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Perfluoroalkylated compounds in the eggs and feathers of resident and migratory seabirds from the Antarctic Peninsula

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ABSTRACT

In this study, we investigated factors that influence the differences in exposure of perfluoroalkyl acids (PFAAs) from eight species of Antarctic seabirds, including *Pygoscelis* penguins, *Stercorarius maccormicki,* and *Macronectes giganteus*. We analyzed the relationship between foraging ecology (based on $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ values) and PFAAs accumulated in eggs and breast feathers. Ten out of 15 targeted PFAAs were detected in eggs compared to eight in feathers. Mean ∑PFAA concentrations in feathers ranged from 0.47 in *P. antarcticus* to 17.4 ng/g dry weight (dw) in *S. maccormicki*. In eggs, ∑PFAA concentrations ranged from 3.51 in *P. adeliae* to 117 ng/g dw in *S. maccormicki*. The highest concentrations of most PFAAs were found in trans-equatorial migrators such as *S. maccormicki*, probably due their high trophic position and higher concentrations of PFAAs in the Northern Hemisphere compared to the Southern Hemisphere. Based on stable isotopes correlations, our results suggest that the trophic position ($\delta^{15}N$) and the foraging area ($\delta^{13}C$ and $\delta^{34}S$) influence PFAAs concentrations in Antarctic seabirds. Our results point to the possibility that long-distance migratory birds may have as bio-vectors in the transport of pollutants, including PFCAs, in Antarctic environments, although this must be further confirmed in future studies using a mass balanced approach, such as extractable organofluorine (EOF).

1. Introduction

The Antarctic continent is absent of permanent native human residents and industrial activities, but despite this, significant levels of several contaminants have been reported in its ecosystems (Bargagli, 2008; Jerez et al., 2011; Polito et al., 2016). Research stations, tourism, and large-scale krill fishing have intensified the human presence on the continent, generating local anthropogenic impacts in the Antarctic region. However, the main entry way of pollutants into the Antarctic environment derives globally and not locally (Bargagli, 2008). The relative isolation of the polar regions in relation to other ecosystems, combined with shorter food chains, makes them important research sites for studying the environmental behavior of pollutants, including their trophodynamics along the food chain (Gao et al., 2020a).

Among these pollutants, perfluoroalkyl acids (PFAAs) are a widely distributed emerging pollutants, being found in places far from their manufacturing source, such as Antarctica (Gao et al., 2020a; Roscales et al., 2019). Although it is not clear which form of transport is dominant, studies indicate that PFAAs can reach different regions of the globe through the ocean and/or atmospheric currents (Young and Mabury, 2010; Zhao et al., 2012). Among PFAAs, previous studies focused primarily on long-chain perfluoroalkyl carboxylic acids (PFCAs) and

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perfluoroalkyl sulfonic acids (PFSAs) (Buck et al., 2011; Groffen et al., 2020). Perfluorooctane sulfonate (PFOS– $C_8F_{17}SO_3H$) and perfluorooctanoic acid (PFOA- $C_7F_{15}COOH$) draw special attention for their persistence, potential health effects, and global distribution, and are the most widely detected long-chain PFAAs in the environment, wildlife and humans around the world (Buck et al., 2011; Ericson Jogsten et al., 2012; Groffen et al., 2017). The highest PFOS and PFOA concentrations in humans were reported to be 164 ng/mL from U.S.A and 256 ng/mL from Korea, respectively (Sinclair et al., 2020). So et al. (2006) also measured amounts of PFAS in human breast milk, in which PFOS has been reported at 360 ng/L and PFOA at 210 ng/L. Exposure to PFAAs can cause diseases such cancer, altered metabolisms, impaired liver function, chronic kidney damage, cardiovascular diseases, probable thyroid, and other hormonal malfunction or imbalances (Podder et al., 2021).

PFOS and PFOA were listed as Persistent Organic Pollutants (POPs) by the Stockholm Convention since 2009 and 2019 respectively, which resulted in regulations that aimed to reduce the levels of these compounds in the environment (Filipovic et al., 2015; Stockholm Convention, 2021). However, since the early 2000s, developing Asian countries have increased their PFAAs production and emissions (Xie et al., 2013). Linked to this, the production of other PFAAs compounds such as polyfluorinated compounds (e.g., fluorotelomer sulfonate - FTSA) and short-chain PFAAs (e.g., $C_4HF_9O_3S$ - perfluorobutane sulfonic acid - PFBS), which are often used as alternatives to PFOS and PFOA, are still increasing, and the impact of these alternative substances on the environment is still not clear (Groffen et al., 2017; Wang et al., 2013).

Seabirds are valuable sentinels of environmental pollution, due to their high trophic position, wide distribution, and longevity. Among the Antarctic birds, penguins constitute the largest avian biomass in the region, presenting populations distributed in Antarctic lands. Therefore they can be useful indicators of local and regional pollution (Espejo et al., 2017; Jerez et al., 2011; Metcheva et al., 2006; Padilha et al., 2021). In addition to resident birds, the migratory ones, such as South Polar Skua (*Stercorarius maccormicki*) and Antarctic Tern (*Sterna vittata*), may act as carriers of contaminants to Antarctica, as they migrate during the southern winter and can reach more contaminated regions northwards (Costa et al., 2019).

Eggs provide an useful biomonitoring tool for assessing avian exposure to contaminants, including PFAAs, in many regions of the world (Groffen et al., 2017). Regarding feathers, there is still ongoing debate regarding their suitability in PFAAs monitoring, since there is a need for further studies to clarify the correlation of PFAAs with internal organs and the contribution of external contamination in feathers concentrations (Jaspers et al., 2019). Additionally, avian eggs reflect contaminant exposure of maternal tissue, because maternal lipid, protein, and organic contaminants are deposited into eggs during its synthesis (Drouillard and Norstrom, 2001). Feathers are associated with the bloodstream during growth, thus internal contaminants, such as metals and persistent organic pollutants, are incorporated throughout the feather growth period (Costa et al., 2019; Groffen et al., 2020; Jaspers et al., 2006; Løseth et al., 2019). Therefore, feathers constitute a potentially important detoxification pathway for organic and inorganic pollutants.

Little is known about the contamination of seabird species by PFAAs in Antarctica (Larramendy and Soloneski, 2015; Munoz et al., 2017; Roscales et al., 2019). Previous studies on Antarctic environment have shown that the Antarctic Circumpolar Current is responsible for providing a protective barrier against the transport of PFAAs through the water (Bengtson Nash et al., 2010) which may contribute to the low concentrations of many PFAAs in Antarctica relative to other continents (Schiavone et al., 2009; Tao et al., 2006). However, the atmospheric transport of PFAAs to the Antarctic environment seems to be relevant, since studies reported air levels of PFAAs in Antarctica is similar to northern latitudes (Cai et al., 2012; Dreyer et al., 2009).

The factors that influence the exposure of Antarctic seabirds to PFAAs are not well understood, mainly for migratory species that exhibit marked interspecific differences in their foraging ecology. However, some of the complexities involved in understanding the feeding ecology as well as the migration patterns of seabirds can be clarified using stable isotope analysis (SIA) to infer trophic position ($\delta^{15}N$), foraging areas ($\delta^{13}C$), and origin of food (i.e. benthic *vs.* pelagic, $\delta^{34}S$) of these animals (Cherel et al., 2014; Cherel and Hobson, 2007; Herman et al., 2017).

The present study aims to evaluate the species-specific differences in PFAAs accumulation among resident and migratory Antarctic seabirds through feather and eggs analysis of 15 PFAAs (four PFSAs and 11 PFCAs). Feather and eggs were used to observe how the pattern of PFAAs concentrations is distributed across different matrices of Antarctic birds. Simultaneously, stable isotopes were used to test the influence of multiple spatial and ecological factors on these accumulated concentrations, analyzing whether possible interspecific differences are due to habitat contamination, sources of food or differences in trophic positions.

