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Highlights

- PFAS and TEs detected in the feathers of Wilson's storm petrel and Cape petrel.
- Wilson's storm petrel has higher PFAS levels due to Northern Hemisphere migration.
- PFAS exposure is not strongly correlated with trophic position.
- PFUnDA concentrations indicate a pattern of biodilution.
- Migration patterns do not seem to influence trace element (TEs) concentrations.

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Assessing the Trophic Ecology and Migration on the Exposure of Cape Petrels and Wilson's Storm Petrels from Antarctica to Perfluoroalkylated Substances, Trace and Major Elements

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Abstract

Chemical pollution is a global concern as contaminants are transported and reach even the remote regions of Antarctica. Seabirds serve as important sentinels of pollution due to their high trophic position and wide distribution. This study examines the influence of migration and trophic ecology on the exposure of two Antarctic seabirds, Wilson's storm petrel (*Oceanites oceanicus* - Ooc), and Cape petrel (*Daption capense* - Dca), to chemical elements and perfluoroalkyl substances (PFAS). Our methodology involved assessing the concentration of these pollutants in feather samples obtained from carcasses, offering a practical means for monitoring contamination. Trace and major element concentrations were comparable in both species, suggesting that migratory patterns have a minimal impact on exposure levels. However, Ooc had higher concentration of PFAS compared to Dca (mean, ng g^{-1}dry weight, PFOA: Ooc:0.710, Dca:0.170; PFTrDA: Ooc:0.550, Dca:0.360, and PFTeDA: Ooc:1.01, Dca:0.190), indicating that migration to the more polluted Northern Hemisphere significantly affects PFAS exposure. Furthermore, while no strong associations were found between either trace elements or PFAS and the three stable isotopes ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$), a negative association was observed between PFUnDA and $\delta^{15}N$, hinting at potential biodilution. The research concludes that the migratory patterns of these seabird species affect their PFAS exposure, underscoring the critical need for further exploration and understanding of these relationships to better inform conservation strategies.

Keywords: metals, PFAS, seabirds, feathers, polar environment

1. Introduction

Antarctica is the only continent without permanent human residents or industrial activities, making the region pristine with lower anthropogenic pressures than the rest of the globe (Abrams, 1985; Bargagli, 2008; Jerez et al., 2011; Metcheva et al., 2010; Polito et al., 2016). However, due to the long-range transport of contaminants and the increasing number of research stations and tourist activities, Antarctica has been experiencing various environmental impacts, including the rising concentrations of several contaminants such as trace elements, which are concerning for living organisms due to their bioaccumulative nature and potential toxicity (Bargagli, 2008; Jerez et al., 2011;

Padilha et al., 2021; Tin et al., 2009). Trace elements occur naturally in the environment, but anthropogenic activities such as mining, agriculture and industry, can render them bioavailable in various ecosystems, including Antarctica (Bargagli, 2008). The isolation of the region, along with shorter food chains, makes Antarctica an important site for pollution studies (Gao et al., 2020). Although, the primary source of pollution in Antarctica comes by long-range global transport, the King George Island, chosen for this study, houses several research stations and is a popular location for tourist activities, which significantly contribute to the local input of contamination in the area (Espejo et al., 2018a; Jerez et al., 2011; Tin et al., 2009).

In addition to trace elements, emerging anthropogenic compounds such as perfluoroalkyl substances (PFAS) can also be found in Antarctica, far from their production sites (Gao et al., 2020; Roscales et al., 2019). Many PFAS are resistant to fat, oil, water, and heat, making them useful in stain- and water-resistant fabrics, specific packaging for fatty foods, non-stick cookware, among many other applications (Buck et al., 2011). Although the exact transport mechanism is not yet fully understood, PFAS can reach other regions of the globe through atmospheric and/or oceanic currents (Young & Mabury, 2010; Zhao et al., 2012), and exposure to PFAS can cause various health issues such as cancer, liver dysfunction, chronic kidney damage, among others (Podder et al., 2021). Some PFAS, including perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorohexane sulfonic acid (PFHxS) have been regulated and banned under the Stockholm Convention, an international agreement created to protect human health and the environment from a range of persistent pollutants (Stockholm Convention, 2023). However, the production of alternative compounds continues to increase, and their impacts are still not fully understood (Filipovic et al., 2015; Groffen et al., 2017; Stockholm Convention, 2018; Wang et al., 2013).

Seabirds are important sentinels of pollution due to their high trophic position, wide distribution, and longevity (Espejo et al., 2018b; Jerez et al., 2011; Metcheva et al., 2006; Padilha et al., 2021), and migratory birds can carry contaminants to Antarctica, as they travel to more polluted regions during the southern winters and return to breed during the summer (Cipro et al., 2018; Costa et al., 2019). Wilson's storm petrels (*Oceanites oceanicus*) are known for their extensive migration distances and are frequently observed in the northern hemisphere (Flood & Fisher, 2010; Kitching, 2002; Nakamura et al., 1983; Warham, 1990), while Cape petrels *(Daption capense*) only reaches the waters of the southern Atlantic Ocean (BirdLife International, 2018; Croxall & Wood, 2002). Feeding is the primary route through which avian species are exposed to pollutants, which can accumulate in organs such as the liver or kidneys (Burger, 1993; Bargagli, 2008; Celis et al., 2018). Subsequently, pollutants can be eliminated through the molting process and sequestered in feathers (Burger, 1993; Bargagli, 2008; Celis et al., 2018).

Feathers are connected to the bloodstream during their growth, incorporating contaminants during their formation (Costa et al., 2019; Groffen et al., 2020; Jaspers et al., 2006; Løseth et al., 2019). They serve as an important pathway for the detoxification of organic and inorganic pollutants (Burger, 1993; Jaspers et al., 2019; Rutkowska et al. 2018). While feathers are recommended as an alternative to invasive matrices, such as organs and tissues, in the analysis of metals and POPs, limited information is currently available for emerging contaminants leaving uncertainties about the usefulness of feathers for studying other pollutants such as PFAS (Jaspers et al., 2019). For PFAS and similar substances, the correlations between feather concentrations and internal tissue concentrations are still unclear (Jaspers et al., 2019; Pacyna-Kuchta, 2023). While some authors have reported moderate correlations and proposed feathers as a useful non-invasive matrix for monitoring PFAS exposure (Gómez-Ramírez et al., 2017), others recommend prioritizing different matrices such as plasma over feathers for PFAS analyses (Løseth et al., 2019). Additionally, correlations vary among PFAS compounds and may be influenced by the specific feather types and bird species (Groffen et al. 2020). This ambiguity is due to the limited number of studies conducted on this topic, highlighting the urgent need for further research.

