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Persistent organic pollutants (POPs) in killer whales (*Orcinus orca*) from the Crozet Archipelago, southern Indian Ocean

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ABSTRACT

Persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs), are ubiquitous environmental contaminants of which significant concentrations are reported in upper trophic level animals. In 1998, we collected blubber biopsy samples ($n = 11$) from killer whales (*Orcinus orca*) inhabiting the coastal waters around Possession Island, Crozet Archipelago, southern Indian Ocean, for contaminant analyses. Despite inhabiting an isolated region far removed from industrial activities, these killer whales can presently be considered among the most PCB-contaminated cetaceans in the southern hemisphere, with concentrations ranging from 4.4 to 20.5 mg/kg lipid weight (lw). PCDD levels ranged from below the detection limit (5 ng/kg) to 77.1 ng/kg lw and PCDF levels from below the detection limit (7 ng/kg) to 36.1 ng/kg lw. Over 70% of our study animals had PCB concentrations which exceeded a 1.3 mg/kg PCB threshold established for endocrine disruption and immunotoxicity in free-ranging harbour seals, suggesting that organic contaminants cannot be ruled out as an additional threat to this declining population.

1. Introduction

Polychorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/Fs) are persistent organic pollutants (POPs). They are hydrophobic, have moderate vapour pressure, and low reactivity that allow them to be readily transported in the environment. "Global distillation" was described as the process by which POPs evaporate in the warmer regions and are then transported in the atmosphere towards the poles where they condense and are deposited. Cold regions, such as the Arctic and the Antarctic, have thus been described as important sinks for these contaminants (Wania and Mackay, 2001).

PCBs were extensively used by industrialized nations until the late 70s when they were largely banned. They were detected for the first time in the Antarctic environment in the early 70s. Atmospheric transport is believed to be the dominant pathway for PCB contamination in Antarctica where local sources are thought to be restricted to electrical equipment at isolated research stations (Risebrough et al., 1990).

PCDD/Fs are formed as by-products during different industrial and thermal processes such as emissions from metallurgical industries, municipal incinerators, pulp and paper mills, and the manufacture of chlorinated chemicals. Atmospheric transport is also thought to be the dominant pathway for the delivery of dioxins and furans to the Antarctic along with minor local sources such as incinerators at research stations (Lugar et al., 1996).

As long lived, high level trophic feeders, marine mammals tend to bioaccumulate POPs in lipid tissues. Marine mammals from Europe, North America, Asia, and the Arctic have been found to be particularly contaminated with PCBs (Bergman et al., 2001; Kajiwara et al., 2006; Muir et al., 2000; Ross et al., 2000). Marine mammal-eating transient killer whales (*Orcinus orca*) from the Northeastern Pacific Ocean are reported as among the most PCB-contaminated marine mammals in the world (Ross et al., 2000) and killer whales from Norway are the most PCB-contaminated animals in the Arctic (Wolkers et al., 2007).

The biology of killer whales from the coastal waters of Possession Island, Crozet Archipelago, southern Indian Ocean, has been studied since the late 1980s, but no information exists on their exposure to POPs. Killer whales are sighted in the area year round but some photo-identified individuals have been seen at the nearby Kerguelen Island and close to the Antarctic continent. Killer whales in the Crozet Archipelago feed on a variety of prey including fish, penguins (*Eudyptes* sp.), southern elephant seals (*Mirounga leonina*) and occasionally, large cetaceans (Guinet, 1991). Between 1988 and 2002, this population declined by 50% due to the decline

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of an important prey species (the southern elephant seal), interactions with the Patagonian toothfish (*Dissostichus eleginoides*) longline fishery, and/or emigration of individuals or groups from the coastal waters of the Crozet Archipelago (Poncelet et al., in press).

POPs are known to cause hormone disruption, immunosuppression, and reproductive failure in other marine mammals (Mos et al., 2007a; Reijnders, 1986; Ross et al., 1995; Tabuchi et al., 2006). Such persistent contaminants can represent a population-level conservation threat to killer whales (Ross, 2006), with heavy POP accumulation largely due to their high trophic position and long lifespan (Hickie et al., 2007). In analyzing PCB, PCDD, and PCDF concentrations in blubber biopsies taken from the declining Crozet Archipelago population, we aimed to provide a much-needed baseline for these priority contaminants, and to characterize associated health risks.

2. Materials and methods

2.1. Sampling

The study was carried out in the Crozet Archipelago, southern Indian Ocean (46°25′S; 51°59′E) (Fig. 1). Lightweight pneumatic darts were used to biopsy killer whales inhabiting the coastal waters of Possession Island. The variable-power dart projector and its stainless-steel, 6.4 mm diameter tip, as well as a full description of the sampling procedure, is described elsewhere (Barrett-Lennard et al., 1996). This method was adapted to enable shore-based, rather than ship-based, collections.