2. Material and methods

2.1. Study area and sampling

All samplings were performed at King George Island (61°50′-62°15′S and 57°30′-59° 00′W) in the South Shetland Archipelago, Antarctic Peninsula (Fig. 1, Table 1), during 2010–2011, 2012–2013 austral summers and in the reproductive period of the birds. This study presents two groups of seabirds: resident and migratory. *Pygoscelis* penguins (Adélie - *Pygoscelis adeliae,* Chinstrap - *P. antarcticus*, Gentoo - *P. papua*) are the resident seabirds in the present study due to their circumpolar distribution (Jerez et al., 2013). As migratory birds in the present study, we have selected species with different migration patterns, since the South Polar Skua (*Stercorarius maccormicki*) is dispersed by routes through the Atlantic and Pacific oceans, reaching the Northern Hemisphere during the winter (Cruwys, 2008; Kopp et al., 2011). On the other hand, Snowy Sheathbill (*Chionis albus*), Antarctic Tern (*Sterna vittata*), Southern Giant Petrel (*Macronectes giganteus*), and Kelp Gull (*Larus dominicanus*) disperse in marine environments of the Southern Hemisphere during winter (Patterson and Hunter, 2000; Watson, 1975).

We sampled breast feathers of *P. adeliae, P. antarcticus*, *P. papua*, *S. maccormicki, S. vittate*, and *C. albus*. The feathers of *L. dominicanus* and *M. giganteus* were opportunistically collected from the ground of their colonies following the protocol: 10 to 20 contour feathers (feathers on the chest, abdomen, or back) at three distinct points inside each colony, and each point collected in the same colony was considered as an individual. The *Pygoscelis* penguins, *Sterna vittata*, and *Chionis albus* were captured with long-handled fish nets, and the *S. maccormicki* were captured using a snare trap. Feathers were packed in individual "zip" type polyethylene bags, and samples were kept at room temperature in dark conditions until the time of analysis. Each captured animal was banded with an aluminum ring, weighed, and measured (wing and tail size, Table S1 of the Supplementary material) with a digital caliper or ruler as described by Sick et al. (1997).

Non-viable eggs of penguins (*P. papua, P. adeliae,* and *P. antarcticus*), *S. maccormicki,* and *S. vittata* were collected in breeding territories, found abandoned outside the nests. The non-viable eggs were collected and stored in decontaminated jars and kept frozen for later lyophilization.

2.2. Sample preparation

All feather samples 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). After this procedure the feathers were cut into small pieces using ceramic scissors. For stable isotope measurements, feather samples were additionally

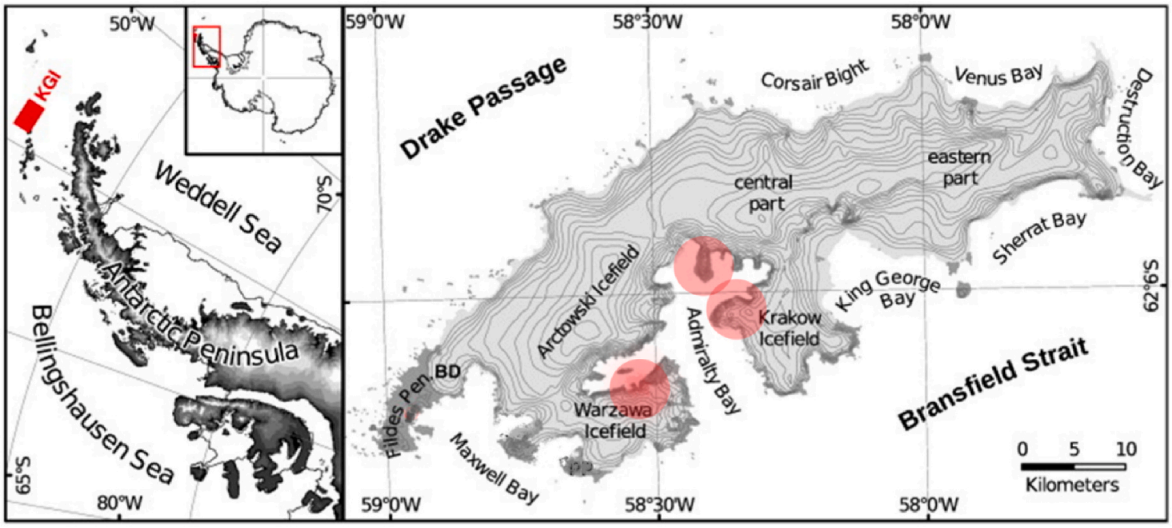

Fig. 1. Map of the Antarctic Peninsula, highlighting King George Island. The sampling points are marked as a red circle (Adapted from Rückamp et al., 2011). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Sampling data (tissue, species, state of maturity, and number of individuals - *n*) from King George Island in the Antarctic Peninsula during 2010–2013 and 2013–2014 austral summers.

	Species	Year of feather sampling	N feathers	Year of egg sampling	N eggs
Migratory	*Chionis albus*	2010–2011	7		–
	Larus dominicanus	2010–2011	12		–
	Macronectes giganteus	2010–2011	24		–
	Stercorarius maccormicki	2010–2013	17	2010–2011	38
	Sterna vittata	2010–2011	27	2010–2011	8
Resident	*Pygoscelis adeliae*	2010–2011	16	2010–2013	17
	P. antarcticus	2010–2011	13	2010–2013	22
	P. papua	2010–2011	15	2010–2013	24

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). The non-viable eggs were kept frozen until they were lyophilized and stored in PFAAs-free plastic tubes for further analysis. For extraction of PFAAs from the feathers and eggs, protocols described by Groffen et al. (2021) and (Powley et al., 2005) were used respectively. The used abbreviation of the target PFAAs are according to Buck et al. (2011; Table S2).

2.3. Chemical reagents

The isotopically mass-labelled internal standards (ISTDs; Wellington Laboratories, Guelph Canada) contained a chemical purity of >98% and isotopic purities of ≥99% or > 94% per ^{13}C or ^{18}O, respectively. Additionally, HPLC grade acetonitrile (ACN; Acros Organics BVBA, Belgium), methanol (VWR International, Belgium), ammonium hydroxide (Filter Service N.V, Belgium) and Milli-Q (18.2 mΩ; TOC: 2.0 ppb; Merck Millipore, Belgium) were used.

2.4. Chemical extraction

For the extraction of PFAAs from the feathers, a protocol described by Groffen et al. (2021) was used with minor modifications as follow. Approximately 100 mg of each sample was weighed and stored in 50 mL polypropylene (PP) tubes. After adding 10 mL of methanol, the samples were vortex-mixed during 1 min and stored for 48 h at room temperature and then centrifuged (4 °C, 10 min, 2400 rpm; 1037×*g*, Eppendorf centrifuge 5804 R). The supernatant was transferred into a 15 mL PP tube, spiked with 10 ng of each ISTD and dried completely using a rotational-vacuum-concentrator (Martin Christ, RVC 2–25, Osterode am Harz, Germany). After reconstituting the samples with 2 mL of a 2% ammoniumhydroxide solution in ACN, the samples were vortex-mixed and filtrated through an Ion Chromatography Acrodisc 13 mm Syringe Filter with 0.2 μm Supor (PES) Membrane (VWR International, Leuven, Belgium) into a PP auto-injector vial.