Conversely, although more studies have investigated the exposure of seabirds to trace elements, there is still a need for further research on factors affecting their accumulation, such as migration (Colominas-Ciuró et al., 2018; Espejo et al., 2018a; Herman et al., 2017; Jerez et al., 2013; Metcheva et al., 2010). Similarly, there is limited knowledge about the contamination of emerging pollutants in Antarctic seabirds (Larramendy & Soloneski, 2015; Munoz et al., 2017; Roscales et al., 2019), and the factors that influence their exposure, especially in migratory birds. A valuable tool that can provide clearer insights into these matters is stable isotope analysis (SIA) of carbon, nitrogen, and sulfur (Cherel et al., 2014; Cherel & Hobson, 2007; Herman et al., 2017). In differentiating between inshore and offshore food items, carbon ratios expressed as per mill ‰ $\delta^{13}C$ play a crucial role, whereas nitrogen ratios ($\delta^{15}N$) are essential indicators of trophic positions (Cherel et al., 2014; Dehnhard et al., 2020; Polito et al., 2016). Furthermore, sulfur ratios ($\delta^{34}S$) serve the purpose of distinguishing marine and terrestrial habitats (Connolly et al., 2004). Thus, SIA can be used to investigate how migration patterns and different trophic ecologies may influence the exposure of Antarctic seabirds to pollutants (Wing et al., 2021).

Therefore, in order to fill these knowledge gaps, this study aimed to assess the influence of migration and trophic ecology ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) on the exposure of two Antarctic migratory bird species, Wilson's storm petrel (*Oceanites oceanicus*), and Cape petrel (*Daption capense*), to concentrations of 18 elements and 15 perfluoroalkyl acids

(PFAS). Both species nest on King George Island in the Antarctic Peninsula, and exposure to pollutants was assessed through feather analysis. Our objective was to understand the influence of migration and trophic ecology on pollutant accumulation and thereby contribute to the protection of these species. Our hypotheses were: (1) Wilson's storm petrel, migrating to the Northern Hemisphere, is exposed to elevated levels of trace elements and PFAS compared to Cape petrel, which migrates within the Southern Hemisphere, due to greater industrialization and population density in the Northern Hemisphere; and (2) trophic ecology influences the concentration of trace elements and PFAS in migratory birds.

2. Material and methods

2.1 Sampling and sample preparation

Carcasses of Cape petrel and of Wilson's storm petrel were sampled at King George Island (61°50'-62°15'S and 57°30'-59° 00'W) in the South Shetland Archipelago, Antarctic Peninsula region, during 2010-2011, 2012-2013 and 2013-2014 austral summers (Figure 1). Wings were retrieved from the remains of Cape petrels and Wilson's storm petrels within their breeding colonies, a feasible approach considering that predatory and scavenging birds typically consume all parts of deceased birds, leaving the wings intact. Notably, these wings are often found intact in Antarctica, facilitating species identification (Souza et al., 2020). The wings were packed in individual zip-lock polyethylene bags and stored at room temperature (approx. 24ºC) until the analysis.

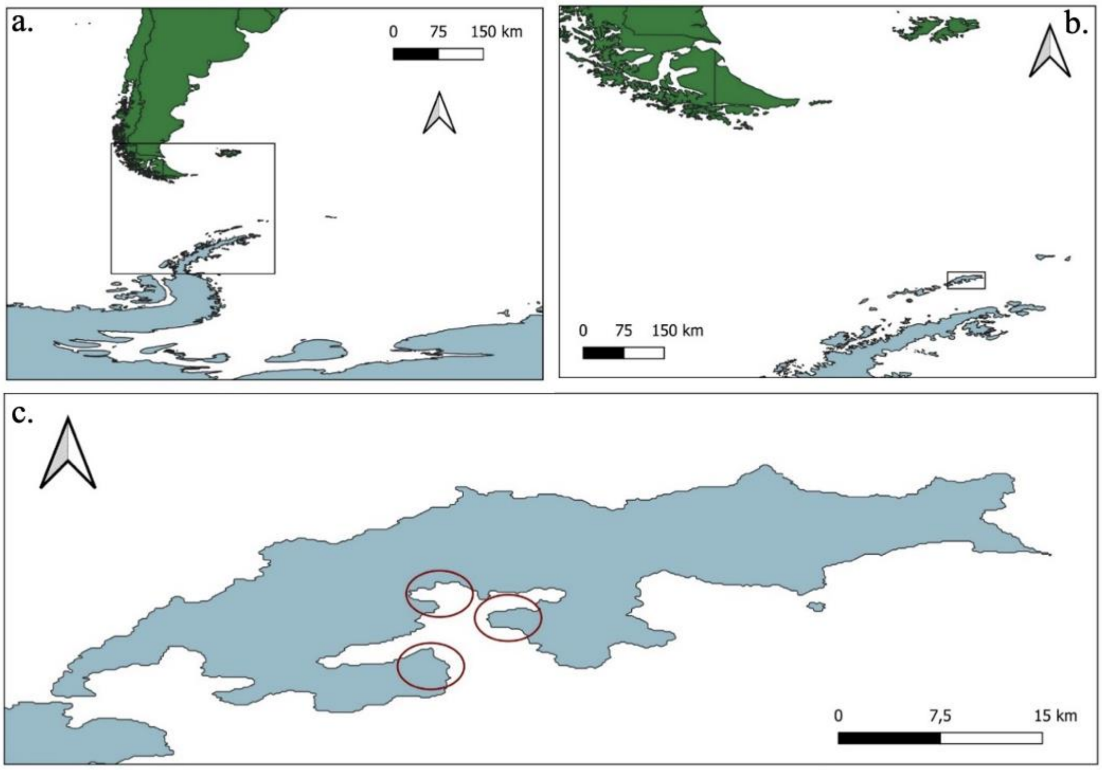


Figure 1 - Map of the study area: a) Antarctic Peninsula in relation to southern South America b) Antarctic peninsula with the King George Island shown in the rectangle; c) King George Island (61º50'-62º15´S and 57º30'-59º00'W) with specific sampling locations marked in red.

Initially, the primary feather (P9) was removed from each wing. Then, the feathers were washed three times with a sequence of 1) Milli-Q ultrapure water (Merck Millipore, USA), 2) 0.01% EDTA (Spectrum, Tedia, USA), and 3) Milli-Q ultrapure water (Merck Millipore, USA), for eliminating external contamination, and then the samples were oven-dried at 50 °C for 24 h (Marques et al., 2007). Subsequently, the feathers were cut into small pieces using ceramic scissors. For stable isotope analysis, the samples were additionally washed with a chloroform/methanol (2:1, v: v, suprapur Merck, Germany) solution and dried at 50 °C for 48 h (Padilha et al., 2021; 2023).

