# ORIGINAL PAPER



# Trace elements in invertebrates and fish from Kerguelen waters, southern Indian Ocean

Caio V. Z. Cipro<sup>1,2</sup> • Y. Cherel<sup>3</sup> • P. Bocher<sup>1</sup> • F. Caurant<sup>1</sup> • P. Miramand<sup>1</sup> • P. Bustamante<sup>1</sup>

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**Abstract** Given the lack of background data on essential and non-essential trace elements in invertebrates and fish known to be the predominant prey of marine mammals and seabirds breeding at the Kerguelen Islands, this study intends to provide these results of great influence for predators in higher trophic levels. To this end, plankton organisms (9 species/4 phyla), mollusks (2 bivalves and 2 squid species) and fishes (8 benthic and 10 pelagic species) from Kerguelen waters were analysed for cadmium (Cd), copper (Cu), mercury (Hg) and zinc (Zn). Individual concentrations of non-essential elements (particularly Cd) showed larger variation in comparison with essential ones likely due to their homeostasis. Thus Cd ranged over 4 orders of magnitude; however, Hg ranged only 1, without significant correlation to trophic level. Instead, ecological parameters (benthic/mesopelagic habitat and feeding ecology) showed a more important influence on the results. Concerning seashore organisms, bivalves collected inside the Gulf of Morbihan had higher Cd concentrations compared to those from the Kerguelen shelf, suggesting a local

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- ☐ Caio V. Z. Cipro caiovzc@usp.br
- Littoral Environnement et Sociétés (LIENSs), UMR 7266, CNRS-Université de La Rochelle, 2 rue Olympe de Gouges, 17042 La Rochelle Cedex 01, France
- <sup>2</sup> Laboratório de Química Orgânica Marinha, Instituto Oceanográfico, Universidade de São Paulo, São Paulo, SP 05508-120, Brazil
- Centre d'Etudes Biologiques de Chizé, UMR 7372, CNRS-Université de La Rochelle, BP 14, 79360 Villiers-en-Bois, France

source of Cd, such as runoff water from bird colonies. Comparison with the literature showed metal concentrations in invertebrates and fishes from Kerguelen Islands somewhat lower than those in the Antarctic area, with Hg prevailing in benthic species and Cd in pelagic ones. In contrast to Hg, Cd values of squids, jellyfish and the amphipod *Themisto gaudichaudii* were significantly higher than all other species. Finally, top predators foraging in this area that can be subject to potentially high Hg and Cd exposure through their diet at Kerguelen are reviewed.

 $\begin{tabular}{ll} \textbf{Keywords} & Plankton \cdot Myctophid \cdot Food web \cdot Metals \cdot \\ Trace & elements \cdot Kerguelen \end{tabular}$ 

### Introduction

The Southern Ocean constitutes a particular environment for marine biota where human inputs of metals are supposed to be very low. Several essential elements such as iron (Fe) or copper (Cu) are poorly concentrated and/or bioavailable in these waters and could therefore act as limiting factors for phytoplankton (e.g. Coale 1991). In higher trophic level organisms, low Cu and zinc (Zn) concentrations in regard to organisms from temperate regions have been found in crustaceans and mollusks (e.g. Rainbow 1989; Petri and Zauke 1993; Bustamante et al. 1998a, 2003), raising the question of how these organisms can cope with essential element-supposed deficiency. Several hypotheses have been suggested to answer this question such as a relatively higher efficiency of mechanisms of element uptake compared to similar organisms from non-deficient areas and/or the replacement of essential elements by non-essential ones in biochemical reactions or in enzymes. To date, such replacement has only



been evidenced for Zn substitution by Cd in carbonic anhydrase from marine diatoms (Lane and Morel 2000; Lane et al. 2005; Xu et al. 2008). In this context, the interactions between essential and non-essential elements in invertebrates and fish from the Southern Ocean appear poorly documented and, moreover, baseline values necessary for the study of such interactions are even scarcer, if not inexistent in the literature.

Despite the comparatively low inputs of non-essential elements, very high concentrations of Cd and Hg have been reported in several organisms from distinct trophic levels in Antarctic and subantarctic environments (Sanchez-Hernandez 2000; Bustamante et al. 2003; Dos Santos et al. 2006; Bargagli 2008). Population growth and industrial development in several countries of the Southern Hemisphere are changing the global pattern of persistent anthropogenic contaminants and new classes of chemicals have already been detected in the Southern Ocean (e.g. Bargagli 2008; von Waldow et al. 2010; Carravieri et al. 2014a). Very high concentrations of both Cd and Hg were also found in the tissues of top predators such as seabirds and marine mammals from the Southern Ocean (see the review of Sanchez-Hernandez 2000). These high trophic level vertebrates are mainly exposed to trace elements through their food (Muirhead and Furness 1988; Aguilar et al. 1999) and some specific prey highly contribute to the exposure to a given element. For example, cephalopod consumption is well known to provide elevated concentrations of Cd under a bioavailable form (Bustamante et al. 1998b, 2002) and mesopelagic fish contain high amounts of methyl-Hg (e.g. Monteiro et al. 1996; Chouvelon et al. 2012). However, there are only a few data on invertebrates and fish to provide background for explaining the high Cd and Hg concentrations in the top predators from the Southern Ocean. Therefore, it is of major concern to provide data about lower trophic level organisms they feed on to give a more comprehensive and evidence supported basis to their contamination pattern. In addition to that, age, trophic position, sex, size among other ecological parameters likely play a role in trace element concentrations in these prey organisms (e.g. Locarnini and Presley 1995; Dehn et al. 2006; McIntyre and Beauchamp 2007).

Situated near the Polar Front, the Kerguelen Islands are a particularly important area for breeding seabirds and for mammals (see Guinet et al. 1996). Specifically, this archipelago hosts a large and highly diverse avian assemblage (35 different breeding species according to Weimerskirch et al. 1989) and 13 species of marine mammals (3 mysticetes, 7 odontocetes and 3 pinnipeds; Borsa 1997). According to their reproduction strategies, many seabird species catch their prey in the highly productive waters around the Archipelago and feed on a few key species of marine organisms, including some

crustaceans (e.g. euphausiids, hyperiids, copepods), fish (e.g. myctophids, notothenioids) and cephalopods (e.g. oceanic squids) (Guinet et al. 1996; Bocher et al. 2001; Cherel and Hobson 2005; Cherel et al. 2010). Their exposure to contaminants and that of their offspring is therefore determined by the concentrations in these lower trophic level organisms consumed specifically in this area, at least during the breeding period.

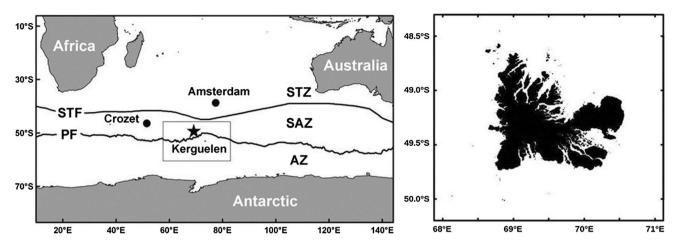
In this context, the present study was conducted to document selected trace element concentrations in zooplankton, mollusks and fishes around the Kerguelen Islands to provide understanding on the degree of metal contamination in low trophic level organisms being the prey of seabirds and marine mammals. To this end, Cd, Cu, Hg and Zn have been analysed in organisms belonging to different phyla of pelagic invertebrates and in 17 coastal and oceanic fish species to cover the main categories of prey species of the Kerguelen seabird community and of the marine mammals foraging in these waters. The non-essential elements Cd and Hg constitute the main metals of concern for wild vertebrates because of their known toxicity (Scheuhammer 1987; Tan et al. 2009; Tartu et al. 2013). In turn, Cu and Zn can be disturbed by the interaction of Cd and Hg on their regulation proteins such as the metallothioneins (e.g. Øverjordet et al. 2015). The levels of these trace elements were compared within the benthic and pelagic food webs and were globally compared with similar organisms from other marine ecosystems, when available. Finally, the significance of key species in contaminants transfer towards top predators was examined.

#### Materials and methods

### Sampling of organisms

Pelagic and benthic organisms were successively collected in the waters surrounding the Kerguelen Island Archipelago (Fig. 1) during the austral summers from 1997 to 1999. Information on these organisms are summarised in Table 1. In coastal waters, pelagic zooplankton mainly constituted by hyperiid amphipods (Themisto gaudichaudii) and copepods (Paraeuchaeta antarctica) was sampled inside the Morbihan Gulf in March 1997 with an ORI-net (2 m<sup>2</sup>, 1-mm mesh aperture). In this area, several benthic fish species (mostly Notothenidae) were also collected by net fishing overnight (Table 1). Outside the gulf, hyperiid amphipods (T. gaudichaudii), euphausiids (Euphausia vallentini, E. frigida and E. triacantha) and six myctophid species were collected in the eastern part of the peri-insular shelf in February 1998, using a International Young Gadoid Pelagic Trawl (IYGPT trawl; opening:  $12 \times 7$  m) with 10-mm mesh size in the cod-end. Other





**Fig. 1** Kerguelen location in the Southern Indian Ocean among the French Southern Lands (*left*) and detailed map (*right*). STZ, SAZ and AZ stand for, respectively, the subtropical, sub-Antarctic and

Antarctic zones, whereas STF and PF stand for the subtropical and polar fronts. Taken from Cipro et al. (2014)

pelagic materials (gelatinous plankton, planktonic crustaceans, squid and fish) were sampled during February 1999 on cruises of the RV "La Curieuse". Benthic fish were collected by bottom trawl used for commercial fishery in the Southern Kerguelen shelf. The samples of the copepod Thysanoessa sp. were obtained from stomach contents of the South Georgian diving petrel collected during investigations on the diet of this species (Bocher et al. 2003) and potential effects of partial digestion must be taken into account. Mussels were collected by hand on the shore during low tides in January 1999. Immediately after collection, the organisms were separated by species, then sex and size or age classes whenever possible (E. vallentini above and below 25 mm, and Champsocephalus gunnari adults and juveniles, respectively), and frozen in plastic bags or vials. Then, samples were stored at -20 °C until analysis. All organisms were analysed whole, except the mussels, which had their shells removed.

### Sample preparation and analysis

Length (mm) and mass (g) of fish and squids were thoroughly determined, as well as the sex, whenever possible (i.e. when size and maturity allowed so), and their gut content was removed. In the case of myctophids, otoliths were taken out to ensure identification of the species. Fish and squids were systematically treated individually, except *Harpagifer* sp. (12 individuals resulted in 4 samples). In contrast, all other invertebrates were pooled, except the jellyfish, which were treated individually. Pooling was primarily made because of analytical reasons, in order to gather enough mass to attend protocol specifications. Sample characteristics, i.e. family, species, length, weight and sex (for squid, fish and some crustacean species), are given in Table 1. Trophic level is assessed based on the

personal data of the co-authors, mostly based on stomach contents. Six of the seventeen fish species had also their trophic levels determined by stable isotope ratio of nitrogen published in other studies (Cherel et al. 2010). Since the difference between these two methods was lower than one trophic level, only the former will be further considered during data interpretation.