For the extraction of PFAAs from the eggs, a protocol described by Powley et al. (2005) was used with minor modifications as follow. After removal of the shell, the samples were freeze-dried prior to the extractions. Each sample (50 mg) was spiked with 10 ng ISTD, after which 300 μL of Milli-Q and 10 mL of ACN was added. The samples were vortex-mixed, sonicated for 3 × 10 min (Branson 2510) and left overnight on a shaking plate (135 rpm, room temperature, GFL 3020, VWR International, Leuven, Belgium). After centrifugation (4 °C, 10 min, 1037×*g*, Eppendorf centrifuge 5804 R), the supernatant was reduced until approximately 0.5 mL by using a rotational-vacuum-concentrator (Martin Christ, RVC 2–25, Osterode am Harz, Germany). The concentrated extract and 2 times 250 μL ACN, which was used to rinse the tubes, were added to an Eppendorf tube containing 50 mg graphitized carbon powder (Supelclean ENVI-Carb, Sigma-Aldrich, Belgium) and 50 μL glacial acetic acid. These tubes were vortex-mixed for 1 min and centrifuged (4 °C, 10 min, 10,000 rpm; 9279.4×*g*, Eppendorf centrifuge 5415 R). The cleaned-up extracts were dried almost completely and reconstituted in 2 mL of a 2% ammoniumhydroxide solution in ACN and filtrated as described above for the feathers.

2.5. UPLC-MS/MS analysis

Ultra-performance liquid chromatography-tandem ES (−) mass spectrometry (UPLC-MS/MS, ACQUITY, TQD, Waters, Milford, MA, USA) was used to analyze the target analytes (i.e., four PFSAs (PFBS, PFHxS, PFOS, and PFDS) and 11 PFCAs (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA). The individual analytes were separated using an ACQUITY BEH C18 column (2.1 × 50 mm; 1.7 μm, Waters, USA). To retain PFAA contamination from the system, an ACQUITY BEH C18 pre-column (2.1 × 30 mm; 1.7 μm, Waters, USA) was inserted between the solvent mixer and the injector. The mobile phase solvents consisted of 0.1% formic acid in water (A) and 0.1% formic acid in ACN (B). The flow rate was set at 450

μL/min at a partial loop injection of 6 μL. The solvent gradient started at 65% A, decreased to 0% A in 3.4 min and returned to 65% A at 4.7 min. The analytes were identified and quantified using multiple reaction monitoring (MRM) of two diagnostic transitions per analyte. The MRM transitions, cone voltages and collision energy of each target analyte, including the ISTDs, are displayed in Table S3 of the Supplementary material and were validated by Groffen et al. (2019). All results are expressed in dry weight (dw).

2.6. Quality assurance

Calibration curves, with a highly significant linear fit for all target analytes (all $p < 0.001$; $R^2 > 0.98$), have been constructed by (Groffen et al., 2021, 2019). Procedural blanks were added per batch of 20–25 samples as quality control and contained 10 mL of methanol for the feathers and 10 mL of ACN for the eggs. The methanol-blanks contained minor contamination with PFOA (0.05–0.15 ng/g ww), PFDA (<LOQ – 0.28 ng/g ww) and PFUnDA (<LOQ – 0.25 ng/g ww), which were subtracted from concentrations in samples from the same batch. In addition, instrumental blanks (ACN 100%) were analyzed on a regular basis to prevent crossover contamination of the samples. Individual PFAAs were quantified using the most suitable ISTD based on ionization and extraction efficiency (Groffen et al., 2019) and were those closest in terms of functional group and carbon-chain length (Table S3 of the Supplementary material). The individual limits of quantification (LOQs) were determined in matrix based on a signal-to-noise (S/N) ratio of 10 and are displayed in Table S4 of the Supplementary material.

2.7. Stable isotope measurements

Stable isotope measurements were performed via continuous flow - elemental analysis - isotope ratio mass spectrometry (CF-EA-IRMS) using a Vario MICRO cube C–N–S elemental analyzer (Elementar Analysensysteme GmBH, Hanau, Germany) coupled to an IsoPrime100 isotope ratio mass spectrometer (Isoprime, Cheadle, United Kingdom). Isotopic ratios were conventionally expressed as δ concentrations in ‰ (Coplen, 2011) and relative to the international standards: Vienna Pee Dee Belemnite, for carbon; Atmospheric Air, for nitrogen; and Vienna Canyon Diablo Troilite, for sulfur. We used International Atomic Energy Agency (IAEA, Vienna, Austria) certified reference materials IAEA-C6 ($\delta^{13}C$ values = −10.8 ± 0.5‰; mean ± SD), IAEA-N2, ($\delta^{15}N$ values = 20.3 ± 0.2‰; mean ± SD) and IAEA-S1 ($\delta^{34}S$ values = −0.3‰ ± 0.01‰; mean ± SD) as primary analytical standards. As secondary analytical standards we used sulfanilic acid ($\delta^{13}C$ values = −25.9 ± 0.3; $\delta^{15}N$ values = −0.12 ± 0.4; $\delta^{34}S$ values = 5.9 ± 0.6; mean ± SD in each case). Isotopic ratios of samples were calibrated using primary analytical standards. Standard deviations on multi-batch replicate measurements of secondary analytical (sulfanilic acid) and lab standards (feathers) analyzed interspersed among samples (one replicate of each standard every 15 analyses) were 0.2‰ for both $\delta^{13}C$ values and $\delta^{15}N$ values and 0.4‰ for $\delta^{34}S$ values.

2.8. Statistical analysis

The statistical analyses were performed in R (Jackson et al., 2011; "R Core Team (2020). — European Environment Agency," n. d.) statistical software and STATISTICA software (version 10; StatSoft Inc, USA). For statistical analysis, concentrations < LOQ were replaced to a value equal to f x LOQ where f is the frequency, i. e the number of samples in which the compound was detected divided by the total number of samples analyzed (Parente et al., 2018). Non-parametric (Spearman rank correlation test-r, Mann-Whitney, and Kruskal-Wallis) tests were used. A Kruskal-Wallis test was used for comparing PFAA concentration and stable isotope values among different species. The post hoc tests were conducted to test pairwise comparisons. Mann-Whitney *U* test was used to evaluate the possibility of a significant difference between the concentrations of PFAAs between resident and migratory birds, and to verify possible annual differences. Spearman rank correlation test was used to describe $\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$ values and PFAAs concentration in tissues. We analyzed the relationship between PFAAs concentrations among ten species of resident and migratory seabirds using a principal component analysis (PCA).Before analysis, data was rank transformed for standardization and to deal with values below the limit of quantification (LOQ). When the compounds had almost all the samples below the LOQ they were excluded from the analyses. The PCAs, for both feathers and eggs, included species and habit as supplementary qualitative variables. Feather PCA also included isotopes as supplementary quantitative variables, since the measurements of stable isotopes were only carried out in the feather matrix. The inclusion of isotopes as variables in the PCA was made to observe whether there was also an influence of trophic ecology on the differences in PFAA concentrations between species. Biplots showing $\delta^{34}S$, $\delta^{15}N$, and $\delta^{13}C$ values in Antarctic seabirds were made.

3. Results

The dominant compound among PFAAs was PFUnDA in both matrices (Tables 2 and 3; Figs. 2 and 3). More compounds could be detected in eggs than in feathers samples (i.e., ten compounds were detected in eggs compared to eight compounds detected in feathers for a total of 15 compounds measured, Tables 2 and 3; Fig. 2). It was not possible to correlate the egg to the parents in the present study since the non-viable eggs were found abandoned outside the nests. Mean ∑PFAA concentrations in feathers ranged from 0.47 as the lowest concentration to 17.4 ng/g dry weight (dw) as the highest from *P. antarcticus* to *S. maccormicki*. In eggs, ∑PFAA concentrations ranged from 3.51 as the lowest concentration to 116.6 ng/g dw as the highest from *P. adeliae* to *S. maccormicki*. There was no significant difference between the samples of feathers and eggs collected in different years for each species in the present study ($p > 0.05$). Additionally, no significant interannual difference was observed for samples of feathers and eggs of *S. maccormicki* ($p > 0.05$) and eggs of *Pygoscelis* penguins ($p > 0.05$).

