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Trace elements in Antarctic fish species and the influence of foraging habitats and dietary habits on mercury levels

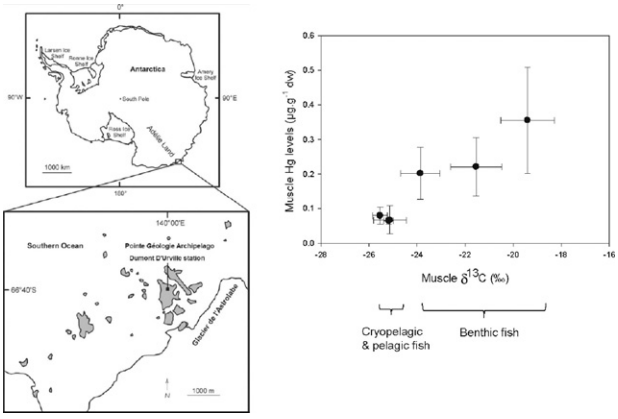
Aurélie Goutte [a,*], Yves Cherel [b], Carine Churlaud [c], Jean-Pierre Ponthus [a], Guillaume Massé [d], Paco Bustamante [c]

[a] École Pratique des Hautes Études (EPHE), SPL, UPMC Univ Paris 06, UMR 7619 METIS, F-75005, 4 place Jussieu, Paris, France
[b] Centre d'Etudes Biologiques de Chizé, UMR 7372, CNRS-Université de La Rochelle, 79360 Villiers-en-Bois, France
[c] Littoral Environnement et Sociétés (LIENSs), UMR 7266, CNRS-Université de la Rochelle, 2 rue Olympe de Gouges, 17000 La Rochelle, France
[d] Unité Mixte Internationale Takuvik, Pavillon Alexandre-Vachon, Université Laval, QC, Québec, Canada

HIGHLIGHTS

- Trace elements and stable isotopes were analyzed in seven Antarctic fish species.
- Levels of trace elements in liver and in muscle differed among species.
- Hg load was higher in benthic fish than in cryopelagic and pelagic fish.
- These findings could be due to the high methylation rate of Hg in the sediment.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aims at describing and interpreting concentration profiles of trace elements in seven Antarctic fish species (N = 132 specimens) off Adélie Land. Ichthyofauna plays a key role in the Antarctic ecosystem, as they occupy various ecological niches, including cryopelagic (ice-associated), pelagic, and benthic habitats. Firstly, trace element levels in the studied specimens were similar to those previously observed in fish from the Southern Ocean. Apart from manganese and zinc, concentrations of arsenic, cadmium, copper, iron, mercury (Hg), nickel, selenium and silver differed among fish species. Muscle $\delta^{13}C$ and $\delta^{15}N$ values were determined to investigate whether the fish foraging habitats and dietary habits could explain Hg levels. Species and foraging habitat ($\delta^{13}C$) were strong predictors for variations of Hg concentrations in muscle tissues. The highest Hg contamination was found in shallow benthic fish compared to cryopelagic and pelagic fish. This pattern was likely due to the methylation of Hg in the coastal sediment and the photodemethylation by ultraviolet radiation in surface waters.

* Corresponding author.
E-mail address: aurelie.goutte@ephe.sorbonne.fr (A. Goutte).

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1. Introduction

Trace elements, from natural and anthropogenic sources are increasingly released in the environment (Sen and Peucker-Ehrenbrink, 2012) and are ultimately deposited in the ocean. Long-range transport to the open ocean happens through oceanic currents and atmospheric circulation, followed by wet and dry deposition processes (SCOR, 2007). Moreover the ocean plays a critical role in the biogeochemical cycle of trace metals, through chemical and biological reactions in the water column (Morel and Price, 2003; SCOR, 2007). For instance, mercury (Hg) is deposited through the atmosphere in its inorganic form (HgII) and is methylated (Me–Hg) in the ocean, thereby being more bioavailable for marine biota. In that respect, marine ecosystems could be particularly exposed to toxic metals, even in remote and isolated areas (Fitzgerald et al., 1998; Ebinghaus et al., 2002).

Although the contamination pattern of Arctic marine biota by trace elements has been well described (Atwell et al., 1998; AMAP, 1998, 2011), such investigations have been less abundant in the Southern Ocean (de Moreno et al., 1997; Sanchez-Hernandez, 2000; Bargagli, 2008). Moderate to high levels of trace metals have been reported in Antarctic and subantarctic zooplankton (Rainbow, 1989; Petri and Zauke, 1993), benthic octopuses (Bustamante et al., 1998), fish (Honda et al., 1983; Bargagli et al., 1998a,b; Marquez et al., 1998; Bustamante et al., 2003), seabirds (Blévin et al., 2013; Carravieri et al., 2014a) and marine mammals (Szefer et al., 1993). This could raise matters of environmental concerns, since some metals, such as Hg, cadmium (Cd) and lead (Pb), cause health problems in vertebrates, including endocrine disruption, DNA damage, immunotoxicity and reprotoxicity (UNEP, 2010a,b; Wolfe et al., 1998). On the other hand, some elements (e.g. copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), zinc (Zn)) play essential biological roles, often as cofactors or part of cofactors in enzymes and structural elements of proteins.

