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South polar skua (Catharacta maccormicki) as biovectors for long-range transport of persistent organic pollutants to Antarctica☆

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ABSTRACT

Migratory bird species may serve as vectors of contaminants to Antarctica through the local deposition of guano, egg abandonment, or mortality. To further investigate this chemical input pathway, we examined the contaminant burdens and profiles of the migratory South polar skua (*Catharacta maccormicki*) and compared them to the endemic Adélie penguin (*Pygoscelis adeliae*). A range of persistent organic pollutants were targeted in muscle and guano to facilitate differentiation of likely exposure pathways. A total of 56 of 65 targeted analytes were detected in both species, but there were clear profile and magnitude differences between the species. The South polar skua and Adélie penguin muscle tissue burdens were dominated by *p,p′*-dichlorodiphenyldichloroethylene (mean 5600 ng g^{-1} lw and 330 ng g^{-1} lw respectively) and hexachlorobenzene (mean 2500 ng g^{-1} lw and 570 ng g^{-1} lw respectively), a chemical profile characteristic of the Antarctic and Southern Ocean region. Species profile differences, indicative of exposure at different latitudes, were observed for polychlorinated biphenyls (PCBs), with lower chlorinated congeners and deca-chlorinated PCB-209 detected in South polar Skua, but not in Adélie penguins. Notably, the more recently used perfluoroalkyl substances and the brominated flame retardants, hexabromocyclododecane and tetrabromobisphenol A, were detected in both species. This finding suggests local exposure, given the predicted slow and limited long-range environmental transport capacity of these compounds to the eastern Antarctic sector.

1Introduction

Persistent organic pollutants (POPs) are a suite of toxic, anthropogenic chemicals that resist degradation and bioaccumulate in organisms. They have the capacity to reach remote ecosystems far from their point of release and as such are ubiquitous in the global environment (Corsolini, 2009; Hung et al., 2013; UNEP, 2001). Long-range environmental transport through, for example, large-scale atmospheric and oceanic transport, has resulted in a portion of these chemicals being redistributed to colder regions of the planet where their persistence is further prolonged (Blais et al., 2005; Blais et al., 2007; Corsolini et al., 2011; Hale et al., 2006; Wania and Mackay, 1996). Polar regions thus serve as environmental sinks for the world's POP burden and represent important focus regions for global POP monitoring and research (Bengtson Nash, 2011; Bengtson Nash et al., 2017, 2021; Wania and Su, 2004). Atmospheric and ocean currents are, however, not the only environmental pathways by which POPs may reach Polar latitudes. Migratory species that spend part of their life-history foraging at lower

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latitudes have been shown to play a role in biologically mediated long-range environmental transport to Polar regions (Blais et al., 2005; Blais et al., 2007; Corsolini et al., 2011; Hale et al., 2006; Wild et al., 2014). Although this pathway is still poorly understood, biovector transport is likely to be of increasing importance in the context of altered species ranges in warming polar climates (Parmesan, 2006; UNEP/AMAP, 2011; Walther et al., 2002). The most recent Arctic Monitoring and Assessment (AMAP) report on Climate Change Trends and Impacts (AMAP, 2021), summarises the rapid and transformational changes occurring to Arctic ecosystems. Similar shifts may be anticipated in the South Polar region, driven by e.g. changed ocean circulation serving to introduce new phytoplankton assemblages; increased ocean productivity; and the exploitation of milder Antarctic climatic conditions by temperate consumers, leading to novel trophic linkages and ecosystem dynamics. Altered species ranges and trophic interactions, particularly among species across the Antarctic Circumpolar Current, carry marked potential for the introduction of contaminant to Antarctica (Bengtson Nash et al., 2010).

The high bioaccumulation and biomagnification potential of POPs facilitates biovector transport via avian biota. Both the atmospheric and oceanographic circulation patterns of the Antarctic region limit direct north-south transport of air masses and water bodies (Rintoul, 2000; Schneider and Sobel, 2007). As such, both water bodies and air masses from north of the Antarctic Convergence are expected to carry comparatively higher POP burdens due to the influence of diverse hemispheric pollution sources (Bengtson Nash et al., 2010). Antarctic migratory species that spend the austral winter feeding outside of Antarctica may therefore exhibit different profiles and higher levels of POPs compared to endemic species foraging entirely south of the Antarctic Convergence.

South polar skua (hereafter SPS; *Catharacta maccormicki*) breed during summer in Antarctica but undertake extensive north-south migrations during the austral winter (Kopp et al., 2011). They have often been shown to possess significantly higher POP burdens than Antarctic biota with life histories and foraging ranges entirely restricted to the Antarctic region (Bengtson Nash et al., 2010; Focardi, 1995). As such, they may ultimately serve as biovectors of POP contamination to Antarctica through local deposition of guano, abandonment of eggs, and mortality (Roosens et al., 2007; Roscales et al., 2016). While the contribution to the overall POP budget of the region via this pathway is likely to be small compared to other Long Range Environmental Transport pathways, it may carry a disproportionate local ecological and toxicological impact. While SPS do not form large colonies, they breed close to Adélie penguin colonies and form a long-term association with the same territory for breeding and feeding, and as a result, highly concentrated areas of pollution may be generated through accumulation of guano and carcasses in locations of elevated ecological and conservation importance (Robinson et al., 2018; Roosens et al., 2007).

The role of biologically mediated long range environmental transport of chemicals to the Antarctic was explored in the present study by targeting a range of POPs, both legacy and recently annexed under the Stockholm Convention, as well as a current-use industrial chemical. Chemical contaminants were targeted in muscle and guano of the highly migratory SPS, and of an archetypal endemic Antarctic bird species, the Adélie penguin (hereafter AP; *Pygoscelis adeliae*). This experimental design was used to test the hypothesis that the different trophic level of these two species is the primary driver of differential POP exposure and accumulation, whilst differences in winter foraging range is the main driver behind contrasting exposure profiles.