3.1. Perfluoroalkyl acids in feathers

The concentrations of PFOA, PFUnDA, PFDoDA, PFTrDA, PFTeDA were detectable in migratory and resident seabirds; while PFHxA and PFDA were detectable only in migratory ones (Table 2, Fig. 2). PFOS was not detectable in any of the resident species, but it was detectable in one migratory seabird (*S. maccormicki*). The concentrations of PFBA, PFPeA, PFHpA, PFNA, PFBS, PFHxS, and PFDS were below the detection limit for all species of seabirds. There was no significant correlation between the morphometric measurements (Table S1 of the Supplementary material) of seabirds and the concentrations of PFAAs ($p > 0.05$ in all cases).

Comparing migratory with resident seabirds, significantly higher values of PFHxA ($U = 352$, $p < 0.001$), PFDA ($U = 0$, $p < 0.001$), PFUnDA ($U = 1188$, $p < 0.001$), and PFTeDA ($U = 2396$, $p = 0.032$) were observed in migratory animals.

Profiles based on the relative contribution of the studied compounds to PFAAs were dominated by ΣPFCAs (89–100%), with PFUnDA being the prevalent compound (20–65% of ΣPFAAs) for all species (Fig. 2). PFSAs represented 11% of ΣPFAAs in *S. maccormicki*. Considering all migratory species, the prevalent compound was PFUnDA (22–63%). In resident seabirds' species the contributions of PFCAs were 100%, with PFUnDA being the prevalent compound, mean of 40% of ΣPFAAs in all resident species together, followed by PFOA (14%–37%) > PFTeDA > PFDoDA > PFTrDA.

To better characterize our groups a PCA was used. The first principal component (PC1) explained 36.1% (Fig. 3A, Table S5) of the total variability in the dataset, with the strongest positive contributions from PFTrDA (0.91), PFTeDA (0.90), and the weakest one from PFOA

Table 2
Median concentrations and ranges (min-max; ng/g dw) of PFAAs, $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ in feathers of resident and migratory seabirds from King George Island, Antarctic Peninsula, Antarctica. The concentrations of PFBA, PFPeA, PFHpA, PFNA, PFBS, PFHxS, and PFDS were below the detection limit for all species and therefore omitted from the Table. ∑PFAAs was represented by the average ± standard deviation of the sums of each individual. P-values *<0.05; **<0.01; ***<0.001.

	Species		PFHxA	PFOA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFOS	∑PFAAs	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
Migratory	*Chionis albus* n = 7	**Median**	<0.97	1.41*	1.29	1.81	<0.32*	<0.17	<0.55	<0.98	4.67 ±	−20.2	10.5	17.5
		min-max	<0.97–1.81	1.11–1.74	<1.19–1.43	<1.41–1.43	<0.32–0.39	–	–	–	1.17*	−17–−22.3	9.8–11.3	16.9–18.8
	Stercorarius maccormicki n = 17	**Median**	<0.97**	<1.06	0.3	1.55	<0.32***	0.58**	2.15**	<0.98***	8.09 ±	−17.5	12.6	13.7***
		min-max	–	<1.06–1.9	<1.19–1.71	<1.41–3.96	<0.32–1.69	<0.17–1.99	<0.55–7.4	<0.98–2.62	5.18**	−19.3–−16.6	11.2–14.1	10.7–15.8
	Larus dominicanus n = 12	**Median**	<0.97	<1.06***	<1.19	<1.41	<0.32	<0.17	<0.55	<0.98	3.78 ±	−18.1*	11.1	16.9
		min-max	<0.97–2.48	<1.06–2.82	<1.19–1.98	<1.41–2.31	–	–	–	–	1.43*	−20.1–−17.4	10.4–11.8	12.1–17.6
	Macronectes giganteus n = 24	**Median**	<0.97	<1.06	<1.19***	1.61	<0.32	<0.17	<0.55	<0.98	2.46 ±	−21.2*	12.9	17.5
		min-max	<0.97–1.54	<1.06–1.57	<1.19–1.83	<1.41–2.14	–	–	–	–	1.12*	−23.6–−15.1	11.4–13.7	15.8–18.9
	Sterna vittata n = 27	**Median**	<0.97	<1.06	<1.19	1.47	<0.32	<0.17	<0.55	<0.98	2.57 ±	−24.6	9.12**	17.2
		min-max	<0.97–2.18	<1.06–1.68	<1.19–2	0.73–2.35	–	–	–	–	0.95*	−34.4–−16.7	7.6–11.2	15.8–19

	Species		PFHxA	PFOA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFOS	∑PFAAs	$\delta^{13}C$ values (‰)	$\delta^{15}N$ values (‰)	$\delta^{34}S$ values (‰)
Resident	*Pygoscelis adeliae* n = 16	**Median**	<0.97	0.20	<1.19	<1.41***	<0.32	<0.17	<0.55	<0.98	1.54 ±	−24.3	9.82**	14.9
		min-max	–	0.20–1.94	–	<1.41–1.71	<0.32–0.61	<0.17–0.33	<0.55–1.31	–	0.46*	−25.8–−23	9–10.7	13.5–17.6
	P. antarcticus n = 13	**Median**	<0.97	0.33	<1.19	<1.41	<0.32***	<0.17	<0.55	<0.98	1.48 ±	−25.3	9.29**	13.9*
		min-max	–	0.20–1.97	–	<1.41–2.47	–	–	–	–	1.03*	−27.2–−24.4	8.3–9.77	12.8–15.2
	P. papua n = 15	**Median**	<0.97	0.14***	<1.19	<1.41	<0.32	<0.17	<0.55	<0.98	2.21±	−24.5	9.8**	15.7
		min-max	–	0.14–1.63	–	<1.41–1.90	<0.32–0.59	<0.17–1.01	<0.55–3.78	–	1.54*	−25.5–−24.1	9.16–10.1	14.2–16.3

Table 3
Median concentrations and ranges (min-max; ng/g dw) of PFAAs in eggs of resident and migratory seabirds from King George Island, Antarctic Peninsula, Antarctica. PFBA, PFPeA, PFBS, PFHxS, and PFDS concentrations were below the detection limit for all species and therefore omitted from the Table. P-values *<0.05; **<0.01; ***<0.001.

			PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFOS	∑PFAAs
Migratory	*S. maccormicki* n = 38	**Median**	<2.05	<1.93	2.44	<0.54	3.17*	6.42***	1.66*	<0.72–7.6	3.30*	0.97	4.38***	35.1 ±
		Min-max	<2.05–6.25	–	1.17–11.8	<0.54–1.26	<0.59–5.31	<0.94–23.1	<0.72–7.6	0.3–37.4	0.36–37.9	<0.59	<1.09–32.6	24.7*
	S. vittata n = 8	**Median**	<2.05	<1.93	1.91	<0.54	2.22	4.25	0.86	0.96	<0.59	<1.09		29.0 ±
		Min-max	<2.05–4.15	<1.93–83.7	0.97–2.17	–	1.27–4.44	2.78–6.1	<0.72–1.05	0.63–1.16	–	–		30.9*
Resident	*P. adeliae* n = 17	**Median**	<2.05	<1.93	1.77	<0.54	2.8	4	<0.72	0.55	<0.59	<1.09		11.0 ±
		Min-max	<2.05–2.74	–	<0.82–2.56	–	<0.59–3.83	<0.94–6.8	<0.72–1.51	0.24–1.21	–	–		3.01*
	P. antarcticus n = 22	**Median**	2.16	<1.93	1.37***	2.43	<0.59	2.27	<0.72	0.64	<0.59	<1.09		13.3 ±
		Min-max	<2.05–6.04	–	<0.82–2.7	1.07–4.2	–	2.78–5.9	<0.72–1.86	0.29–1.88	–	–		2.33*
	P. papua n = 24	**Median**	2.42*	<1.93	2.33	<0.54	2.43	4.27	<0.72	0.64	<0.59	1.57**		14.8 ±
		Min-max	<2.05–7.65	–	0.86–4.95	–	1.07–4.2	2.78–5.9	<0.72–1.86	0.29–1.9	–	<1.09–4.45		2.69*