Samples were dried for two to three days at 50 °C to a constant weight and then homogenised. Next, two aliquots of approx. 100-300 mg each (according to availability) of homogenised dry sample were digested with 5 ml of 65% HNO<sub>3</sub> and 0.3 ml of 70% HClO<sub>4</sub> during 72 h at 80 °C. When the solution was clear, acids were evaporated and the obtained residues were dissolved in 10 ml 0.3 N nitric acid. Cd, Cu and Zn were analysed using a flame and graphite furnace atomic absorption spectrophotometer Varian 250 Plus with deuterium background correction. For Hg, aliquots ranging from 5 to 20 mg of dried material were analysed directly in an Advanced Mercury Analyser spectrophotometer (Altec AMA 254). Hg determination involved evaporation of Hg by progressive heating until 700 °C was reached and then held under oxygen atmosphere for 3 min, followed by an amalgamation on a goldnet. Afterwards, the net was heated to liberate the collected mercury, and subsequently measured by UV atomic absorption spectrophotometry.

Quality assurance was assessed using dogfish liver DOLT-2 (NRCC) and dogfish muscle DORM-2 (NRCC) as reference materials. Such standards were analysed and treated under the same conditions as the samples, with errors in regard to the certified values remaining below 5% in both cases. Detection limits were 0.004 for Cd, 0.5 for Cu, 0.005 for Hg, and 3  $\mu$ g g<sup>-1</sup> dry weight (dw) for Zn. All trace element concentrations in Kerguelen Islands marine organisms are reported in  $\mu$ gg<sup>-1</sup>dw unless stated otherwise.



Table 1 Sample characteristics together with water content in the whole organisms (for dry/wet wt metal concentrations conversion)

Class or family Species	Sample size (N)	Length (mm)	Fresh weight (*: g or *: mg)	Sex	Water content (%)	Collection zone	Functional group
Taxa							
Cnidarians							
Jellyfish	3	_	7-50#	_	$91 \pm 3$	Shelf waters	Filter-feeder
Ctenophora							
Beroe sp.	15 <sup>a</sup>	_	1.6-2.3#	_	$92 \pm 1$	Shelf waters	Filter-feeder
Crustaceans							
Euphausiacea							
Euphausia frigida	90 <sup>a</sup>	14–18	11-29*	_	$80 \pm 2$	Eastern Shelf waters	Herbivore
E. triacantha	15 <sup>a</sup>	27-36	137-410*	_	$70 \pm 3$	Eastern Shelf waters	Herbivore
E. vallentini (small)	32 <sup>a</sup>	16-24	19-88*	_	$61 \pm 3$	Eastern Shelf waters	Herbivore
E. vallentini (large)	60 <sup>a</sup>	25-30	24-96*	_	$73 \pm 3$	Eastern Shelf waters	Herbivore
Thysanoessa sp.	$60^{a}$	5-20	1-53*	_	$76 \pm 5$	Stomach content	Omnivore
Copepoda							
Paraeuchaeta antarctica	60 <sup>a</sup>	5–10	6–18*	\$	64 ± 2	Coastal waters (Morbihan)	Carnivore 1
Paraeuchaeta antarctica	125 <sup>a</sup>	3–5	4–8	3	69 ± 1	Coastal waters (Morbihan)	Carnivore 1
Amphipoda							
Themisto gaudichaudii	100 <sup>a</sup>	14-17	31-51*	_	$71 \pm 2$	Coastal waters (Morbihan)	Carnivore 1
Themisto gaudichaudii	32 <sup>a</sup>	17-27	54-224*	_	$71 \pm 1$	Eastern Shelf waters	Carnivore 1
Cephalopods							
Ommastrephidae							
Todarodes angolensis Onychoteuthidae	11	197–221	129–214#	6 ♂, 5 ♀	$77 \pm 3$	Shelf waters	Carnivore 1–2
Moroteuthis ingens	8	103-257	44-472#	4 ♂, 4 ♀	$79 \pm 1$	Shelf waters	Carnivore 1–3
Bivalvia				97 1			
Mytilidae							
Mytilus edulis desolationis	36 <sup>a</sup>	30–78	1.9–42#	-	$88 \pm 4$	Cap Noir, Port-aux-Français, Mayes, Foch	Filter-feeder
Aulacomya atra	27 <sup>a</sup>	38-97	4.8-65#	_	$80 \pm 4$		Filter-feeder
Tunicates							
Salpa thompsoni	9 <sup>a</sup>	33-42	3.1-5.4#	_	$95 \pm 0$	Shelf waters	Herbivore
Salpa thompsoni	12 <sup>a</sup>	33-44	3.1-5.9#	_	$94 \pm 2$	Shelf waters	Herbivore
Fishes							
Centrolophidae							
Icichthys australis	8	212-312	125-416#	5 ♂, 3 ♀	$74 \pm 13$	Shelf waters	Carnivore 1–2
Channichthyidae							
Channichthys rhinoceratus	13	257–420	212–563#	5 ♂, 8 ♀	$79 \pm 3$	Shelf waters (Morbihan)	Carnivore 2–3
Champsocephalus gunnari (adults)	10	299–328	164–232#	5 ♂, 5 ♀	$74 \pm 1$	Shelf waters	Carnivore 1–2
C. gunnari (juveniles)	10	122-154	127-154	ND	$74 \pm 1$	Shelf waters	Carnivore 1
Congiopodidae							
Zanclorhynchus spinifer	6	126–163	34–83#	3 ♂, 3 ♀	$70 \pm 3$	Southern Shelf waters	Carnivore 1–2
Gempylidae  Paradiplospinus	1	370	67#	₫	70	Oceanic waters	Carnivore 1–3
<i>gracilis</i> Harpagiferidae							



Table 1 continued

Class or family Species	Sample size (N)	Length (mm)	Fresh weight (*: g or *: mg)	Sex	Water content (%)	Collection zone	Functional group
Harpagifer sp.	12ª	54–75	3.8-9.1#	_	$72 \pm 4$	Shelf waters(Morbihan)	Carnivore 1–2
Myctophidae							
Electrona antarctica	15	48-78	1.3-4.4#	ND	$62 \pm 2$	Oceanic waters	Carnivore 1–2
Gymnoscopelus fraseri	15	65-82	2.5-5.5#	ND	$69 \pm 1$	Oceanic waters	Carnivore 1–2
G. nicholsi	4	129-164	22-42#	4 ♀	$61 \pm 6$	Oceanic waters	Carnivore 1–2
G. piabilis	14	114–162	17–44#	5 ♂, 9 ♀	$71 \pm 3$	Oceanic waters	Carnivore 1–2
Protomyctophum bolini	15	49-58	1.2-2.2#	ND	$66 \pm 2$	Oceanic waters	Carnivore 1
P. tenisoni	15	34-42	0.3-0.7#	ND	$73 \pm 2$	Oceanic waters	Carnivore 1
Notothenidae							
Gobionotothen acuta	1	177	82#	9	75	Coastal waters (Morbihan)	Carnivore 1–2
Lepidonotothen squamifrons	10	234–310	177–386#	5 ♂, 5 ♀	$74 \pm 2$	Shelf waters (Morbihan)	Carnivore 1–2
Notothenia cyanobrancha	1	195	160#	\$	77	Shelf waters (Morbihan)	Carnivore 1
N. rossii	13	137–288	57–450#	5 ♂, 7 ♀, 1 ND	$78 \pm 3$	Coastal waters (Morbihan)	Carnivore 2–3
Paranotothenia magellanica	6	147–168	74–119#	2 ♂, 4 ♀	78 ± 1	Shelf waters (Morbihan)	Carnivore 1–2
Stomidae							
Stomias sp.	14	102-178	1.1-4.7#	ND	$81 \pm 6$	Oceanic waters	Carnivore 3

<sup>&</sup>lt;sup>a</sup> Individuals in pooled samples

Water contents allowing recalculations of the metal concentrations from dw to wet weight (ww) are given in Table 1.

## Statistical analyses

Statistical analyses were performed in Microsoft Excel 2007 and Statsoft Statistica 11 and 12. Before analyses, data were checked for normality of distribution and homogeneity of variances using Shapiro–Wilk and Brown–Forsythe tests, respectively, followed by ANOVA and post hoc Tukey HSD. Spearman's or Pearson's correlations are used to assess the degree of monotonic or linear dependence, respectively, between two variables. A t-test was used to assess whether female and male datasets differed when available. All statistically significant results were set at  $\alpha=0.05$  and all presented correlations should be assumed significant unless stated otherwise.

# **Results**

Metal concentrations in invertebrates and fishes from the Kerguelen Island waters are presented in Table 2. Cu, Hg and Zn concentrations showed, in a general way, a lesser

degree of variability when compared to Cd. Indeed, Cu, Hg and Zn average concentrations vary one order of magnitude each, whereas Cd ranged over three orders of magnitude.

Regarding the influence of biological factors in the results, the only crustacean species for which gender comparison was possible was *Paraeuchaeta antarctica*. All four trace elements presented significant differences between males and females, these latter showing significantly higher Cd (p < 0.001), Cu (p = 0.004) and Zn (p = 0.015) levels than males. This difference can be attributed to their considerably higher length and weight (Table 1). Concerning Hg, significantly higher (p = 0.037) concentrations were found in males than in females.

In cephalopods, there were no differences on metal concentrations between males and females (for *Todarodes angolensis* Cd,  $p_{t\text{-test}} = 0.149$  and Hg,  $p_{t\text{-test}} = 0.867$ ; for *Moroteuthis ingens* Cd,  $p_{t\text{-test}} = 0.206$  and Hg,  $p_{t\text{-test}} = 0.923$ ); moreover, no correlation (neither Pearson's nor Spearman's) between biometrics and metal concentrations were found. In fish, metal concentrations showed no significant difference between the sexes nor correlation with the biometric parameters (total length and total weight) with a few exceptions concerning Cd and Hg. Cd



Table 2 Metal concentrations ( $\mu g\ g^{-1}\ dry\ wt$ ) of organisms from the Kerguelen Islands