2.2 ICP MS and UPLC analysis and stable isotope measurements

The measurements of various elements, including both trace elements (such as lithium [Li], beryllium [Be], chromium [Cr], iron [Fe], manganese [Mn], nickel [Ni], copper [Cu], zinc [Zn], arsenic [As], selenium [Se], rubidium [Rb], strontium [Sr], cadmium [Cd], tin [Sn], barium [Ba], and lead [Pb]) and major elements (specifically magnesium [Mg] and calcium [Ca]), was conducted utilizing the methodology delineated in Padilha et al. (2021). The inclusion of major elements in our study stems from their biological importance and environmental interactions, as these components are integral to various physiological processes within seabirds and are indicative of the broader ecological dynamics and nutritional availability in their habitats. For instance, Mg is vital for birds, particularly in nerve impulse conduction, muscle contraction, and overall energy production, while Ca is crucial for bone formation and eggshell production in breeding seabirds (Newman et al. 1997; Shastak et al, 2015, Roman et al., 2023).

Briefly, 0.1 g of dry powdered feathers were acid digested in the microwave in Teflon vessels, with 5 mL of nitric acid (HNO_3, 65% suprapur Merck, Germany), 2 mL of hydrogen peroxide (H_2O_2, 30% suprapur Merck, Germany) and 1 mL of Milli-Q ultrapure water (Merck Millipore, USA). Subsequently, the samples were transferred to Falcon tubes and adjusted to a final volume of 50 mL. The solution was quantified using an inductively coupled plasma mass spectrometry (ICP MS; Perkin Elmer 9000). The measurements of the stable isotopes $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ were conducted using continuous flow elemental analysis-isotope ratio mass spectrometry (CF-EA-IRMS; OPTIMA) using a Vario MICRO cube CeNeS elemental analyzer (Elementar Analysensysteme GmBH, Hanau, Germany) coupled to an IsoPrime100 isotope ratio mass spectrometer (Isoprime, Cheadle, United Kingdom) according to Padilha et al. (2021).

The determination of PFAS concentrations and their analysis followed the methods described in Groffen et al. (2021). Around 100 mg of each specimen was measured and placed in 50 mL polypropylene (PP) containers. Upon introducing 10 mL of methanol, the specimens underwent vortex agitation for a minute and then settled at ambient temperature for 48 hours. This was followed by a centrifugation step (4 °C, 10 min, 2400 rpm; 1037×g, using an Eppendorf 5804 R centrifuge). The resultant clear liquid was decanted into a 15 mL PP container, with an addition of 10 ng of every internal standard (ISTD), and subsequently fully evaporated with a rotary vacuum device (Martin Christ, RVC 2–25, Osterode am Harz, Germany). Afterward, the specimens were reconstituted using 2 mL of a 2% ammonium hydroxide solution mixed with ACN. These specimens were then vortex-agitated and filtered utilizing a 13 mm Ion Chromatography Acrodisc Syringe Filter featuring a 0.2 μm Supor (PES) Membrane (supplied by VWR International, Leuven, Belgium) and ultimately poured into a PP auto-injector container. Ultra-performance liquid chromatography-tandem ES (−) mass spectrometry (UPLC-MS/MS, ACQUITY, TQD, Waters, Milford, MA, USA) was used to measure four perfluoroalkane sulfonic acids (PFBS, PFHxS, PFOS, and PFDS) and eleven perfluoroalkane carboxylic acids (PFBA, PFPeDA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA) were selected as target analytes. For quality control of the samples, the procedures are further explained in Padilha et al. (2023) and Padilha et al. (2022) for trace elements and PFAS, respectively. The abbreviations utilized for the target PFAS are consistent with those proposed by Buck et al. (2011; see Table S1 in the Supplementary Material). Further specifications such as MRM transitions, cone voltages, and collision energy for each target analyte, inclusive of the ISTDs, are detailed in Table S2, with validations provided by Groffen et al. (2019). All data are reported in dry weight (dw). Calibration curves were established by Groffen et al. (2021, 2019), demonstrating a highly significant linear fit for all target analytes ($p < 0.001$; R2 > 0.98). To ensure data quality control, procedural blanks containing 10 mL of methanol were introduced for every batch of 20–25 samples. The methanol blanks exhibited minimal contamination with PFOA (0.0500–0.150 ng/g ww), PFDA (<LOQ – 0.280 ng

g^{-1} ww), and PFUnDA (<LOQ – 0.250 ng g^{-1} ww), and these contaminant levels were subtracted from the concentrations of samples within the same batch. Additionally, instrumental blanks (100% ACN) were regularly analyzed to prevent cross-contamination between injections. The quantification of individual PFAS was conducted using the most appropriate internal standard (ISTD) based on ionization and extraction efficiency, as detailed in Groffen et al. (2019), selecting ISTDs that closely matched the functional group and carbon-chain length. The individual limits of quantification (LOQs) were established within the matrix, employing a signal-to-noise (S/N) ratio of 10 (refer to Table S3 in the Supplementary material).

2.3 Statistical analysis

The statistical analyses were performed using R software (Jackson et al., 2011; R Core Team, 2023). Due to the non-normality of the data, all data were logarithmically transformed (base 10), and parametric tests were utilized. Student's t-test was employed to compare chemical elements, PFAS concentrations, and stable isotope values between the two species.

Correlation matrices were constructed to examine the relationships between trace elements and stable isotopes, as well as between PFAS and stable isotopes using the package "corrplot".

To analyze the relationship between PFAS concentrations in the two species of migratory seabirds, a Principal Component Analysis (PCA) was conducted. The inclusion of isotopes as variables in the PCA aimed to observe whether trophic ecology also influenced the differences in PFAS and element concentrations between species.

To explore ecological niches across various species, the SIBER (Stable Isotope Bayesian Ellipses in R) method was utilized, incorporating $\delta^{15}N$ and $\delta^{13}C$ data (Jackson et al., 2011). The SEAb (Standard Ellipse Area Bayesian), a Bayesian-derived estimate of the standard ellipse area, was used to compare niche widths among groups. This estimation was based on the dimensions of the generated ellipse areas and their predicted posterior distributions. Groups with similar SEAb values indicate analogous isotopic niche widths, suggesting a reliance on a similar assortment of prey species and/or foraging habitats.

3. Results

3.1 Trace and major elements, stable isotopes, and trophic niche

The concentrations of the elements (Li, Be, Mg, Ca, Cr, Fe, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Ba, and Pb) and the values of stable isotopes $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ detected in the feathers of Cape Petrel and Wilson's storm petrel from King George Island, Antarctic Peninsula, are presented in Table 1.