Briefly, biopsy sampling was conducted from shore with a fine fishing line attached to the dart in order to retrieve biopsies taken posterior to, and below, the dorsal fin of the animal. Samples of epidermal, dermal, and hypodermal tissue typically weighed approximately 0.5 g. Skin from the biopsy samples was preserved in dimethyl sulphoxyde and a saturated salt solution and stored at 4 °C for DNA extraction. Blubber from the biopsies was placed in pesticide grade hexane-rinsed glass vials with aluminium foil-covered caps and stored at −20 °C for contaminant analyses. 11 blubber biopsies were collected from nine different killer whales. Genetic results from the present samples, combined with the photo-identification work conducted previously (Guinet, 1991), enabled a determination of sex as well as age class for each of the nine individuals.

2.2. Contaminant analyses

Blubber samples were analyzed for PCDDs, PCDFs, and mono-ortho, di-ortho, and non-ortho (planar) PCBs. Thawed blubber was ground in a porcelain mortar and pestle with 200 g of anhydrous sodium sulphate and spiked with a mixture of ^{13}C-labelled PCBs, PCDDs, and PCDFs. The blubber-sodium sulphate mixture was transferred to an extraction column and extracted with 250 mL of 1:1 dichloromethane/hexane (DCM/hex) from a glass column by gravity flow. The extract was evaporated to dryness and the lipid content of the samples was determined. Analyses of cleaned-up samples were conducted by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Procedural blanks were analyzed along with samples to assess the integrity of the analytical procedures. Details on the sample clean-up, instrumental analysis condition used, quantification protocols, criteria used for congener identification and the quality assurance/quality control (QA/QC) measures undertaken for the HRGC/HRMS analysis of all the analytes of interest are described elsewhere (Ikonomou et al., 2001; Rantaleinen et al., 1998).

2.3. Data analysis

Two killer whales were biopsied twice allowing for replicate comparison. For one of these two whales, contaminant concentrations differed between the two samples. However, in the case of this individual, one of the biopsies was taken on the dorsal ridge just behind the dorsal fin. This sample was low in lipid content, not representative of a typical biopsy and therefore eliminated from our analysis. For the other whale, the two biopsies provided similar results (2.3% and 8.6% difference between the two samples for PCBs and PCDDs/Fs, respectively). Average contaminant concentrations were considered for this whale. Although we were unable to age sampled individuals, we were able to divide our study animals into three categories for POP comparisons: juvenile females ($n = 3$), adult females ($n = 5$) and adult male ($n = 1$).

All the concentrations were expressed on a lipid weight basis (lw) and were blank-corrected as well as recovery-corrected using the stable isotope dilution method based on ^{13}C-labelled PCB, PCDD, and PCDF spikes (Ikonomou et al., 2001) (the recovery ranges were a mean of 60% for PCBs (range 20–95%), 82% for PCDDs (50–105%), and 81% for PCDFs (60–100%)).

Many congeners were not detected. When congeners were undetected, substitutions were applied according to the following

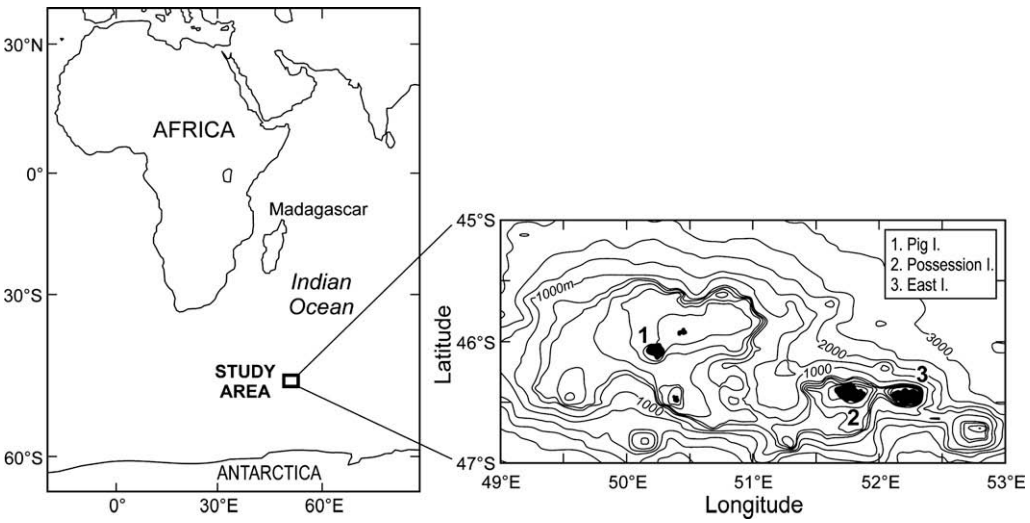

Fig. 1. Killer whales were sampled around Possession Island, Crozet Archipelago, in the southern Indian Ocean.