Group		N	Cd		Cu		Hg		Zn	
Species	Family		Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Ctenophora										
Beroe sp.	Beroidae	$3^{a}$	$0.077 \pm 0.009$	0.070-0.088	$6.7 \pm 0.2$	6.4–6.9	$0.054 \pm 0.010$	0.045-0.065	$642 \pm 58$	582–697
Euphausids										
Euphausia frigida	Euphausiidae	4 e	$0.137 \pm 0.047$	0.109-0.207	$5.8 \pm 0.1$	5.7–5.8	$0.023 \pm 0.002$	0.021-0.025	$43 \pm 3$	41–43
E. triacantha	Euphausiidae	$3^{a}$	$0.289 \pm 0.025$	0.260-0.306	$14.9 \pm 6.7$	4.3–19.8	$0.036 \pm 0.006$	0.029 - 0.041	$55 \pm 2$	53–57
E. vallentini (small)	Euphausiidae	$3^{a}$	$0.500 \pm 0.217$	0.278-0.711	$17.8 \pm 2.1$	15.4–19.5	$0.042 \pm 0.003$	0.039-0.045	$58 \pm 9$	52-68
E. vallentini (large)	Euphausiidae	$3^{a}$	$0.659 \pm 0.093$	0.589-0.765	$30.0\pm1.0$	29.0-30.9	$0.017 \pm 0.001$	0.016-0.018	$39 \pm 3$	37–43
Thysanoessa sp.	Euphausiidae	8 <sub>a</sub>	$3.66 \pm 1.80$	1.38–6.26	$33.7 \pm 12.8$	12.8-45.4	$0.067 \pm 0.031$	0.024-0.125	$30 \pm 11$	10-47
Copepods										
Paraeuchaeta antarctica ( <table-cell-rows></table-cell-rows>	Euchaetidae	$3^{a}$	$2.11 \pm 0.05$	2.06-2.16	$8.8\pm1.1$	7.7–9.8	$0.038 \pm 0.019$	0.023-0.060	$245\pm66$	197–321
P. antarctica (3)	Euchaetidae	$3^{a}$	$0.81 \pm 0.05$	0.78-0.87	$4.9 \pm 0.4$	4.4–5.2	$0.072 \pm 0.002$	0.071-0.074	$87 \pm 9$	77–92
Amphipods										
Themisto oaudichaudii (coast)	Hyperridae	4 <sub>a</sub>	$28.5 \pm 7.4$	21.2–38.8	$12.5 \pm 0.7$	11.9–13.4	$0.026 \pm 0.005$	0.022-0.034	$52 \pm 3$	48–55
T. gaudichaudii (shelf)	Hvperridae	4a	$73.4 \pm 7.2$	70.4–81.7	$16.0 \pm 7.1$	11.8–24.2	$0.024 \pm 0.002$	0.023-0.027	$82 \pm 5$	80–88
Tunicates										
Salpa thompsoni	Salpidae	$3^{a}$	$0.624 \pm 0.066$	0.583-0.700	$19.9 \pm 5.5$	14.9–25.7	$0.033 \pm 0.003$	0.030-0.035	$969 \pm 142$	821-1104
Salpa thompsoni	Salpidae	$3^{a}$	$2.154 \pm 0.135$	2.066–2.310	$7.7 \pm 1.8$	5.6-9.0	$0.015 \pm 0.001$	0.013-0.016	$367 \pm 82$	302-458
Cnidarians										
Jellyfish	Not determined	3	$29.0 \pm 30.8$	9.98–64.53	$7.4 \pm 0.9$	6.8-9.4	$0.081 \pm 0.015$	0.067-0.097	$353 \pm 305$	142–703
Mollusks										
Moroteuthis ingens	Onychoteuthidae	∞	$29.6 \pm 20.0$	0.09-0.9	$39.4 \pm 14.2$	23.2–60.7	$0.099 \pm 0.063$	0.034-0.215	$66 \pm 20$	19–81
Todarodes angolensis	Ommastrephidae	11	$79.4 \pm 41.8$	17.5–172.3	$80.3 \pm 39.4$	50.2-194	$0.100 \pm 0.058$	0.057-0.270	$107 \pm 27$	59–158
Mytilus edulis desolationis	Mytilidae	$12^{\mathrm{a}}$	$6.50 \pm 5.83$	2.27–27.71	$6.2\pm1.9$	3.57-9.08	$0.273 \pm 0.187$	0.113-0.647	$83 \pm 25$	48.7–125
Aulacomya atra	Mytilidae	$9^{a}$	$9.11 \pm 4.79$	4.05–18.49	$8.5\pm2.1$	5.9–12.7	$0.208 \pm 0.116$	0.105-0.417	$135\pm39$	84.2–221
Benthic fish										
Channichthys rhinoceratus	Channichthyidae	13	$0.173 \pm 0.125$	0.022-0.484	$1.8\pm0.4$	1.3–2.7	$0.345 \pm 0.296$	0.058-0.870	$79 \pm 26$	50-128
Gobiotothen acuta	Notothenidae	_	I	0.063	I	2.9	ı	0.075	I	88
Harpagifer sp.	Harpagiferidae	4 <sub>a</sub>	$0.404 \pm 0.091$	0.330-0.536	$3.5\pm0.5$	3.0-3.9	$0.230 \pm 0.084$	0.128 - 0.334	$107 \pm 19$	80–123
Lepidonotothen squamifrons	Notothenidae	10	$0.475 \pm 0.198$	0.232-0.808	$1.5\pm0.4$	1.1–2.5	$0.150 \pm 0.089$	0.063-0.271	$43 \pm 9$	31–58
Notothenia cyanobrancha	Notothenidae	П	I	0.323	I	2.1	ı	0.216	1	49
N. rossii	Notothenidae	13	$0.134 \pm 0.043$	0.084-0.229	$3.0 \pm 1.0$	1.6-4.9	$0.145 \pm 0.053$	0.072-0.260	$47 \pm 9$	27–58
Paranotothenia magellanica	Notothenidae	9	$0.288 \pm 0.234$	0.095-0.650	$2.2 \pm 0.2$	1.9–2.6	$0.106 \pm 0.019$	0.075-0.126	57 ± 4	53-64
Zanclorhynchus spinifer	Congiopodidae	9	$0.781 \pm 0.320$	0.322-1.173	$1.8\pm0.2$	1.5-2.1	$0.067 \pm 0.013$	0.054-0.083	$40 \pm 6$	35–52
Pelagic fish										



17-20 20–35 15–31 SD+ $19 \pm 1$ 22 ± 27 ± 3 32 ± 4 H ++++28 56 Zn 54 0.059 - 0.1350.041-0.112 0.028 - 0.0490.046 - 0.1000.094 - 0.4240.096 - 0.2000.067-0.333 0.053 - 0.0980.026 - 0.041 $\pm 0.026$  $0.086 \pm 0.022$  $\pm 0.005$  $0.066 \pm 0.015$  $\pm 0.047$  $\pm 0.006$  $0.179 \pm 0.078$  $\pm 0.014$ 0.197 - 0.101+Mean 0.036 0.137 0.075 0.036 0.064 NA 1.4 - 2.91.6 - 2.92.4-4.8 0.6 - 1.5SD $2.4 \pm 0.8$  $2.1 \pm 0.5$  $3.2 \pm 0.6$  $2.2 \pm 0.7$  $2.3 \pm 0.3$  $1.2 \pm 0.2$  $2.7 \pm 0.4$  $3.6 \pm 0.5$ 1.5 +Mean Cn 0.105 - 0.3410.289-0.744 0.355-1.176 0.132-0.506 0.256-0.929 0.180 - 0.3920.453 - 1.8260.143-2.320 0.164 0.112 0.454 0.101 0.233  $\pm 0.755$  $0.188 \pm 0.063$  $\pm 0.267$ SD + $0.270 \pm$ + $\mathbb{H}$  $^{\rm H}$ +++0.887 0.903 Mean 0.556 0.496 0.251 1.168  $\mathcal{C}^{\mathsf{g}}$ 5 4 4 15  $\geq$ Channichthyidae **Channichthyidae** Centrolophidae Myctophidae Myctophidae Myctophidae Myctophidae Myctophidae Myctophidae Gempylidae Stomidae Champsocephalus gunnari Paradiplospinus gracilis Protomyctophum bolini Gymnoscopelus fraseri C. gunnari (juveniles) Electrona antarctica Icichthys australis Fable 2 continued Stomias sp. G. nicholsi G. piabilis P. tenisoni Species

correlated significantly with total length in L. squamifrons (r = 0.723, p = 0.018) and with both length and weight in G. fraseri (r = 0.704, p = 0.005 and 0.862, p < 0.001,respectively). Interestingly, a significant negative correlation of Cd with both biometric parameters was found for juvenile C. gunnari (r = -0.702, p = 0.023 and -0.636,p = 0.048) and Protomyctophum tenisoni (r = -0.549, p = 0.034 and -0.627, p = 0.012). In turn, Hg correlated (Spearman's rank) significantly with total length in Gymnoscopelus piabilis (r = 0.591, p = 0.033) and Lepidonotothen squamifrons (r = 0.670, p = 0.034), with weight in *Protomyctophum bolini* (r = 0.697, p = 0.004) and with both length and weight (shown respectively) in Channichthys rhinoceratus (r = 0.843, p = 0.02 and r = 0.802, p = 0.07), G. fraseri (r = 0.771, p = 0.001 for both), Notothenia rossii (r = 0.554, p = 0.049) and r = 0.577, p = 0.038) and Zanclorhynchus spinifer (r = 0.959, p = 0.002 and r = 0.965, p = 0.002). Finally, in regard to between-element relationships, Cd and Hg levels correlated with one another significantly in Champsocephalus gunnari (total, r = 0.947, p < 0.001) and G. fraseri (r = 0.843, p < 0.001).

Concerning Bivalves, two mussel species (the blue mussel, Mytilus edulis desolationis and the Magellan mussel, Aulacomya atra) sampled in four different locations (Foch, Cap Noir, Port-aux-Français and Mayes Island) were analysed in the present study. A significant negative correlation (Spearman's rank) between Cd and Cu (r = -0.725, p = 0.039) was found in the blue mussel, and also in the Magellan mussel (r = -0.798, p = 0.004). This latter species presented yet significant correlations between Cu and total weight (r = -0.682, p = 0.042), Cd and total weight (r = 0.673, p = 0.048) and Cd and Hg (r = -0.702, p = 0.034). When all samples (both species) are considered together, there is a significant correlation between Cd and total weight (r = 0.547, p = 0.007) and also a significant negative correlation between Cd and Cu (r = -0.537, p = 0.009).

# Discussion

Pooled samples

The main objective of this study was to provide baseline levels in a wide range of phyla which constitute the prey for high trophic level organisms such as large fish, seabirds and marine mammals. The species collected in the present study represent a wide range of ecological groups from the pelagic/benthic and neritic/oceanic communities from the Kerguelen Island waters. The size of the collected organisms falls within the range of the size preyed by top predators from this area and, more specifically, from the large seabird community that includes 35 species (Weimerskirch et al. 1989).



# Influence of biological factors on metal concentrations

Among factors influencing metal concentrations, sex differences were found for the crustacean Paraeuchaeta antarctica. Higher concentrations of Cd, Cu and Zn in female P. antarctica might be due to the fact that metals are highly retained by copepods and Cd, Cu and Zn bioaccumulation with the size is likely to have played a major role in this difference, not necessarily via diet, but also possibly via the dissolved phase, in a passive way (Wang et al. 1996; Wang and Fisher 1998) or else via a possible remobilisation due to sexual maturation, as further discussed. In contrast to Cd, Cu and Zn, higher Hg concentrations in males is likely due to the fact that the sampled females could have already reached sexual maturity size and have excreted Hg in the laid eggs. Indeed, maternal transfer may act as a major pathway for Hg(II) and methyl-Hg elimination in crustaceans (Tsui and Wang 2004). The size of the specimens analysed here ranged from 5 to 10 mm, whereas this species presents CV (last copepodite stage) at  $6.5 \pm 0.3$  mm and CVI (adults) at  $8.7 \pm 0.4$  mm (Bocher et al. 2002); therefore, the sample set likely contained sexually mature individuals.

In cephalopods, the lack of difference in Cd and Hg concentrations between males and females is surprising considering the sexual dimorphism in both species, females reaching larger sizes than males in both squid species. Indeed, sexual dimorphism and ontogenic effects can influence in metal concentrations in cephalopods (e.g. Pierce et al. 2008; Chouvelon et al. 2011). The absence of variation of metal concentrations in both cephalopod species is likely due to the limited number of specimens of each sex and limited size range for both *T. angolensis* and

M. ingens. Nevertheless, metal concentrations found in both squid species were among the highest for all the species from the present study, especially for Cd. Cephalopods are considered as superbioaccumulators of many trace elements and their capacity to bioaccumulate remarkable Cd levels was already shown in several environments (Martin and Flegal 1975; Miramand and Guary 1980; Miramand and Bentley 1992; Dorneles et al. 2007; Penicaud et al. 2017), including Kerguelen waters (Bustamante et al. 1998b). Even though the specific proteins involved in Cd bioaccumulation are not fully known, its significant correlation (Spearman's rank) with Zn (r = 0.902) in T. angolensis (the highest Cd level) would suggest the involvement of MTLP in Cd detoxification even such proteins seem not to be the main detoxification pathway in cephalopods (Bustamante et al. 2002; Penicaud et al. 2017). For Hg as well, cephalopods were among the most contaminated species. Within this group, Hg is mainly under the highly bioavailable organic form (Bustamante et al. 2006) and therefore they represent a significant source of this element for their predators.