2. Methods

2.1. Study species

Two species were selected for the present study, SPS and AP. SPS breed along the Antarctic coast, laying eggs from November through December. This flying seabird migrates during the austral winter to the northern Pacific, Indian and Atlantic Oceans (Kopp et al., 2011; Weimerskirch et al., 2015). SPS are opportunistic scavengers, often feeding on fish stolen from other seabirds, as well as on AP eggs and chicks (Baker and Barbraud, 2001; Pietz, 1987). There are no population estimates of SPS for the Mawson, Davis and Casey station regions of the current study, but the total population across all regions is likely to number in the several thousands (Wilson et al., 2016). AP breed in dense colonies from October through February in rocky coastal areas around Antarctica (Ainley, 2002). During the austral summer, breeders forage close to their breeding colony, but during winter they can swim distances of several thousand kilometres from their breeding colonies to forage, though never north of the Antarctic Convergence in the current study region (Ballard et al., 2010). AP diet consists primarily of krill and small fish, such as Antarctic silverfish (*Pleuragramma antarcticum* Perciformes; Nototheniidae), with some regional preferences in diet observed (Emslie and Patterson, 2007). Population estimates of AP across the Antarctic region lie around 9.55 million breeding age birds (Southwell et al., 2017).

2.2. Sample collection

Pectoral muscle samples from SPS ($n = 7$) adults and AP chick ($n = 5$) carcasses were collected from areas near AP breeding colonies during the 2012/2013 and 2013/14 austral summers. Fresh SPS ($n = 21$) and AP ($n = 14$) guano samples were collected from these locations during the 2013/14 austral summer. The breeding colonies sampled were located between 2 and 30 km from Australia's three permanent Antarctic research stations along the East Antarctic coastline; Mawson (muscle: (SPS) $n = 3$; (AP) $n = 2$. Guano: (SPS) $n = 13$; (AP); $n = 9$), Davis (muscle: (SPS) $n = 1$. Guano: (SPS) $n = 5$; (AP) $n = 5$), and Casey (muscle: (SPS) $n = 3$; (AP) $n = 3$. Guano: (SPS); $n = 3$) (Fig. 1). Details of the collection locations and year for each sample can be found in Table SI-3 to Table SI-5.

Fresh guano samples were collected from the surface of snow or rock using solvent-washed stainless-steel or wooden spatulas and placed into furnaced, solvent-rinsed amber glass jars. Carcasses or parts of carcasses were collected whole and wrapped in aluminium foil and placed in sealed plastic zip-lock bags. All samples were then stored at −20 °C for transportation and storage prior to chemical analysis. Sub-sampling occurred at Griffith University in Brisbane, Australia. Subsequent chemical analyses for organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs) were conducted at the University of Antwerp, Belgium and for perfluoroalkyl substances (PFASs) at Aarhus University, Denmark. Bulk Stable Isotope (SI) analysis of muscle was performed at the University of Liège, Belgium.

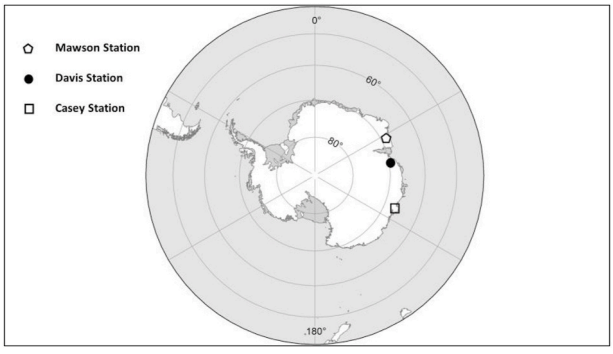

Fig. 1. Sampling Locations. The geographical location of Australia's three all-year Antarctic stations, where SPS and AP carcasses and guano were collected.

2.3. Stable isotope analysis

Stable Isotope analysis provides a quantitative tool for the investigation of foraging ecology, and therefore the interpretation of the dietary contaminant exposure pathway of an individual or species. $\delta^{13}C$ values allow for discrimination between the dietary carbon sources, often referred to as the foraging ecosystem, based upon characteristic ranges in the values of the respective primary producers which remain largely unchanged throughout the food chain. By contrast, $\delta^{15}N$ are typically enriched (trophic enrichments) along the food chain in a predictable fashion, thus serving as a quantitative proxy for an individual's trophic position (Eisenmann et al., 2016).

Species trophic level and carbon source were examined by bulk muscle stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope analysis. Freeze-dried muscle (mean ± SD: 1.65 ± 0.32 mg) was crimped into a tin combustion cup. Stable carbon and nitrogen isotope ratios were determined using isotopic ratio mass spectrometry (Isoprime 100, Isoprime, UK) coupled in continuous flow to an elemental analyser (Vario microtube, Elementar, Germany). Stable isotope ratios were expressed in δ notation in ‰ and relative to the international references; Vienna Pee Dee Belemnite (for carbon) and atmospheric air (for nitrogen). International Atomic Energy Agency (IAEA, Vienna, Austria) certified reference materials sucrose (IAEA-C-6; $\delta^{13}C = -10.8‰ \pm 0.5‰$; mean ± SD) and ammonium sulphate (IAEA-N-2; $\delta^{15}N = 20.3‰ \pm 0.3‰$; mean ± SD) were used as primary analytical standards. Glycine (Merck, Darmstadt, Germany; $\delta^{13}C = -47.5 \pm 0.3‰$; $\delta^{15}N = 2.25 \pm 0.3‰$; means ± SD) was used as the secondary analytical standard. The standard deviations on multi-batch replicate measurements of secondary and internal lab standards (amphipod crustacean muscle) interspersed with samples (one replicate of each standard every 15 analyses) were 0.3‰ for $\delta^{13}C$ and 0.2‰ for $\delta^{15}N$.

Published SI values for Antarctic and Australian species were used to provide references for SI values measured in the present study (Table SI-1). These included blood SI values from AP adults and chicks, SPS adults, as well as local prey samples such as Antarctic krill (*Euphausia superba*) and Antarctic silverfish (*Pleuragramma antarcticum*) collected in Adélie Land (Cherel, 2008). Blood samples from short-tailed shearwater (*Puffinus tenuirostris*), adults and chicks, were also used as a reference for Australian birds known to forage at both high and low latitudes (Cherel et al., 2005). Possible extra-Antarctic prey samples, i.e., local Australian krill species (*Euphausia* vallentini, and *Nyctiphanes australis*) (Cherel et al., 2005) were also included.

