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Wide range of metallic and organic contaminants in various tissues of the Antarctic prion, a planktonophagous seabird from the Southern Ocean



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Trace elements and POPs were measured in various tissues of 10 Antarctic prions.
- Residue diversity was notable given the species' small size and low trophic position.
- Cd. Se. BDE 183 and 209 showed noticeably high internal tissue concentrations.
- · Several POPs showed inter- and intra-tissue correlations, indicating co-exposure.
- Blood was validated as a good bioindicator of internal tissue As and Hg levels.



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ABSTRACT

Trace elements (n = 14) and persistent organic pollutants (POPs, n = 30) were measured in blood, liver, kidney, muscle and feathers of 10 Antarctic prions (Pachyptila desolata) from Kerguelen Islands, southern Indian Ocean, in order to assess their concentrations, tissue distribution, and inter-tissue and inter-contaminant relationships. Liver, kidney and feathers presented the highest burdens of arsenic, cadmium and mercury, respectively. Concentrations of cadmium, copper, iron, and zinc correlated in liver and muscle, suggesting that uptake and pathways of metabolism and storage were similar for these elements. The major POPs were 4,4'-DDE, mirex, PCB-153 and PCB-138. The concentrations and tissue distribution patterns of environmental contaminants were overall in accordance with previous results in other seabirds. Conversely, some Antarctic prions showed surprisingly high concentrations of BDE-209. This compound has been rarely observed in seabirds before, and its presence in Antarctic prions could be due to the species feeding habits or to the ingestion of plastic debris. Overall, the study shows that relatively lower trophic level seabirds (zooplankton-eaters) breeding in the remote southern Indian Ocean are exposed to a wide range of environmental contaminants, in particular cadmium, selenium and some emerging-POPs, which merits further toxicological investigations.

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Trace elements and persistent organic pollutants (POPs) are commonly found in terrestrial and aquatic ecosystems worldwide (Walker et al., 2012). These environmental contaminants come from both natural and anthropogenic sources, and can exhibit toxic properties causing endocrine dysfunction, mutagenesis, or reproductive and behavioural disturbances (e.g., Scheuhammer, 1987; AMAP, 2004; Walker et al., 2012). Although polar marine environments are isolated from the major emission sources, they are reached by trace elements and POPs through atmospheric and oceanic transport (Fitzgerald et al., 2007; Galbán-Malagón et al., 2013). Many contaminants, such as mercury (Hg) and POPs bioaccumulate in organisms and biomagnify in food webs (Morel et al., 1998; Fisk et al., 2001). Thus, polar marine predators usually bear high burdens of contaminants (Bustnes et al., 2003; Bargagli, 2008), with exposure being governed by various factors such as foraging habitat and trophic position (Fisk et al., 2001; Carravieri et al., 2013). Seabirds are often considered to be ideal models to biomonitor contaminants in the marine environment, since they forage over large geographic areas and feed at different trophic levels (Furness and Camphuysen, 1997). In contrast to Arctic species (e.g., Braune et al., 2005; Dietz et al., 2009), contaminant exposure of Southern Ocean seabirds has received little attention, although pioneer studies have reported a wide diversity of compounds in their tissues (Bocher et al., 2003; Tao et al., 2006; Anderson et al., 2010).

Several tissues have been used to evaluate seabird contamination, particularly feathers (e.g., Bustnes et al., 2002; Seco Pon et al., 2011), blood (e.g., González-Solís et al., 2002; Bustnes et al., 2007) and soft tissues such as liver (e.g., Colabuono et al., 2012; Jerez et al., 2013). The interpretation of contaminant burdens in these tissues depends on the understanding of contaminant dynamics within the whole organism. For instance, blood has a transport role for contaminants, and circulating concentrations are believed to reflect short-term dietary exposure (Burger and Gochfeld, 1997). On the other hand, the liver and kidney are specifically involved in contaminant detoxification and/or storage, while muscles could function as a temporary storage tissue (Lewis and Furness, 1991). Finally, feathers are known to sequester both metallic and organic contaminants during their synthesis (Burger, 1993; García-Fernández et al., 2013). Overall, however, these mechanisms are still poorly known for the large majority of environmental contaminants. Namely, there have been only few comprehensive studies that have simultaneously guantified trace elements and POPs in a suite of seabird tissues, and that have investigated between-contaminant and between-tissue relationships (Eagles-Smith et al., 2008; Colabuono et al., 2012). Data are particularly lacking for low trophic level seabirds, because they usually bear lighter burdens of contaminants than top predators, with residues being more difficult to detect.