In fish, the significant negative correlation of Cd with both biometric parameters (size and weight) for *C. gunnari* and *P. tenisoni* could be due to a higher Cd exposure in earlier life stages (due to diet, habitat or maternal transfer), with a growth dilution effect taking place and concentrations decreasing thereafter. Benthic organisms present, in a general way, overall lower Cd values when compared to pelagic ones (Fig. 2), and this is in accordance with previous studies describing *C. gunnari* as benthopelagic, but with a shift from the pelagic to the benthic environment as the fish grow (Kock 2005a, b). Concerning Hg, the correlations found between this element and biometrics are likely related to the bioaccumulation of Hg as the fish

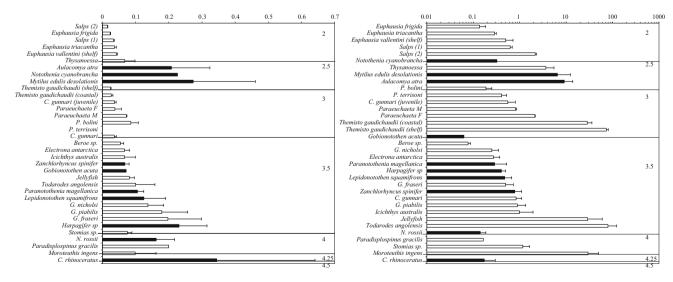


Fig. 2 Hg (*left* linear scale) and Cd (*right* log scale) concentrations ( $\mu g g^{-1} dw$ ) stratified by trophic level. Benthic species in black, pelagic ones in white



grow. Moreover, benthic species presented mostly higher Hg levels than pelagic ones (Fig. 2). In sediments, organic carbon and microbial activity play an important role on Hg bioavailability as microorganisms highly contribute to the methylation of inorganic Hg (Andersson et al. 1990), enhancing the exposure of benthic species to Hg. In regard to Cd and Hg positive significant correlations with size and weight in C. gunnari and G. fraseri, it would mean that these species are simultaneously exposed to sources of both contaminants. This could be due to the consumption (1) of one specific prey that presents high concentrations of Cd and Hg or (2) of several prey that present conversely high concentrations of Cd or Hg. The second hypothesis seem more likely in regard to C. gunnari, since its diet in a subantarctic environment (South Georgia Archipelago) comprised a large proportion of Antarctic krill Euphausia superba, knowing that Euphausids had comparatively high Hg levels (See Table 2) and, more importantly, the hyperiid amphipod T. gaudichaudii (with very high Cd levels) as the most frequent prey (Kock et al. 1994). In regard to G. fraseri, it feeds mainly on copepods and, to a lesser extent, on the Euphausid *Thysanoessa* spp. (Saunders et al. 2015), both presenting high Cd and Hg concentrations (Table 2). Therefore, it seems reasonable to state that the first one of the previous hypotheses would be more likely in this case.

The influence of the trophic position on metal concentrations is examined in Fig. 2, which presents the concentrations of Cd and Hg stratified by trophic level. In this regard, stable isotope ratios of nitrogen bring slightly superior data for trophic levels (TLs) of six fish species included in the present study (Cherel et al. 2010), all of them inferior to one trophic level: 0.9 TL for *Protomyctophum bolini*, 0.7 TL for *Gymnoscopelus nicholsi*, 0.5 TL for *P. tenisoni*, 0.3 TL for *Electrona antarctica* and *G. fraseri* and finally 0.2 TL for *G. piabilis*. The difference between these TLs obtained by different methods was negligible and did not change the stratification of concentrations along the TLs.

Cd concentrations ranged over 4 orders of magnitude, i.e. from  $0.063~\mu g~g^{-1}$  in *Gobionotothen acuta* to  $79.4~\mu g~g^{-1}$  in *T. angolensis* across the different trophic levels, interestingly, a relatively similar pattern to the one reported for an Arctic marine food web (Macdonald and Sprague 1988). Moreover, a large intraspecific variation is shown by different taxa as well, such as in salps and specially crustaceans (Table 2). However, no significant correlation between Cd concentrations and the trophic level of the species was found in our sampling, suggesting that Cd is not biomagnified within our sampling set. However, it is important to remark that the increase in trophic level within our sample set does not always infer a direct food—consumer link between the sampled organisms, so

biomagnification *strictu sensu* must be regarded with caution. Moreover, samples were taken in different years and interannual and local differences are possible as well. Also, the transfer of Cd appears to be more related to the species rather than to the trophic level itself, as previously shown in other environments (Miramand et al. 1999; Pigeot et al. 2006). This specificity is likely related to Cd bioaccumulation capacities which are particularly elevated for some taxa such as the hyperiid amphipods *Themisto* sp. (e.g. Ritterhoff and Zauke 1997) and cephalopods (e.g. Bustamante et al. 1998a, 2002; Dorneles et al. 2007, Penicaud et al. 2017), or particularly weak as in most marine fish species (Wang 2002; Kojadinovic et al. 2007).

The lack of biomagnification is apparently repeated for Hg in our set of samples, contrary to what is previously reported for local avifauna (Blévin et al. 2013; Carravieri et al. 2014b). It is important to remark that Hg biomagnification concerns its main organic form, i.e. methyl-Hg, due to its high bioavailability (e.g. Kannan et al. 1998), whereas our analyses were made only for total Hg. A much higher assimilation efficiency is displayed for methyl-Hg than for inorganic Hg and a slight variation in this property may determine whether or not some of the element is biomagnified (Reinfelder et al. 1998). Yet, the proportion of methyl-Hg is poorly documented for low trophic level prey in the Southern Ocean. This issue clearly deserves further research in this ecologically important and representative oceanographic area.

# Sessile organisms as indicators of possible secondary metal sources

In mussels, the positive correlation between Cd and weight and the negative correlation between Cd and Cu suggest that as they grow, the homeostatically controlled Cu is proportionally surpassed by the bioaccumulative Cd in their organisms, likely bound to metallothioneins (Klaassen et al. 1999). Indeed, mussels produce Cd-induced metallothioneins (Mackay et al. 1993) and Cd can displace essential metals such as Cu and Zn normally associated to these proteins (Amiard et al. 2006). Tukey post-hoc tests resulted in separated groups for Cd (raw data for average lot length and mass and trace element concentrations are available as Online Resource 1): one group containing samples from Foch, Cap Noir and Port-aux-Français; and the second one, from Port-aux-Français and Mayes (always in crescent order). This result suggests some local Cd source enrichment inside the Gulf of Morbihan, where Port-aux-Français, the largest human settlement in the area (between 45 in austral winter and 120 people in austral summer) and Mayes are both located. Conversely, both other locations (Foch and Cap Noir) are exposed to the open ocean, in the northern shore. This is apparently

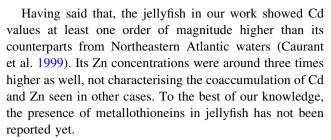


contrary to the T. gaudichaudii data (Table 2), which presented levels for continental shelf samples three times higher than coastal ones. However, the average individual weight of these amphipods from the continental shelf samples was around three times the one from coastal samples, and therefore there is likely an influence from age and, thus, from bioaccumulation. A strong effect of age is confirmed by a previous study on the closely related species T. libellula from the Greenland Sea (Ritterhoff and Zauke 1997). Nevertheless, a growth dilution effect should be expected for the continental shelf samples, which leaves two hypotheses: whether exposure is increased for larger individuals, or the influence of local Cd sources within the Gulf of Morbihan is not as important to T. gaudichaudii as it is for mussels. Since the literature presents related species (T. japonica and probably T. gaudichaudii as well) switching from herbivory to carnivory during their life cycles (Pakhomov and Perissinotto 1996), the first hypothesis remains more likely, corroborating the existence of a local Cd secondary source.

Using fish for comparison did not prove to be helpful, since the only two species collected inside the Gulf were benthic (N. rossii and P. magellanica) and there was an evident bias in Cd levels towards pelagic species, as stated above, possibly because of Cd-enriched upwelled waters around the archipelago (Bustamante et al. 1998b, 2003). For coastal sites inside the Morbihan Bay, another source can be suspected. Indeed, Mayes provides diverse and highly suitable breeding sites for large colonies of burrowing petrels, which breed there in very high densities (Weimerskirch et al. 1989), with up to 6 burrows per square metre (Mougeot et al. 1998). Seabird faeces can alter the trace metal composition in soils (Headley 1996) and, therefore, colonies might work as secondary trace metal sources (see Choy et al. 2010; Espejo et al. 2014). Water percolating bird colonies has already been shown to have an important role in the exposure of terrestrial flora to contaminants in Antarctic lands (Cipro et al. 2011). It is therefore plausible to assume an analogous effect for the mussels when this water reaches the sea. Nevertheless, this subject deserves further investigation.

# Comparison with similar ecosystems in other regions

Table 3 presents a comparison of the obtained results with those from the literature despite the scarcity of data for equivalent organisms in similar environments, which reinforces the need for studies such as this one. Therefore, taxonomic, geographic and ecological differences might present some bias that has to be taken into account when interpreting the data.



For Ctenophora, our results are somewhat closer to the ones for the North Atlantic Ocean than the ones for the Mediterranean, suggesting an influence from local conditions. Tunicates presented results for Cd and Cu in a reasonable agreement with the ones from the literature.

Crustaceans, in turn, showed some differences: in a general way, *Euphausia* spp. values of Cd, Cu and Zn are lower than those in organisms from Antarctica and *Thysanoessa* spp. values for Cd were higher than those in organisms from the Bering Sea, closer to pollution sources than Kerguelen Islands (Zauke et al. 2003). So, the difference might be due to a species-specific reason or in a lesser extent, to the influence of water masses dynamics.

As for mollusks, bivalves presented lower values when compared to Antarctic filter feeders, even if the previously discussed influence of a local source is considered (Ahn et al. 1996; Bargagli 2001). Cephalopods, on the other hand, presented similar Hg levels when compared to another subantarctic environment, Macquarie Island (McArthur et al. 2003) or slightly superior when compared to branchial hearts concentrations from samples collected off Amsterdam Islands (Kojadinovic et al. 2011), which is located north of the Polar Front. Care must be taken when comparing digestive gland data (Kojadinovic et al. 2011) to muscle or even whole organism data, since this organ might present higher concentrations, even if it does not greatly contribute to the total Hg burden in some oceanic squids (Bustamante et al. 2006).