2.4. Organochlorine pesticides; polychlorinated biphenyls, and brominated flame retardant analysis

The analytical procedures for OCPs, PCBs, and BFRs followed protocols earlier established by Eulaers et al. (2011). Briefly, muscle tissue from single individuals (median = 4.43 g; range = 3.41–5.88 g) or pooled guano from single sites and collection years (median = 4.90 g; range = 1.29–5.75 g) were analysed. Guano samples were combined based on location to meet minimum sample requirements. This resulted in two composite analytical AP guano samples from an original 14 samples (one for locations near Mawson Station and Davis Station respectively), and 18 SPS from an original 21 collected guano samples (13 analytical samples for Mawson Station, 3 for Davis Station, and 2 for Casey Station). All samples were dried and homogenized with 1 g of Na_2SO_4, spiked with an internal standard mixture consisting of PCB-143 (CB-143), polybrominated diphenyl ether 77 (BDE-77), ε-hexachlorocyclohexane (ε-HCH), ^{13}C-tetrabromobisphenol-A (^{13}C-TBBPA), labelled α-, β-, and γ-diastereoisomers of hexabromocyclododecane (^{13}C-α, ^{13}C-β and ^{13}C-γ-HBCDD) prior to hot soxhlet extraction for 2.5 h using a hexane:acetone mixture (3:1; v:v). The extract was further cleaned using sulphuric acid and acidified silica Purified extracts were fractionated using Silica Bond Elut™ SPE cartridges (500 mg, 3 mL, Agilent Technologies). The first fraction (F_1), containing PCBs, OCPs and polybrominated diphenylethers (PBDEs), was eluted with 8 mL of hexane, and the second fraction (F_2), containing HBCDDs and TBBPA with 8 mL of dichloromethane. Both fractions were evaporated to dryness under a gentle nitrogen flow and reconstituted in *iso*-octane (F_1) or methanol (F_2) prior to quantification.

Medium and highly chlorinated PCB congeners (IUPAC: CB-105, -128, −146, −156, −170, −171, −174, −177, −180, −183, −187, −194, −196/203, −199, −206 and −209), PBDE congeners (IUPAC: BDE-28, -47, −49, −99, −100, −153, −154 and −183), HCH-isomers (*α*-, *β*-, and *γ*-HCH) and chlordane compounds (oxychlordane (OxC), *trans*- (TN) and *cis*-nonachlor (CN), and *trans*- (TC) and *cis*-chlordane (CC)) were quantified using a gas chromatograph (GC; Agilent GC 6890, Palo Alto, CA, USA; DB-5 capillary column of 30 m × 0.25 mm x 0.25 μm) coupled to a mass spectrometer (MS; Agilent MS 5973) operated in electron capture negative ionization mode. The remaining PCB congeners (IUPAC: CB-28, -49, −52, −74, −95, −99, −101, −110, −118, −138, −149, −151 and −153), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane and metabolites (*p,p′*- and *o,p′*-DDT; *p,p′*- and *o,p′*-DDD; *p,p′*-DDE), were quantified using a GC equipped with an HT-8 capillary column (25 m × 0.22 mm × 0.25 μm; SGE Analytical Science, Zulte, Belgium), coupled to an MS operated in electron impact mode. The BFRs HBCDD and TBBPA were quantified using a liquid chromatography system (LC; Agilent LC 1100 series) equipped with a Luna C18 (2) reversed phase column (150 mm × 2 mm; 3 μm particle size; Phenomenex, Utrecht, the Netherlands) coupled to a tandem mass spectrometer (Agilent 6410).

Pesticide/GC grade solvents and reagents were obtained from Merck KGaA Chemicals (Darmstadt, Germany) and Acros Organics (Geel, Belgium). A procedural blank was analysed every seven samples. Interlaboratory comparisons have shown the high analytical accuracy and precision of the analytical methods employed (Gill et al., 2004; Kucklick et al., 2009). Analytical results of all compounds were blank subtracted using their average procedural blank values. The limit of quantification (LOQ) was defined as three times the standard deviation of the procedural blanks, or, for analytes not detectable in blanks, calculated from a 10:1 signal-to-noise ratio. LOQs in muscle ranged from 0.01 to 0.20 ng g^{-1} wet weight (ww) or 0.25–10.00 ng g^{-1} lipid weight (lw), while those in guano ranged from 0.01 to 0.20 ng g^{-1} dry weight (dw). A complete list of LOQs is provided in Tables SI-3,4.

2.5. Perfluoroalkyl substance analysis

There were insufficient sample volumes for all muscle tissue samples to be analysed for PFAS compounds, so only samples with large enough volumes to cover both PFAS and OCPs, PCBs, and BFRs analysis were used (SPS; $n = 3$; AP; $n = 4$). The extraction method for PFAS was based on that of Ahrens et al. (2009). In summary, approximately 5 g of muscle tissue sample was homogenized and a 1 g aliquot weighed into a polypropylene tube and spiked with 10 ng of an internal standard mixture (Table SI-2). Native and labelled compounds were purchased as mixtures from Wellington Laboratories (Guelph, ON, Canada). Muscle samples were extracted with 5 mL of acetonitrile twice for 30 min in an ultrasonic bath at 30 °C. The combined extract was cleaned using Supelclean ENVI-Carb® cartridges (100 mg, 1 mL, 100–400 mesh, Supelco, USA), conditioned with acetonitrile followed by 20 % acetic acid in acetonitrile. The sample extract was eluted with methanol, reduced to dryness and reconstituted in methanol/2 mM ammonium acetate (50:50, v:v) for quantification.

Samples were analysed for perfluorooctanesulfonamide (PFOSA) together with nine perfluorinated carboxylates, i.e. perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorotridecanoate (PFTrA) and perfluorotetradecanoate (PFTeA), and five sulfonates, i.e. perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluoroheptanesulfonate (PFHpS),

perfluorooctanesulfonate (PFOS), perfuorodecanesulfonate (PFDS). Quantification was performed by using an Agilent 1200 Series HPLC (Agilent, Palo Alto, CA, USA). The HPLC was interfaced to a QTrap 5500 (AB Sciex, Framingham, CT, USA) equipped with a Turbulon Ion Spray source operating in negative ionization mode. The system used a C18 Kinetex column (2.6 μm particle diameter, 2.1 × 150 mm, Phenomenex, Torrance, CA, USA) Quantification was performed using response factors calculated by a five-point calibration curve from 0.10 to 40.00 ng g^{-1} ww. The samples were extracted and analysed in batches together with a procedural blank. The LOQwas defined as three times the standard deviation of the concentrations calculated in the blanks ($n = 8$). The LOQs of the analysed compounds are summarized in Table SI-5.

