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1 **Perfluoroalkylated compounds in the eggs and feathers of resident and migratory seabirds**

2 **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).

Keywords: PFAA, Perfluorinated substances, PFOS, biomonitoring, contamination, stable isotopes

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68 **1. Introduction**

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

78 Among these pollutants, perfluoroalkyl acids (PFAAs) are a widely distributed emerging
79 pollutants, being found in places far from their manufacturing source, such as Antarctica (Gao et
80 al., 2020a; Roscales et al., 2019). Although it is not clear which form of transport is dominant,
81 studies indicate that PFAAs can reach different regions of the globe through the ocean and/or
82 atmospheric currents (Young and Mabury, 2010; Zhao et al., 2012a). Among PFAAs, previous
83 studies focused primarily on long-chain perfluoroalkyl carboxylic acids (PFCAs) and
84 perfluoroalkyl sulfonic acids (PFSAs) (Buck et al., 2011; Groffen et al., 2020). Perfluorooctane
85 sulfonate (PFOS- $C_8F_{17}SO_3H$) and perfluorooctanoic acid (PFOA- $C_7F_{15}COOH$) draw special
86 attention for their persistence, potential health effects, and global distribution, and are the most
87 widely detected long-chain PFAAs in the environment, wildlife and humans around the world
88 (Buck et al., 2011; Ericson Jogsten et al., 2012; Groffen et al., 2017). The highest PFOS and PFOA

89 concentrations in humans were reported to be 164 ng/mL from U.S.A and 256 ng/mL from Korea,
90 respectively (Sinclair et al., 2020). So et al. (2006) also measured amounts of PFAS in human
91 breast milk, in which PFOS has been reported at 360 ng/L and PFOA at 210 ng/L. Exposure to
92 PFAAs can cause diseases such cancer, altered metabolisms, impaired liver function, chronic
93 kidney damage, cardiovascular diseases, probable thyroid, and other hormonal malfunction or
94 imbalances (Podder et al., 2021).

95 PFOS and PFOA were listed as Persistent Organic Pollutants (POPs) by the Stockholm
96 Convention since 2009 and 2019 respectively, which resulted in regulations that aimed to reduce
97 the levels of these compounds in the environment (Filipovic et al., 2015; Stockholm Convention,
98 2021). However, since the early 2000s, developing Asian countries have increased their PFAAs
99 production and emissions (Xie et al., 2013). Linked to this, the production of other PFAAs
100 compounds such as polyfluorinated compounds (e.g., fluorotelomer sulfonate- FTSA) and short-
101 chain PFAAs (e.g., $C_4HF_9O_3S$ - perfluorobutane sulfonic acid - PFBS), which are often used as
102 alternatives to PFOS and PFOA, are still increasing, and the impact of these alternative substances
103 on the environment is still not clear (Groffen et al., 2017; Wang et al., 2013).

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

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

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

132 The factors that influence the exposure of Antarctic seabirds to PFAAs are not well
133 understood, mainly for migratory species that exhibit marked interspecific differences in their
134 foraging ecology. However, some of the complexities involved in understanding the feeding

135 ecology as well as the migration patterns of seabirds can be clarified using stable isotope analysis
136 (SIA) to infer trophic position ($\delta^{15}N$), foraging areas ($\delta^{13}C$), and origin of food (i.e. benthic *vs.*
137 pelagic, $\delta^{34}S$) of these animals (Cherel et al., 2014; Cherel and Hobson, 2007; Herman et al., 2017).
138 The present study aims to evaluate the species-specific differences in PFAAs accumulation
139 among resident and migratory Antarctic seabirds through feather and eggs analysis of 15 PFAAs
140 (four PFSAs and 11 PFCAs). Feather and eggs were used to observe how the pattern of PFAAs
141 concentrations is distributed across different matrices of Antarctic birds. Simultaneously, stable
142 isotopes were used to test the influence of multiple spatial and ecological factors on these
143 accumulated concentrations, analyzing whether possible interspecific differences are due to habitat
144 contamination, sources of food or differences in trophic positions.

145 **2. Material and methods**

146 **2.1 Study area and sampling**

147 All samplings were performed at King George Island (61°50'-62°15'S and 57°30'-59°
148 00'W) in the South Shetland Archipelago, Antarctic Peninsula (Figure 1, Table 1), during 2010-
149 2011, 2012-2013 austral summers and in the reproductive period of the birds. This study presents
150 two groups of seabirds: resident and migratory. *Pygoscelis* penguins (Adélie - *Pygoscelis adeliae,*
151 Chinstrap - *P. antarcticus*, Gentoo - *P. papua*) are the resident seabirds in the present study due to
152 their circumpolar distribution (Jerez et al., 2013). As migratory birds in the present study, we have
153 selected species with different migration patterns, since the South Polar Skua (*Stercorarius*
154 *maccormicki*) is dispersed by routes through the Atlantic and Pacific oceans, reaching the Northern
155 Hemisphere during the winter (Cruwys, 2008; Kopp et al., 2011). On the other hand, Snowy
156 Sheathbill (*Chionis albus*), Antarctic Tern (*Sterna vittata*), Southern Giant Petrel (*Macronectes*

157 *giganteus*), and Kelp Gull (*Larus dominicanus*) disperse in marine environments of the Southern
158 Hemisphere during winter (Patterson and Hunter, 2000; Watson, 1975).

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

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

173 **2.2 Sample preparation**

174 All feather samples were washed three times with a sequence of 1) Milli-Q ultrapure water
175 (Merck Millipore, USA), 2) 0.01% EDTA (Spectrum, Tedia, USA) and 3) Milli-Q ultrapure water
176 (Merck Millipore, USA), for eliminating external contamination, and then the samples were oven-
177 dried at 50 °C for 24 h (Marques et al., 2007). After this procedure the feathers were cut into small
178 pieces using ceramic scissors. For stable isotope measurements, feather samples were additionally
179 washed with a chloroform/methanol (2:1, v: v, suprapur Merck, Germany) solution, and dried at

180 50 °C for 48 h (Padilha et al., 2021). The non-viable eggs were kept frozen until they were
181 lyophilized and stored in PFAAs-free plastic tubes for further analysis. For extraction of PFAAs
182 from the feathers and eggs, protocols described by Groffen et al. (2021) and (Powley et al., 2005)
183 were used respectively. The used abbreviation of the target PFAAs are according to Buck et al.
184 (2011; Table S2).