For benthic fish species, Antarctic organisms (Table 3) presented levels for both Cd and Hg one order of magnitude higher than in the present study. For pelagic ones, the only truly pelagic neritic fish present in all sizes throughout the water column is *Pleuragramma antarctica* (Wöhrmann et al. 1997). For this species, Brasso et al. (2014) present Hg data averaging  $0.014 \mu g g^{-1}$  for juveniles and  $0.021 \mu g^{-1}$  for adults (for whole fish, after conversion to dry weight). This is an apparent contradiction to the trend previously discussed (Antarctic organisms with higher levels than subantarctic ones); however, this species feeds on a lower trophic level than the ones in Table 3 and also lives in shallower shelf waters (Giraldo et al. 2011; Pinkerton et al. 2013), which makes it less exposed to these contaminants. Nevertheless, Goutte et al. (2015) present an average of 0.065  $\mu g g^{-1}$  for P. antarcticum collected in



Table 3 Comparison of heavy metal concentrations in organisms from the Kerguelen Islands with those from the literature (range or mean  $\pm$  SD, in  $\mu g g^{-1} dw$ )

Taxa Cnidarians Ilnidantified iallyfish						
ped jellvfich						
	Southern Indian Ocean	$29.0 \pm 30.8$	$7.4 \pm 0.9$	$0.081 \pm 0.015$	$353 \pm 305$	Present study
Pelagia noctiluca Med	Mediterranean Sea	0.4	2.0	ı	46	Romeo et al. (1987)
Velella velella	Mediterranean Sea	$1.2\pm0.5$	$5.7 \pm 0.7$	I	$118 \pm 34$	Romeo et al. (1987)
Velella velella	Mediterranean Sea	$2.7 \pm 0.9$	$9.3\pm1.9$	I	$100\pm18$	Romeo et al. (1987)
Sagartia troglodytes Sein	Seine estuary, France	0.06	5.8	1	238	Miramand et al. (2001)
Ctenophora						
Beroe sp. Sour	Southern Indian Ocean	$0.077 \pm 0.009$	$6.7 \pm 0.2$	$0.054 \pm 0.010$	$642 \pm 58$	Present study
Beroe ovate Med	Mediterranean Sea	$1.4\pm0.4$	$2.8\pm0.8$	1	$29 \pm 9$	Romeo et al. (1992)
Beroe ovate Nor	North Atlantic	0.16	2.0	ı	52	Dubé (1982)
Tunicates						
Salpa thompsoni Sout	Southern Indian Ocean	$0.624 \pm 0.066$	$19.9 \pm 5.5$	$0.033 \pm 0.003$	$969 \pm 142$	Present study
Salpa thompsoni Sout	Southern Indian Ocean	$2.154 \pm 0.135$	$7.7 \pm 1.8$	$0.015 \pm 0.001$	$367 \pm 82$	Present study
S. maxima Med	Mediterranean Sea	$0.4 \pm 0.4$	$5.9 \pm 2.4$	1	$79 \pm 20$	Romeo et al. (1992)
S. fusiformis Med	Mediterranean Sea	$1.1\pm1.0$	$6.6\pm4.9$	ı	$64 \pm 28$	Romeo et al. (1992)
Euphausiacea						
Euphausia frigida Sout	Southern Indian Ocean	0.109-0.207	5.7-5.8	0.021-0.025	41–43	Present study
E. triacantha Sout	Southern Indian Ocean	0.260-0.306	4.3–19.8	0.029-0.041	53–57	Present study
E. triacantha Sout	Southern Ocean	0.6	31	1	402	Hennig et al. (1985)
E. superba	Western Antarctic Peninsula	0.13-0.75	37.8-140	0.0131-0.0489	35.2–51.3	Locarnini and Presley (1995)
E. vallentini Sou	Southern Indian Ocean	0.278-0. 765	15.4–30.9	0.016-0.045	37–68	Present study
Thysanoessa longipes Beri	Bering Sea	0.36-1.14	I	ı	88-69	Hamanaka and Tsujita (1981)
Thysanoessa sp. Sour	Southern Indian Ocean	1.38-6.26	12.8–45.4	0.024-0.125	10-47	Present study
Copepoda						
Paraeuchaeta antarctica Sout	Southern Indian Ocean	0.78-2.16	4.4–9.8	0.023-0.074	77–321	Present study
Calanus hyperboreus Baff	Baffin Bay, Canadian Arctic	$1.62 \pm 0.79$	$1.55 \pm 0.57$	$0.025 \pm 0.017$	$17.73 \pm 0.65$	Campbell et al. (2005)
Several species Fran	Fram strait, Arctic	0.32-0.75	4.0–7.5	0.31-0.68	79–351	Ritterhoff and Zauke (1997)
Gre	Greenland Sea	0.12-0.69	3.8–5.9	0.2-0.5	86–389	
Pooled (Eurytemora affinis, Acartia Sein clausi and Temora longicomis)	Seine estuary, high salinity	$0.9 \pm 0.4$	$15 \pm 6$	I	$260 \pm 68$	Miramand et al. (1998)
Sein	Seine estuary, low salinity	$5.5 \pm 2.1$	$47 \pm 27$	I	$480\pm190$	
Several species Wec	Weddel Sea, Antarctica	2.3–14.4	1	1	I	Kahle and Zauke (2003)
Amphipoda						
Themisto gaudichaudii Sour	Southern Indian Ocean	21.2–81.7	11.8–24.2	0.022-0.034	48–88	Present study
Themisto gaudichaudii Aro	Around 60°S170°E (Polar Front)	$118\pm81$	$34 \pm 26$	ı	$529 \pm 238$	Hennig et al. (1985)



Table 3 continued

Themisto gaudichaudii ~45/55°S 170°E (N of the Themisto gaudichaudii Antarctica Themisto compressa Northeastern Atlantic Euphausia superba Antarctica Paramoera walkeri Terra Nova Bay, Antarctica Bivalvia Adamussium colbecki (digestive gland) Terra Nova Bay, Antarctica Mytilus edulis desolationis Southern Indian Ocean Aulacomya atra Cephalopods Moroteuthis ingens Southern Indian Ocean Moroteuthis ingens Southern Indian Ocean Anderodes angolensis Southern Indian Ocean	~45/55°S 170°E (N of the Front) Antarctica Northeastern Atlantic Antarctica ferra Nova Bay, Antarctica ferra Nova Bay, Antarctica Maxwell Bay, Antarctica Southern Indian Ocean Southern Indian Ocean	29 ± 23 10.8-117 35.5-108 0.15-1.5 5.1-10.9 55.7 ± 27 11.5 ± 4.1 6.50 ± 5.83 9.11 ± 4.79 	38 ± 24 11.2-79.3 18.6-66.7 30.0-85.5 - 38.1 ± 5.0 6.23 ± 1.95 8.49 ± 2.08 39 ± 14 - 80 ± 39 179 ± 87.5		587 ± 560 44.6-82.6 58.5-109 42.0-74.8 - 153 ± 39 83 ± 25 135 ± 39 66 ± 20	Hennig et al. (1985) Rainbow (1989) Hennig et al. (1985) Hennig et al. (1985) Bargagli et al. (1996) Bargagli et al. (1996) Present study Present study McArthur et al. (2003) Present study McArthur et al. (2003) Present study
isto gaudichaudii isto compressa nusia superba noera walkeri ussium colbecki (digestive gland) nula elliptica (digestive gland) ts edulis desolationis omya atra oods teuthis ingens reuthis ingens	Atlantic  1y, Antarctica  1y, Antarctica  Antarctica  n Ocean  n Ocean	10.8–117 35.5–108 0.15–1.5 5.1–10.9 55.7 ± 27 11.5 ± 4.1 6.50 ± 5.83 9.11 ± 4.79 	11.2-79.3 18.6-66.7 30.0-85.5 - 38.1 ± 5.0 6.23 ± 1.95 8.49 ± 2.08 39 ± 14 - - - 80 ± 39 179 ± 87.5		$44.6-82.6$ $58.5-109$ $42.0-74.8$ $153 \pm 39$ $83 \pm 25$ $135 \pm 39$ $66 \pm 20$	Rainbow (1989) Hennig et al. (1985) Hennig et al. (1985) Bargagli et al. (1996) Bargagli (2001) Ahn et al. (1996) Present study Present study Present study McArthur et al. (2003) Present study Koiadinovic et al. (2011)
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a atra is ingens is ingens i angolensis	n Ocean n Ocean	$9.11 \pm 4.79$ $29.6 \pm 20.0$ $ 70.4 \pm 41.8$	$8.49 \pm 2.08$ $39 \pm 14$ - $80 \pm 39$ $179 \pm 87.5$	$0.208 \pm 0.116$ $0.099 \pm 0.063$ $0.086 \pm 0.017$ $0.100 \pm 0.058$ $0.42 \pm 0.17$	$135 \pm 39$ 66 ± 20	Present study Present study McArthur et al. (2003) Present study Koiadinovic et al. (2011)
is ingens is ingens : angolensis	n Ocean	$29.6 \pm 20.0$ - 70.4 + 41.8	$39 \pm 14$ - $80 \pm 39$ $179 \pm 87.5$	$0.099 \pm 0.063$ $0.086 \pm 0.017$ $0.100 \pm 0.058$ $0.42 \pm 0.17$	66 ± 20 -	Present study McArthur et al. (2003) Present study Koiadinovic et al. (2011)
sis	n Ocean	$29.6 \pm 20.0$ - 70.4 + 41.8	$39 \pm 14$ - $80 \pm 39$ $179 \pm 87.5$	$0.099 \pm 0.063$ $0.086 \pm 0.017$ $0.100 \pm 0.058$ $0.42 \pm 0.17$	66 ± 20 -	Present study McArthur et al. (2003) Present study Koiadinovic et al. (2011)
sis	7	- 70.4 + 41.8	$-80 \pm 39$ $179 \pm 87.5$	$0.086 \pm 0.017$ $0.100 \pm 0.058$ $0.42 \pm 0.17$	1	McArthur et al. (2003) Present study Koiadinovic et al. (2011)
	ınd	70.4 + 41.8	$80 \pm 39$ 179 ± 87.5	$0.100 \pm 0.058$ $0.42 \pm 0.17$		Present study Koiadinovic et al. (2011)
	n Ocean	7.4 T 41.0	$179 \pm 87.5$	$0.42 \pm 0.17$	$107 \pm 27$	Koiadinovic et al. (2011)
Todarodes fillipovae (branchial heart) Southern Indian Ocean	n Ocean	$34.3 \pm 19.7$			$65.6 \pm 15.0$	() are an are arrest
Todarodes fillipovae (digestive gland) Southern Indian Ocean	n Ocean	$246 \pm 187$	$218 \pm 196$	$0.14 \pm 0.06$	$94.3 \pm 66.1$	Kojadinovic et al. (2011)
Benthic fish						
Notothenia rossii Southern Indian Ocean	n Ocean	$0.134 \pm 0.043$	$3.0\pm1.0$	$0.145 \pm 0.053$	$47 \pm 9$	Present study
N. coriiceps (body) Livingston Island, Antarctica	and, Antarctica	$0.28 \pm 0.02$	$1.64 \pm 1.78$	1	$93.05\pm2.15$	Beltcheva et al. (2011)
N. coriiceps (muscle) Adelie Land, Antarctica	Antarctica	I	I	$0.221 \pm 0.085$	I	Goutte et al. (2015)
N. coriiceps (liver) Adelie Land, Antarctica	Antarctica	$9.032 \pm 3.215$	$11.8 \pm 4.1$	ı	$119 \pm 17$	Goutte et al. (2015)
Notothenia spp. Admiralty Bay, Antarctica	', Antarctica	I	I	0.0163	64.6	dos Santos et al. (2006)
Trematomus newnesi Admiralty Bay, Antarctica	', Antarctica	ı	I	0.016	99.1	dos Santos et al. (2006)
Trematomus newnesi (kidney) Terra Nova Bay, Antarctica	1y, Antarctica	$1.86 \pm 0.89$	I	1	ı	Bargagli et al. (1996)
T. bernachii McMurdo Sound, Antarctica	nd, Antarctica	1	I	$0.0539 \pm 0.0321$	I	Wintle et al. (2015)
Pelagic fish						
Electrona antarctica Southern Indian Ocean	n Ocean	$0.270 \pm 0.101$	$2.1\pm0.5$	$0.066 \pm 0.015$	$22 \pm 3$	Present study
Dissostichus eleginoides Scotia Sea, Antarctica	ıtarctica	0.003	0.17	0.005	I	Stoeppler and Brandt (1979)
Dissostichus eleginoides South Georgia		ı	I	$0.23 \pm 0.01$	I	Guynn and Peterson (2008)
Dissostichus eleginoides Prince Edwards Islands	s Islands	ı	I	$0.8 \pm 0.07$	I	Guynn and Peterson (2008)
Dissostichus eleginoides Chilean ZEE around 40°S	round 40°S	1	I	$0.73 \pm 0.10$	I	Guynn and Peterson (2008)
Dissostichus eleginoides Macquarie Island	pun	ı	I	$0.33 \pm 0.12$	I	McArthur et al. (2003)
Dissostichus eleginoides Southern Ocean	Southern Ocean (Pacific sector)	ı	I	0.43 (0.15-0.97)	I	Hanchet et al. (2012)
Dissostichus mawsoni Southern Ocean	Southern Ocean (Pacific sector)	1	I	0.16 (0.02–0.70)	I	Hanchet et al. (2012)
Antimora rostrata Southern Ocean	Southern Ocean (Pacific sector)	I	I	0.19 (0.04-0.68)	I	Hanchet et al. (2012)