2.6. Statistical analyses

The cosine theta similarity metric (cos θ) (John, 1986) was employed to compare the similarity of PCB, OCP, and PBDE congener profiles between AP and SPS muscle tissue and between guano of AP and SPS. This metric calculates the cosine of the angle between two multivariate vectors. The cos θ metric is calculated from the formula for a Euclidean dot product of two vectors according to:

$$\cos\theta = \frac{\sum_{k=1}^{n}(x_{ak}.x_{sk})}{\sqrt{\sum_{k=1}^{n}x_{ak}^2}\cdot\sqrt{\sum_{k=1}^{n}x_{sk}^2}}$$

where, x_{ak} is the concentration (ng g^{-1} lw) of congener k in AP muscle tissue or guano, x_{sk} is the concentration of the same congener in SPS muscle tissue or guano and n the number of PCB, OCP or PBDE congeners analysed. Values of cos θ can range from 0.0 to 1.0, with 1.0 representing a perfect match, and 0.0 indicating perpendicular vectors and no similarity between the congener profiles (Saba and Boehm, 2011). This approach has been used previously to quantify the similarity of PCB congener profiles in sediment and air (Du and Rodenburg, 2007; Magar et al., 2005; Rodenburg et al., 2011; Saba and Boehm, 2011). For cos θ analysis, analyte concentrations below the LOQ were substituted for half LOQ, to reduce the influence of samples with non-detection, overestimating the similarity between congener profiles (Kang et al., 2010; Loppi et al., 2015). For all other analysis, and when presenting other statistics such as means and standard error, analyte concentrations below the LOQ were treated as zero (0), reducing the risk of overestimating contaminant profiles.

A Multi-Dimensional Scaling (MDS) diagram, based on a presence/absence transformation and Bray-Curtis resemblance matrix, was produced in PRIMER v.7 to visualize chemical profile differences in bird muscle tissues. MDS plots represent dissimilarities between two objects by distance on a diagram, such that objects more similar are closer together than objects that are less similar.

Paired comparisons to test significance of the difference of means between species chemical concentrations was done by Wilcoxon's matched pairs test (by Statistica v7.1).

3. Results and discussion

3.1. Trophic position separation and extra-antarctic foraging

δ^{15}N values measured in APs (range; +9.03 to +10.72‰) were consistent with values previously reported for blood collected from AP adults and chicks (Cherel, 2008), and aligned with the expected trophic enrichment when compared to published values for Antarctic krill (Figure SI-1) (Cherel, 2008). Similarly, SPS muscle δ^{15}N values (range; +11.65 to +14.08‰) corresponded with δ^{15}N values obtained for red blood cells of SPS chicks from Adélie Land (+11.4‰) (Carravieri et al., 2017), and placed the SPS individuals sampled in the present study as feeding approximately one trophic position (assuming trophic enrichment of 3.4‰) (Post, 2002) higher than the AP individuals studied here.

Reference δ^{13}C values were utilised to discriminate foraging in Antarctica versus lower latitudes (Figure SI-1). The δ^{13}C values of APs (range; −26.28 to −24.72‰) all adhered closely to those expected from a low trophic level Antarctic diet (≤-25‰; Figure SI-1) (Cherel, 2008; Eisenmann et al., 2016). By contrast, there was increased heterogeneity among SPS individuals, where six of the studied individuals showed δ^{13}C values (range; −24.22 to −21.44‰) intermediate between those of typical Antarctic and typical Tasmanian (−20‰) foraging grounds (Figure SI-1). However two SPSs showed δ^{13}C values (−14.46 and −18.98‰) more closely associated with lower latitude provisioning (Figure SI-1). This apparent bimodal distribution in δ^{13}C values suggests high inter-individual variation in the geographical origin of energetic provisioning. This could be influenced by a number of factors, such as life-stage, individual foraging, and by the inter-individual differences in the time spent in Antarctica immediately prior to death.

A study by Cherel et al. (2005) on Tasmanian-breeding Short-tailed shearwaters reported stable isotope values in surveyed chicks comparable those in the present study for SPSs. By contrast, adult shearwaters had values close to those of APs (Figure SI-1). These authors concluded that chicks received a mixture of Antarctic- and Tasmanian-sourced food, while parents fed exclusively on Antarctic prey (Cherel et al., 2005). By extension, SPS δ^{13}C values in the current study may also reflect an integrated signal resulting from a mixture of Antarctic and lower latitude feeding.

3.2. Contaminant burdens

Of the 65 pollutants targeted, all but nine, namely CB-52, CB-49 and CB-95, α-HCH and five PFASs (PFBS, PFHpS, PFOSA, PFHxA and PFHpA) were detected in the muscle and guano of either of the investigated bird species (Table SI-6). Whilst there was a marked difference in the tissue concentrations measured between the species, reflecting their respective trophic position, the relative contributions of compounds to the overall contaminant profiles of SPS and AP generally showed a moderate degree of commonality (cos $\theta \geq 0.6$). This indicates a similar trophic magnification pathway, as might be expected through a direct predator/prey comparison such as is this. When all chemical data of bird muscle tissue were compiled for MDS analysis based on presence/absence similarity however, differences were sufficient to separate the data by species (Fig. 2), indicating species profile distinctions, unrelated to relative profile contribution or absolute concentrations.

In both species, muscle and guano burdens were dominated by *p,p′*-DDE and HCB, previously and consistently reported as the dominant legacy POPs accumulating in Antarctic food webs (Bengtson Nash et al., 2008; Bengtson Nash et al., 2013; Bustnes et al., 2006; Court et al., 1997; Poulsen et al., 2013; Waugh et al., 2014). Some distinct differences in the PCB profiles were indicative of extra-Antarctic exposure for SPS, whilst the unexpected presence of the recently used PFASs and HBCDD in both species raised the possibility of local Antarctic sources.

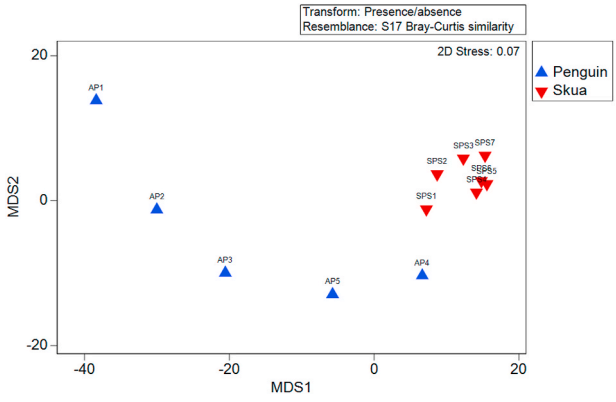

Fig. 2. MDS Plot of all bird muscle chemical data.