Table 1 - Concentrations of trace and major elements, in µg g^{-1} dry weight, and values of $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ (median, mean, and min-max) in feathers of Cape Petrel (*Daption capense*) and Wilson's storm petrel (*Oceanites oceanicus*).

Tissue	Species	Elements	Li	Be	Mg	Ca	Cr	Fe	Mn	Ni	Cu	Zn	As
Feather	*Oceanites oceanicus* n=23	Median	0.0300	0.0100	616	913	0.230	94.0	11.5	0.340	15.8	83.3	0.140
		Mean	0.0700	0.0100	676	4939	0.480	390	16.6	1.01	23.9	92.2	0.200
		Min-Max	0.0100-0.480	0.0100 - 0.0600	263-1619	953-52902	0.0400-1.59	43.8-1304	1.27-106	0.160-7.70	5.03-61.9	29.4-218	0.0800-0.400
	Daption capense n=25	Median	0.110	0.0100	1350	2100	0.300	440	18.0	0.560	26.8	93.4	0.150
		Mean	0.120	0.0100	1387	1632	20.6	513	14.3	1.75	27.9	93.6	0.160
		Min-Max	0.0400-0.300	<LD-0.0600	490-1870	970-53000	0.0400-12.0	80.0-1400	1.90-88.0	0.270-2.00	15.8-46.1	70.6 -120	0.0300-0.410

Tissue	Species	Elements	Se	Rb	Sr	Cd	Sn	Ba	Pb	$\delta^{13}C$	$\delta^{15}N$	$\delta^{34}S$
Feather	*Oceanites oceanicus* n=23	Median	6.75	0.140	15.8	0.0900	0.290	0.160	0.260	-20.5	12.1	17.8
		Mean	8.66	0.190	29.9	1.04	0.0200	1.79	0.230	-23.6	11.8	17.8
		Min-Max	4.36-17.6	0.0400-0.820	9.86-43.8	<LD-3.12	0.0700-0.780	0.0600-0.400	0.0600-3.77	-51.3- -17.4	8.86-14.2	16.3-18.8
	Daption capense n=25	Median	7.90	0.560	22.0	0.290	0.0300	1.11	0.540	-24.5	9.28	17.5
		Mean	7.16	0.320	22.9	0.270	0.0300	1.86	0.300	-24.9	8.85	17.5
		Min-Max	6.98-14.5	0.180-1.33	14.7-32.3	0.140-0.600	0.0100-0.0400	0.860-4.58	0.0900-0.910	-26.5--24.5	7.48-9.28	16.6-17.5

The Student's t-test conducted to evaluate differences between the concentrations of various variables in the two species under study, only revealed significant differences for Li ($p = 0.02$, $t = -2.49$, $df = 19.5$), Mg ($p < 0.001$, $t = -4.79$, $df = 21.4$), Rb ($p = 0.04$, $t = -2.20$, $df = 21.9$), Ca ($p = 0.004$, $t = 3.25$, $df = 22.1$), and $\delta^{15}N$ ($p < 0.001$, $t = 6.60$, $df = 19.4$). As observed in Figure 2, Cape Petrel shows higher average concentrations of Li, Mg, and Rb compared to Wilson's storm petrel, while Wilson's storm petrel exhibits higher average concentrations of Cd and $\delta^{15}N$.

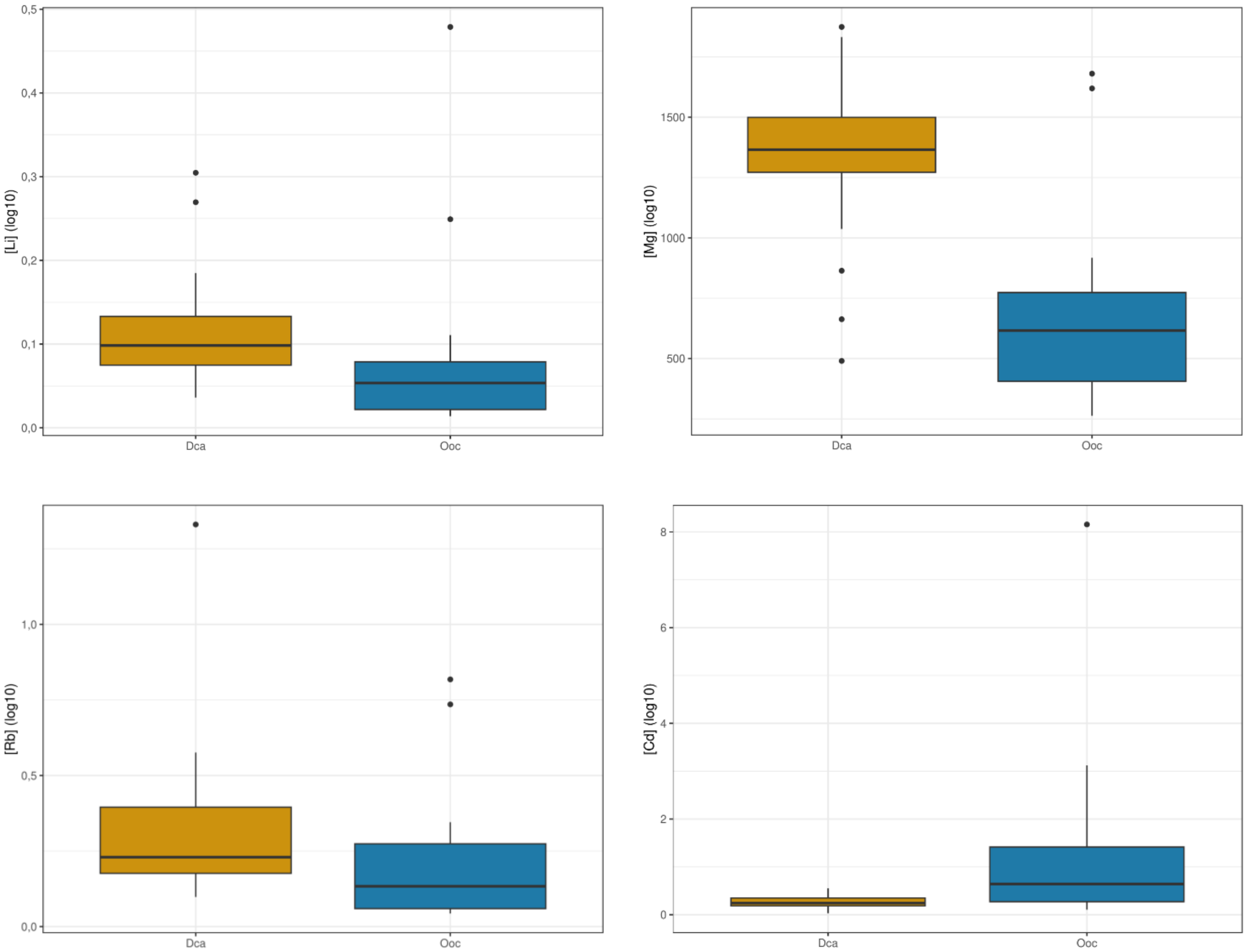
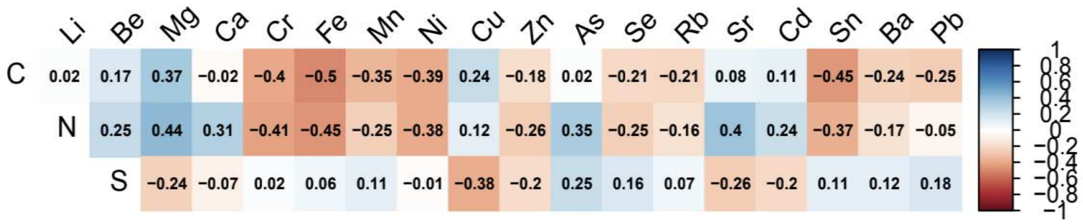