Hanchet et al. (2012) Brasso et al. (2014) Brasso et al. (2014) Goutte et al. (2015) Zn 0.38 (0.01-1.10)  $0.065 \pm 0.009$  $0.021 \pm 0.009$  $0.014 \pm 0.004$ Cn g Southern Ocean (Pacific sector) Ross Sea shelf, Antarctica Ross Sea shelf, Antarctica Adélie Land, Antarctica Location Pleuragramma antarcticum antarcticum (juvenile) P. antarcticum (adult) Macrourus whitsoni Fable 3 continued Species

Adélie Land, Antarctica, much similar to the concentration we found for *E. antarctica*.

Taking all the previous information into account, Kerguelen marine invertebrates and fish seemed to present lower metal concentrations when compared to other sub-Antarctic and especially to Antarctic environments, with the exception of some particular species, notably *T. gaudichaudii* (see also Stoeppler and Nürnberg 1979; Hennig et al. 1985; Rainbow 1989; Kahle and Zauke 2003; McArthur et al. 2003; Guynn and Peterson 2008; Beltcheva et al. 2011 and the comparison in Table 3).

# Implications concerning the transfer to predators

Because all of the species investigated here constitute to a wide extent, primary or secondary prey for seabirds breeding on the Kerguelen Islands, it is important to provide information on their exposure to trace elements. This is especially important for the non-essential Cd and Hg which can have toxic effects at different levels on wild vertebrates (e.g. Gallien et al. 2001; Tan et al. 2009; Goutte et al. 2014; Tartu et al. 2013). In addition to linking prey and predator, this section is intended to highlight the fact that some of the accumulation/magnification occur not only in high trophic levels.

In regard to Cd, the main homogenous group after Tukey HSD was composed by all species but T. gaudichaudii, jellyfish and both the cephalopods. T. gaudichaudii is an important part of local macrozooplankton and the main prey for local planktivorous seabirds (Bocher et al. 2001), therefore their main Cd source (Bocher et al. 2003). Jellyfish showed a Cd concentration one to two orders of magnitude higher than the fish, similar to the findings of Caurant et al. (1999). Jellyfish could therefore represent a vector for Cd transfer, since their energetic value is likely very low (Caurant et al. 1999) so their predators should ingest a large amount of them to satisfy their energetic needs. Cephalopods, in turn, may also function as vectors for Cd transfer to top predators (e.g. Bustamante et al. 1998a; Lahaye et al. 2005). This role is even more evident at higher latitudes as they showed somewhat higher Cd concentrations in Antarctic and subantarctic areas when compared to temperate and tropical waters (e.g. Dorneles et al. 2007; Pierce et al. 2008; Kojadinovic et al. 2011). Since cephalopods are present in the diet of several predators from Kerguelen Islands such as albatrosses or elephant seals (Guinet et al. 1996; Cherel et al. 2000, 2004; Lescroël et al. 2004), their role as Cd vectors is evident. Reported concentrations in the kidney of seabirds from other subantarctic areas such as Gough Island in the South Atlantic Ocean clearly highlighted that seabirds feeding on squids displayed higher



concentrations that crustacean- and fish-feeder species (Muirhead and Furness 1988).

Hg, as previously presented, had a much less speciesspecific distribution, with less interspecific variation when compared to Cd, even though some stratification within the trophic levels could be detected. No statistical difference was found among all invertebrates taken together (Tukey HSD) and, concerning the fish, only Notothenia rossii, Gymnoscopelus piabilis, G. fraseri and C. rhinoceratus (in crescent Hg concentration) departed from a homogenous group that contained all the other species. The unicorn icefish C. rhinoceratus presented elevated Hg concentrations, which is consistent with its feeding ecology (Kock 2005a, b): indeed, the diet of juveniles is composed by crustaceans and then adults shift to forage on various notothenioids (mostly benthic) and mesopelagic fish in a lesser extent. In turn, mesopelagic fish, notably the myctophids, are among the most Hg contaminated. Therefore, predators relying on benthic or benthopelagic prey, as the gentoo penguin *Pygoscelis papua* (Lescroël and Bost 2005) or mesopelagic fish, such as elephant seals Mirounga leonina (Cherel et al. 2008) and the white-chinned petrel Procellaria aequinoctialis (Delord et al. 2010), would be highly exposed to Hg.

The present study highlights that not only top predators will be exposed to elevated amounts of Cd and Hg through their diet when consuming specific types of prey, but also lower trophic level organisms can be subject to the same effect. Zooplankton-eating predators are exposed to Cd especially if they consume the amphipod T. gaudichaudii (i.e. Halobaena caerulea, Pachyptila desolata, P. belcheri, Pelecanoides georgicus and P. urinatrix, according to Bocher et al. 2003). Cephalopod-eating species as the wandering albatross (Diomedea exulans) and the greatwinged petrel (Pterodroma macroptera) are also highly exposed to Cd but also to Hg which is consistent with the concentrations recorded in their internal tissues and their feathers (Muirhead and Furness 1988; Stewart et al. 1999; Anderson et al. 2009; Bustamante et al. 2016; Tavares et al. 2013) and also with blood (Anderson et al. 2010; Carravieri et al. 2014a). Finally, fish eating species, as the grey (Procellaria cinerea) or the white-chinned petrel (Procellaria aequinoctialis) are highly exposed (see Stewart et al. 1999; Anderson et al. 2009; Cipro et al. 2014) to Hg through the consumption of mesopelagic and benthic fish (Delord et al. 2010).

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#### References

- Aguilar A, Borrell A, Pastor T (1999) Biological factors affecting variability of persistent pollutant levels in cetaceans. J Cetacean Res Manag 1:83–116
- Ahn I-Y, Lee SH, Kim KT, Shim JH, Kim D-Y (1996) Baseline heavy metal concentrations in the Antarctic clam, Laternula elliptica in Maxwell Bay, King George Island, Antarctica. Mar Pollut Bull 32:592–598. doi:10.1016/0025-326X(95)00247-K
- Amiard J-C, Amiard-Triquet C, Barka S, Pellerin J, Rainbow PS (2006) Metallothioneins in aquatic invertebrates: their role in metal detoxification and their use as biomarkers. Aquat Toxicol 76:160–202. doi:10.1016/j.aquatox.2005.08.015
- Anderson ORJ, Phillips RA, Mcdonald RA, Shore RF, Mcgill RAR, Bearhop S (2009) Influence of trophic position and foraging range on mercury levels within a seabird community. Mar Ecol Prog Ser 375:277–288. doi:10.3354/meps07784
- Anderson ORJ, Phillips RA, Shore RF, McGill RAR, McDonald RA, Bearhop S (2010) Element patterns in albatrosses and petrels: influence of trophic position, foraging range, and prey type. Environ Pollut 158:98–107. doi:10.1016/j.envpol.2009.07.040
- Andersson I, Parkman H, Jernelöv A (1990) The role of sediments as sink or source for environmental contaminants—a case study of mercury and chlorinated organic compounds. Limnol Jena 20:347–359
- Bargagli R (2001) Trace metals in Antarctic organisms and the development of circumpolar biomonitoring networks. Rev Env Contam Toxicol 171:53–110
- Bargagli R (2008) Environmental contamination in Antarctic ecosystems. Sci Total Environ 400:212–226. doi:10.1016/j.scitotenv. 2008.06.062
- 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. doi:10.1007/BF02329071
- Beltcheva M, Metcheva R, Peneva V, Marinova M, Yankov Y, Chikova V (2011) Heavy metals in Antarctic notothenioid fish from South Bay, Livingston Island, South Shetlands (Antarctica). Biol Trace Elem Res 141:150–158. doi:10.1007/s12011-010-8739-5
- Blévin P, Carravieri A, Jaeger A, Chastel O, Bustamante P, Cherel Y (2013) Wide Range of Mercury Contamination in Chicks of Southern Ocean Seabirds. PLoS ONE 8:e54508. doi:10.1371/journal.pone.0054508
- Bocher P, Cherel Y, Labat J, Mayzaud P, Razouls S, Jouventin P (2001) Amphipod-based food web: *Themisto gaudichaudii* caught in nets and by seabirds in Kerguelen waters, southern Indian Ocean. Mar Ecol Prog Ser 223:261–276. doi:10.3354/meps223261
- Bocher P, Cherel Y, Alonzo F, Razouls S, Labat JP, Mayzaud P, Jouventin P (2002) Importance of the large copepod Paraeuchaeta antarctica (Giesbrecht, 1902) in coastal waters and the diet of seabirds at Kerguelen, Southern Ocean. J Plankton Res 24:1317–1333. doi:10.1093/plankt/24.12.1317