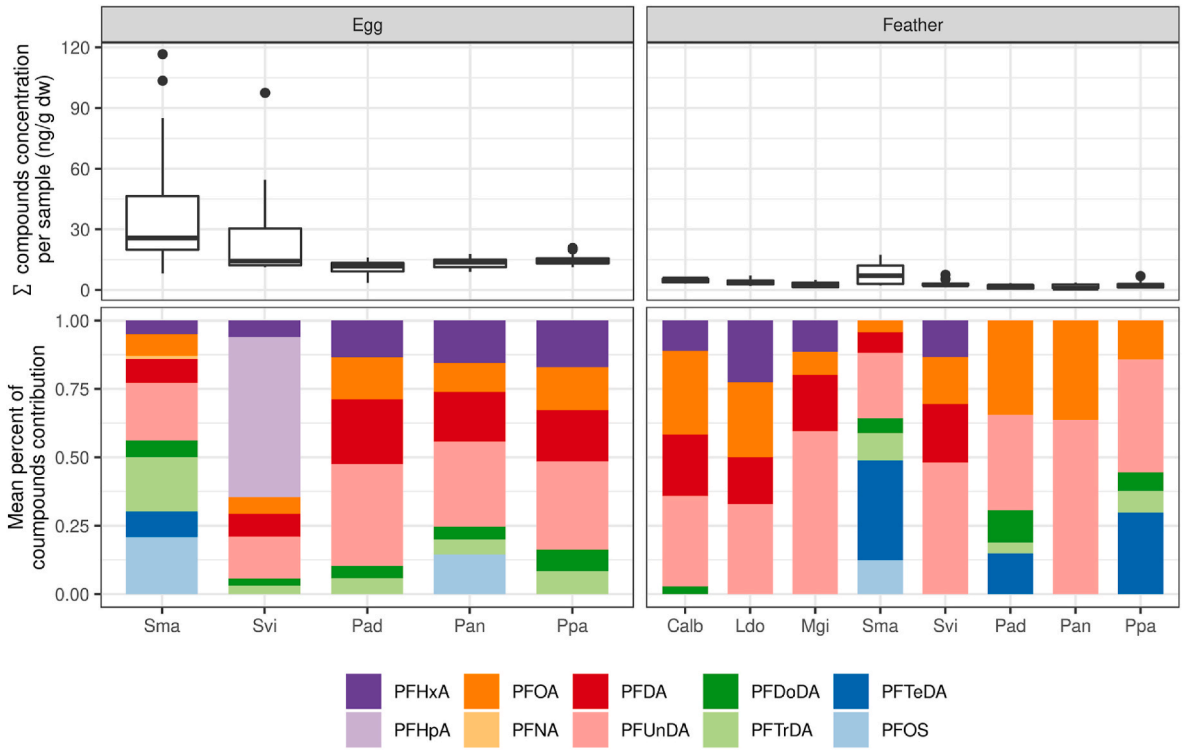

Fig. 2. Sum of compounds and relative contribution of individual PFAAS to ∑PFAAs (ng/g dw) in feathers and eggs of *C. albus* (Calb), *L. dominicanus* (Ldo), *M. giganteus* (Mgi), *S. maccormicki* (Sma), *S. vittata* (Svi), *P. adeliae* (Pad), *P. antarcticus* (Pan), and *P. papua* (Ppa) from Antarctic Peninsula.

(−0.12). The second principal component (PC2) expressed 25% (Fig. 3A, Table S5) of the variation with the strongest positive contributions from PFOA (0.87). There was a clear overlap among the PFAAs and stable isotope profiles between migratory and resident seabirds (Fig. 3A).

The pattern of PFAAs contamination in feathers (Table 2) in the present study was as follows: *S. maccormicki* > *C. albus* > *L. dominicanus* > *S. vittata* > *M. giganteus* > *S. vittata* > *P. papua* > *P. adeliae* > *P. antarcticus.*

Comparing the compounds detected in feathers only in migratory seabirds, the concentrations of PFDoDA, PFTrDA, PFTeDA were below the detection limit for *S. vittata, L. dominicanus,* and *M. giganteus* (Table 2). PFHxA ($H = 63.3$, $p < 0.001$), PFOA ($H = 54$, $p < 0.001$), PFDA ($H = 50.3$, $p < 0.001$), PFDoDA ($H = 79.6$, $p < 0.001$), and PFTrDA ($H = 79.8$, $p < 0.001$) differed among species. The PFHxA concentrations of *S. maccormicki* ($p = 0.01$) were significantly lower compared to the other seabird species. PFOA concentrations were significantly higher in *C. albus* ($p = 0.03$) and *L. dominicanus* ($p < 0.001$) compared to the others. The PFDA concentrations were significantly lower in *M. giganteus* ($p < 0.001$), and no significant differences were found for the other species of migratory seabirds. PFDoDA concentrations were significantly higher in *C. albus* ($p = 0.03$) and *S. maccormicki* ($p < 0.001$) compared to the others. Concentrations of PFTrDA and PFTeDA were significantly higher in *S. maccormicki* (PFTrDA: $p = 0.008$; PFTeDA: $p = 0.008$) compared to the other migratory seabirds.

Comparing the compounds detected in feathers only in resident seabirds (Table 2). PFOA ($H = 17.7$, $p = 0.001$), PFUnDA ($H = 13.9$, $p = 0.001$), PFDoDA ($H = 31.9$, $p < 0.001$), PFTrDA ($H = 35.2$, $p < 0.001$), and PFTeDA ($H = 35.2$, $p < 0.001$) differed among species. The PFOA concentrations were significantly lower in *P. papua* ($p < 0.001$) compared to the other two penguin species. The PFUnDA concentrations were significantly lower in *P. adeliae* ($p < 0.001$) compared to *P. papua*. The PFDoDA concentrations were significantly lower in *P. antarcticus* ($p < 0.001$) compared to the other two penguin species. PFTrDA and PFTeDA concentrations ranged from *P. papua* ($p = 0.035$) > *P. adeliae* ($p = 0.003$) > *P. antarcticus* ($p < 0.001$).

3.2. Perfluoroalkyl acids in eggs

Significant differences in egg PFAAs concentrations among the resident and migratory seabirds were observed for all detected analytes for both groups (Table 3, Fig. 2). The concentrations of PFHxA, PFOA, PFDA, PFUnDA, PFDoDA, PFTrDA and PFOS were detectable in the group of resident and migratory seabirds, while PFHpA, PFTeDA were detectable only in the group of migratory seabirds. PFBA, PFPeA, PFBS, PFHxS and PFDS concentrations were below the detection limit in eggs of all investigated species.

The pattern of PFAAs contamination in eggs (Table 3) in the present study was as follows: *S. maccormicki* > *S. vittata* > *P. papua* > *P. antarcticus* > *P. adeliae.*

Profiles based on the relative contribution (Fig. 2) of the studied compounds to PFAAs were dominated by ΣPFCAs (78–100%). PFHpA was the predominant compound in eggs of migratory birds (0–62%), followed by PFOS > PFUnDA > PFTrDA. The predominant compound in the eggs of resident birds was PFUnDA (mean 36%), followed by PFDA > PFHxA > PFOA.

The first principal component (PC1) explained 40.6% (Fig. 3B, Table S6) of the total variability in the dataset, with the strongest positive contributions from PFTrDA (0.84), PFTeDA (0.81), PFUnDA (0.81), and the weakest one from PFHpA (−0.18). The second principal component (PC2) expressed 14.5% (Fig. 3B, Table S6), with the strongest positive contributions from PFHxA (0.68), PFOA (0.62). There is a clear overlap between migratory and residents with a higher tendency of separation than reported in the feathers. However, as in the feathers, the horizontal axis tends to separate Northern Hemisphere migratory birds from Southern Hemisphere birds.