Figure 2. Boxplots representing the differences in concentrations of Li, Mg, Rb, Cd, and N, on a log10, between Cape Petrel (*Daption capense*, Dca) and Wilson's storm petrel (*Oceanites oceanicus,* Ooc). The whiskers indicate the maximum and minimum values, while the box represents the interquartile range with the central line representing the median value for each analyzed group.

Regarding the correlation matrices between elements and stable isotopes (Figure 3), a moderate negative correlation (-0.5) can be observed between Fe and $\delta^{13}C$ in Cape Petrel, and a moderate negative correlation (-0.5) between Be and $\delta^{13}C$ in Wilson's storm petrel.

a.



b.

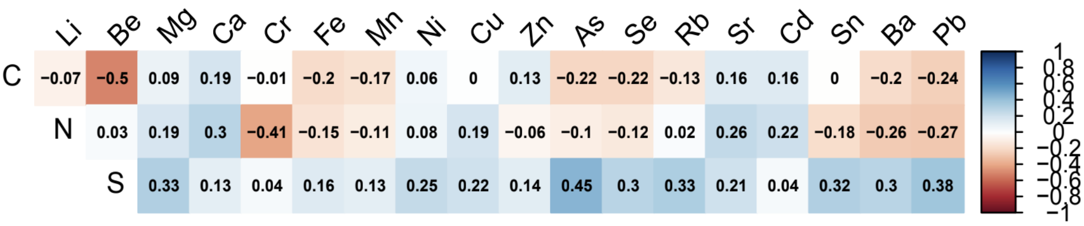


Figure 3 - Correlation matrices between trace and major elements and stable isotopes of $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ in feathers of Cape Petrel (a) and Wilson's storm petrel (b).

The results of the SIBER metrics (Figure 4) show that Wilson's storm petrel has a larger total niche area compared to Cape Petrel (14.6‰^{2} > 5.40‰^{2}), as well as a considerably larger standard ellipse area (Figure 4) (6.14‰^{2} > 1.87‰^{2}). There is no overlap between the standard ellipse areas of both species.

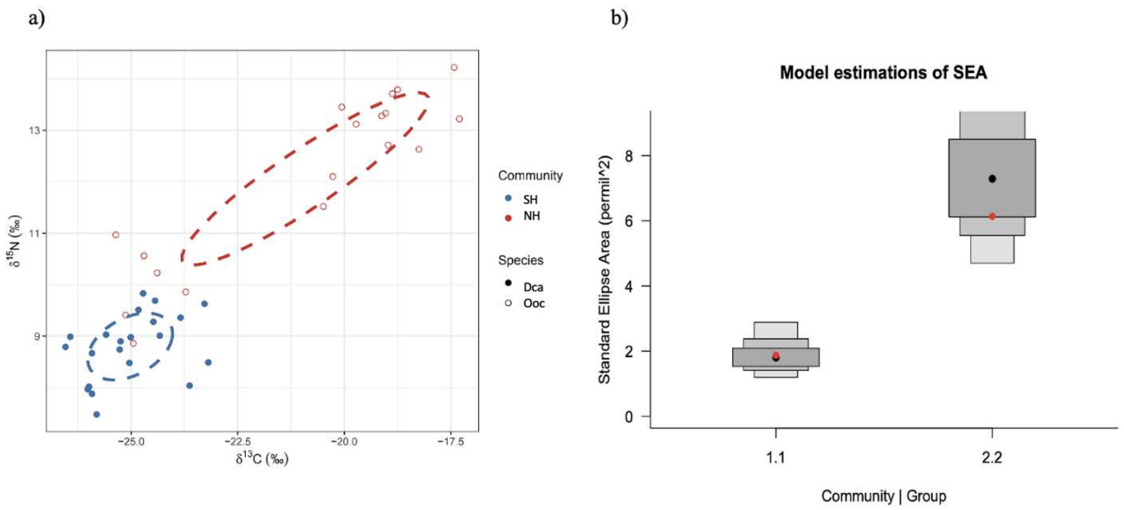


Figure 4 – a) Size of trophic niche and their respective standard ellipses for Cape petrel (Dca, *Daption capense*; SH, Southern Hemisphere) and Wilson's storm petrel (Ooc, *Oceanites oceanicus*; HN, Northern Hemisphere) and b) the areas of the standard ellipses for (Dca , 1.1) and Ooc, 2.2) (B).

Principal Component Analysis (Figure S1a) revealed that the first principal component explains 27.8% of the variance in the samples, with Mn, Rb, and Li making the highest contributions (Figure S2). The second principal component explains 15.3% of the variance in the samples, with Cr, Sn, and Ni making the highest contribution. Additionally, there is an overlap observed between the two species.

3.2 Perfluoroalkyl acids and stable isotopes

PFBA, PFPeA, PFHpA, PFNA, PFBS, PFHxS, PFOS, and PFDS could not be detected in any of the samples and were removed from further analyses. The concentrations of the other perfluoroalkyl acids (PFHxA, PFOA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA) and the values of stable isotopes $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ detected in the feathers of Cape petrel and Wilson's storm petrel are presented in Table 2 in ng g^{-1} due to their lower concentration compared to chemical elements.

Table 2 – Concentration of (median, mean, and min-max in ng g^{-1} dry weight) of PFAS and stable isotope values ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) in the feathers of Cape petrel (*Daption capense*) and Wilson's storm petrel (*Oceanites oceanicus*).

