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From Antarctica to the subtropics: Contrasted geographical concentrations of selenium, mercury, and persistent organic pollutants in skua chicks (*Catharacta* spp.)☆

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ABSTRACT

Seabirds integrate bioaccumulative contaminants *via* food intake and have revealed geographical trends of contamination in a variety of ecosystems. Pre-fledging seabird chicks are particularly interesting as bioindicators of chemical contamination, because concentrations in their tissues reflect primarily dietary sources from the local environment. Here we measured 14 trace elements and 18 persistent organic pollutants (POPs) in blood of chicks of skuas that breed in four sites encompassing a large latitudinal range within the southern Indian Ocean, from Antarctica (Adélie Land, south polar skua *Catharacta maccormicki*), through subantarctic areas (Crozet and Kerguelen Islands, brown skua *C. lonnbergi*), to the subtropics (Amsterdam Island, *C. lonnbergi*). Stables isotopes of carbon ($\delta^{13}C$, feeding habitat) and nitrogen ($\delta^{15}N$, trophic position) were also measured to control for the influence of feeding habits on contaminant burdens. Concentrations of mercury (Hg) and selenium (Se) were very high at all the four sites, with Amsterdam birds having the highest concentrations ever reported in chicks worldwide (4.0 ± 0.8 and 646 ± 123 μg g^{-1} dry weight, respectively). Blood Hg concentrations showed a clear latitudinal pattern, increasing from chicks in Antarctica to chicks in the subantarctic and subtropical islands. Interestingly, blood Se concentrations showed similar between-population differences to Hg, suggesting its involvement in protective mechanisms against Hg toxicity. Chicks' POPs pattern was largely dominated by organochlorine pesticides, in particular DDT metabolites and hexachlorobenzene (HCB). Skua chicks from subantarctic islands presented high concentrations and diversity of POPs. By contrast, chicks from the Antarctic site overall had the lowest concentrations and diversity of both metallic and organic contaminants, with the exception of HCB and arsenic. Skua populations from these sites, being naturally exposed to different quantities of contaminants, are potentially good models for testing toxic effects in developing chicks in the wild.

1. Introduction

Anthropogenic activities have profoundly modified physical and chemical processes at the Earth's surface, with pervasive environmental pollution being one of the major consequences. Global fluxes of trace elements such as mercury (Hg), lead (Pb) and arsenic (As) are exceedingly influenced by human activities (mining, fossil fuel combustion, construction; Rauch and Pacyna, 2009; Sen and Peucker-Ehrenbrink, 2012). In addition, a multitude of synthetic chemicals have been released into the environment, with some of them, such as the highly toxic persistent organic pollutants (POPs, www.pops.int) being still widespread and threatening ecosystems worldwide. The ocean plays a critical role in the biogeochemical cycle of trace elements (Coale et al., 1996; SCOR Group,

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2007) and in the global dynamics of POPs (Dachs et al., 2002; Nizzetto et al., 2010). Yet there is still a significant dearth of knowledge on the distributions of trace elements and POPs in the World Ocean. Seabirds can be effectively used as bioindicators of contamination in vast oceanic regions, because they integrate the contamination of their food webs through bioaccumulation and biomagnification mechanisms over large spatial scales, and breed on land in colonies where they are easily accessible (Elliott and Elliott, 2013). Despite their interest as bioindicators, still little is known on seabird contaminant exposure, in particular for trace elements such as copper (Cu), iron (Fe) or selenium (Se) (but see e.g. Anderson et al., 2010; Borgå et al., 2006; Fromant et al., 2016). These trace elements are essential for biological processes within a narrow window of concentrations, but can lead to deleterious effects outside of it (deficiency below and toxicity above), and have the potential to interact with other metallic and organic contaminant uptake, storage, and toxic effects (Walker et al., 2012). In particular, Se has a well-known protecting role against Hg toxicity (Khan and Wang, 2009), yet only a few studies have quantified Hg-Se co-exposure and interaction in seabirds (but see e.g. Carvalho et al., 2013; Cipro et al., 2014; González-Solís et al., 2002). Furthermore, large-scale trace element and POPs distributions in the World Ocean are poorly known, especially in the Southern Hemisphere (SCOR Group, 2007), and seabirds could help in understanding potential geographical differences in their bioavailability. Seabird species with large distributions are particularly useful as bioindicators, because the comparison of distinct populations allow inferring geographical differences in contamination of food webs with a limited phylogenetic bias (Brasso et al., 2015; Carravieri et al., 2016; Roscales et al., 2016).

