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Urban proximity while breeding is not a predictor of perfluoroalkyl substance contamination in the eggs of brown pelicans

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1 **ABSTRACT**

2 Identifying sources of exposure to chemical stressors is difficult when both target organisms and
3 stressors are highly mobile. While previous studies have demonstrated that populations of some
4 organisms proximal to urban centers may display increased burdens of human-created chemicals
5 compared to more distal populations, this relationship may not be universal when applied to organisms
6 and stressors capable of transboundary movements. We examined eggs of brown pelicans (*Pelecanus*
7 *occidentalis*), a nearshore seabird with daily movements ranging from local to 50 km and annual
8 migrations ranging from year-round residency to 1,500 km. Thirty-six eggs from three breeding colonies
9 located at increasing distances to a major urban center (Charleston, South Carolina, USA) were analyzed
10 for concentrations of per- and polyfluoroalkyl substances (PFAS). Areas of high use for each colony
11 during the breeding season were also assessed via the tracking of adult pelicans from each colony using
12 GPS-PTT satellite transmitters and overlapped with measures of relative urbanization via land cover
13 data. We report potentially significant Σ PFAS concentrations in the eggs of pelicans (175.4 ± 120.1 ng/g
14 w wt. SD), driven largely by linear perfluorooctane sulfonate (n-PFOS) (48 – 546 ng/g w wt.). Residues of
15 the precursor compound perfluorooctane sulfonamide (FOSA) were also present in pelican eggs,
16 suggesting continued exposure of local wildlife beyond implemented phaseouts of some PFAS. For most
17 analytes, egg concentrations did not exhibit a significant spatial structure despite some differentiation in
18 high-use areas unlike similar data for another regional apex predator, the bottlenose dolphin (*Tursiops*
19 *truncatus*). We suggest that the partially migratory nature of brown pelicans during the non-breeding
20 season, combined with daily ranges that may extend to 50 km from local point sources, may have
21 homogenized exposure across individuals. Charleston likely remains a major source for PFAS in the
22 overall region, however, given the high concentrations observed as well as known releases of PFAS in
23 the nearshore environment.

24 **KEYWORDS**

25 Brown pelican; perfluoroalkyl substances; urban; tracking; GPS; seabird

26 **1.1 INTRODUCTION**

27 Ranging behaviors of highly mobile organisms can expose these species to lethal and sublethal
28 stressors not experienced by more sedentary organisms (Jodice & Suryan 2010, Mello et al. 2016, Odsjö
29 1975). The risks to vagile organisms are amplified when the stressors themselves are also mobile in
30 nature, capable of affecting organisms across relatively broad spatial or temporal scales (Cabrera-Cruz et
31 al. 2018, Henkel et al. 2012). The opportunity for individuals far from local sources of exposure to
32 encounter the stressor should be greater when both organism and stressor are capable of frequently
33 moving among systems, compared to organisms which occupy a distinct spatiotemporal distribution
34 removed from the stressor or for which the stressor is relatively concentrated in a given area. Proximity
35 to sources of environmental stressors may therefore only be a good predictor of exposure for relatively
36 sedentary populations or those with distinct, consistent, or local ranges, and may not be as relevant for
37 highly mobile species interacting with a highly mobile environmental stressor (Adams et al. 2008, Power
38 et al. 2020).

39 Anthropogenic chemicals, including compounds of emergent interest such as per- and
40 polyfluoroalkyl substances (PFAS), can act as mobile stressors because they are capable of long-range
41 dispersal from point sources (Lohmann et al. 2007). PFAS are widespread chemicals that are persistent
42 in both marine and terrestrial environments worldwide (Houde et al. 2006a). Manufactured for their
43 stability and ability to repel both oily and aqueous substances, PFAS have been used for coating paper
44 and packaging products, non-stick cookware, stain-resistant carpet and clothing, as industrial
45 surfactants, and in fire-fighting foams (Sunderland et al. 2019). In production since the 1940s, PFAS
46 contamination in the environment has occurred globally via both direct release and remote transport

47 (Armitage et al. 2009). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), two of the
48 most commonly-detected PFAS, have been observed to be pervasive in the blood of both wildlife and
49 human populations, and are associated with harmful and diverse biological effects across taxa (Fenton
50 et al. 2020, Houde et al. 2006a, Houde et al. 2011, Sunderland et al. 2019).