The present study describes the concentrations of 14 trace elements and 30 POPs (seven polychlorinated biphenyls, PCBs; 12 organochlorine pesticides, OCPs; and 11 polybrominated diphenyl ethers, PBDEs) in several internal tissues and in feathers of 10 Antarctic prions (Pachyptila desolata) from Kerguelen Islands, a remote subantarctic archipelago in the southern Indian Ocean. The Antarctic prion breeds in Antarctic and subantarctic islands, with important populations at South Georgia (southern Atlantic Ocean), Auckland (southern Pacific Ocean) and Kerguelen Islands (Weimerskirch et al., 1989; Marchant and Higgins, 1990). At the latter locality, breeding Antarctic prions forage in cold waters where they prey primarily on swarming crustaceans (pelagic amphipods) to feed their chicks (Weimerskirch et al., 1999; Cherel et al., 2002). The composition of stomach oil indicates that adults also prey on mid-water fish when they feed for themselves (Connan et al., 2007). During the inter-breeding season, birds shift north to the warmer subtropical waters where they moult (Quillfeldt et al., 2015).

Our main goal was to investigate the contaminant distribution pattern, and inter-tissue and inter-contaminant relationships, in order to depict co-exposure and/or similar bioaccumulation and detoxification patterns among contaminants. Furthermore, correlations of soft tissue burdens with blood and/or feather concentrations is necessary to validate the use of these tissues as appropriate proxies of internal contamination, which has surprisingly received little attention in polar seabirds (Henriksen et al., 1998; Bustnes et al., 2003). Based on previous knowledge (Bocher et al., 2003), we expected the liver to bear high contaminant burdens when compared to other organs, and feathers to present high Hg concentrations, considering their excretory role (Braune and Gaskin, 1987). Given the relatively low trophic level, and thus potentially low contaminant exposure of Antarctic prions, we expected overall low contaminant concentrations in this species when compared to higher trophic level seabirds from the same environments.

2. Materials and methods

2.1. Sample collection and preparation

Ten freshly dead Antarctic prions trapped in the vegetation (*Acaena adscendens*) were opportunistically collected on January 26th, 2012, on the Kerguelen archipelago ($49^{\circ}21'S$, $70^{\circ}18'E$), southern Indian Ocean. Only intact specimens were collected and then stored at -20 °C until dissection. Age and breeding status of birds were not known. However, because in Kerguelen Islands Antarctic prions' eggs are laid in December (incubation of the single white egg takes 44–46 days) and chicks fledge at 45–55 days old (Weimerskirch et al., 1989) these birds cannot be newly fledged chicks.

During necropsies, internal tissues (liver, kidneys and pectoral muscle) were sampled, weighed and wrapped individually in plastic bags and in aluminium foils for trace element and POP analyses, respectively. The stomachs were also dissected in order to check their contents. Plastic debris were found in five individuals. Clotted blood was collected from heart auricles and stored in microtubes at -20 °C. Four body feathers were pulled out from the lower back and stored dry in plastic bags. Birds were first sexed during necropsies by visual gonad examination. Sex was then confirmed using the molecular method described by Fridolfsson and Ellegren (1999). Prior to chemical analyses, internal tissues and blood were freeze-dried, ground to powder and then stored in plastic and glass tubes for trace element and POP analyses, respectively. Feathers were washed to remove surface dirt and adsorbed contaminants in a chloroform-methanol solution and then oven dried as described by Carravieri et al. (2013). For each individual, the four body feathers were pooled to limit potential inter-feather differences in trace element concentrations (Carravieri et al., 2014a); feathers were homogenised by cutting them with scissors into small fragments (1-2 mm). Samples were weighed before and after freezedrying to calculate water content (moisture, see Table S1, Supplementary material).

2.2. Analyses of trace elements

Trace elements were determined in blood, liver, kidney, muscle and feathers. Total Hg analysis was carried out with an advanced mercury analyser (ALTEC AMA 254) on dried tissue aliquots (2–4 mg) following Blévin et al. (2013). All analyses were repeated 2–3 times until having a relative standard deviation < 10%. Accuracy was checked using TORT-2 Lobster Hepatopancreas (NRC, Canada) as certified reference material (CRM) with a certified Hg concentration of 0.27 \pm 0.06 µg g⁻¹ dry weight (dw). Our measured values were 0.267 \pm 0.006 $\mu g~g^{-1}~dw$ (n = 18). Thirteen other elements (silver, Ag; arsenic, As; cadmium, Cd; cobalt, Co; chromium, Cr; copper, Cu; iron, Fe; manganese, Mn; nickel, Ni; lead, Pb; selenium, Se; vanadium, V; and zinc, Zn) were analysed using a Varian Vista-Pro ICP-OES and a Thermo Fisher Scientific X Series 2 ICP-MS (following Métian et al., 2008). Aliquots of the biological samples (30-300 mg) were digested with 6 ml 67-70% HNO3 and 2 ml 34-37% HCl (Fisher Scientific, trace element grade quality), except for feathers (1.8 ml HNO₃ and 0.6 ml HCl).

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