The PFHpA concentrations were above the detection limit only for *S. vittata* eggs. The PFNA and PFTeDA concentrations were above the detection limit only for *S. maccormicki* eggs. PFTrDA ($H = 56.5$, $p < 0.001$), PFHxA ($H = 21.3$, $p < 0.001$), PFOA ($H = 39$, $p < 0.001$), PFDA ($H = 39$, $p < 0.001$), PFUnDA ($H = 25.5$, $p < 0.001$), and PFDoDA ($H = 48.6$, $p < 0.001$) concentrations differed among species. The

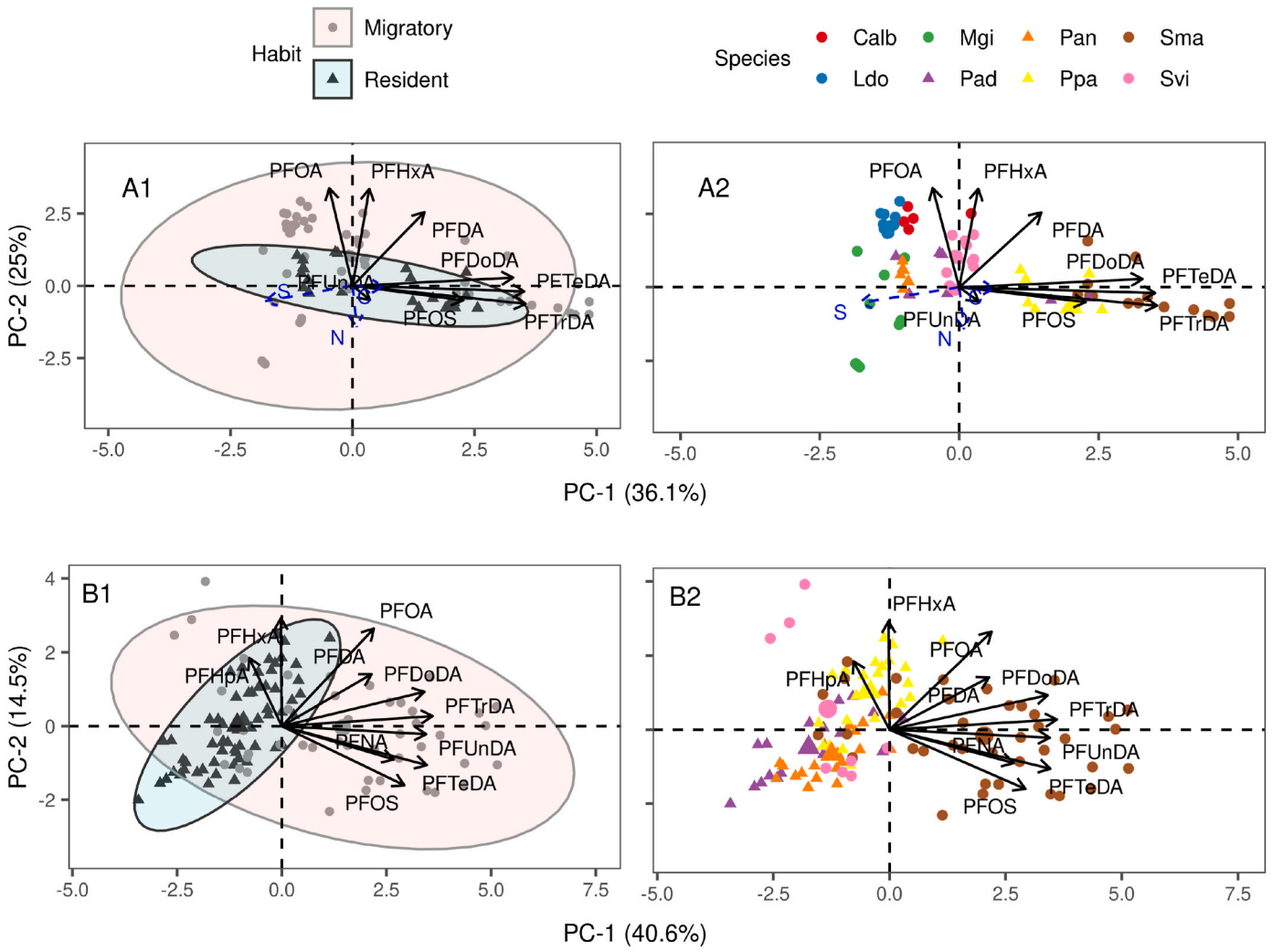

Fig. 3. PCA feather (A1 and A2) and egg (B1 and B2) of migratory and resident seabirds from Antarctic Peninsula.

concentrations of PFTrDA were significantly higher in *S. maccormicki* ($p = 0.04$) compared to the other analyzed species. The PFOS concentrations were above the detection limit only for *S. maccormicki* and *P. papua*. *S. maccormicki* ($U = 229$, $p = 0.004$) showed significantly higher concentrations of PFOS than *P. papua* eggs.

The concentrations of PFHxA were significantly higher in *P. papua* ($p = 0.014$) than in *P. adeliae* ($p < 0.001$) and *S. maccormicki* ($p = 0.001$). The concentrations of PFOA were significantly lower in *P. antarcticus* ($p < 0.001$) than *S. maccormicki* ($p = 0.002$) and *P. papua* eggs ($p < 0.001$). The PFDA concentrations were significantly higher in *S. maccormicki* ($p = 0.011$) than in *P. antarcticus* ($p = 0.011$) eggs. The PFUnDA concentrations were significantly higher in *S. maccormicki* ($p < 0.001$) than in *P. adeliae* ($p < 0.001$) and *P. antarcticus* ($p < 0.001$). The concentrations of PFDoDA were significantly higher in *S. maccormicki* ($p = 0.046$) and *P. papua* eggs ($p = 0.012$) than in the other *Pygoscelis* spp.

3.3. Stable isotope ratios and PFAAs patterns

Spearman rank correlation matrix between PFAAs and stable carbon showed positively significant correlations among $\delta^{13}C$ values and five compounds (PFDA, PFUnDA, PFTrDA, PFTeDA, and PFOS), and significantly negative between $\delta^{13}C$ values and PFOA (Fig. 4). Significant positive correlations were found between $\delta^{15}N$ values and three compounds (PFUnDA, PFTrDA, and PFTeDA), and significantly negative correlations considering $\delta^{15}N$ values and PFOA (Fig. 4). The $\delta^{34}S$ values concentrations showed positive and significant correlation with

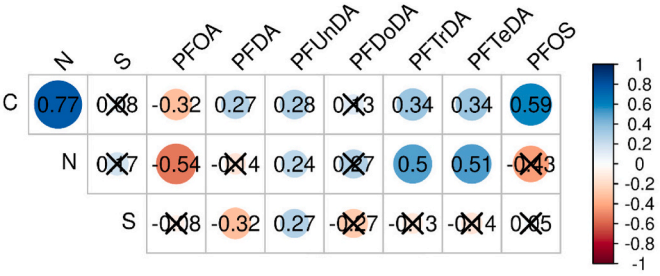

Fig. 4. Spearman rank correlation matrix between PFAAs and C ($\delta^{13}C$), N ($\delta^{15}N$), and S ($\delta^{34}S$) in feathers of seabirds from the Antarctic Peninsula. Significant correlations (rs, $p < 0.05$) are shown in blue (positive) and red (negative). The color intensity is related to the rs value, while non-significant correlations are marked with an X. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

PFUnDA, and significantly negative with PFDA (Fig. 4). There is a significantly positive correlation between $\delta^{13}C$ and $\delta^{15}N$, but no significant correlation was observed between $\delta^{15}N$ x $\delta^{34}S$, and $\delta^{34}S$ x $\delta^{13}C$ (Fig. 4).

