this way.

Conclusions

Due to the very high concentrations of cadmium in both *Benthoctopus thielei* and *Graneledone* sp., these cephalopods probably play an important role in the process of Cd transfer to top vertebrate predators in this region. Cd is well known for its accumulation in the kidneys of vertebrates, where at high doses it causes renal diseases (Nicholson et al. 1983; Nogawa 1984; Lauwerys 1990). For human consumption, a "provisional tolerable weekly intake" of 400–500 μg Cd per person has been proposed by the World Health Organisation (Andersen et al. 1987). This is approximately 1 μg/kg body weight for most individuals or 55–70 μg/day. In Kerguelen, the daily consumption by marine predators of one small octopus (about 10 g wet weight) is sufficient to reach the equivalent of this dose. Thus, Kerguelen top predators which have cephalopods in their diets could achieve high levels of Cd in their tissues, as in the South Atlantic Ocean where cephalopod-eating albatrosses have high levels of cadmium in their kidneys and livers (Muirhead and Furness 1988). In this context, research on Cd levels in tissues of top marine vertebrates from Kerguelen Islands, with particular attention on the kidney, is of particular interest.

Acknowledgments We thank Pascal Robidou for collecting octopuses on the French trawler "Kerguelen de Trémarec" in February 1994, and Guy Duhamel for providing us with other specimens collected in May/June 1995. This work was supported financially by the Conseil Régional Poitou-Charentes, the Usine des Terres Rares de La Rochelle, Rhône-Poulenc, the Institut Français pour la Recherche et la Technologie Polaires and the Terres Australes et Antarctiques Françaises.

References

Adams NJ, Klages NT (1989) Temporal variation in the diet of the gentoo penguin *Pygoscelis papua* at sub-Antarctic Marion Island. Colon Waterbirds 12:30–36

Ahn IY, Lee SH, Kim KT, Shim JH, Kim DY (1996) Baseline heavy metal concentrations in the antarctic clam, *Laternula elliptica* in Maxwell Bay, King George Island, Antarctica. Mar Pollut Bull 32:592–598

Aime S, Botta M, Camurati I (1989) NMR studies of 1-dopa melanin-manganese (II) complex in water solution. J Inorg Biochem 35:1–9

Andersen A, Julshamn K, Ringdal O, Mørkøre J (1987) Trace elements intake in the Faroe Islands. II. Intake of mercury and other elements by consumption of pilot whales (*Globicephalus meleanus*). Sci Tot Environ 65:63–68

Bargagli R, Nelli L, Ancora S, Focardi S (1996) Elevated cadmium accumulation in marine organisms from Terra Nova Bay (Antarctica). Polar Biol 16:513–520

Barghigiani C, D'Ulivo A, Zamboni R, Lampugnani L (1993) Interaction between selenium and cadmium in *Eledone cirrhosa* of the Northern Tyrrhenian Sea. Mar Pollut Bull 26:212–216

Berkman PA, Nigro M (1992) Trace metal concentrations in scallops around Antarctica: extending the Mussel Watch Programme to the Southern Ocean. Mar Pollut Bull 24:322–323

Bost CA (1991) Variation spatio-temporelle des ressources marines et stratégies adaptatives des oiseaux côtiers: le cas du Manchot papou (*Pygoscelis papua*). Thesis, University of Paris

Boutier B, Chiffoleau JF (1986) La contamination par le cadmium en Gironde et son extension sur le plateau continental. IFREMER, Brest

Boyle PR (1990) Prey handling and salivary secretions in octopuses. In: Barnes M, Gibson RN (eds) Trophic relationships in the marine environment. Proceedings of the 24th European Marine Biology Symposium. Aberdeen University Press, Aberdeen, pp 541–552

Brown CR, Klages NTW (1987) Seasonal and annual variation in diets of macaroni (*Eudyptes chrysolophus*) and southern rockhopper (*E. chrysocome chrysocome*) penguins at sub-Antarctic Marion Island. J Zool Lond 212:7–28

Bryan GW (1973) The occurrence and seasonal variation of trace metals in the scallops *Pecten maximus* (L.) and *Chlamys opercularis* (L.). J Mar Biol Assoc UK 53:145–166

Bryan GW (1976) Heavy metal contamination in the sea. In: Johnston R (ed) Marine pollution, ch 3. Academic Press, London, pp 185–302