185 **2.3 Chemical reagents**

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

191 **2.4 Chemical extraction**

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

202 For the extraction of PFAAs from the eggs, a protocol described by Powley et al. (2005)
203 was used with minor modifications as follow. After removal of the shell, the samples were freeze-
204 dried prior to the extractions. Each sample (50 mg) was spiked with 10 ng ISTD, after which 300
205 µL of Milli-Q and 10 mL of ACN was added. The samples were vortex-mixed, sonicated for 3 x
206 10 min (Branson 2510) and left overnight on a shaking plate (135 rpm, room temperature, GFL
207 3020, VWR International, Leuven, Belgium). After centrifugation (4°C, 10 min, 1037 x g,
208 Eppendorf centrifuge 5804R), the supernatant was reduced until approximately 0.5 mL by using a
209 rotational-vacuum-concentrator (Martin Christ, RVC 2-25, Osterode am Harz, Germany). The
210 concentrated extract and 2 times 250 µL ACN, which was used to rinse the tubes, were added to
211 an Eppendorf tube containing 50 mg graphitized carbon powder (Supelclean ENVI-Carb, Sigma-
212 Aldrich, Belgium) and 50 µL glacial acetic acid. These tubes were vortex-mixed for 1 min and
213 centrifuged (4°C, 10 min, 10000 rpm; 9279.4 x g, Eppendorf centrifuge 5415R). The cleaned-up
214 extracts were dried almost completely and reconstituted in 2 mL of a 2% ammoniumhydroxide
215 solution in ACN and filtrated as described above for the feathers.

216 **2.5 UPLC-MS/MS analysis**

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

225 (B). The flow rate was set at 450 µL / min at a partial loop injection of 6 µL. The solvent gradient
226 started at 65% A, decreased to 0% A in 3.4 min and returned to 65% A at 4.7 min. The analytes
227 were identified and quantified using multiple reaction monitoring (MRM) of two diagnostic
228 transitions per analyte. The MRM transitions, cone voltages and collision energy of each target
229 analyte, including the ISTDs, are displayed in Table S3 of the Supplementary material and were
230 validated by Groffen et al. (2019). All results are expressed in dry weight (dw).

231 **2.6 Quality assurance**

232 Calibration curves, with a highly significant linear fit for all target analytes (all $p < 0.001$;
233 $R^2 > 0.98$), have been constructed by (Groffen et al., 2021, 2019). Procedural blanks were added
234 per batch of 20 – 25 samples as quality control and contained 10 mL of methanol for the feathers
235 and 10 mL of ACN for the eggs. The methanol-blanks contained minor contamination with PFOA
236 (0.05 – 0.15 ng/g ww), PFDA (<LOQ – 0.28 ng/g ww) and PFUnDA (<LOQ – 0.25 ng/g ww),
237 which were subtracted from concentrations in samples from the same batch. In addition,
238 instrumental blanks (ACN 100%) were analyzed on a regular basis to prevent crossover
239 contamination of the samples. Individual PFAAs were quantified using the most suitable ISTD
240 based on ionization and extraction efficiency (Groffen et al., 2019) and were those closest in terms
241 of functional group and carbon-chain length (Table S3 of the Supplementary material). The
242 individual limits of quantification (LOQs) were determined in matrix based on a signal-to-noise
243 (S/N) ratio of 10 and are displayed in Table S4 of the Supplementary material.

244 **2.7 Stable isotope measurements**

245 Stable isotope measurements were performed via continuous flow - elemental analysis -
246 isotope ratio mass spectrometry (CF-EA-IRMS) using a Vario MICRO cube C-N-S elemental
247 analyzer (Elementar Analysensysteme GmBH, Hanau, Germany) coupled to an IsoPrime100

248 isotope ratio mass spectrometer (Isoprime, Cheadle, United Kingdom). Isotopic ratios were
249 conventionally expressed as δ concentrations in ‰ (Coplen, 2011) and relative to the international
250 standards: Vienna Pee Dee Belemnite, for carbon; Atmospheric Air, for nitrogen; and Vienna
251 Canyon Diablo Troilite, for sulfur. We used International Atomic Energy Agency (IAEA, Vienna,
252 Austria) certified reference materials IAEA-C6 ($\delta^{13}C$ values = -10.8 ± 0.5‰; mean ± SD), IAEA-
253 N2, ($\delta^{15}N$ values = 20.3 ± 0.2‰; mean ± SD) and IAEA-S1 ($\delta^{34}S$ values = -0.3‰ ± 0.01‰; mean
254 ± SD) as primary analytical standards. As secondary analytical standards we used sulfanilic acid
255 ($\delta^{13}C$ 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
256 case). Isotopic ratios of samples were calibrated using primary analytical standards. Standard
257 deviations on multi-batch replicate measurements of secondary analytical (sulfanilic acid) and lab
258 standards (feathers) analyzed interspersed among samples (one replicate of each standard every 15
259 analyses) were 0.2‰ for both $\delta^{13}C$ values and $\delta^{15}N$ values and 0.4‰ for $\delta^{34}S$ values.