Tissue	Species	Compounds	PFHxA	PFOA	PFDA	PFUnDA	PFDoDA
Feather	*Daption capense* n=25	Median	0.340	0.0800	0.370	1.56	0.0200
		Mean	0.690	0.170	0.670	1.72	0.0500
		Min-Max	0.340 – 2.21	0.0800 – 1.29	0.370 - 1.73	0.870 – 5.36	0.0200 - 0.380
	Oceanites oceanicus n=23	Median	0.250	0.390	0.510	1.67	0.150
		Mean	0.730	0.710	0.900	1.71	0.310
		Min-Max	0.260-2.29	0.390-1.56	0.510-2.20	0.890-3.61	0.150-0.700
Tissue	Species		PFTrDA	PFTeDA	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
Feather	*Daption capense* n=25	Median	0.0500	0.0600	-25.0	8.93	15.5
		Mean	0.360± 0.710	0.190± 0.360	-24.7± 1.76	9.01± 1.19	17.5± 0.550
		Min-Max	0.0500-2.81	0.0600-1.29	-26.5- -18.1	7.48-13.5	16.6-18.4
	Oceanites oceanicus n=23	Median	0.370	0.180	-19.9	12.7	17.8
		Mean	0.550	1.01	-20.9	12.1	17.7
		Min-Max	0.120-2.39	0.180-6.13	-25.4 - -19.9	8.86-14.2	16.3-18.8

The t-test revealed significant differences for PFOA ($p < 0.001$, $t = -8.06$, $df = 37.9$), PFDA ($p = 0.01$, $t = -2.61$, $df = 36.9$), PFDoDA ($p < 0.001$, $t = -9.56$, $df = 37.9$), PFTrDA ($p = 0.01$, $t = -2.85$, $df = 36.7$), PFTeDA ($p < 0.001$, $t = -4.30$, $df = 37.8$), and

$\delta^{15}N$ ($p < 0.001$, $t = -6.74$, $df = 32.4$) between the two species, with the highest concentrations being observed in Wilson's storm petrel. Profiles based on the relative contribution (Figure 5) of the studied compounds to PFAS were dominated by ΣPFCAs (100%). As observed in Figure 5, Wilson's storm petrel exhibits higher average concentrations for ∑PFAS (ng g^{-1} dw) compared to Cape petrel, with the predominance of PFUnDA.

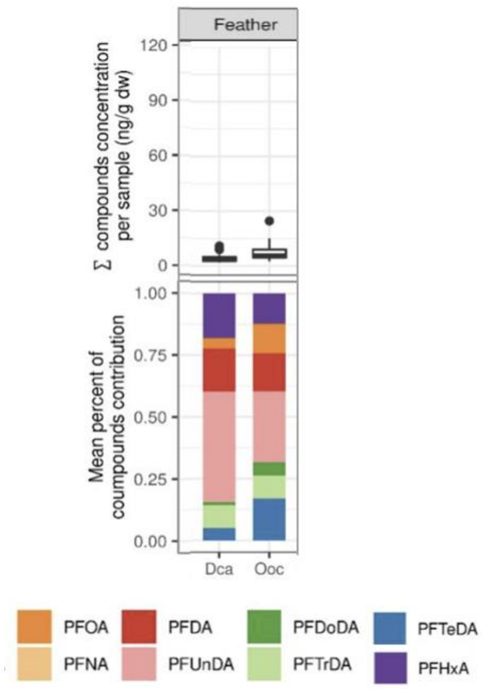
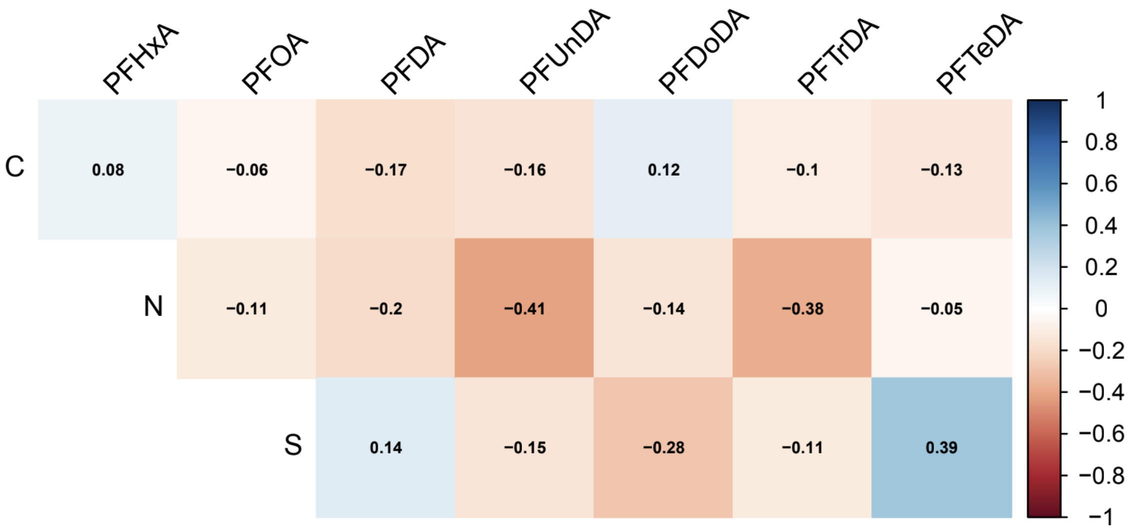


Figure 5. The sum of quantified PFAS compounds and relative contribution (percent) of individual PFAS to ∑PFAS (ng g^{-1} dw) in feathers of Cape petrel (*Daption capense*, Dca) and Wilson's storm petrel (*Oceanites oceanicus*, Ooc) from King George Island, Antarctic Peninsula.

Regarding the correlation matrices between PFAS and stable isotopes (Figure 6), most of the existing correlations are weak, with more pronounced moderate correlations observed between PFUnDA and $\delta^{15}N$ (-0.41) in Cape petrel, and between PFTeDA and δ^{34} (-0.47) in Wilson's storm petrel.

a.



b.

Figure 6. Correlation matrices (Pearson) between PFAS and stable isotopes of $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ in feathers of Cape petrel (*Daption capense*) (a) and Wilson's storm petrel (*Oceanites oceanicus*) (b).

The PCA(Figure S1b) revealed that the first principal component explains 27.8% of the sample variance, with $\delta^{15}N$, $\delta^{13}C$, and PFDoDA making the highest contributions

(Figure S3). The second principal component explains 21.1% of the sample variance, with PFUnDA and PFTrDA making the highest contributions. There is no clear overlap between the two species.

4. Discussion

Our results indicate that migratory behaviors do not significantly impact the trace and major element concentrations in either studied species. However, we observed a difference in PFAS accumulation, with Wilson's storm petrel showing higher concentrations for multiple compounds compared to Cape petrel, likely due to the former's broad-ranging migration and higher trophic position. Trophic ecology exhibited more significant correlations with PFAS concentrations compared to elements, emphasizing the complex interplay between environmental factors, diet, and contaminant accumulation.