- Bocher P, Caurant F, Miramand P, Cherel Y, Bustamante P (2003) Influence of the diet on the bioaccumulation of heavy metals in zooplankton-eating petrels at Kerguelen archipelago, Southern Indian Ocean. Polar Biol 26:759–767. doi:10.1007/s00300-003-0552-6
- Borsa P (1997) Seasonal trends in the occurrence of marine mammals in the golfe du Morbihan, Kerguelen Islands. Mar Mammal Sci 13:314–316. doi:10.1111/j.1748-7692.1997.tb00635.x
- Brasso R, Lang J, Jones C, Polito M (2014) Ontogenetic niche expansion influences mercury exposure in the Antarctic silverfish Pleuragramma antarcticum. Mar Ecol Prog Ser 504:253–263. doi:10.3354/meps10738
- Bustamante P, Caurant F, Fowler SW, Miramand P (1998a)
  Cephalopods as a vector for the transfer of cadmium to top
  marine predators in the north-east Atlantic Ocean. Sci Total
  Environ 220:71–80
- Bustamante P, Cherel Y, Caurant F, Miramand P (1998b) Cadmium, copper and zinc in octopuses from Kerguelen Islands, Southern Indian Ocean. Polar Biol 19:264–271. doi:10.1007/ s003000050244
- Bustamante P, Cosson RP, Gallien I, Caurant F, Miramand P (2002) Cadmium detoxification processes in the digestive gland of cephalopods in relation to accumulated cadmium concentrations. Mar Environ Res 53:227–241
- Bustamante P, Bocher P, Cherel Y, Miramand P, Caurant F (2003)
  Distribution of trace elements in the tissues of benthic and pelagic fish from the Kerguelen Islands. Sci Total Environ 313:25–39. doi:10.1016/S0048-9697(03)00265-1
- Bustamante P, Lahaye V, Durnez C, Churlaud C, Caurant F (2006)
  Total and organic Hg concentrations in cephalopods from the
  North Eastern Atlantic waters: influence of geographical origin
  and feeding ecology. Sci Total Environ 368:585–596. doi:10.
  1016/j.scitotenv.2006.01.038
- Bustamante P, Carravieri A, Goutte A, Barbraud C, Delord K, Chastel O, Weimerskirch H, Cherel Y (2016) High feather mercury concentrations in the wandering albatross are related to sex, breeding status and trophic ecology with no demographic consequences. Environ Res 144:1–10. doi:10.1016/j.envres. 2015.10.024
- Campbell LM, Norstrom RJ, Hobson KA, Muir DCG, Backus S, Fisk AT (2005) Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). Sci Total Environ 351–352:247–263. doi:10.1016/j.scitotenv.2005.02.043
- Carravieri A, Bustamante P, Tartu S, Meillère A, Labadie P, Budzinski H, Peluhet L, Barbraud C, Weimerskirch H, Chastel O, Cherel Y (2014a) Wandering albatrosses document latitudinal variations in the transfer of persistent organic pollutants and mercury to southern ocean predators. Environ Sci Technol 48:14746–14755. doi:10.1021/es504601m
- Carravieri A, Cherel Y, Blévin P, Brault-Fravrou M, Chastel O, Bustamante P (2014b) Mercury exposure in a large subantarctic avian community. Environ Pollut 190C:51–57. doi:10.1016/j. envpol.2014.03.017
- Caurant F, Bustamante P, Bordes M, Miramand P (1999) Bioaccumulation of cadmium, copper and zinc in some tissues of three species of marine turtles stranded along the French Atlantic Coasts. Mar Pollut Bull 38:1085–1091. doi:10.1016/S0025-326X(99)00109-5
- Cherel Y, Hobson KA (2005) Stable isotopes, beaks and predators: a new tool to study the trophic ecology of cephalopods, including giant and colossal squids. Proc Biol Sci 272:1601–1607. doi:10.1098/rspb.2005.3115
- Cherel Y, Weimerskirch H, Trouvé C (2000) Food and feeding ecology of the neritic-slope forager black-browed albatross and its relationships with commercial fisheries in Kerguelen waters.

  Mar Ecol Prog Ser 207:183–199. doi:10.3354/meps207183

- Cherel Y, Duhamel G, Gasco N (2004) Cephalopod fauna of subantarctic islands: new information from predators. Mar Ecol Prog Ser 266:143–156. doi:10.3354/meps266143
- Cherel Y, Ducatez S, Fontaine C, Richard P, Guinet C (2008) Stable isotopes reveal the trophic position and mesopelagic fish diet of female southern elephant seals breeding on the Kerguelen Islands. Mar Ecol Prog Ser 370:239–247. doi:10.3354/ meps07673
- Cherel Y, Fontaine C, Richard P, Labat J-P (2010) Isotopic niches and trophic levels of myctophid fishes and their predators in the Southern Ocean. Limnol Oceanogr 55:324–332. doi:10.4319/lo. 2010.55.1.0324
- Chouvelon T, Spitz J, Cherel Y, Caurant F, Sirmel R, Mèndez-Fernandez P, Bustamante P (2011) Inter-specific and ontogenic differences in  $\delta 13C$  and  $\delta 15N$  values and Hg and Cd concentrations in cephalopods. Mar Ecol Prog Ser 433:107–120. doi:10. 3354/meps09159
- Chouvelon T, Spitz J, Caurant F, Mèndez-Fernandez P, Autier J, Lassus-Débat A, Chappuis A, Bustamante P (2012) Enhanced bioaccumulation of mercury in deep-sea fauna from the Bay of Biscay (north-east Atlantic) in relation to trophic positions identified by analysis of carbon and nitrogen stable isotopes. Deep Sea Res I 65:113–124. doi:10.1016/j.dsr.2012.02.010
- Choy ES, Gauthier M, Mallory ML, Smol JP, Douglas MSV, Lean D, Blais JM (2010) An isotopic investigation of mercury accumulation in terrestrial food webs adjacent to an Arctic seabird colony. Sci Total Environ 408:1858–1867. doi:10.1016/j.scito tenv.2010.01.014
- Cipro CVZ, Yogui GT, Bustamante P, Taniguchi S, Sericano JL, Montone RC (2011) Organic pollutants and their correlation with stable isotopes in vegetation from King George Island, Antarctica. Chemosphere 85:393–398. doi:10.1016/j.chemosphere. 2011.07.047
- Cipro CVZ, Cherel Y, Caurant F, Miramand P, Méndez-Fernandez P, Bustamante P (2014) Trace elements in tissues of white-chinned petrels (*Procellaria aequinoctialis*) from Kerguelen waters, Southern Indian Ocean. Polar Biol 37:763–771. doi:10.1007/ s00300-014-1476-z
- Coale KH (1991) Effects of iron, manganese, copper, and zinc enrichments on productivity and biomass in the subarctic Pacific. Limnol Oceanogr 36:1851–1864. doi:10.4319/lo.1991.36.8.1851
- Dehn L-A, Follmann EH, Thomas DL, Sheffield GG, Rosa C, Duffy LK, O'Hara TM (2006) Trophic relationships in an Arctic food web and implications for trace metal transfer. Sci Total Environ 362:103–123. doi:10.1016/j.scitotenv.2005.11.012
- Delord K, Cotté C, Péron C, Marteau C Pruvost P, Gasco N, Duhamel G, Cherel Y, Weimerskirch H (2010) At-sea distribution and diet of an endangered top predator: relationship between white-chinned petrels and commercial longline fisheries. Endanger Species Res 13:1–16. doi:10.3354/esr00309
- Dorneles PR, Lailson-Brito J, Dos Santos RA, da Costa PAS, Malm O, Azevedo AF, Torres JPM (2007) Cephalopods and cetaceans as indicators of offshore bioavailability of cadmium off Central South Brazil Bight. Environ Pollut 148:352–359. doi:10.1016/j.envpol.2006.09.022
- dos Santos IR, Silva-Filho EV, Schaefer C, Sella SM, Silva CA, Gomes V, Passos MJACR, Ngan PV (2006) Baseline mercury and zinc concentrations in terrestrial and coastal organisms of Admiralty Bay, Antarctica. Environ Pollut 140:304–311. doi:10. 1016/j.envpol.2005.07.007
- Dubé J (1982) Étude de la distribution de quelques metaux dans le zooplancton de deux ecosystèmes du Saint-Laurent. Université du Québec, Quebec
- Espejo W, Celis JE, González-Acuña D, Jara S, Barra R (2014) Concentration of trace metals in excrements of two species of



penguins from different locations of the Antarctic Peninsula. Polar Biol 37:675–683. doi:10.1007/s00300-014-1468-z

- Gallien I, Caurant F, Bordes M, Bustamante P, Miramand P, Fernandez B, Quellard N, Babin P (2001) Cadmium-containing granules in kidney tissue of the Atlantic white-sided dolphin (Lagenorhyncusacutus) off the Faroe Islands. Comput Biochem Physiol C 130:389–395
- Giraldo C, Cherel Y, Vallet C, Mayzaud P, Tavernier E, Moteki M, Hosie G, Koubbi P (2011) Ontogenic changes in the feeding ecology of the early life stages of the Antarctic silverfish (*Pleuragramma antarcticum*) documented by stable isotopes and diet analysis in the Dumont d'Urville Sea (East Antarctica). Polar Sci 5:252–263. doi:10.1016/j.polar.2011.04.004
- Goutte A, Bustamante P, Barbraud C, Delord K, Weimerskirch H, Chastel O (2014) Demographic responses to mercury exposure in two closely related Antarctic top predators. Ecology 95:1075–1086. doi:10.1890/13-1229.1
- Goutte A, Cherel Y, Churlaud C, Ponthus J-P, Massé G, Bustamante P (2015) Trace elements in Antarctic fish species and the influence of foraging habitats and dietary habits on mercury levels. Sci Total Environ 538:743–749. doi:10.1016/j.scitotenv.2015.08.103
- Guinet C, Cherel Y, Ridoux V, Jouventin P (1996) Consumption of marine resources by seabirds and seals in Crozet and Kerguelen waters: changes in relation to consumer biomass 1962–85. Antarct Sci 8:23–30
- Guynn KD, Peterson MS (2008) Mercury concentrations in the Patagonian toothfish, *Dissostichus eleginoides* Smitt 1898, among three distinct stocks. Polar Biol 31:269–274. doi:10.1007/s00300-007-0354-3
- Hamanaka T, Tsujita T (1981) Cadmium and zinc concentrations in zooplankton in the subarctic region of the North Pacific. J Oceanogr Soc Jpn 37:160–172. doi:10.1007/BF02309053
- Hanchet SM, Tracey D, Dunn A, Horn P, Smith N (2012) Mercury concentrations of two toothfish and three of its prey species from the Pacific sector of the Antarctic. Antarct Sci 24:34–42. doi:10. 1017/S0954102011000654
- Headley AD (1996) Heavy metal concentrations in peat profiles from the high Arctic. Sci Total Environ 177:105–111. doi:10.1016/0048-9697(95)04867-7
- Hennig H, Eagle G, McQuaid C, Rickett L (1985) Metal Concentrations in Antarctic Zooplankton Species. In: Siefried W, Condy P, Laws R (eds) Antarctic nutrient cycles and food webs. Springer, Berlin, pp 656–661
- Kahle J, Zauke GP (2003) Trace metals in Antarctic copepods from the Weddell Sea (Antarctica). Chemosphere 51:409–417. doi:10. 1016/S0045-6535(02)00855-X
- Kannan K, Smith RG Jr, Lee RF, Windom HL, Heitmuller PT, Macauley JM, Summers JK (1998) Distribution of total mercury and methyl mercury in water, sediment, and fish from South Florida Estuaries. Arch Environ Contam Toxicol 34:109–118. doi:10.1007/s002449900294
- Klaassen CD, Liu J, Choudhuri S (1999) Metallothionein: an intracellular protein to protect against cadmium toxicity. Annu Rev Pharmacol Toxicol 39:267–294. doi:10.1146/annurev. pharmtox.39.1.267
- Kock K-H (2005a) Antarctic icefishes (Channichthyidae): a unique family of fishes. A review, Part II. Polar Biol 28:897–909. doi:10.1007/s00300-005-0020-6
- Kock K-H (2005b) Antarctic icefishes (Channichthyidae): a unique family of fishes. A review, Part I. Polar Biol 28:862–895. doi:10. 1007/s00300-005-0019-z
- Kock KH, Wilhelms S, Everson I, Groger J (1994) Variations in the diet composition and feeding intensity of mackerel icefish *Champsocephalus gunnari* at South Georgia (Antarctic). Mar Ecol Prog Ser 108:43–58. doi:10.3354/meps108043