51 Exposure to PFAS can vary by physicochemical properties of the compound, toxicokinetic and
52 ecological qualities of the organism at risk, or characteristics of the ecosystem within which the
53 organism resides. For example, PFAS bioaccumulate and biomagnify in apex predators via direct
54 consumption of contaminated prey, making them particularly harmful to species that occupy upper
55 trophic levels (Houde et al. 2006b). Individual exposure can also be affected by intrinsic properties of the
56 ecosystem in which the species forages as well as the behavior of the organism itself. For example,
57 large-scale boundary habitats (i.e. coastal systems) which integrate pollution inputs from both marine
58 and terrestrial domains may present a higher risk to individuals that forage there as opposed to
59 individuals that forage in systems that tend to function as isolated units or have less input from adjacent
60 systems (i.e. pelagic habitats or upland systems) (Crain et al. 2009). Furthermore, exposure potential
61 may not be spatially predictable within an ecosystem, and different aspects of the abiotic environment
62 may serve to collect or distribute risk. For example, although areas with high levels of urban
63 development can concentrate anthropogenic stressors such as toxic pollutants (Adams et al. 2014,
64 Gewurtz et al. 2016), the transport capabilities of many ecological toxicants can result in high levels of
65 exposure even to organisms relatively far from source inputs (Robuck et al. 2020). The long-range
66 broadcasting of risk may thus create a heterogenous exposure landscape that is not defined simply by
67 the location of the source.

68 Our goal was to assess PFAS concentrations in the eggs of a highly mobile apex predator
69 breeding near an urbanized landscape. Charleston, South Carolina, USA is a rapidly developing city
70 located within a complex coastal morphology of rivers, estuaries, and nearshore marine environments.

71 Prior research suggests that habitats in the Charleston region have significantly elevated levels of PFAS
72 relative to other regions (Keller et al. 2005, Houde et al. 2006b, Vander Pol et al. 2012, Bangma et al.
73 2017). For example, White et al. (2015) reported sediment PFAS concentrations from estuarine habitats
74 in and around Charleston Harbor in excess of any other previously examined U.S. city, with
75 approximately half of tested sites within the study area above the global median concentration for PFOS
76 (0.54 ng/g d wt.). Bottlenose dolphins (*Tursiops truncatus*) resident within the harbor possess plasma
77 PFAS levels comparable to occupationally exposed humans and are some of the highest recorded in
78 marine mammals globally (Houde et al. 2005, Houde et al. 2006b, Fair et al. 2013, Fair & Houde 2018).
79 Several fish species frequently consumed by both humans and wildlife in the Charleston area also were
80 commonly above recommended levels for safe consumption by mammals, posing a potentially
81 significant health risk (Fair et al. 2019).

82 Here we assess concentrations of 24 PFAS in 36 eggs of a locally abundant seabird, the Eastern
83 brown pelican (*Pelecanus occidentalis carolinensis*). Pelicans nest colonially on only 2-3 islands within
84 the vicinity of Charleston in any given year, and these islands and the colonies on them vary in both
85 distance from the urban center (~ 2 – 35 km) as well as in the number of breeding adults (~ 250 – 3000
86 pairs). We hypothesized there would be an inverse relationship between distance to Charleston Harbor
87 and ΣPFAS, with birds breeding closer to the urban center and therefore also closer to likely point
88 sources acquiring greater toxicity burdens. Therefore, we sought to (i) assess the presence of PFAS in
89 pelican eggs from the Charleston Harbor region relative to published values for other seabird eggs
90 collected from other locales and (ii) investigate the influence of urban habitat use on concentrations of
91 PFAS in pelican eggs using movement data from an additional subset of GPS-tracked adult pelicans from
92 each colony.