Ichthyofauna plays a key role in the Antarctic ecosystems, as they constitute a link between lower (copepods, euphausiids) and higher (seabirds, seals) levels of the trophic web (La Mesa et al., 2004). Moreover Antarctic fish occupy most of the available ecological niches, including cryopelagic (ice-associated), pelagic, benthic and epibenthic habitats (La Mesa et al., 2004; Cherel et al., 2011). Antarctic fish species are thus appropriate to assess the respective contribution of foraging habitat and diet in both the inter- and intra-specific variations of trace element concentrations. As a result of bioaccumulation and bioamplification processes within trophic webs (Atwell et al., 1998; Morel et al., 1998; Bargagli et al., 1998a), the concentrations of biomagnifiable trace element are supposed to increase with higher trophic level organisms. In addition, foraging habitat may shape the levels of exposure to trace metals. Due to the high Hg bioavailability in coastal bottom water around the Antarctic shelf (Fitzgerald et al., 2007), benthic fish species are expected to have higher Hg levels than species foraging in the water column and underneath the sea ice.

The present study was carried out in the Pointe Géologie archipelago, Adélie Land, Antarctica, which contains a rich marine ecosystem with a high density of epibenthic organisms, pelagic fish, seabirds and marine mammals (Micol and Jouventin, 2001; Gutt et al., 2007). The first goal of this study was to describe the concentrations of 13 trace elements in the liver (silver (Ag), arsenic (As), Cd, cobalt (Co), chromium (Cr), Cu, Fe, Mn, Ni, selenium (Se), vanadium (V), and Zn) and in the muscle (Hg) of seven Antarctic fish species (N = 132 specimens) off Adélie Land. The second objective aims at exploring the influence of feeding strategies in driving Hg variations in Antarctic fish, by interpreting the ratios of stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in fish muscle. In the marine environment, the $\delta^{13}C$ values are mainly used to indicate inshore versus offshore, or pelagic versus benthic contribution to food intake. Moreover, consumers are typically enriched in ^{15}N relative to their food and consequently the $\delta^{15}N$ values serve as indicators of a dietary habits and trophic position (Vanderklift and Ponsard, 2003).

2. Materials and methods

2.1. Study area, species and sample collection

This study was carried out from the 24th of April 2010 to 17th of January 2012 in the Pointe Géologie Archipelago (Adélie Land, Antarctica, 66°40′ S, 140°01′ E). Table 1 provides general information about the samples analyzed in this study. *Pleuragramma antarcticum* is the dominant pelagic fish in high-Antarctic waters (La Mesa et al., 2004; La Mesa and Eastman, 2012) and was collected over the continental slope (66°18′S and 141°56′E) from the Research Icebreaker Astrolabe using an Isaacs-Kidd Midwater Trawl (IKMT). The six other species were caught near-shore underneath the sea ice and up to 87-meter-deep in the vicinity of the station. The cryopelagic (Hoshiai et al., 1989) fish *Pagothenia borchgrevinki* were caught in cracks in the sea ice, using fishing rods at a depth of less than one meter. Most of the benthic species (*Notothenia coriiceps*, *Trematomus bernacchii*, *Trematomus hansoni*, *Trematomus pennellii*, Gon and Heemstra, 1990) were caught by using fish traps on the sea bottom, or by paying out line until we felt contact with the bottom and then reeled in just enough to keep our lure from hanging bottom. The fish *Trematomus newnesi*, known to feed in the water column or at the undersurface of ice in near shore shallow areas (Gon and Heemstra, 1990), was collected in the water column using a fishing rod. Each fish was identified to the species level based on morphological criteria. Individuals were measured (total length; nearest mm) and weighed (nearest g). These morphometric measures were not taken for the 9 *P. antarcticum*, because they had head or caudal fin removed while fishing with the IKMT net. Samples of white muscle (N = 129) and liver (N = 75) were excised and immediately frozen at −80 °C until analysis in the laboratory. Since amounts of liver samples were limited, it was not possible to analyze both Hg and the 12 other elements in liver samples. Hence, Hg concentrations were determined in muscle samples and the 12 other elements in liver samples.

2.2. Trace element analyses

Freeze-dried samples were powdered and homogenized. The total Hg concentrations in the muscle were determined by analyzing Hg directly with an Advanced Mercury Analyzer (ALTEC AMA 254) on aliquots ranging from 5 to 50 mg of freeze-dried sample weighed to the nearest 0.01 mg (Bustamante et al., 2006). All analyses were repeated 2–3 times for each sample until having a relative standard deviation <10%. The analysis of Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Se, V and Zn were determined in liver samples according to Kojadinovic et al. (2011). Briefly, 60 to 300 mg samples were microwave digested in a mixture of 6 mL of 65% HNO3 (VWR Quality SUPRAPUR) and 2 mL of 30% HCl (VWR Quality SUPRAPUR), except for the samples with a weight below 100 mg: 3 mL HNO3 and 1 mL HCl. Then the samples were diluted to 50 mL (25 mL for the samples with a weight below 100 mg) with ultrapure water. The 12 elements were then analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (Varian Vista-Pro ICP-OES) and Mass Spectrometry (ICP-MS II Series Thermo Fisher Scientific). To avoid trace element contamination, all glass and plastic utensils used were soaked in a bath of nitric acid (50 mL in 2 L) for a minimum of 48 h, rinsed in ultrapure water and dried under a laminar hood before use. Accuracy and reproducibility of the preparation were tested by preparing analytical blanks and replicates of lobster hepatopancreas (TORT-2) and dog-fish liver (DOLT-3) reference standards (National Research Council, Canada) along with each set of samples. Results for the certified reference materials were in good agreement with the certified values and recovery rates varied from 83% to 109%. The detection limits ($\mu g \cdot g^{-1}$ dry wt) were 0.005 (Hg), 0.02 (Ag, Cd, Co, Cr), 0.1 (Cu, Mn, Se), 0.2 (As), 0.3 (Ni), 0.33 (V), and 3.3 (Fe, Zn). Trace element concentrations are expressed in $\mu g \cdot g^{-1}$ dry weight (dw).