260 **2.8 Statistical analysis**

261 The statistical analyses were performed in R (Jackson et al., 2011; "R Core Team (2020).
262 — European Environment Agency," n.d.) statistical software and STATISTICA software (version
263 10; StatSoft Inc., USA). For statistical analysis, concentrations <LOQ were replaced to a value
264 equal to f x LOQ where f is the frequency, i.e the number of samples in which the compound was
265 detected divided by the total number of samples analyzed (Parente et al., 2018). Non-parametric
266 (Spearman rank correlation test-r, Mann-Whitney, and Kruskal-Wallis) tests were used. A
267 Kruskal-Wallis test was used for comparing PFAA concentration and stable isotope values among
268 different species. The post hoc tests were conducted to test pairwise comparisons. Mann-Whitney
269 U test was used to evaluate the possibility of a significant difference between the concentrations
270 of PFAAs between resident and migratory birds, and to verify possible annual differences.

271 Spearman rank correlation test was used to describe $\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$ values and PFAAs
272 concentration in tissues. We analyzed the relationship between PFAAs concentrations among ten
273 species of resident and migratory seabirds using a principal component analysis (PCA). Before
274 analysis, data was rank transformed for standardization and to deal with values below the limit of
275 quantification (LOQ). When the compounds had almost all the samples below the LOQ they were
276 excluded from the analyses. The PCAs, for both feathers and eggs, included species and habit as
277 supplementary qualitative variables. Feather PCA also included isotopes as supplementary
278 quantitative variables, since the measurements of stable isotopes were only carried out in the
279 feather matrix. The inclusion of isotopes as variables in the PCA was made to observe whether
280 there was also an influence of trophic ecology on the differences in PFAA concentrations between
281 species. Biplots showing $\delta^{34}S$, $\delta^{15}N$, and $\delta^{13}C$ values in Antarctic seabirds were made.

282 **3. Results**

283 The dominant compound among PFAAs was PFUnDA in both matrices (Table 2 and 3;
284 Figure 2 and 3). More compounds could be detected in eggs than in feathers samples (i.e., ten
285 compounds were detected in eggs compared to eight compounds detected in feathers for a total of
286 15 compounds measured, Table 2 and 3; Figure 2). It was not possible to correlate the egg to the
287 parents in the present study since the non-viable eggs were found abandoned outside the nests.
288 Mean ∑PFAA concentrations in feathers ranged from 0.47 as the lowest concentration to 17.4 ng/g
289 dry weight (dw) as the highest from *P. antarcticus* to *S. maccormicki*. In eggs, ∑PFAA
290 concentrations ranged from 3.51 as the lowest concentration to 116.6 ng/g dw as the highest from
291 *P. adeliae* to *S. maccormicki*. There was no significant difference between the samples of feathers
292 and eggs collected in different years for each species in the present study ($p > 0.05$). Additionally,

293 no significant interannual difference was observed for samples of feathers and eggs of *S.*
294 *maccormicki* ($p > 0.05$) and eggs of *Pygoscelis* penguins ($p > 0.05$).
295
296 **3.1 Perfluoroalkyl acids in feathers**
297 The concentrations of PFOA, PFUnDA, PFDoDA, PFTrDA, PFTeDA were detectable in
298 migratory and resident seabirds; while PFHxA and PFDA were detectable only in migratory ones
299 (Table 2, Figure 2). PFOS was not detectable in any of the resident species, but it was detectable
300 in one migratory seabird (*S. maccormicki*). The concentrations of PFBA, PFPeA, PFHpA, PFNA,
301 PFBS, PFHxS, and PFDS were below the detection limit for all species of seabirds. There was no
302 significant correlation between the morphometric measurements (Table S1 of the Supplementary
303 material) of seabirds and the concentrations of PFAAs ($p > 0.05$ in all cases).
304 Comparing migratory with resident seabirds, significantly higher values of PFHxA ($U =$
305 352, $p < 0.001$), PFDA ($U = 0$, $p < 0.001$), PFUnDA ($U = 1188$, $p < 0.001$), and PFTeDA ($U =$
306 2396, $p = 0.032$) were observed in migratory animals.
307 Profiles based on the relative contribution of the studied compounds to PFAAs were
308 dominated by ΣPFCAs (89−100%), with PFUnDA being the prevalent compound (20 - 65% of
309 ΣPFAAs) for all species (Figure 2). PFSAs represented 11% of ΣPFAAs in *S. maccormicki.*
310 Considering all migratory species, the prevalent compound was PFUnDA (22 – 63%). In resident
311 seabirds' species the contributions of PFCAs were 100%, with PFUnDA being the prevalent
312 compound, mean of 40% of ΣPFAAs in all resident species together, followed by PFOA (14% -
313 37%) > PFTeDA > PFDoDA > PFTrDA.
314 To better characterize our groups a PCA was used. The first principal component (PC1)
315 explained 36.1% (Figure 3A, Table S5) of the total variability in the dataset, with the strongest

316 positive contributions from PFTrDA (0.91), PFTeDA (0.90), and the weakest one from PFOA (-
317 0.12). The second principal component (PC2) expressed 25% (Figure 3A, Table S5) of the
318 variation with the strongest positive contributions from PFOA (0.87). There was a clear overlap
319 among the PFAAs and stable isotope profiles between migratory and resident seabirds (Figure
320 3A).

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

324 Comparing the compounds detected in feathers only in migratory seabirds, the
325 concentrations of PFDoDA, PFTrDA, PFTeDA were below the detection limit for *S. vittata, L.*
326 *dominicanus,* and *M. giganteus* (Table 2). PFHxA ($H = 63.3$, $p < 0.001$), PFOA ($H = 54$, $p <$
327 0.001), PFDA ($H = 50.3$, $p < 0.001$), PFDoDA ($H = 79.6$, $p < 0.001$), and PFTrDA ($H = 79.8$, $p <$
328 0.001) differed among species. The PFHxA concentrations of *S. maccormicki* ($p = 0.01$) were
329 significantly lower compared to the other seabird species. PFOA concentrations were significantly
330 higher in *C. albus* ($p = 0.03$) and *L. dominicanus* ($p < 0.001$) compared to the others. The PFDA
331 concentrations were significantly lower in *M. giganteus* ($p < 0.001$), and no significant differences
332 were found for the other species of migratory seabirds. PFDoDA concentrations were significantly
333 higher in *C. albus* ($p = 0.03$) and *S. maccormicki* ($p < 0.001$) compared to the others.
334 Concentrations of PFTrDA and PFTeDA were significantly higher in *S. maccormicki* (PFTrDA: p
335 $= 0.008$; PFTeDA: $p = 0.008$) compared to the other migratory seabirds.