Bryan GW (1984) Pollution due to heavy metals and their compounds. In: Kinne O (ed) Marine ecology, vol 5 part 3. Wiley, Chichester, pp 1289–1431

Cherel Y, Klages NTW (1997) A review of the food of albatrosses. In: Robertson G, Gales R (eds) Albatrosses biology and conservation. Surrey Beatty, Chipping Norton, Australia, pp 113–136

Clarke MR (1985) Cephalopods in the diet of cetaceans and seals. Rapp Comm Int Mer Médit 29 :211–219

Clarke MR (1996) Cephalopods as prey. III. Cetaceans. Philos Trans R Soc Lond Ser B 351:1053–1065

Clarke MR, McLeod N (1982) Cephalopods remains in the stomachs of eight Weddell seals. Br Antarct Surv Bull 57:33–40

Croxall JP, Prince PA (1996) Cephalopods as prey. I. Seabirds. Philos Trans R Soc Lond Ser B 351:1023–1043

Eisler (1981) Trace metal concentrations in marine organisms. Pergamon Press, New York

Finger JM, Smith JD (1987) Molecular association of Cu, Zn, Cd and ^{210}Po in the digestive gland of the squid *Nototodarus gouldi*. Mar Biol 95:87–91

Fox DL, Updegraff DM (1943) Adenochrome a glandular pigment in the branchial hearts of the octopus. Arch Biochem 1:339–356

Francesconi KA, Moore EJ, Joll LM (1993) Cadmium in the saucer scallop, *Amussium balloti*, from western Australian waters: concentrations in adductor muscle and redistribution following frozen storage. Aust J Mar Freshwater Res 44:787–797

Ghiretti-Magaldi A, Giuditta A, Ghiretti F (1958) Pathways of terminal respiration in marine invertebrates. I. The respiratory system in cephalopods. J Cell Comp Physiol 52:389–429

Guary JC, Fowler SW (1982) Experimental studies on the biokinetics of plutonium and americium in the cephalopod *Octopus vulgaris*. Mar Ecol Prog Ser 7:327–335

Guary JC, Higgo JJW, Cherry RD, Heyraud M (1981) High concentrations of transuranic and natural radioactive elements in the branchial hearts of the cephalopods *Octopus vulgaris*. Mar Ecol Prog Ser 4:123–126

Hennig HFKO, Eagle GA, McQuaid CD, Rickett LH (1985) Metal concentrations in Antarctic zooplankton species. In: Siefried WR, Condy PR, Laws RM (eds) Antarctic nutrient cycles and food webs. Springer, Berlin Heidelberg New York, pp 656–661

Imber MJ (1991) Feeding ecology of Antarctic and sub-Antarctic Procellariiformes. Acta XX Congressus Internationalis Ornithologici. New zealand Ornithological Congress Trust Board, Wellington, pp 1402–1412

Koubbi P, Ibaez F, Duhamel G (1991) Environmental influences on spatio-temporal oceanic distribution of ichthyoplankton around the Kerguelen Islands (Southern Ocean). Mar Ecol Prog Ser 72:225–238

Laidig TE, Adams PB, Baxter CH, Butler JL (1995) Feeding on euphausiids by *Octopus rubescens*. Calif Fish Game 81:77–79

Larsson B, Tjalve H (1978) Studies on the melanin-affinity of metal ions. Acta Physiol Scand 104:479–484

Lauwerys RR (1990) Cadmium. In: Toxicologie industrielle et intoxication professionnelle. Masson, Paris, pp 136–149

Martin JH, Flegal AR (1975) High copper concentrations in squid livers in association with elevated levels of silver, cadmium, and zinc. Mar Biol 30:51–55

Mauri M, Orlando E, Nigro M, Regoli F (1990) Heavy metals in the Antarctic scallop *Adamussium colbecki*. Mar Ecol Prog Ser 67:27–33

McQuaid CD (1994) Feeding behaviour and selection of bivalve prey by *Octopus vulgaris* Cuvier. J Exp Mar Biol Ecol 177:187–202

Miramand P, Bentley D (1992) Concentration and distribution of heavy metals in tissues of two cephalopods, *Eledone cirrhosa* and *Sepia officinalis*, from the French coast of the English Channel. Mar Biol 114:407–414