3.3. Organochlorine pesticides

The OCP profiles of the two study species showed a high degree of similarity (cos $\theta = 0.82$; Fig. 1), although concentrations measured in SPS muscle were up to two orders of magnitude higher than those in AP muscle. The different life stages of SPS (adults) and AP (chicks) sampled for the present study must be noted in these and following, concentration comparisons, as should the relatively small sample numbers available. Similarly, body condition assessment of neither species could be performed, which is known to significantly impact tissue burdens of lipophilic contaminants in SPS and other marine megafauna (Bengtson Nash, 2018; Bengtson Nash et al., 2013; Midthaug et al., 2021). Nonetheless these data provide novel baseline information for comparison. The most abundant OCPs in these SPS samples were *p,p′*-DDE (mean = 5560 ng g^{-1} lw) and HCB (mean = 2540 ng g^{-1} lw) whilst for AP, the order of these dominant compounds was reversed (*p,p′*-DDE: mean = 330 ng g^{-1} lw; HCB: mean = 570 ng g^{-1} lw and mean). The ratio of *p,p′*-DDT: *p,p′*-DDE was similar in both species suggesting that exposure to a similarly degraded source of DDT (Roosens et al., 2007).

Of the three HCH isomers, *β*-HCH shows the highest resistance to environmental degradation and the highest biomagnification potential due to higher K_{oa} and K_{ow} values (Hansen, 2006). *β*-HCH is, however, also less volatile. As a result, *β*-HCH is typically the dominant HCH isomer observed in biota outside of Polar regions (Corsolini et al., 2006;

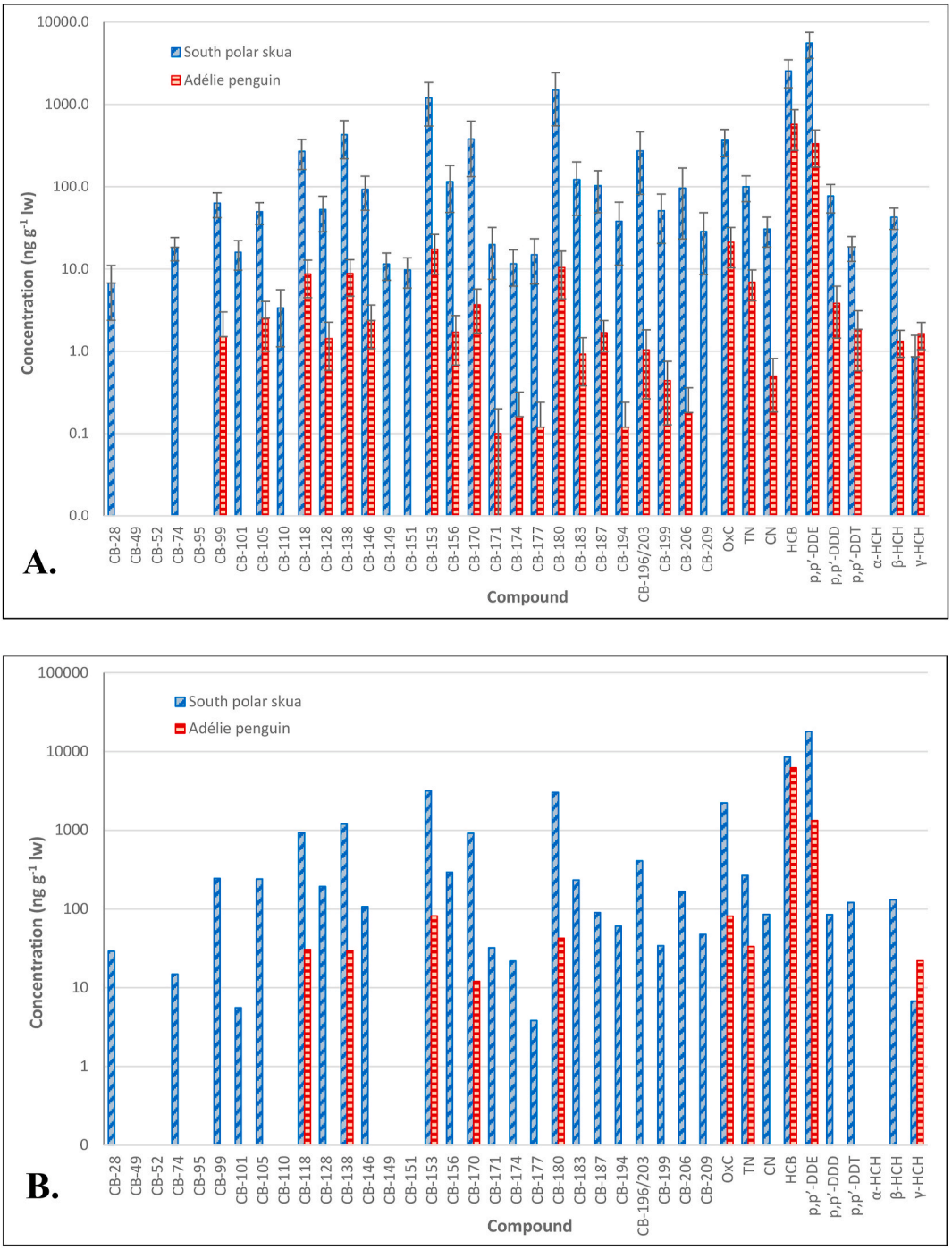

Fig. 3. Mean (±SE) PCB and OCP concentrations (log scale) in muscle (A) and guano (B) of South polar skua and Adélie penguin. Standard error values unavailable for guano as composite samples were used.

Hansen, 2006; Willett et al., 1998), whilst the majority of HCH exposure in Antarctic biota is to α-HCH and γ-HCH (Cincinelli et al., 2011; Corsolini et al., 2006). For both species, β- and γ-HCH were detected, whereas α-HCH was not. γ-HCH was found at higher concentrations in AP muscle than in SPS muscle (mean = 1.60 ng g^{-1} lw versus 0.90 ng g^{-1} lw). The dominance of β-HCH over γ-HCH in SPS muscle profile suggests exposure to a newer, less degraded source of HCH outside of Antarctica. Similarly, the elevated levels of γ-HCH in AP tissue reflect the isomer's effective poleward deposition.