336 Comparing the compounds detected in feathers only in resident seabirds (Table 2). PFOA
337 ($H= 17.7$, $p = 0.001$), PFUnDA ($H = 13.9$, $p = 0.001$), PFDoDA ($H = 31.9$, $p < 0.001$), PFTrDA
338 ($H= 35.2$, $p < 0.001$), and PFTeDA ($H= 35.2$, $p < 0.001$) differed among species. The PFOA

339 concentrations were significantly lower in *P. papua* ($p < 0.001$) compared to the other two penguin
340 species. The PFUnDA concentrations were significantly lower in *P. adeliae* ($p < 0.001$) compared
341 to *P. papua*. The PFDoDA concentrations were significantly lower in *P. antarcticus* ($p < 0.001$)
342 compared to the other two penguin species. PFTrDA and PFTeDA concentrations ranged from *P.*
343 *papua* ($p = 0.035$) > *P. adeliae* ($p = 0.003$) > *P. antarcticus* ($p < 0.001$).

344 **3.2 Perfluoroalkyl acids in eggs**

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

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

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

357 The first principal component (PC1) explained 40.6% (Figure 3B, Table S6) of the total
358 variability in the dataset, with the strongest positive contributions from PFTrDA (0.84), PFTeDA
359 (0.81), PFUnDA (0.81), and the weakest one from PFHpA (-0.18). The second principal
360 component (PC2) expressed 14.5% (Figure 3B, Table S6), with the strongest positive contributions
361 from PFHxA (0.68), PFOA (0.62). There is a clear overlap between migratory and residents with

362 a higher tendency of separation than reported in the feathers. However, as in the feathers, the
363 horizontal axis tends to separate Northern Hemisphere migratory birds from Southern Hemisphere
364 birds.

365 The PFHpA concentrations were above the detection limit only for *S. vittata* eggs. The
366 PFNA and PFTeDA concentrations were above the detection limit only for *S. maccormicki* eggs.
367 PFTrDA ($H = 56.5$, $p < 0.001$), PFHxA ($H = 21.3$, $p < 0.001$), PFOA ($H = 39$, $p < 0.001$), PFDA
368 ($H = 39$, $p < 0.001$), PFUnDA ($H = 25.5$, $p < 0.001$), and PFDoDA ($H = 48.6$, $p < 0.001$)
369 concentrations differed among species. The concentrations of PFTrDA were significantly higher
370 in *S. maccormicki* ($p = 0.04$) compared to the other analyzed species. The PFOS concentrations
371 were above the detection limit only for *S. maccormicki* and *P. papua*. *S. maccormicki* ($U= 229$, p
372 $= 0.004$) showed significantly higher concentrations of PFOS than *P. papua* eggs.

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

381 **3.3 Stable isotope ratios and PFAAs patterns**

382 Spearman rank correlation matrix between PFAAs and stable carbon showed positively
383 significant correlations among $\delta^{13}C$ values and five compounds (PFDA, PFUnDA, PFTrDA,
384 PFTeDA, and PFOS), and significantly negative between $\delta^{13}C$ values and PFOA (Figure 4).

385 Significant positive correlations were found between $\delta^{15}N$ values and three compounds (PFUnDA,
386 PFTrDA, and PFTeDA), and significantly negative correlations considering $\delta^{15}N$ values and
387 PFOA (Figure 4). The $\delta^{34}S$ values concentrations showed positive and significant correlation with
388 PFUnDA, and significantly negative with PFDA (Figure 4). There is a significantly positive
389 correlation between $\delta^{13}C$ and $\delta^{15}N$, but no significant correlation was observed between $\delta^{15}N$ x
390 $\delta^{34}S$, and $\delta^{34}S$ x $\delta^{13}C$ (Figure 4).
391 The values of $\delta^{15}N$ ($H = 70.1$, $p < 0.001$), $\delta^{13}C$ ($H = 70.6$, $p < 0.001$), and $\delta^{34}S$ ($H = 88.8$,
392 $p < 0.001$) differed among species. *Pygoscelis* species ($p = 0.009$) and *S. vittata* ($p = 0.009$) showed
393 significantly lower $\delta^{15}N$ values compared to the other species of seabirds (Table 2, Figure 5). *S.*
394 *maccormicki* ($p < 0.001$), *M. giganteus* ($p = 0.02$), and *L. dominicanus* ($p = 0.02$) showed
395 significantly higher $\delta^{13}C$ values compared to the other species of seabirds (Table 2, Figure 5).
396 Regarding $\delta^{34}S$ values, *S. maccormicki* ($p < 0.001$) and *P. antarcticus* (0.04) showed significantly
397 lower values compared to *C. albus, M. giganteus*, and *S. vittata* (Table 2, Figure 5).
398
399 **4. Discussion**
400 Clearly, Antarctic seabirds are exposed to PFAAs concentrations that will rely upon intra-
401 specific and inter-specific driving factors (e.g., tissues, sex, sampling location, biology, …).
402 Migratory seabirds showed higher concentrations of most PFAAs than resident species. The higher
403 concentrations of PFSAs and PFCAs in migratory seabirds compared to *Pygoscelis* penguins agree
404 with differences in their trophic positions ($\delta^{15}N$ values) and foraging area ($\delta^{13}C$ and $\delta^{34}S$ values).
405 Trophic ecology (i.e., diet and foraging strategies), metabolic factors (i.e., sex, molting and
406 breeding status), migration patterns (trans-equatorial movements of seabirds), and sources of

407 PFAAs (i.e., point sources and long-range transport) may influence in the interspecific differences

408 found in this study.