- Kojadinovic J, Potier M, Le Corre M, Cosson RP, Bustamante P (2007) Bioaccumulation of trace elements in pelagic fish from the Western Indian Ocean. Environ Pollut. doi:10.1016/j.envpol. 2006.07.015
- Kojadinovic J, Jackson CH, Cherel Y, Jackson GD, Bustamante P (2011) Multi-elemental concentrations in the tissues of the oceanic squid *Todarodes filippovae* from Tasmania and the southern Indian Ocean. Ecotoxicol Environ Saf 74:1238–1249. doi:10.1016/j.ecoenv.2011.03.015
- Lahaye V, Bustamante P, Spitz J, Dabin W, Das K, Pierce GJ, Caurant F (2005) Long-term dietary segregation of common dolphins *Delphinus delphis* in the Bay of Biscay, determined using cadmium as an ecological tracer. Mar Ecol Prog Ser 305:275–285. doi:10.3354/meps305275
- Lane TW, Morel FM (2000) A biological function for cadmium in marine diatoms. Proc Natl Acad Sci USA 97:4627–4631. doi:10. 1073/pnas.090091397
- Lane TW, Saito MA, George GN, Pickering IJ, Prince RC, Morel FMM (2005) A cadmium enzyme from a marine diatom. Nature 434:42. doi:10.1038/434455a
- Lescroël A, Bost CA (2005) Foraging under contrasting oceanographic conditions: the gentoo penguin at Kerguelen Archipelago. Mar Ecol Prog Ser 302:245–261. doi:10.3354/meps302245
- Lescroël A, Ridoux V, Bost CA (2004) Spatial and temporal variation in the diet of the gentoo penguin (*Pygoscelis papua*) at Kerguelen Islands. Polar Biol 27:206–216. doi:10.1007/s00300-003-0571-3
- Locarnini S, Presley B (1995) Trace element concentrations in Antarctic krill, *Euphausia superba*. Polar Biol 15:283–288
- Macdonald C, Sprague J (1988) Cadmium in marine invertebrates and arctic cod in the Canadian Arctic. Distribution and ecological implications. Mar Ecol Prog Ser 47:17–30. doi:10.3354/meps047017
- Mackay EA, Overnell J, Dunbar B, Davidson I, Hunziker PE, Kägi JH, Fothergill JE (1993) Complete amino acid sequences of five dimeric and four monomeric forms of metallothionein from the edible mussel Mytilus edulis. Eur J Biochem 218:183–194
- 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. doi:10.1007/BF00393752
- McArthur T, Butler ECV, Jackson GD (2003) Mercury in the marine food chain in the Southern Ocean at Macquarie Island: an analysis of a top predator, Patagonian toothfish (*Dissostichus eleginoides*) and a mid-trophic species, the warty squid (Moroteuthis ingens). Polar Biol 27:1–5. doi:10. 1007/s00300-003-0560-6
- McIntyre JK, Beauchamp DA (2007) Age and trophic position dominate bioaccumulation of mercury and organochlorines in the food web of Lake Washington. Sci Total Environ 372:571–584. doi:10.1016/j.scitotenv.2006.10.035
- 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 24:738–788
- Miramand P, Fichet D, Bentley D (1998) Concentrations en métaux lourds (Cd, Cu, Pb, Zn) observées le long du gradient de salinité dans le réseau trophique pélagique de l'estuaire de la Seine. Comptes Rendus l'Académie des Sci Sci la terre des planètes 327:259–264
- Miramand P, Pigeot J, Guyot T, Fichet D (1999) Ecotoxicologie intégrée de l'espèce à l'écosystème. Océanis 25:581–608
- Miramand P, Guyot T, Rybarczyk H, Elkaim B, Mouny P, Dauvin JC, Bessineton C (2001) Contamination of the biological



compartment in the Seine estuary by Cd, Cu, Pb, and Zn. Estuaries 24:1056–1065

- Monteiro LR, Costa V, Furness RW, Santos RS (1996) Mercury concentrations in prey fish indicate enhanced bioaccumulation in mesopelagic environments. Mar Ecol Prog Ser 141:21–25
- Mougeot F, Genevois F, Bretagnolle V (1998) Predation on burrowing petrels by the brown skua (Catharacta skua lönnbergi) at Mayes Island, Kerguelen. J Zool Lond 244:429–438. doi:10.1017/S0952836998003136
- 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. doi:10.1016/0025-326X(88)90599-1
- Øverjordet IB, Kongsrud MB, Gabrielsen GW, Berg T, Ruus A, Evenset A, Borgå K, Christensen G, Jenssen BM (2015) Toxic and essential elements changed in black-legged kittiwakes (*Rissa tridactyla*) during their stay in an Arctic breeding area. Sci Total Environ 502:548–556. doi:10.1016/j.scitotenv.2014.09.058
- Pakhomov EA, Perissinotto R (1996) Trophodynamics of the hyperiid amphipod Themisto gaudichaudi in the South Georgia region during late austral summer. Mar Ecol Prog Ser 134:91–100. doi:10.3354/meps134091
- Penicaud V, Lacoue-Labarthe T, Bustamante P (2017) Metal bioaccumulation and detoxification processes in cephalopods: a review. Environ Res 155:123–133. doi:10.1016/j.envres.2017. 02.003
- Petri G, Zauke G-P (1993) Trace metal in the crustaceans in the Antarctic Ocean. Ambio 1(22):529–536
- Pierce GJ, Stowasser G, Hastie LC, Bustamante P (2008) Geographic, seasonal and ontogenetic variation in cadmium and mercury concentrations in squid (Cephalopoda: Teuthoidea) from UK waters. Ecotoxicol Environ Saf 70:422–432. doi:10.1016/j. ecoenv.2007.07.007
- Pigeot J, Miramand P, Guyot T, Sauriau P-G, Fichet D, Le Moine O, Huet V (2006) Cadmium pathways in an exploited intertidal ecosystem with chronic cadmium inputs (Marennes-Oléron, Atlantic coast, France). Mar Ecol Prog Ser 307:101–114
- Pinkerton MH, Forman J, Bury SJ, Brown J, Horn P, O'Driscoll RL (2013) Diet and trophic niche of Antarctic silverfish Pleuragramma antarcticum in the Ross Sea, Antarctica. J Fish Biol 82:141–164. doi:10.1111/j.1095-8649.2012.03476.x
- Rainbow P (1989) Copper, cadmium and zinc concentrations in oceanic amphipod and euphausiid crustaceans, as a source of heavy metals to pelagic seabirds. Mar Biol 103:513–518
- Reinfelder JR, Fisher NS, Luoma SN, Nichols JW, Wang WX (1998)

  Trace element trophic transfer in aquatic organisms: a critique of the kinetic model approach. Sci Total Environ 219:117–135
- Ritterhoff J, Zauke G-P (1997) Influence of body length, life-history status and sex on trace metal concentrations in selected zooplankton collectives from the Greenland Sea. Mar Pollut Bull 34:614–621. doi:10.1016/S0025-326X(96)00181-6
- Romeo M, Gnassia-Barelli M, Carre C (1987) Trace metals: Cd, Cu, Pb and Zn in gelatinous macroplankton from the Northwestern Mediterranean. Water Res 21:1287–1292
- Romeo M, Gnassia-Barelli M, Carre C (1992) Importance of gelatinous plankton organisms in the storage and transfer of trace metals in the north-western Mediterranean. Mar Ecol Prog Ser 82:267–274
- Sanchez-Hernandez JC (2000) Trace element contamination in Antarctic ecosystems. Rev Env Contam Toxicol 166:83–127

- Saunders RA, Collins MA, Ward P, Stowasser G, ShreeveR Tarling GA (2015) Distribution, population structure and trophodynamics of Southern Ocean Gymnoscopelus (Myctophidae) in the Scotia Sea. Polar Biol 38:287–308. doi:10.1007/s00300-014-1584-9
- Scheuhammer AM (1987) The chronic toxicity of aluminium, cadmium, mercury, and lead in birds: a review. Environ Pollut 46:263–295
- Stewart F, Phillips R, Bartle J (1999) Influence of phylogeny, diet, moult schedule and sex on heavy metal concentrations in New Zealand Procellariiformes. Mar Ecol Prog Ser 178:295–305
- Stoeppler M, Nürnberg HW (1979) Comparative studies on trace metal levels in marine biota. Ecotoxicol Environ Saf 3:335–351. doi:10.1016/0147-6513(79)90023-X
- Tan SW, Meiller JC, Mahaffey KR (2009) The endocrine effects of mercury in humans and wildlife. Crit Rev Toxicol 39:228–269. doi:10.1080/10408440802233259
- Tartu S, Goutte A, Bustamante P, Angelier F, Moe B, Clément-Chastel C, Bech C, Gabrielsen GW, Bustnes JO, Chastel O (2013) To breed or not to breed: endocrine response to mercury contamination by an Arctic seabird. Biol Lett 9:1–4. doi:10.1098/rsbl.2013.0317
- Tavares S, Xavier JC, Phillips RA, Pereira ME, Pardal MA (2013) Influence of age, sex and breeding status on mercury accumulation patterns in the wandering albatross Diomedea exulans. Environ Pollut 181:315–320. doi:10.1016/j.envpol.2013.06.032
- Tsui MTK, Wang WX (2004) Uptake and Elimination Routes of Inorganic Mercury and Methylmercury in Daphnia magna. Environ Sci Technol 38:808–816. doi:10.1021/es034638x
- von Waldow H, Macleod M, Scheringer M, Hungerbühler K (2010) Quantifying remoteness from emission sources of persistent organic pollutants on a global scale. Environ Sci Technol 44:2791–2796. doi:10.1021/es9030694
- Wang W (2002) Interactions of trace metals and different marine food chains. Mar Ecol Prog Ser 243:295–309. doi:10.3354/ meps243295
- Wang W, Fisher NS (1998) Accumulation of trace elements in a marine copepod. Limnol Oceanogr 43:273–283. doi:10.4319/lo. 1998 43 2 0273
- Wang W-X, Reinfelder JR, Lee B-G, Fisher NS (1996) Assimilation and regeneration of trace elements by marine copepods. Limnol Oceanogr 41:70–81. doi:10.4319/lo.1996.41.1.0070
- Weimerskirch H, Zotier R, Jouventin P (1989) The avifauna of the Kerguelen Islands. EMU 89:15–29
- Wintle NJP, Sleadd IM, Gundersen DT, Kohl K, Buckley BA (2015) Total mercury in six Antarctic Notothenioid fishes. Bull Environ Contam Toxicol 95:557–560. doi:10.1007/s00128-015-1594-5
- Wöhrmann APA, Hagen W, Kunzmann A (1997) Adaptations of the Antarctic silverfish Pleuragramma antarcticum (Pisces: Nototheniidae) to pelagic life in high-Antarctic waters. Mar Ecol Prog Ser 151:205–218
- Xu Y, Feng L, Jeffrey PD, Shi Y, Morel FMM (2008) Structure and metal exchange in the cadmium carbonic anhydrase of marine diatoms. Nature 452:56–61. doi:10.1038/nature06636
- Zauke G-P, Clason B, Savinov VM, Savinova T (2003) Heavy metals of inshore benthic invertebrates from the Barents Sea. Sci Total Environ 306:99–110. doi:10.1016/S0048-9697(02)00487-4