93

94 **METHODS**

95 **2.1 Sample collection and processing**

96 Eggs for contaminant analysis were collected from three breeding colonies of Eastern brown pelicans
97 located at progressively greater distances from urban Charleston (Figures 1 & 2). Castle Pinckney (32°
98 46' 26'' N, 79° 54' 40'' W) is an urban seabird colony centrally located on a small shell island within the
99 harbor and has hosted approximately 250 breeding pairs of brown pelicans near-annually since
100 individuals first started nesting in 1999 (Jodice et al. 2007). Bird Key Stono (32° 38' 00'' N, 79° 58' 04'' W)
101 is a larger sand island located at the mouth of the Stono River approximately 17 km to the southwest of
102 Charleston Harbor. This island is a regionally important nesting site for brown pelicans, with
103 approximately 3,000 nesting pairs annually since recolonization in 2014 (Jodice et al. 2007, F. Sanders
104 2021). Deveaux Bank (32° 32' 46'' N, 80° 11' 30'' W) has hosted annual breeding pairs of brown pelicans
105 since 1989, with an average count of 1,300 nests per year (Jodice et al. 2007). Deveaux Bank is located
106 approximately 37 km southwest of Charleston Harbor at the outflow of the North Edisto River.

107 Thirty-six eggs were collected in total, with efforts split evenly among colonies ($n = 12$ per
108 breeding site). All eggs were collected between 10 May 2019 and 15 May 2019, with procedures
109 approximating those of Vander Pol et al. (2012). Briefly, eggs were floated to estimate approximate age,
110 with an effort made to collect eggs in as early a stage of incubation as possible. Brown pelicans typically
111 lay a clutch of three eggs, and we aimed to collect first-laid eggs as these tend to have higher
112 concentrations of maternally transferred chemical compounds than second- and third-laid eggs (Vicente
113 et al. 2015, Parolini et al. 2021). The laying order of eggs was based on visual inspection of shell
114 cleanness. Only eggs which sank in water were collected for analysis, with resting angles ranging from
115 approximately 0°- 60° relative to the bottom of the floating vessel (Rush et al. 2007). Only one egg was
116 collected per nest, and an attempt was made to distribute the collection throughout the spatial
117 footprint of the colony ($\sim 0.01 \text{ km}^2$).

118 Eggs were transported from the colony to an off-site refrigerator (4°C) until homogenization.
119 Egg contents were separated from the shell and homogenized using a bag mixer (BagMixer 400 W,
120 Interscience Laboratories, Inc.) in non-filter 400 mL polyolefin blender bags (BagLight PolySilk,
121 Interscience Laboratories, Inc.). Aliquots of homogenized sample (15 mL) were then transferred to
122 polypropylene vials via individual transfer pipettes and stored at -80°C until sample extraction and
123 analysis (March 2020).

124 **2.2 Sample preparation and analysis**

125 Sample preparation and analysis followed a modified protocol based on Chu & Letcher (2008).
126 Sample aliquots were thawed at room temperature, and 0.5 g of homogenate were weighed into
127 polypropylene centrifuge tubes and spiked with 20 µL of isotopically labeled internal standard (0.5
128 ng/µL). Samples were extracted with 4 mL 10 mM potassium hydroxide (KOH) in methanol (MeOH) and
129 vortexed. Following sonication (20 min) and centrifugation (2 min x 4000 rpm), the resulting supernatant
130 was transferred to 15 mL polypropylene tubes. Remaining pellets received a secondary wash of 4 mL 10
131 mM KOH in MeOH, sonication, and centrifugation (10 min x 4000 rpm), with supernatant decanted and
132 added to the prior fraction.

133 Supernatant samples were diluted with 80 mL of Milli-Q (MQ) water prior to solid phase
134 extraction (SPE). Waters Oasis WAX cartridges (Waters Corp.) were preconditioned with 4 mL 0.1%
135 ammonium hydroxide (NH₄OH) in MeOH, 4 mL MeOH, and 4 mL MQ water. Samples were then loaded
136 onto cartridges at an approximate flow rate of 1 drop/sec. Cartridges were then allowed to dry under
137 vacuum for 5 min and eluted with 4 mL MeOH and 4 mL 0.1% NH₄OH in MeOH. Eluent was collected in
138 15 mL polypropylene tubes containing 200 mg ENVI Carb sorbent. Following vortexing and
139 centrifugation (10 min x 4,000 rpm), the resulting supernatant was transferred to 50 mL polypropylene
140 tubes. The ENVI Carb sorbent was rinsed with MeOH, centrifuged, and the resulting supernatant was
141 decanted and combined with the prior sample fraction. Samples were evaporated to dryness, and

142 reconstituted using 50:50 water:MeOH with 2 mL ammonium acetate. Solutions were microcentrifuged
143 at 15,000 rpm for 15 min and transferred to autosampler vials for analysis.