409 **4.1 Migration and the PFAAs**

410 Migratory seabirds that migrate to the Northern Hemisphere (*S. maccormicki*) had higher

411 PFAAs concentrations than seabirds migrating only within the Southern Hemisphere. These data

412 were expected because of the well-known industrialization of the Northern Hemisphere compared

413 to the Southern Hemisphere (Ma et al., 2016; Paul et al., 2009).

414 The *S. maccormicki* is a trans-equatorial migrant, disperses widely, reaching the Northern

415 Hemisphere during the southern winter (Cruwys, 2008; Kopp et al., 2011). This top predator is

416 opportunistic, feeding on fish and crustaceans, as well as carrion of seabirds nesting in nearby

417 colonies (Borghello et al., 2019; Cruwys, 2008; Quillfeldt, 2002; Ridoux and Offredo, 1989).

418 Thus, the high trophic position coupled with its migration pattern may explain the high levels of

419 $\delta^{15}N$, $\delta^{13}C$, and PFCAs in *S. maccormicki* compared to the other Antarctic seabirds in the present

420 study. The literature shows that long-chain PFCAs are mainly noticed in seawater outside of the

421 Antarctic Circumpolar Current (Zhao et al., 2012), being more abundant in seawater from northern

422 compared to southern Atlantic latitudes (González-Gaya et al., 2014; Ma et al., 2016). This may

423 explain the relative high levels of PFTrDA and PFTeDA found in *S. maccormicki* and low

424 concentrations in penguins. Previous studies about Antarctic seabirds also demonstrate a similar

425 pattern (Roscales et al., 2019; Tao et al., 2006). Tao et al. (2006) detected long-chain PFCAs in

426 liver, serum, and eggs of northern albatrosses, while the PFCAs concentrations were below the

427 limits of quantitation in livers of albatrosses from the Southern Ocean. Roscales et al. (2019) found

428 higher levels of long-chain PFCAs in plasma of seabirds foraging north of Antarctica than in the

429 resident seabirds. Gao et al. (2020b) found ∑PFAAs 1.85 ± 1.21 ng/g dry weight (dw) (present

430 study: 2.62 ± 1.54 ng/g dw) in feathers of *P. papua,* and like in our study, reported low
431 concentrations of long-chain PFCAs in penguins.

432 The PFCAs were more predominant in our samples than PFSAs, since PFBS, PFHxS, and
433 PFDS were not detected in any of the samples, and PFOS was only detected in feather of *S.*
434 *maccormicki* and eggs of *S. maccormicki* and *P. antarcticus*. Tao et al. (2006) observed similar
435 concentrations of PFOS in *S. maccormicki* eggs (2.5 ng/g ww), which indicate that the
436 concentrations of PFOS have remained constant over the years in the south polar skua. Leat et al.
437 (2013) analyzing *S. maccormicki* eggs, detected only PFCAs with nine or more carbon atoms
438 (PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA), whereas for PFSAs, the eight-
439 carbon PFOS dominates. Our results showed a similar pattern, since PFDA, PFUnDA, PFDoDA,
440 PFTrDA, PFTeDA, and PFOS were detected in *S. maccormicki* eggs. The reported better ability
441 of PFOS, compared to PFCAs, to biomagnificate and bioaccumulate in polar food webs (Kelly et
442 al., 2009; Roscales et al., 2019) could explain the higher values of PFOS in *S. maccormicki* feathers
443 and eggs in the present study. Thus, migration could result in higher exposure to PFSAs, and
444 consequently higher concentrations of PFOS in comparison to resident behavior, as previously
445 demonstrated for PFAAs in plasma blood of migratory and resident Antarctic seabirds (Roscales
446 et al., 2019).

447 Studies performed in birds from Northern Hemisphere have shown a higher exposure to
448 PFSAs compared to the Southern ones. The Great skua (*Stercorarius skua*) from the North Atlantic
449 showed values of PFOS an order of magnitude greater than (mean 23 ng/g ww) *S. maccormicki*
450 (2.2 ng/g ww) from the present study (Leat et al., 2013). The literature has shown PFOS
451 concentrations in plasma of *S. skua* from Northern Hemisphere (mean 31 ng/g ww) an order of
452 magnitude greater than in brown skuas from the Falklands (Leat et al., 2013; Roscales et al., 2019).

453 Li et al. (2018) observed higher PFSAs concentrations in feathers samples of accipiter birds from
454 Tibetan Plateau (mean range: 0.59 – 6.12 ng/g, dw) compared to the present study.

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

463 Despite *S. vittata* presents $\delta^{15}N$ values and diet similar to penguins (Casaux et al., 2008),
464 higher concentrations of PFAAs were observed, which may be due to their migratory pattern, since
465 this species migrates to more polluted places such as southern Africa and South America (Cruwys,
466 2008).

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

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

483 **4.2 PFAAs and the stable isotopes**

484 In the present study, PFUnDA, PFTrDA, and PFTeDA showed a significant positive
485 correlation with trophic position (δ^{15}N values), indicating a biomagnification potential of these
486 compounds. The literature has shown less or no biomagnification for PFCAs compounds (Lescord
487 et al., 2015; Simonnet-Laprade et al., 2019), which contradicts our findings. Unlike (Kelly et al.,
488 2009), who observed a positive and significant correlation between δ^{15}N values and PFOS, we did
489 not observe a correlation between δ^{15}N values and any PFSAs. (Lopez-Antia et al., 2021) observed,
490 based on δ^{15}N values and δ^{13}C values data, that black-backed gulls (*Larus fuscus*) with a
491 predominantly marine diet have higher exposure to PFOS. Our results also showed that PFOS,
492 PFDA, PFUnDA, PFTrDA and PFTeDA present a correlation with foraging areas (δ^{13}C values).
493 The correlations between PFUnDA and δ^{34}S values in our study suggest an important contribution
494 from coastal or benthic food webs. The latter statement is based on the fact that producers from
495 open marine and pelagic environments typically have higher δ^{34}S values concentrations compared
496 to coastal benthic sediment-associated producers (Connolly et al., 2004).