Species concentration differences in guano were more pronounced than those in muscle tissue with SPS guano contaminant levels on average 10 times higher than those in AP guano ($p = 0.01$, AP: 21 ± 92 ng g^{-1} lw, SPS 276 ± 878 ng g^{-1} lw). As with the muscle concentrations, SPS guano was dominated by *p,p′*-DDE (mean = 18000 pg g^{-1} dw) with HCB being the second highest OCP (mean = 800 pg g^{-1} dw). For AP guano this pattern was again reversed (*p,p′*-DDE: mean = 1300 pg g^{-1} dw; HCB = 6200 pg g^{-1} dw). OxC was the third highest OCP in both muscle and guano for both SPS and AP (mean: 2230 pg g^{-1} dw and 81 pg g^{-1} dw, respectively). The only other OCPs detectable in AP guano were TN and γ-HCH, whereas all OCPs analysed for, except for α-HCH, were detected in SPS guano.

The OCP pollutant profiles of SPS and AP guano were less similar to each other than muscle samples ($\cos\theta = 0.60$; Fig. 3). The main driver of this profile difference between AP muscle and guano was that CN, *p,p′*-DDD, *p,p′*-DDT and β-HCH were detectable in muscle but not in guano. As these compounds were found at the lowest concentration of all OCPs in muscle, their absence from guano is perhaps not surprising considering the lipophilic nature of these compounds, and in this matrix they may fall below the method's LOQ.

3.4. Polychlorinated biphenyls

The PCB congener profiles of SPS and AP muscle were moderately similar ($\cos\theta = 0.81$) although concentrations were two to three orders of magnitude higher in SPS ($p < 0.001$, Fig. 3). The more persistent congeners, i.e. CB-118, -138, −153, −170 and −180 dominated the muscle profiles (Court et al., 1997). Together, the hepta- and hexa-PCB congeners CB-153 and -180 made up over 50 % of the muscle PCB burden in the migratory SPS (range: 200–7000 ng g^{-1} lw) and 40 % in the endemic AP (range: 2–53 ng g^{-1} lw).

Despite overall similarities between the species-specific PCB profiles, there were some marked differences. Of the 29 PCB congeners analysed for, only 3 were not detected in SPS whereas 10 were not detectable in AP. Furthermore, in SPS, hexa- and hepta-chlorinated PCBs contribute approximately equally to the profile. By contrast, hexa-chlorinated PCBs constitute a higher proportion in AP (Figure SI-2). Relatively higher accumulation of higher chlorinated PCB congers in SPS likely reflects a number of factors. Firstly, foraging closer to source regions results in greater exposure to higher chlorinated and less volatile PCB congeners (Bustnes et al., 2006; Cipro et al., 2013; Corsolini et al., 2007; Tanabe et al., 1986). Secondly, a higher position in the food chain results in a longer exposure pathway associated with several stages of metabolic conversion and/or elimination. Indeed, a change in dominance from tri-, tetra- and penta-PCBs in Antarctic krill and fish (Bengtson Nash et al., 2008), to hexa-PCBs in AP and finally hexa- and hepta-PCBs in SPS is often observed. This pattern suggests stepwise removal of more readily metabolised, lower chlorinated PCBs, combined with resistance of the larger PCB congeners to metabolic conversion and hence their consistent biomagnification along this Antarctic food chain (Bengtson Nash et al., 2008; Corsolini et al., 2011). In addition to trophic level and foraging proximity to emissions sources, species-specific differences in detoxification ability can also not be discounted as influencing the observed detection of lower chlorinated PCB congeners in SPS but not AP muscle, (CB-28, -74, −101, −110, −149 and −151). Finally, this pattern may also simply also be an artefact of method detection levels and species trophic position, with SPS having greater potential for bioaccumulating levels above the LOQ.

CB-209 was consistently detected in SPS, but not AP muscle. This pattern is consistent with exposure of the migratory SPS during extra-Antarctic foraging, as the relatively large molar mass and low vapour pressure of this congener renders it less likely to undergo effective atmospheric long-range transport.

Overall, the PCB profiles of SPS muscle and guano (Figure SI-3) appeared very similar to each other ($\cos\theta = 0.96$), whilst the similarity of PCB profiles of AP muscle and guano was slightly less ($\cos\theta = 0.79$). By contrast, there was a high degree of dissimilarity evident between SPS and AP guano pollutant profiles ($\cos\theta = 0.45$). SPS guano contained PCB concentrations 1 to 2 orders of magnitude higher than that of AP (Fig. 3). As seen with muscle tissue, CB-153 and -180 dominated PCB profiles of both species' guano. However, unlike in muscle, only 5 of 29 targeted PCB congeners, i.e., CB-118, -138, −153, −170 and −180, were above the LOQ in AP guano compared to 23 quantified congeners in SPS guano.

3.5. Brominated flame retardants

Concentrations of BFRs were found to be higher in SPS compared to AP muscle, however the difference was less pronounced than that observed for other contaminant groups. BFR profiles on the other hand, showed a relatively higher degree of dissimilarity between the species ($\cos\theta = 0.6$) (Fig. 4).

The PBDE profile of AP muscle was consistent with the penta-BDE technical mixture, being dominated by tetra- and penta-BDE congeners (Figure SI-4). This pattern of contamination has previously been observed in AP eggs from King George Island near the Antarctic Peninsula (Yogui and Sericano, 2009) and also AP from the east Antarctic sector (Lewis et al., 2020). SPS muscle, on the other hand, was relatively depleted in penta-brominated congeners and showed higher levels of hexa-BDEs. It has previously been suggested that higher brominated PBDE burdens in Antarctic migratory seabirds are most likely attributed to exposure occurring north of the Antarctic Convergence (Yogui and Sericano, 2009). Notably, the sum of penta-BDE congeners BDE-47, -99 and −100 muscle concentrations contributed over 90 % of the total PBDE burden in AP while only 47 % in the migratory SPS. The latter profile contribution is closer to that found in seabirds from the north-western Pacific Ocean, near Japan and China, including in the herring gull (*Larus argentatus*), which shares a similar opportunistic scavenger niche as SPS (Wan et al., 2008; Watanabe et al., 2004). Emissions of PBDEs from local Antarctic human activities (e.g. research stations) in the study region have previously been evidenced (Wild et al., 2014), hence *in-situ* Antarctic exposure must also be considered in interpretation of these results.