Miramand P, Guary JC (1980) High concentrations of some heavy metals in tissues of the Mediterranean octopus. Bull Environ Contam Toxicol 24:783–788

Miramand P, Guary JC (1981) Association of americium-241 with adenochromes in the branchial hearts of the cephalopod *Octopus vulgaris*. Mar Ecol Prog Ser 4:127–129

Muirhead SJ, Furness RW (1988) Heavy metal concentrations in the tissues of seabirds from Gough Island, South Atlantic Ocean. Mar Pollut Bull 19:278–283

Nakahara M, Koyanagi T, Ueda T, Shimizu C (1979) Peculiar accumulation of cobalt-60 by the branchial hearts of octopus. Bull Jpn Soc Sci Fish 45:539

Nardi G, Steinberg H (1974) Isolation and distribution of adenochrome(s) in *Octopus vulgaris*. Comp Biochem Physiol 48 B:453–461

Nesis KN (1987) Cephalopods of the world. Squids, cuttlefishes, octopuses, and allies. TFH Publications, Neptune City

Nicholson JK, Kendall MD, Osborn D (1983) Cadmium and mercury nephrotoxicity. Nature 304:633–635

Nogawa K (1984) Cadmium. In: Nriagu JO (ed) Changing metal cycles and human health. Springer, Berlin Heidelberg New York, pp 275–284

Petri G, Zauke GP (1993) Trace metal in the crustaceans in the Antarctic Ocean. Ambio 22:529–536

Plancke J (1977) Phytoplankton biomass and productivity in the Subtropical Convergence area and shelves of the western Indian subantarctic islands. In: Llano GA (ed) Adaptations within antarctic ecosystems. Proceedings of the third SCAR Symposium on Antarctic Biology, Washington, DC, Aug 26–30, 1974. Smithsonian Institution, Washington, DC, pp 51–73

Renzoni A, Bacci E, Falciai L (1973) Mercury concentration in the water, sediments and fauna of an area of the Tyrrhenian coast. Revue Int Oceanogr Med 31–32:17–45

Rocca E (1969) Copper distribution in *Octopus vulgaris* Lam. hepatopancreas. Comp Biochem Physiol 28:67–82

Rodhouse PG, Nigmatullin ChM (1996) Role as consummers. Philos Trans R Soc Lond Ser B 351:1003–1022

Rodhouse PG, White MG (1995) Cephalopods occupy the ecological niche of epipelagic fish in the Antarctic Polar Front Zone. Biol Bull Woods Hole Mass 189:77–80

Rodhouse PG, Arnbom TR, Fedak MA, Yeatman J, Murray AWA (1992) Cephalopod prey of the southern elephant seal, *Mirounga leonina*. Can J Zool 70:1007–1015

Sarzanini C, Mentasti E, Abollino O, Fasano M, Aime S (1992) Metal content in *Sepia officinalis* melanin. Mar Chem 39:243–250

Schipp R, Hevert F (1978) Distribution of copper and iron in some central organs of *Sepia officinalis* (Cephalopoda). A comparative study by flamless atomic absorption and electron microscopy. Mar Biol 47:391–399

Simkiss K, Taylor M, Mason AZ (1982) Metal detoxification and bioaccumulation in molluscs. Mar Biol Lett 3:187–201

Smith JD, Plues L, Heyraud M, Cherry RD (1984) Concentrations of the elements Ag, Al, Ca, Cd, Cu, Fe, Mg, Pb and Zn, and the radionuclides ^{210}Pb and ^{210}Po in the digestive gland of the squid *Nototodarus gouldi*. Mar Environ Res 13:55–68

Tanaka T, Hayashi Y, Ishizawa M (1983) Subcellular distribution and binding of heavy metals in the untreated liver of the squid; comparison with data from the livers of cadmium and silver exposed rats. Experientia 39:746–748

Ueda T, Nakahara M, Ishii T, Suzuki Y, Suzuki H (1979) Amounts of trace elements in marine cephalopods. J Radiat Res 20:338–342

Zauke GP, Petri G (1993) Metal concentrations in Antarctic crustacean: the problem of background levels. In: Dallinger R, Rainbow PS (eds) Ecotoxicology of metals in invertebrates. Lewis, London, pp 73–101