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

500 **4.3 PFAAs in different matrices**

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

509 The greater number of compounds in eggs (and higher concentrations) could be due to a
510 higher affinity of certain PFAAs to egg proteins compared to keratin (Lopez-Antia et al., 2017;
511 Wang et al., 2019). The literature has demonstrated that PFAAs bind to protein with suitable
512 binding locations, as a ligand or using hydrogen-bonding as powering force to create a complex
513 with protein and ligands in the PFAAs-protein interactions (Bischel et al., 2011; Zhang et al.,
514 2013). Consequently, these compounds are frequently observed in protein-rich tissues such as eggs
515 (Lopez-Antia et al., 2017; Wang et al., 2019) and serum (Gao et al., 2015).

516 Another factor that may also have contributed to interspecific differences in concentrations
517 found in the present study are the species-specific differences in molting. The annual cycles of
518 molting are usually influenced by migratory patterns, in order to optimize flight efficiency and
519 thermoregulation. This is the case of *L. dominicanus*, *S. maccormicki,* and *S. vittata* that present

520 two annual molting process, while the other species present only one annual molt (Watson, 1975).
521 Previous studies have shown that the molt influences the concentrations of trace elements within
522 and among feathers of birds of prey (Dauwe et al., 2003). However, more studies are needed to
523 verify whether the same is true for PFAAs.

524 **4.4 Joint assessment of aspects that contribute to exposure of Antarctic seabirds to PFAAs**

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

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

540 We observed that the migration, especially trans-equatorial migration, has an important
541 role in the exposure of birds to long-chain PFCAs, since the lowest concentrations were reported
542 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.

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567 Figures and tables

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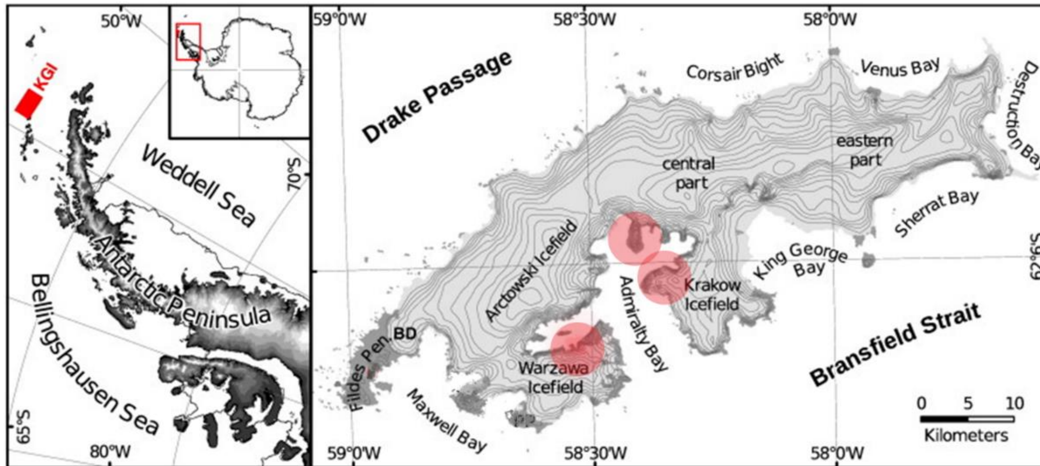

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570 Figure 1. Map of the Antarctic Peninsula, highlighting King George Island. The sampling points are marked as a red
571 circle (Adapted from Rückamp et al., 2011).

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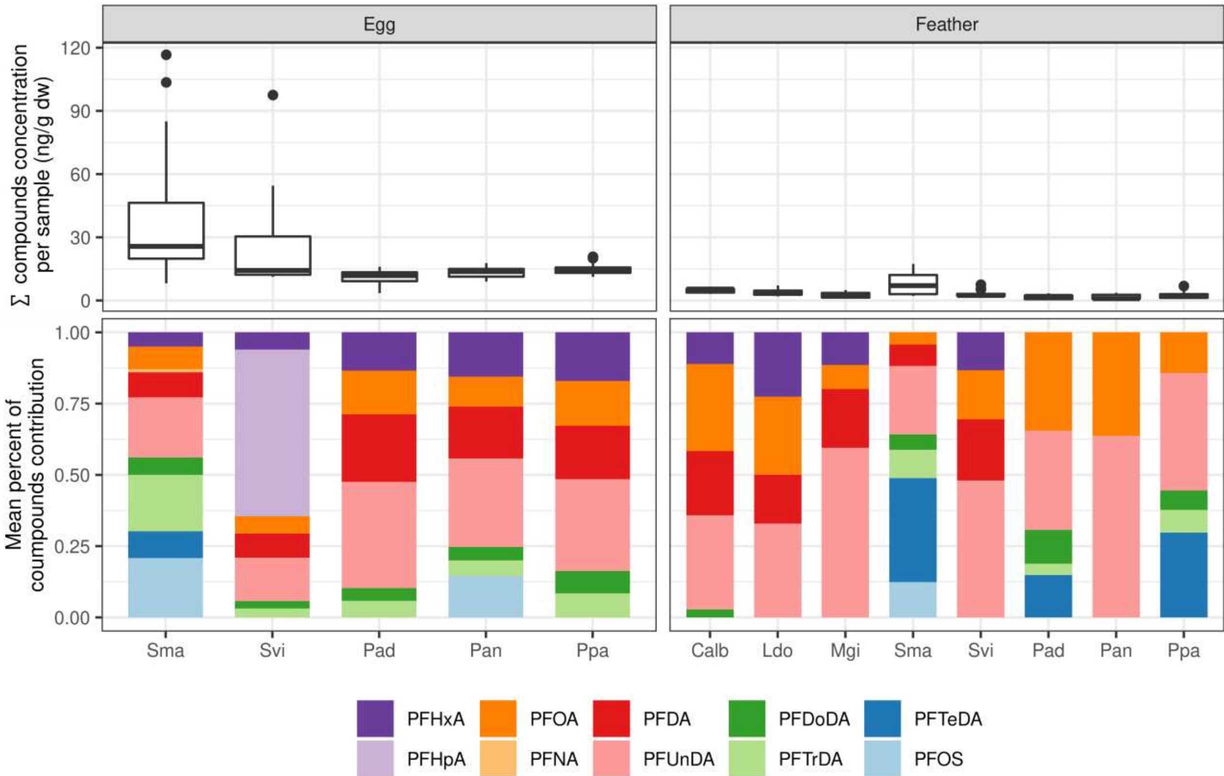