144 Sample extracts were analyzed for 24 PFAS using an Agilent (Santa Clara, CA, U.S.A.) 6460 triple
145 quadrupole liquid chromatograph tandem mass spectrometer (LC-MS/MS) equipped with an Agilent
146 1290 Infinity Flex Cube online SPE, following previously published methods with slight modifications
147 (Weber et al. 2017). A 100 μ L aliquot of each sample extract was injected and loaded onto an Agilent
148 Zorbax SB-Aq (4.6 x 12.5 mm; 5 μ m) online SPE cartridge with 0.85 mL of 0.1% formic acid at a flow rate
149 of 1 mL min^{-1} . Following sample loading, analytes were eluted from the SPE cartridge and loaded onto
150 an Agilent Poroshell 120 EC-C18 (3.0 x 50 mm; 2.7 μ m) reversed-phase HPLC column using ammonium
151 acetate (2 mM) in MQ water (A) and ammonium acetate (2mM) in MeOH (B) at a flow rate of 0.5 mL
152 min^{-1} and a column temperature of 50°C. Initial gradient conditions were 97% A and 3% B. From 0.85 to
153 3.5 min the gradient was linearly increased to 54% B and from 3.5 to 15 mins, linearly increased to 85%
154 B, before increasing to 100% B and maintaining at 100% B from 15.5 to 16.5 mins. Sample analytes were
155 introduced to the tandem mass spectrometer after being ionized with an electrospray ionization source
156 operated in negative ion mode at a temperature of 300°C, gas flow rate of 13 L min^{-1} , and nebulizer
157 pressure of 45 psi.

158 **2.3 Quality assurance and quality control**

159 Matrix spikes and procedural blanks were included with the sample set to monitor matrix
160 effects, process recovery, and background contamination. Matrix effects were addressed using a 7-point
161 matrix-matched curve, made up of chicken egg homogenate extracted in an identical fashion to egg
162 samples, and spiked with native and isotope-labelled standards directly prior to analysis. The chicken
163 egg matrix used for the curve contained trace levels of n-PFOS and was corrected for background n-
164 PFOS using the average of triplicate chicken egg samples taken through the extraction. Recoveries for
165 detected compounds ranged from 27 - 150% for FOSA, perfluorotridecanoate (PFTTrDA), and

166 perfluorotetradecanoate (PFTeDA) having the lowest recoveries due to predictable loss of these
167 analytes during sample preparation (Taniyasu et al. 2005). Excluding these outliers, average analyte
168 recovery ranged from 63 - 150%, with an average recovery of 78%. Data reported in this study were not
169 blank corrected, due to low levels of process contamination identified in procedural blanks. Method
170 detection limits (MDLs) were defined as procedural blank levels of a given analyte plus 3 times the
171 standard deviation. In the absence of quantifiable blank concentrations, the lowest curve point (0.25
172 ng/mL) was deemed the method detection limit. Values below MDLs were considered zero for
173 summation purposes. Summary statistics and group comparisons were derived using uncensored data
174 analyzed using the *cenfit* function in the R package *NADA* version 1.6 - 1.1 (Lee 2020) to account for
175 artifacts of left-censored data (Helsel 2011). Significant differences in contaminant concentrations
176 among colonies were assessed using both uncensored and censored log-transformed data. The *cenfit*
177 function in the R package *NADA*, which uses Kaplan-Meier (KM) model estimates, was used to evaluate
178 group differences via Peto & Peto modification of the Gehan-Wilcoxon test. Left-censored data was also
179 assessed for significant differences by habitat and compound using Kruskal-Wallis tests followed by
180 post-hoc application of Dunn's test for multiple comparisons.