Both HBCDDs (recently annexed under the Stockholm Convention), and the current-use BFR, TBBPA, were detected in both the migratory and endemic study species. This is only the third time that HBCDDs have been reported in Antarctic biota (Kim et al., 2021; Kim et al., 2015), with previous studies confirming biomagnification along Antarctic food chains. Although all three targeted HBCDD stereoisomers were found in higher concentrations in SPS samples compared to AP samples, the latter were found to have a higher proportion of γ-HBCDD versus β-HBCDD (Fig. 4). Levels of both isomers were however lower than the dominant α-HBCDD which is the most persistent (Ueno et al., 2006). Although industrial manufacture of HBCDD has been ongoing for at least the past three decades (Hussain, 1986), it has been almost entirely restricted to the northern hemisphere (Ueno et al., 2006). While its presence in Antarctica may be a result of long-range environmental transport from HBCDD-containing consumer product emissions in the southern hemisphere, the recent detection in both wastewater and surrounding sediment of two Antarctic research stations (Chen et al., 2015), again raises the possibility of local source emissions. Levels of HBCDDs within a number of bird species in Europe and North America are approaching or have surpassed those of PBDEs (Agrawal et al., 2008; Eulaers et al.,

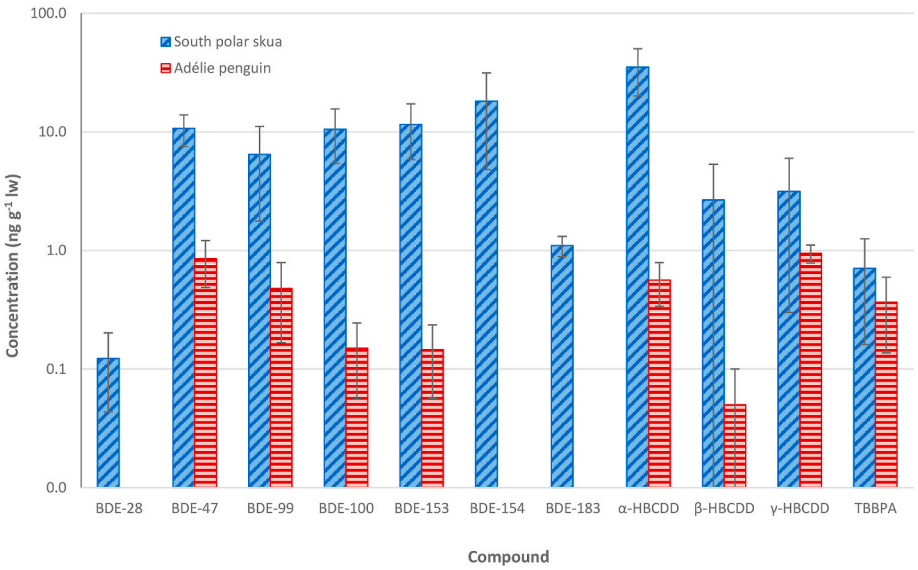

Fig. 4. Mean (±SE) BFR concentrations (log scale) in South polar skua and Adélie penguin muscle.

2014). This appears to be linked to the regulatory lag between the listing of HBCDD relative to PBDEs under the Stockholm Convention (Miller et al., 2014). Although the levels of HBCDD in both SPS and AP penguin muscle were not as high as ΣPBDEs, they were within 30 % of each other. Notably, HBCDD levels observed in SPS and AP muscle in the current study are similar to those found in bird species from the Arctic (Letcher et al., 2010).

TBBPA was detected in muscle of both SPS and AP muscle, which, to the knowledge of the authors, represents the first detection of this compound in any Antarctic matrix. Similar to HBCDDs, the production of TBBPA has been largely limited to the Northern Hemisphere, although its usage in consumer products is widespread (de Wit et al., 2010). TBBPA is predominantly chemically bound through covalent bonding to the polymeric backbone of the resin in its applications and thus tends to have lower bioavailability. As a result the compound is often detected in lower concentrations than PBDEs and HBCDDs in bird tissue, particularly higher trophic level species (Eulaers et al., 2014) This trend was observed also in the current study.

As with muscle, SPS and AP guano were dominated by different PBDE congeners (Fig. 4), although profile differences were less pronounced (cos θ = 0.80). SPS guano contained a higher proportion of hexa-BDEs, whereas the AP guano profile was again more similar to that of the penta-BDE technical mixture. In contrast to muscle, however, the levels of most BFRs detected in guano were similar between both species ($p = 0.86$, AP: 11 ± 14.8 ng g^{-1} lw, SPS 8.5 ± 9.9 ng g^{-1} lw).

A number of analytes that were quantified in muscle tissue were not observed in guano. This anomaly may be attributed to differing matrix LOQs, physiological differences in intestinal uptake and excretion between species, or differences between past dietary exposure (muscle), versus recent, Antarctic dietary exposure (guano).

3.6. Perfluoroalkyl substances

Bengtson Nash (Bengtson Nash et al., 2010) and others (e.g. Schiavone et al., 2009b; Tao et al., 2006), have previously evaluated the distribution of PFAS in diverse Antarctic biota. Collation of existing literature from the region only found evidence of detectable levels of PFAS in migratory bird species as well as in penguin and seal populations resident on the Antarctic Peninsula for which foraging trips could, and likely do, extend into and north of the Antarctic Circumpolar Current. The current detection of PFASs in entirely Antarctic foraging AP colonies may therefore indicate a change in environmental exposure to these compounds, likely through local sources. It should, however, also be noted that the LOQs in the present study were lower than in previous studies (Giesy and Kannan, 2001; Schiavone et al., 2009a; Tao et al., 2006).

Overall, both our migratory and endemic bird species had a similar PFAS profile (cos θ = 0.88) for muscle tissue (guano was not analysed), although concentrations found in SPS muscle were one order of magnitude higher than those in AP muscle (Fig. 6). Differences in the concentrations between both species appear to reflect the different trophic positions rather than profile differences that might flag northern hemisphere exposure for SPS.

In terms of individual PFAS analytes, both AP and SPS muscle samples were dominated by PFOS, with concentrations (ww basis) comparable to those measured in previous studies on eggs and blood of Antarctic birds that feed north of the Antarctic Convergence (Fig. 5) (Schiavone et al., 2009a; Tao et al., 2006). Relatively high levels of PFUnA and PFTrA were also present in the muscle profiles. As with BFRs, PFAS have previously been detected in treated wastewater released from a nearby Antarctic research station, suggesting the possibility of exposure to local sources (Wild et al., 2014). Of note however, is that although muscle samples from this study were dominated by PFOS as well as PFUnA and PFTrA, the latter two compounds were only detectable in low concentrations in wastewater samples (Wild et al., 2014). Wastewater samples were instead dominated by PFOS along with PFOA and PFDS. However the latter two compounds exhibited some of the lowest concentrations among quantified PFAS in the current study (Wild et al., 2014). This discrepancy is suggestive of either an alternate and possibly remote source of these PFASs, or differential uptake and metabolism, and hence bioaccumulation of these compounds.