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576 Figure 2. Sum of compounds and relative contribution of individual PFAAS to ∑PFAAs (ng/g
577 dw) in feathers and eggs of *C. albus* (Calb), *L. dominicanus* (Ldo), *M. giganteus* (Mgi), *S.*
578 *maccormicki* (Sma), *S. vittata* (Svi), *P. adeliae* (Pad), *P. antarcticus* (Pan), and *P. papua* (Ppa)
579 from Antarctic Peninsula.
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596 Table 1. Sampling data (tissue, species, state of maturity, and number of individuals - *n*) from King George Island in

597 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 alba*	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

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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 alba* n=7	**Median**	<0.97	1.41^{*}	1.29	1.81	$<0.32^{*}$	<0.17	<0.55	<0.98	4.67 ± 1.17^{*}	-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	-	-	-		-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 ± 5.18^{**}	-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		-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 ± 1.43^{*}	-18.1^{*}	11.1	16.9
		min-max	<0.97-2.48	<1.06-2.82	<1.19-1.98	<1.41-2.31	-	-	-	-		-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 ± 1.12^{*}	-21.2^{*}	12.9	17.5
		min-max	<0.97-1.54	<1.06 - 1.57	<1.19-1.83	<1.41-2.14	-	-	-	-		-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

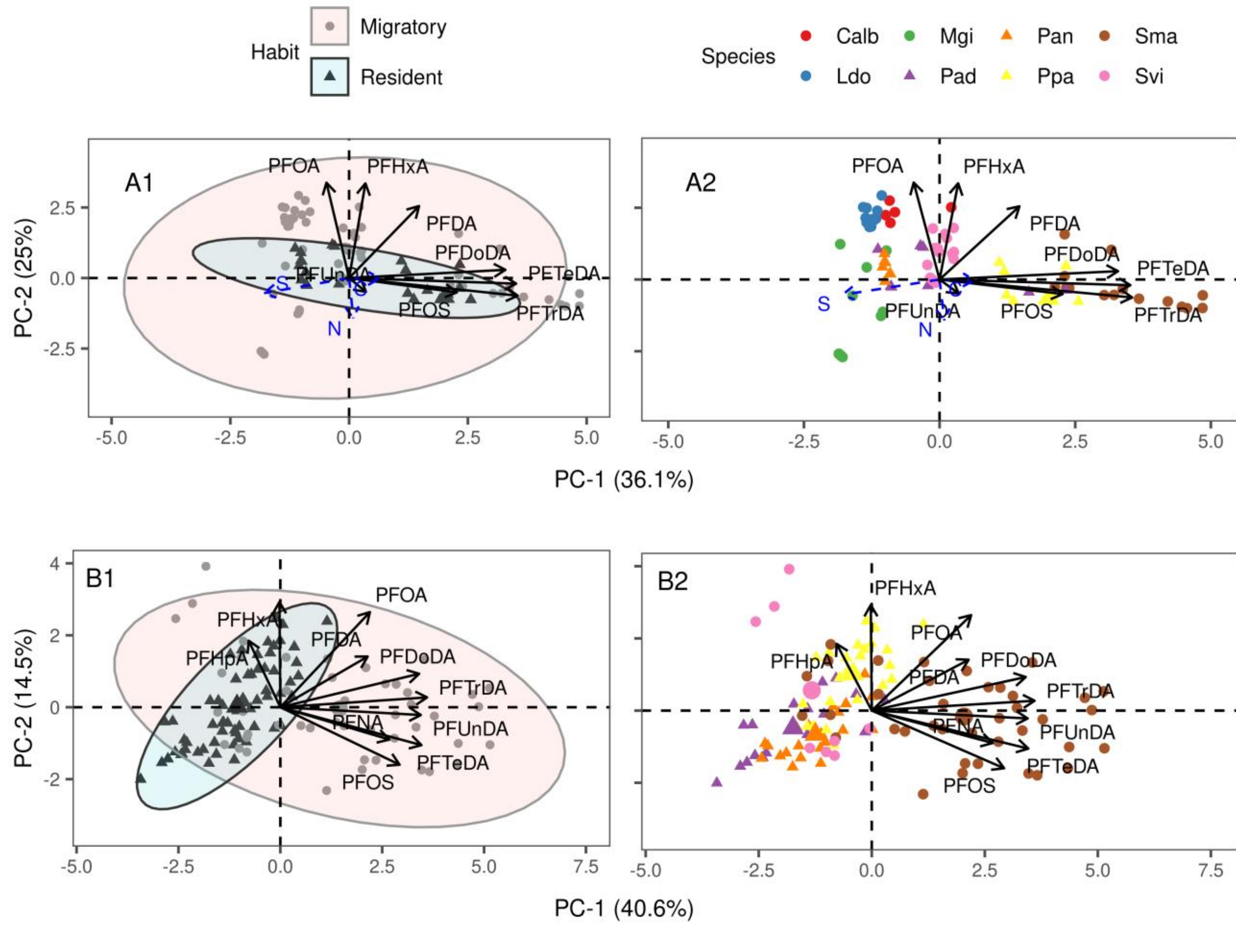
Table 2. (Continued)