The values of $\delta^{15}N$ ($H = 70.1$, $p < 0.001$), $\delta^{13}C$ ($H = 70.6$, $p < 0.001$), and $\delta^{34}S$ ($H = 88.8$, $p < 0.001$) differed among species. *Pygoscelis* species ($p = 0.009$) and *S. vittata* ($p = 0.009$) showed significantly lower $\delta^{15}N$

values compared to the other species of seabirds (Table 2, Fig. 5). *S. maccormicki* ($p < 0.001$), *M. giganteus* ($p = 0.02$), and *L. dominicanus* ($p = 0.02$) showed significantly higher $\delta^{13}C$ values compared to the other species of seabirds (Table 2, Fig. 5). Regarding $\delta^{34}S$ values, *S. maccormicki* ($p < 0.001$) and *P. antarcticus* (0.04) showed significantly lower values compared to *C. albus, M. giganteus*, and *S. vittata* (Table 2, Fig. 5).

4. Discussion

Clearly, Antarctic seabirds are exposed to PFAAs concentrations that will rely upon intra-specific and inter-specific driving factors (e.g., tissues, sex, sampling location, biology, …). Migratory seabirds showed higher concentrations of most PFAAs than resident species. The higher concentrations of PFSAs and PFCAs in migratory seabirds compared to *Pygoscelis* penguins agree with differences in their trophic positions ($\delta^{15}N$ values) and foraging area ($\delta^{13}C$ and $\delta^{34}S$ values). Trophic ecology (i.e., diet and foraging strategies), metabolic factors (i.e., sex, molting and breeding status), migration patterns (trans-equatorial movements of seabirds), and sources of PFAAs (i.e., point sources and long-range transport) may influence in the interspecific differences found in this study.

4.1. Migration and the PFAAs

Migratory seabirds that migrate to the Northern Hemisphere (*S. maccormicki*) had higher PFAAs concentrations than seabirds migrating only within the Southern Hemisphere. These data were expected because of the well-known industrialization of the Northern Hemisphere compared to the Southern Hemisphere (Ma et al., 2016; Paul et al., 2009).

The *S. maccormicki* is a trans-equatorial migrant, disperses widely, reaching the Northern Hemisphere during the southern winter (Cruwys, 2008; Kopp et al., 2011). This top predator is opportunistic, feeding on fish and crustaceans, as well as carrion of seabirds nesting in nearby colonies (Borghello et al., 2019; Cruwys, 2008; Quillfeldt, 2002; Ridoux and Offredo, 1989). Thus, the high trophic position coupled with its migration pattern may explain the high levels of $\delta^{15}N$, $\delta^{13}C$, and PFCAs in *S. maccormicki* compared to the other Antarctic seabirds in the present study. The literature shows that long-chain PFCAs are mainly noticed in seawater outside of the Antarctic Circumpolar Current (Zhao et al., 2012), being more abundant in seawater from northern compared to southern Atlantic latitudes (González-Gaya et al., 2014; Ma et al., 2016). This may explain the relative high levels of PFTrDA and PFTeDA found in *S. maccormicki* and low concentrations in penguins. Previous studies about Antarctic seabirds also demonstrate a similar pattern (Roscales et al., 2019; Tao et al., 2006). Tao et al. (2006) detected long-chain PFCAs in liver, serum, and eggs of northern albatrosses, while the PFCAs concentrations were below the limits of quantitation in livers of albatrosses from the Southern Ocean. Roscales et al. (2019) found higher levels of long-chain PFCAs in plasma of seabirds foraging north of Antarctica than in the resident seabirds. Gao et al. (2020b) found $\sum$PFAAs 1.85 ± 1.21 ng/g dry weight (dw) (present study: 2.62 ± 1.54 ng/g dw) in feathers of *P. papua,* and like in our study, reported low concentrations of long-chain PFCAs in penguins.

The PFCAs were more predominant in our samples than PFSAs, since PFBS, PFHxS, and PFDS were not detected in any of the samples, and PFOS was only detected in feather of *S. maccormicki* and eggs of *S. maccormicki* and *P. antarcticus*. Tao et al. (2006) observed similar concentrations of PFOS in *S. maccormicki* eggs (2.5 ng/g ww), which indicate that the concentrations of PFOS have remained constant over the years in the south polar skua. Leat et al. (2013) analyzing *S. maccormicki* eggs, detected only PFCAs with nine or more carbon atoms (PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA), whereas for PFSAs, the eight-carbon PFOS dominates. Our results showed a similar pattern, since PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, and PFOS were detected in *S. maccormicki* eggs. The reported better ability of PFOS, compared to PFCAs, to biomagnificate and bioaccumulate in polar food webs (Kelly et al., 2009; Roscales et al., 2019) could explain the higher values of PFOS in *S. maccormicki* feathers and eggs in the present study. Thus, migration could result in higher exposure to PFSAs, and consequently higher concentrations of PFOS in comparison to resident behavior, as previously demonstrated for PFAAs in plasma blood of migratory and resident Antarctic seabirds (Roscales et al., 2019).

Studies performed in birds from Northern Hemisphere have shown a higher exposure to PFSAs compared to the Southern ones. The Great skua (*Stercorarius skua*) from the North Atlantic showed values of PFOS

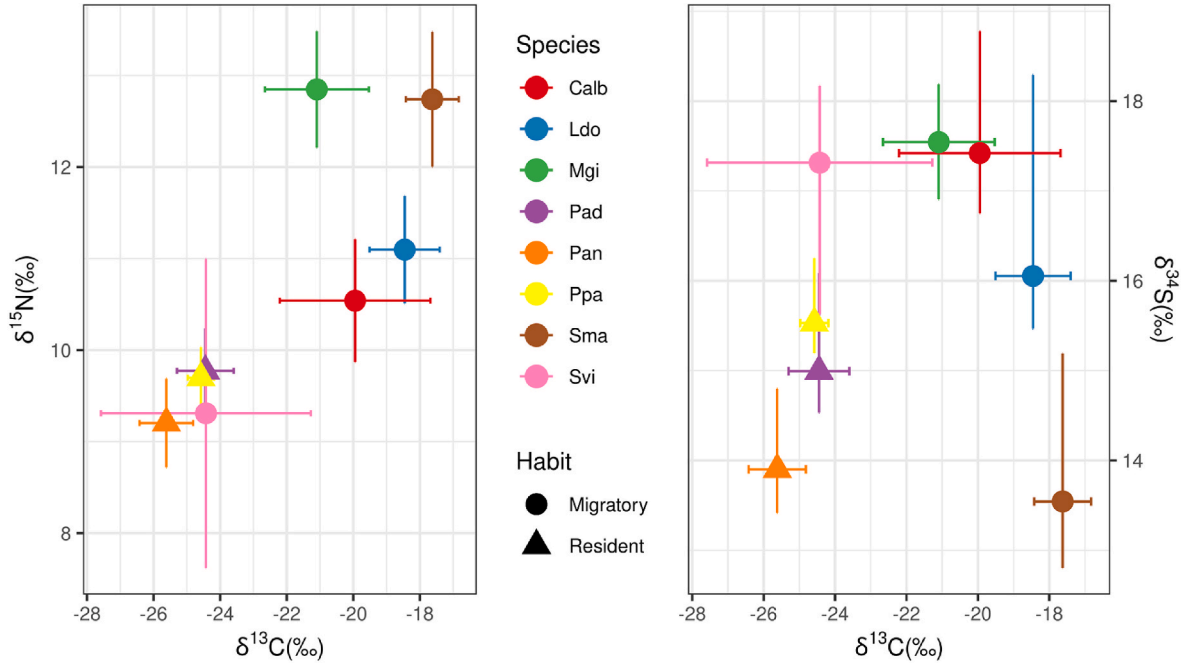

Fig. 5. Mean (±SD) $\delta^{13}C$ x $\delta^{15}N$ values (‰) and $\delta^{13}C$ x $\delta^{34}S$ of in feather samples of migratory and resident seabirds from Antarctic Peninsula.

an order of magnitude greater than (mean 23 ng/g ww) *S. maccormicki* (2.2 ng/g ww) from the present study (Leat et al., 2013). The literature has shown PFOS concentrations in plasma of *S. skua* from Northern Hemisphere (mean 31 ng/g ww) an order of magnitude greater than in brown skuas from the Falklands (Leat et al., 2013; Roscales et al., 2019). Li et al. (2018) observed higher PFSAs concentrations in feathers samples of accipiter birds from Tibetan Plateau (mean range: 0.59–6.12 ng/g, dw) compared to the present study.