4. Conclusion

The present study investigated biologically mediated long-range environmental transport of POPs to Antarctica by examining muscle and guano samples from both a migratory and an endemic bird species. Much larger POP burdens were observed in tissue and, to a lesser extent, in guano of the migratory SPS as compared to the endemic AP. This difference could be explained by their respective trophic positions as evidenced through stable isotope analysis.

The chemical profiles of OCPs in SPS and AP demonstrated a high degree of similarity, indicating similar food web exposure pathways. The experimental design hypothesised that differences in the species

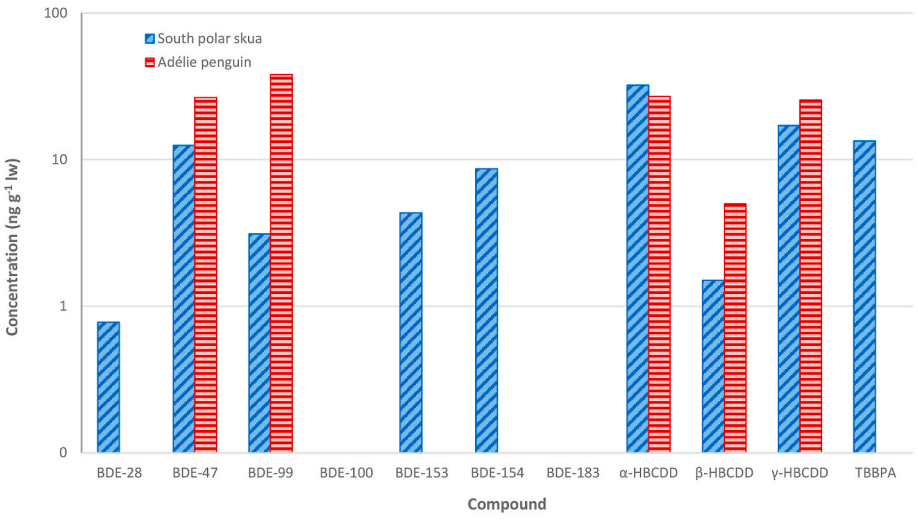

Fig. 5. Mean BFR concentrations in Adélie penguin and South polar skua guano (log scale). Standard error values are unavailable as pooled samples were analysed.

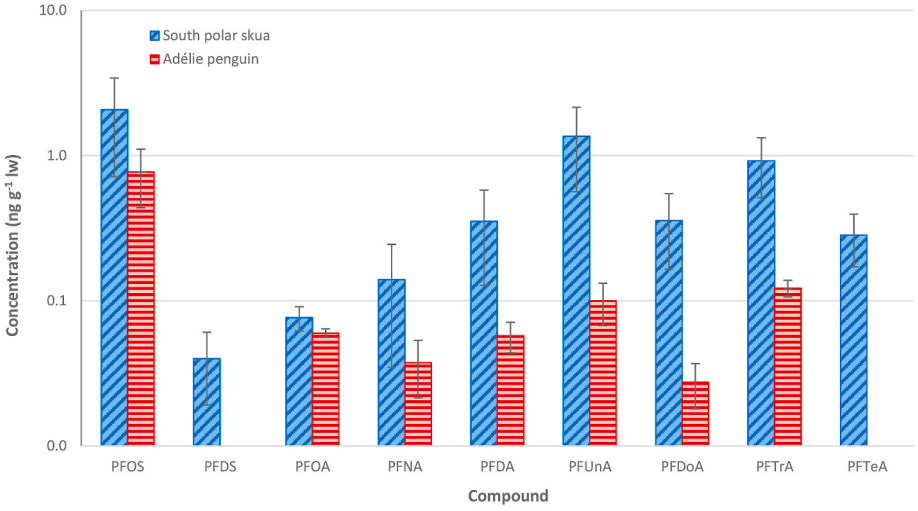

Fig. 6. Mean (±SE) PFAS concentrations (on a log scale) in muscle of South polar skua and Adélie penguin.

profiles of current or recently used chemicals, such as TBBPA, HBCDDs and PFASs, would facilitate discrimination of the respective exposure pathways of the two species. Rather, the results revealed the omnipresence of these compounds in both species. Clearer differentiation of exposure origin was instead derived from legacy POP profiles. These results provide evidence for a greater chemical footprint of present-day local human activities than previously documented, which carries significant implications for international commitments to the Protocol on Environmental Protection to the Antarctic Treaty (ATSecretariat, 2016). Findings contribute further valuable information for the distinction of local versus long-range contaminant sources under long term atmospheric monitoring programs (Bengtson Nash et al., 2021). Although it is not possible from the present study to provide a quantitative estimate on the relative proportion of compound-specific input to the Antarctic region that can be attributed to migratory species, it is clear that both studied bird species are playing a role in the localised biological concentration or focussing of pollutants in the natural environment, into areas of great biological and conservation significance within Antarctica. The role of biologically mediated long-range environmental transport stands to increase as temperate species ranges shift southward in response to warming Antarctic temperatures, serving to increase the potential for novel trophic linkages. Future efforts should focus on a broadened analyte repertoire, including known and unknown Antarctic chemical contaminants, through broadened targeted, as well as untargeted, analytical approaches.

Author statement

Seanan Wild: Conceptualization, Analysis, Investigation, Writing – original draft; Igor Eulaers: Analysis, Investigation, Writing – review & editing. Adrian Covaci: Analysis, Resources, Writing – review & editing. Rossana Bossi: Analysis, Resources, Writing – review & editing. Darryl Hawker: Investigation, Supervision, Writing – review & editing, Roger Cropp: Investigation, Supervision, Writing – review & editing. Colin Southwell: Resources, Writing – review & editing, Louise Emmerson: Resources, Writing – review & editing, Gilles Lepoint: Analysis, Writing – review & editing. Pascale Eisenmann: Analysis, Writing – review & editing. Bengtson Nash: Conceptualization, Resources, Writing – original draft, Supervision, Project administration and Funding Acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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