Food is the main contaminant exposure route in seabirds, thus trophic ecology must be taken into account when evaluating geographical and temporal trends of contamination (Brasso et al., 2015; Braune et al., 2014). By coupling the quantification of environmental contaminants and trophic tracers such as the stable isotopes of carbon and nitrogen (δ^{13}C and δ^{15}N as proxies of foraging habitats and diets, respectively), recent studies on seabirds have highlighted geographical differences in environmental contaminant transfer to predators in the Southern Ocean. Namely, feather Hg concentrations of penguin and albatross species from distinct sites in the Southern Hemisphere indicated potential "hot-spots" of Hg bioavailability, such as Staten Island in the southern Atlantic Ocean (Brasso et al., 2015) or the subtropical waters of the Indian Ocean (Bustamante et al., 2016). In addition, POP exposure of Southern Ocean top predators had different latitudinal patterns in the Southern Atlantic (increasing northward, Roscales et al., 2016) and Indian Oceans (increasing southward, Carravieri et al., 2014). Most of these studies have been conducted in adult seabirds (but see Blévin et al., 2013; Colabuono et al., 2016), where the interpretation of tissue contaminant concentrations may be blurred by confounding factors such as exposure over different temporal and spatial scales (during the breeding *vs* wintering season) (Bourgeon et al., 2013; Fort et al., 2014), thus limiting our capacity to effectively infer geographical differences in exposure.

The present study focuses on two sibling seabird species from the southern Indian Ocean: the south polar skua *Catharacta maccormicki* and the brown skua *C. lonnbergi*. Hg, 13 other trace elements, and 18 persistent organic pollutants (POPs, including organochlorine pesticides, OCPs, and polychlorinated biphenyls, PCBs) were measured in blood of pre-fledging chicks during the same breeding season from four sites that encompass a large latitudinal range: from Antarctica (Adélie Land, *Catharacta maccormicki*), through subantarctic areas (Crozet and Kerguelen Islands, *C. lonnbergi*), to the subtropics (Amsterdam Island, *C. lonnbergi*). Contaminant concentrations in pre-fledging chicks are more easily related to dietary sources than those of adults and represent primarily the local environment (Burger and Gochfeld, 2004). This offers an exceptional opportunity to compare contaminant exposure in geographically distant, but phylogenetically and ecologically closely-related seabird populations. The short time window of sampling also minimises the influence of a potential temporal variation in contaminant concentrations in the skuas' food webs. This work has two main objectives: first, to describe the concentrations of several metallic and organic contaminants in blood of skua chicks, compare it to other seabirds from similar environments, and evaluate potential toxicity; and second to infer potential geographical patterns of exposure within the southern Indian Ocean.

2. Material and methods

2.1. Study sites and sampling procedure

Fieldwork was conducted at four sites of the Terres Australes et Antarctiques Françaises that are representative of different water masses of the southern Indian Ocean, namely Adélie land (66°40′S, 140°01′E) in high-Antarctica, Kerguelen (49°21′S, 70°18′E) and Crozet Archipelagos (46°26′S, 51°45′E) in the subantarctic zone *sensus lato* (between the Polar Front and the Subtropical Front), and Amsterdam Island (37°50′S, 77°31′E) in the subtropics (north of the Subtropical Front). Two sibling species of skuas breed at these sites, the brown skua at Kerguelen, Crozet and Amsterdam Islands, and the south polar skua in Adélie Land. One single well-feathered skua chick per nest was captured by hand before fledging during the 2011–2012 breeding season at all sites (N = 41 across all sites). Blood was sampled from the wing vein with a 2-mL heparinized syringe. Whole blood was centrifuged less than 2 h after sampling, and blood cells and plasma were stored at −20 °C until laboratory analyses in France.

2.2. Diet

Skuas have a high plasticity in feeding methods, being able to (i) scavenge on seabird and marine mammal carcasses, (ii) actively prey upon eggs and seabirds on land, (iii) fish at sea, and (iii) kleptoparatize other seabirds (Furness, 1987; Olsen and Larsson, 1997). During the chick rearing period, parents remain largely on land or coastal habitats to seek food for their offspring, usually exploiting other seabirds' colonies in the vicinity of the nests. At our field station in Adélie Land, south polar skua chicks are mainly fed eggs and carcasses of Adélie penguins *Pygoscelis adeliae* (Centre d'Etudes Biologique de Chizé, CEBC, unpublished data). In the Kerguelen Archipelago, brown skua chicks were sampled at Mayès Island, where skuas rely almost exclusively on small burrowing petrels that breed there, in particular the blue petrel, *Halobaena caerulea*, but also the thin-billed prion, *Pachyptila belcheri* (Mougeot et al., 1998). Skua chick diet at Pointe Basse, Possession Island, Crozet Archipelago, comprises eggs and carcasses of crested penguins (*Eudyptes* spp.), but also introduced black rats *Rattus rattus* (Stahl and Mougin, 1986). Finally, at Amsterdam Island, skua diet is poorly known, but field observations indicate that chicks are fed eggs and carcasses of other seabirds, but also with scavenged subantarctic fur seals, *Arctocephalus tropicalis* and introduced brown rats *Rattus norvegicus*.

2.3. Trace element, POP and stable isotope analyses

Blood is very useful for contaminant evaluation in seabirds: circulating levels are representative of dietary exposure and are in