181 **2.4 GPS Tracking and Spatial Analysis**

182 Movements of representative adult brown pelicans were ascertained via GPS satellite tracking
183 during the nesting period. GPS-equipped pelicans were not the same individuals from which eggs were
184 collected; therefore comparisons between contaminant exposure and movement are population-based
185 (i.e., at the level of the colony) and not individual-based. For the purposes of contaminant exposure, we
186 also assume that habitat use before and after egg laying is approximately equivalent. Adult pelicans
187 typically spend 2-3 weeks at the colony engaged in courtship activities (e.g. nest site selections, mate
188 advertisement, nest construction) prior to egg laying (Schreiber 1977) and during incubation and chick-
189 rearing forage within the vicinity of the colony while mates trade-off incubation, nest attendance, and

190 provisioning duties. A total of 68 solar-powered GPS-PTT units (GeoTrak Inc., North Carolina, USA) were
191 deployed annually in spring/summer from 2017-2020 on adult pelicans during incubation or early (i.e. 2-
192 4 weeks post-hatch) chick-rearing (Castle Pinckney, $n = 20$; Bird Key Stono, $n = 25$; Deveaux Bank, $n =$
193 23). Transmitters weighed ~ 65 g ($10 \times 3.3 \times 3$ cm) and were $\leq 3\%$ body mass of instrumented pelicans
194 (range = 2475 – 4350 g). Adult pelicans were captured at the nest with either a leg or neck lasso and
195 equipped in the field. Transmitters were attached dorsally via a backpack-style harness system as
196 described in Lamb et al. (2017a), and were programmed to record 12 GPS positional fixes per day at 90
197 min intervals between the hours of 10:00 – 02:30 GMT (fixes limited by power availability). Unit error
198 was assumed to be approximate to that of Lamb et al. (2017b), i.e. 4.03 ± 2.79 m. Equipped pelicans
199 were typically released within 20 mins of capture and 50 m of the nest site.

200 We used a recursive detection algorithm in the R package *recurse* (Bracis et al. 2018) to identify
201 nest-site attendance of instrumented pelicans for delimiting breeding locations. Exact nest coordinates
202 were extracted from release locations, with a 250 m radius buffer established around each nest. Regular
203 nest attendance was defined as the presence of locational fixes within the 250 m radius buffer
204 separated by ≤ 168 hrs. This relatively conservative time cutoff was chosen to balance the infrequency
205 of locational fixes compared to the amount of time an adult may spend at the nest, which decreases as
206 chicks age (Sachs & Jodice 2009), with the observation that pelican chicks may be able to survive
207 without provisioning for at least 2 – 3 wks (Shields 2020). All GPS points were then extracted from initial
208 deployment to the last date of nest attendance for each individual. For pelicans that remained near the
209 nest site beyond the breeding season (i.e. non-migratory individuals), a 90-day cutoff was imposed for
210 adults that were initially instrumented with chicks and a 120-day cutoff for adults initially instrumented
211 with eggs, corresponding to the maximum recorded time to successfully raise offspring (Lamb et al.
212 2017b, Shields 2020). We included telemetry data from both incubation and chick-rearing stages in
213 spatial analyses, as the majority of locations were collected during chick-rearing. It should be noted that

214 home ranges tend to decrease in size as chicks age, so estimates of overlap in high-use areas by colony
215 may be somewhat biased towards increased segregation (Geary et al. 2019). However, home range size
216 reduction is driven by increased foraging site fidelity, so that habitats used during chick-rearing are
217 derived from those used during incubation (Geary et al. 2019).

218 Breeding movements included $n = 22,274$ locational fixes and ranged from 12 May – 21 October
219 within each year (mean duration = 34.4 ± 27.8 days). To identify high-use areas for each colony, we
220 utilized a grid-cell based approach based on the number of GPS fixes per cell. To reduce spatial bias
221 introduced by time spent at the nest, all points within 250 m of the relevant breeding colony were
222 removed. A 2.25 km² grid was then imposed over the study area, and the number of locations in each
223 cell was calculated using ArcMap version 10.1 (ESRI, Redlands, California, USA). For each colony, the
224 upper quartile (25%) of grid cells containing the most points was defined as the area of high use and
225 subsequently mapped. The upper quartile was chosen in part because the majority of cells above this
226 threshold contained multiple relocations, indicating high use; additional grid cells beyond this level were
227 populated almost exclusively by single relocations which is likely not reflective of frequent use at the
228 population level.