4.1 Comparative Analysis of PFAS, Trace and Major Element Concentrations in two Antarctic Migratory Seabirds

Limited data are available for the two species under investigation (Souza et al., 2020, Kuepper et al., 2022). Our study observed concentrations of Ca, Cu, Fe, Mg, Se, and Sr (Table 3) at least an order of magnitude higher than those reported by Pacyna et al. (2019). In contrast, the Zn levels (Table 3) recorded by Pacyna et al. (109 $\mu g\ g^{-1}$) were an order of magnitude higher than our findings. It is important to note that while Pacyna et al. collected their samples in 2017, our samples were collected between 2010 and 2014. Such a temporal gap could account for the observed discrepancies, considering potential shifts in environmental conditions and exposures across these years. For the Cape petrel, Souza et al. (2020) reported values for Cd and Se (Cd: 0.020-0.950, Se: 2.24-4.93 μg g-1, dw, table 3) from wing carcass feathers collected between 2010-2014. These values were an order of magnitude lower compared to the current study. Padilha et al. (2023)

observed concentrations of Ca, Cd, Mg, and Cr (Table 3) in breast feathers of Giant petrel (*Macronectes giganteus*), a seabird species with a similar migratory distribution to Cape petrel, at least were an order of magnitude lower than the present study (Patterson & Hunter, 2000). The variations in trace element concentrations highlight the possible impacts of differing environmental conditions, exposure rates, feather types, and time-sensitive factors on the biochemistry of these marine birds (Dauwe et al., 2003; Jerez et al., 2011).

Regarding PFAS concentrations, Padilha et al. (2022) studied 15 PFAS in breast feathers from 8 seabird species collected on King George Island between 2010-2014. In line with our results, both PFTrDA and PFTrDA levels were significantly higher in the South polar skua (*Stercorarius maccormicki*), a transequatorial migrant, similar to the Wilson storm petrel (see details in Table 3). PFUnDA emerged as the dominant compound in our study, a finding also noted by Padilha et al. (2022). Additionally, Gao et al. (2020) assessed PFAS concentrations in Cape petrel wing feathers on King George Island sampled in 2012-2013, recording values (ng g^{-1} dw, mean ± SD) for PFOA (0.0600 ± 0.0200) and PFTrDA (0.06 ± 0.0300) that were an order of magnitude lower than ours. In contrast, Roscales et al. (2019), using blood plasma as a matrix, found PFOS to be the prevalent compound in Antarctic seabirds. Such varied findings suggest different compounds might have distinct affinities to animal matrices, highlighting the importance of further investigations to clarify these variations.

It is worth noting that procuring feathers from deceased specimens offers an apt methodology for monitoring contaminant concentrations (Souza et al., 2020) particularly in understudied species like the Cape petrel and Wilson's storm petrel. Such samples are straightforward to collect, store, and transport, given that they do not necessitate refrigeration. However, the process of collecting feather samples from marine bird carcasses does have its limitations, including the absence of information regarding the seabird's weight, age, or molting status. Despite these limitations, the significant insights garnered from our study affirm the value of this methodology.

While our samples were collected between 2010 and 2014, we contend that they remain pertinent for the investigation of PFAS and trace elements. The enduring nature of these compounds in biotic matrices like feathers mitigates concerns regarding the potential volatility or degradation over time. In the context of PFAS, studies such as that by Sun et al. (2019) have successfully analyzed museum feather samples dating from 1968 to 2015, identifying consistent presence of compounds like FOSA. This suggests that the biotransformation processes in feathers are minimal, lending credibility to the timelessness of our data. Feathers, once removed from the metabolic activity associated with the bird's bloodstream, act as a historical register by effectively 'locking in' the contaminants, thereby serving as a stable matrix for such investigations.

Further, Bond & Lavers (2020) utilized feather samples spanning over a century (1900-2011) to investigate exposure trends for trace elements, including Cd, Hg, and Pb, in Flesh-footed Shearwaters. Their findings not only indicated the temporal shifts in exposure but also validated the methodological approach of using archival biological materials for contemporary environmental forensic purposes. Thus, the temporal gap between sample collection and analysis in our study does not detract from the validity or relevance of our findings. Instead, it highlights the robustness of feathers as a matrix for long-term environmental monitoring, capable of offering invaluable insights into historical pollutant exposure and environmental shifts.

Table 3. Concentration of inorganic and organic pollutants in feathers: A comparison with previous studies.

	Study	Year of sampling	Species	Local	Unit	Ca	Cd	Cu	Fe	Mg	Se	Sr	Cr	Pb	Zn
Inorganic	Pacyna et al. (2019)	2017	Wilson's storm petrel	King George Island	mean µg g^{-1}, dw	96.0	<LD	2.52	20.4	478	1.81	5.77	0.670	0.330	109
	Souza et al. (2020)	2010-2014	Cape petrel	King George Island	Min-max µg g^{-1}, dw		0.0200-0.950				2.24-4.93				
	Padilha et al. (2023)	2010-2014	Giant petrel	King George Island	mean in µg g^{-1} dw	891	0.160	17.0	297	760	5.34	11.3	0.740	0.130	82.0
Organic	Study	Year of sampling	Species		Unit	PFDA	PFTrDA	PFUnDA	PFOA	PFOS					
	Gao et al (2020)	2012-2013	Cape petrel	King George Island	Mean ng g^{-1}, dw	<LD	0.0600	<LD	0.0600	0.770					
	Padilha et al. (2022)	2010-2014	South Polar Skua	King George Island	Median ng g^{-1}, dw	0.300	0.580	1.55	<1.06	<0.980					
			Giant petrel			1.19	<0.170	1.61	<1.06	-					
			Kelp gull			1.19	<0.170	1.41	<1.06	-					

4.2 Influence of Migration and Pollution in Each Hemisphere

In our study, the impact of migration patterns on exposure to trace elements appears to have little influence, given that both Wilson's storm petrel and Cape petrel displayed comparable values of these elements in their feathers, a similarity further substantiated by overlapping data observed in the PCA. However, regarding trace elements, Wilson's storm petrel only showed higher concentrations of Cd compared to Cape petrel. This challenges our initial hypothesis and aligns with studies suggesting higher Cd concentrations in species inhabiting oceanic rather than coastal environments (Espejo et al., 2018b; Jerez et al., 2011). Carbon isotopic data supports the proposition that Wilson's storm petrel has a more oceanic habitat compared to Cape petrel. Although Wilson's storm petrel migrates to the Northern Hemisphere, it is possible that the areas it frequents during migration may not have significantly higher trace elements contamination levels than the areas Cape petrel inhabits. In addition, both species might have similar physiological mechanisms for detoxifying and eliminating these trace elements, which would also contribute to the similar exposure levels found in their feathers. A previous study conducted by Lucia et al. (2012) investigated two different species, *Calidris canutus,* and *Limosa limosa,* and identified similarities in their DNA, particularly in the sequences of genes such as β-actin, acetyl-CoA carboxylase (acc), Cu/Zn superoxide dismutase (sod1), metallothionein (mt), and NADP-dependent malic enzyme. Remarkably, despite the utilization of different detoxification systems, these species exhibited comparable response pathways, which may collectively provide them with similar levels of protection against lipid peroxidation and potential trace element toxicity. Nevertheless, further investigation would be required to definitively identify the factors leading to the lack of observed differences in trace element exposure between the Antarctic seabirds.