	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 ± 0.46*	-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	-		-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 ± 1.03*	-25.3	9.29**	13.9*
		min-max	-	0.20-1.97	-	<1.41-2.47	-	-	-	-		-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± 1.54*	-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	-		-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*	3.30*	0.97	4.38***	35.1 ± 24.7*
		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	<1.09-32.6	
	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 ± 30.9*
		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	-	-	
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 ± 3.01*
		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	-	-	
	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 ± 2.33*
		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	-	-	
	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 ± 2.69*
		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	

30



31
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33 Figure 3. PCA feather (A1 and A2) and egg (B1 and B2) of migratory and resident seabirds from
34 Antarctic Peninsula.
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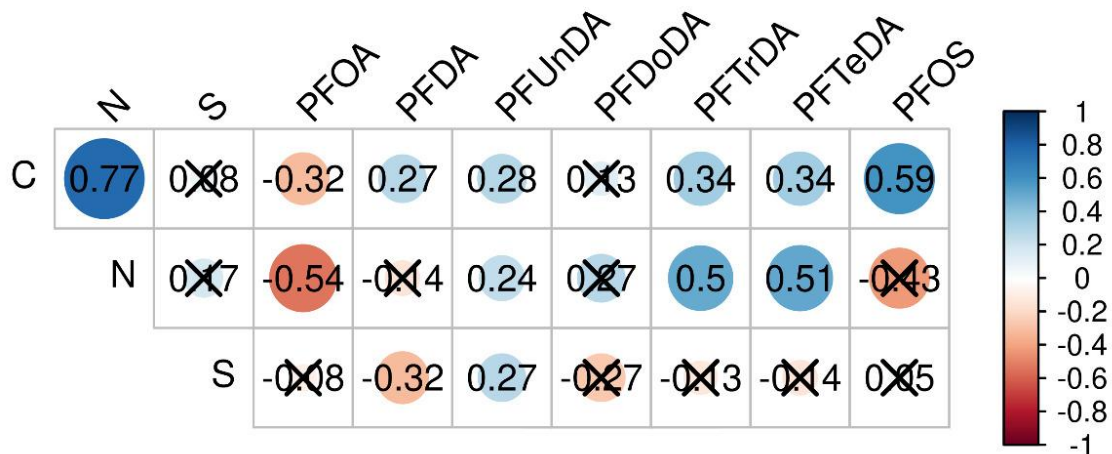

Figure 4. Spearman rank correlation matrix between PFAAs and C ($\delta^{13}C$), N ($\delta^{15}N$), and S ($\delta^{34}S$) in feathers of seabirds from the Antarctic Peninsula. Significant correlations (rs, $p < 0.05$) are shown in blue (positive) and red (negative). The color intensity is related to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

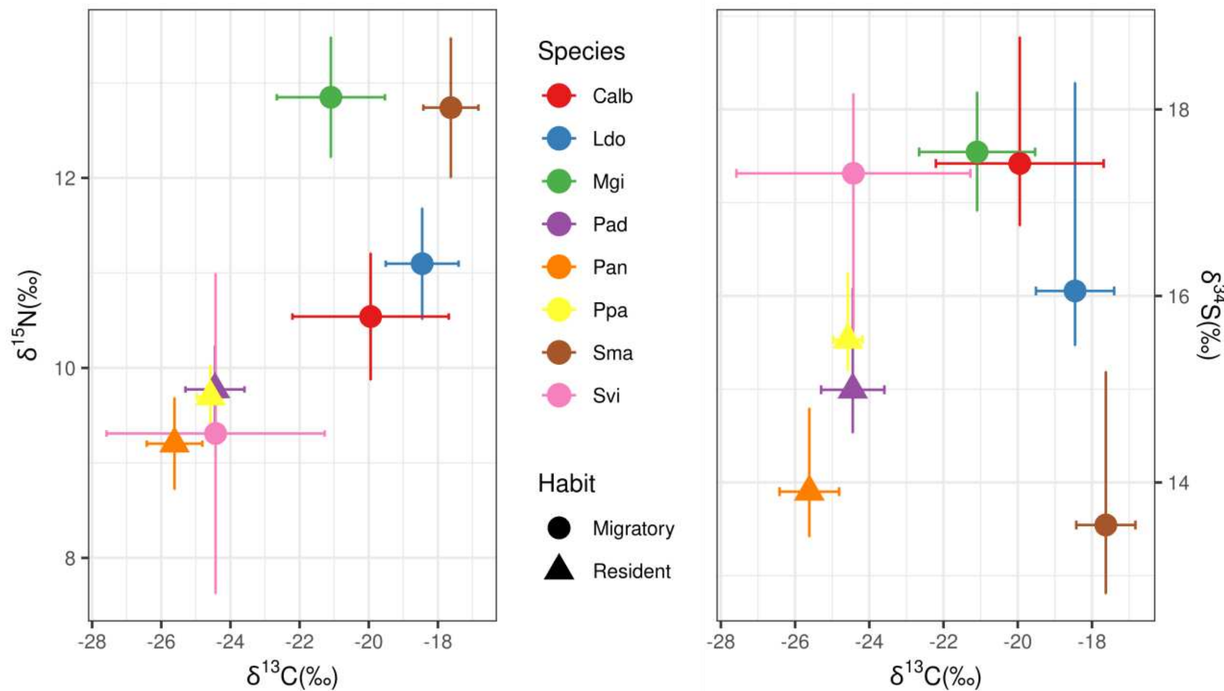

Figure 5. Mean (±SD) $\delta^{13}C$ x $\delta^{15}N$ values (‰) and $\delta^{13}C$ x $\delta^{34}S$ of in feather samples of migratory and resident seabirds from Antarctic Peninsula.

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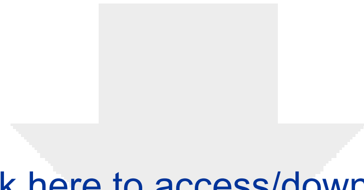

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