M. giganteus are top predators of the sub-Antarctic and Antarctic food webs, feeding on fish, marine mammals, and penguins' carcasses, as confirmed by our $\delta^{15}N$ values results. *M. giganteus* forages in diverse marine regions during the breeding period, which explains the great variability of $\delta^{13}C$ values concentrations (Roscales et al., 2019). Thus, higher concentrations of PFAAs in *M. giganteus* compared to penguins may be explained by their high trophic position and their wide dispersion across southern marine environments. This species can reach the coast of Australia, New Zealand, South Africa and South America, where high levels of PFAAs have been reported compared to Antarctica (González-Gaya et al., 2014; Patterson and Hunter, 2000).

Despite *S. vittata* presents $\delta^{15}N$ values and diet similar to penguins (Casaux et al., 2008), higher concentrations of PFAAs were observed, which may be due to their migratory pattern, since this species migrates to more polluted places such as southern Africa and South America (Cruwys, 2008).

Low PFAAs levels were expected in *Pygoscelis* penguins, owing to their relatively low trophic position, compared to other seabirds in this study, and their resident behavior. In the present study, the concentrations of PFAAs in *P. antarcticus* were lower compared to the other two penguin species. The specialized diet of *P. antarcticus*, which feeds more on krill, compared to generalist strategy presented by *P. papua* and the intermediary one presented by *P. adeliae* (Herman et al., 2017) may explain the significantly lower concentrations of most of PFAAs in feather, and $\delta^{15}N$ values that *P. antarcticus* presents compared to other resident and migratory seabirds.

Our results showed the following pattern of PFAAs concentrations PFUnDA > PFOA > PFTeDA > PFDoDA for *Pygoscelis* feather, and PFUnDA > PFOS > PFDoDA > PFHpA for *P. papua* eggs. This is in line with the findings of (Schiavone et al., 2009) who also observed that among PFCAs, PFUnDA was dominant in penguin eggs. On the other hand, previous studies observed short-chain PFHxA dominated contribution profiles in plasma, guano, and muscle of *P. papua* (Llorca et al., 2012; Roscales et al., 2019). They suggested that metabolic degradation of long-chain PFCAs and direct dietary incorporation might explain this result. This indicates that the PFAAs contributions profiles may vary in different tissues of the animal body.

4.2. PFAAs and the stable isotopes

In the present study, PFUnDA, PFTrDA, and PFTeDA showed a significant positive correlation with trophic position ($\delta^{15}N$ values), indicating a biomagnification potential of these compounds. The literature has shown less or no biomagnification for PFCAs compounds (Lescord et al., 2015; Simonnet-Laprade et al., 2019), which contradicts our findings. Unlike (Kelly et al., 2009), who observed a positive and significant correlation between $\delta^{15}N$ values and PFOS, we did not observe a correlation between $\delta^{15}N$ values and any PFSAs (Lopez-Antia et al., 2021). observed, based on $\delta^{15}N$ values and $\delta^{13}C$ values data, that black-backed gulls (*Larus fuscus*) with a predominantly marine diet have higher exposure to PFOS. Our results also showed that PFOS, PFDA, PFUnDA, PFTrDA and PFTeDA present a correlation with foraging areas ($\delta^{13}C$ values). The correlations between PFUnDA and $\delta^{34}S$ values in our study suggest an important contribution from coastal or benthic food webs. The latter statement is based on the fact that producers from open marine and pelagic environments typically have higher $\delta^{34}S$ values concentrations compared to coastal benthic sediment-associated producers (Connolly et al., 2004).

Altogether, our results appear to suggest that the trophic position, foraging area, and dietary sources influence PFCAs concentrations, and that foraging area influences PFSAs levels in feathers of Antarctic birds.

4.3. PFAAs in different matrices

Feathers and eggs represent an excretion pathway for pollutants that came from different sources (Burger, 1993; Mello et al., 2016). Feathers are often only connected to the blood circulation during its formation (Burger, 1993; Groffen et al., 2020; Jaspers et al., 2006; Løseth et al., 2019), hence integrate bird exposure since the last molt, whereas eggs represent the maternal reserves (Drouillard and Norstrom, 2001). Hence, this could result in differences in accumulated PFAAs, in terms of concentrations as well as in detection frequency of certain analytes. The contributors that probably influence the egg content are mainly the pre-laying and late-winter foraging areas (Cifuentes et al., 2003; Dehnhard et al., 2017; Mello et al., 2016; Polito et al., 2011).

The greater number of compounds in eggs (and higher concentrations) could be due to a higher affinity of certain PFAAs to egg proteins compared to keratin (Lopez-Antia et al., 2017; Wang et al., 2019). The literature has demonstrated that PFAAs bind to protein with suitable binding locations, as a ligand or using hydrogen-bonding as powering force to create a complex with protein and ligands in the PFAAs-protein interactions (Bischel et al., 2011; Zhang et al., 2013). Consequently, these compounds are frequently observed in protein-rich tissues such as eggs (Lopez-Antia et al., 2017; Wang et al., 2019) and serum (Gao et al., 2015).

Another factor that may also have contributed to interspecific differences in concentrations found in the present study are the species-specific differences in molting. The annual cycles of molting are usually influenced by migratory patterns, in order to optimize flight efficiency and thermoregulation. This is the case of *L. dominicanus*, *S. maccormicki,* and *S. vittata* that present two annual molting process, while the other species present only one annual molt (Watson, 1975). Previous studies have shown that the molt influences the concentrations of trace elements within and among feathers of birds of prey (Dauwe et al., 2003). However, more studies are needed to verify whether the same is true for PFAAs.

4.4. Joint assessment of aspects that contribute to exposure of antarctic seabirds to PFAAs

To the best of our knowledge, our study is the first to associating PFAAs exposure with stable isotope values to clarify the influence of multiple spatial and ecological factors using eggs and feathers of Antarctic seabirds. We highlight that: (1) migratory seabird species have higher concentrations of PFSAs and PFCAs in feathers and eggs than resident species; (2) Seabirds that migrate to the Northern Hemisphere have higher concentrations of PFSAs and PFCAs than Southern Hemisphere migratory seabirds and resident ones; (3) Trophic position ($\delta^{15}N$ values), foraging area ($\delta^{13}C$ values), and dietary sources ($\delta^{34}S$ values) influence PFCAs concentrations, and foraging area ($\delta^{13}C$ values) influences PFSAs levels in feathers of Antarctic birds.

In the present study, the difficult access to the reproductive colonies of some seabirds (e.g., *L. dominicanus, C. albus,* and *M. giganteus*) and logistical limitations for moving to different sampling sites made it impossible to collect egg samples from all studied species. Another limitation is that all resident species were penguins, not allowing to control for phylogenetic characteristics, as there are no migratory penguins in the present study. Therefore, we cannot totally exclude that the reported differences reflect a "penguin effect" rather than a "resident/migrant effect".

We observed that the migration, especially trans-equatorial migration, has an important role in the exposure of birds to long-chain PFCAs, since the lowest concentrations were reported in species residing in Antarctica. This may indicate a certain barrier created by the Antarctic

Circumpolar Current to these compounds. However, as shown in the literature, the inputs via atmosphere are relevant. It is worth noting the potential that long-distance migratory birds may have as bio-vectors in the transport of pollutants, including PFCAs, in Antarctic environments, although this has to be further confirmed in future studies using a mass balanced approach, such as extractable organofluorine (EOF). This work serves as a precursor for studies that focus on the potential of migratory birds as vectors of pollutants in remote regions.

Author statement

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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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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