Migration patterns are not the primary determinants of trace element accumulation in migratory birds. Correia et al. (2023) showed differences in elemental concentrations such as As, Pb, and Se in the blood samples of migrating seabirds, attributed mainly to their diet and trophic guilds. Similarly, Kojadinovic et al. (2006) noted the significance of other factors such as diet, age, and health status in migratory birds. Collectively, these studies suggest that the environments and diets of migratory birds play a more crucial role in their exposure to contaminants than their migratory patterns alone.

In focusing on PFAS exposure, Wilson's storm petrel exhibited elevated concentrations of PFOA, PFDA, PFDoDA, PFTrDA, and PFTeDA compared to Cape petrel. This is consistent with findings from Padilha et al. (2022), who found higher PFAS values in trans-equatorial migratory birds. The PCAillustrates a pronounced distinction in PFAS exposure between the two species. Notably, Wilson's storm petrel has a wide-ranging migration pattern, reaching the Northern Hemisphere during the Austral winter via routes through the Atlantic and Pacific Oceans, before returning to the Antarctic environment for summer breeding (Cruwys, 2008; Kopp et al., 2011). This seabird species, a top-level predator, exhibits opportunistic feeding behaviors, consuming fish, and crustaceans, and scavenging from seabirds nesting in proximate colonies (Cruwys, 2008; Quillfeldt, 2002; Ridoux and Offredo, 1989). The higher trophic position, combined with Wilson's storm petrel migration behavior, may account for the elevated values of $\delta^{15}N$, $\delta^{13}C$, and most PFAS compared to Cape petrel. Wilson’s storm petrel displayed the highest levels of PFCAs observed in this study. It is noteworthy that long-chain PFCAs are primarily found in seawater outside the Antarctic Circumpolar Current, being more plentiful in the North Atlantic than in the South Atlantic (González-Gaya et al., 2014; Ma et al., 2016; Zhao et al., 2012). This distribution may explain the high concentrations of PFTrDA and PFTeDA in Wilson's storm petrel and the lower concentrations in Cape petrel. Earlier studies on Antarctic seabirds have demonstrated similar patterns, with higher levels of long-chain PFCAs detected in the plasma of seabirds foraging north of Antarctica than in resident seabirds (Roscales et al., 2019; Tao et al., 2006). Given the higher production of these emergent pollutants in the Northern Hemisphere, it aligns with our initial hypothesis that migrating birds, such as Wilson's storm petrel, venturing into more northern locations would experience greater exposure (Ma et al., 2016; Paul et al., 2009).

4.3 Impact of Trophic Ecology on Contaminant Exposure

The Wilson's storm petrel's diet is based on myctophid (pelagic), krill, carrion, cephalopods, and pelagic crustaceans while the cape petrel eats small crustaceans, fish, and cephalopods, which indicates the higher trophic position occupied by the Wilson' storm petrel (Cruwys, 2008, Fijn et al. 2012). It was further confirmed by our δ15N results, which evidenced the storm petrel's elevated trophic position compared to the cape petrel. When considering the impact of trophic ecology on the concentrations of trace elements in the feathers of Cape petrel and Wilson's storm petrel, we did not find any positive or negative associations between any given element and the three stable isotopes. This contrasts with the findings of Padilha et al. (2023) who observed that foraging area and dietary sources impact Zn, Ba, Sn, and Cd concentrations in migratory seabirds in Antarctica. However, this was not found in the present study.

When investigating the impact of trophic ecology on the concentrations of PFAS in Cape petrel and Wilson's storm petrel, no strong positive correlations were observed between any compound and the three stable isotopes. However, certain compounds, such as PFUnDA, demonstrated a negative correlation with trophic position ($\delta^{15}N$), suggesting biodilution. Interestingly, comparable results were observed in the study by Roscales et al. (2019), and other studies, such as the one by Lescord et al. (2015), have suggested little to no biomagnification capacity for PFCAs. Padilha et al. (2022) revealed that PFCA concentrations in the feathers of Antarctic birds are influenced by factors such as the birds' trophic position ($\delta^{15}N$ values), their foraging area ($\delta^{13}C$ values), and dietary sources ($\delta^{34}S$ values). Similarly, the study also found that PFSA levels are associated with the foraging area of these birds, as suggested by the $\delta^{13}C$ values. These results, collectively, highlight the importance of continuing investigations in this domain to achieve a comprehensive understanding of how trophic ecology can potentially influence the exposure of seabirds to pollutants.

5. Conclusions

Our study aimed to investigate the influence of migration patterns and trophic ecology on pollutant exposure, focusing in particular on trace elements and PFAS in two Antarctic seabird species, Wilson's storm petrel and Cape petrel. Through feather analyses, we provide important insights into the complex connections between the ecology of these birds and their susceptibility to these contaminants.

While the migratory pattern did not significantly affect exposure to trace elements, notable differences were observed in PFAS concentrations between the two studied species, with Wilson's storm petrel exhibiting higher PFAS levels, possibly due to its broader migratory range reaching the Northern Hemisphere. This aligns with our initial hypothesis and prior research indicating higher production of these pollutants in the Northern Hemisphere.

When considering the role of trophic ecology, the study did not find correlations between any given trace element or PFAS and the three stable isotopes ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) in either of the seabird species. However, certain PFAS compounds, such as PFUnDA, demonstrated a negative correlation with trophic position, suggesting biodilution.

While we have started to understand the interplay between migration, trophic ecology, and pollutant exposure, we also acknowledge that there is large variation observed in the accumulation patterns of trace elements and PFAS in these seabird species. Therefore, we recommend continued research into the factors affecting pollutant exposure to obtain a comprehensive understanding. The sample collection method employed in this study, which has been recognized in previous works, serves as a valuable tool, contributing to bridging the knowledge gap for these protected species. Such studies are essential in the broader context of marine ecology and conservation, assisting in the development of more effective strategies for managing and protecting migratory seabird populations in the face of ongoing anthropogenic environmental changes.

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