229 We used the boundaries of 8-digit watersheds along the coastline of South Carolina to describe
230 potential differences in urban habitat use by pelicans from each colony. We chose to use watershed
231 boundaries not only because they are ecologically meaningful for coastal birds, but also because each
232 watershed likely has a varying contaminant profile based on differences in source inputs. Hydrologic unit
233 levels are defined by the U.S. Geological Survey and represent the standard units of measurement for
234 describing watersheds. These definitions correspond to regional, subregional, accounting, and
235 cataloging levels (nested from largest to smallest in size, respectively). 8-digit watersheds correspond to
236 the cataloging level, and are therefore of relatively high resolution. Watershed boundaries were
237 obtained from the S.C. Watershed Atlas (SCDHEC 2020a). Within ArcMap, we calculated the relative

238 percentages of dominant land cover types by watershed following the Anderson Level I Land Use
239 classification system (Anderson 1976) using data from the 2016 USGS National Land Cover Database (Jin
240 et al. 2019). We also calculated the number of facilities with a National Pollutant Discharge Elimination
241 Discharge (NPDES) permit registered in each watershed (SCDHEC 2020b). Finally, the percentage of high-
242 use grid cells for each pelican colony that occurred in each watershed was calculated as a measure of
243 overlap with urbanized habitats, for the purpose of making qualitative comparisons in urban habitat use
244 between colonies. In this way, we expected that eggs from pelican colonies linked to highly urbanized
245 habitat use (i.e., a large percentage of high-use grid cells occurring in watersheds dominated by urban
246 land cover) would contain greater concentrations of PFAS than eggs from pelican colonies linked to
247 lower urban habitat use if urban exposure was indeed a reliable predictor of PFAS contamination (e.g.,
248 Adams et al. 2008) .

249

250 **3.1 RESULTS AND DISCUSSION**

251 Of the 24 PFAS analytes assessed (Table S1), 15 were measured above detection limits in $\geq 50\%$
252 of pelican eggs sampled across colonies (Table 1). Perfluorohexanesulfonic acid (PFHxS), PFOS, PFOA,
253 perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA),
254 perfluorododecanoic acid (PFDoA), and PFTeDA were found in 100% of tested samples. When averaged
255 by colony location, eggs from Deveaux Bank contained the highest mean Σ PFAS concentration ($202 \pm$
256 148 ng/g w wt, $n = 12$), followed by Castle Pinckney (192 ± 137 ng/g w wt, $n = 12$), and Bird Key Stono
257 (132 ± 46 ng/g w wt, $n = 12$), although these differences were not statistically significant likely due to the
258 high variability among samples within colonies (Figure 3). The most abundant compound across all
259 samples was n-PFOS (mean = 127.5 ± 17.5 ; range = 48 – 546 ng/g w wt, $n = 36$). After n-PFOS, the
260 following most abundant compounds included PFDA (12.7 ± 0.8 ; 3 – 25 ng/g w wt), PFUnDA (7.5 ± 0.5 ; 2
261 – 14 ng/g w wt), PFTeDA (6.2 ± 0.5 ; 0 – 15 ng/g w wt), and PFNA (4.1 ± 0.2 ; 1 – 7 ng/g w wt). Of these,

262 only PFNA exhibited significant differences in concentrations among colonies, being higher at Deveaux
263 Bank compared to Castle Pinckney (Figure 4). Other analytes found to significantly differ in
264 concentration among colonies were FOSA, perfluoropentanoic acid (PFPeA), and PFOA although the
265 pattern of differences among colonies differed among analytes (Figure 4). Concentrations of all
266 remaining analytes examined did not differ significantly among colonies. Although few statistical
267 differences were found, we should note some caution may be warranted given the relatively small
268 number of sampled eggs and potential limitations of statistical power.

269 Five watersheds contained at least 10% of high-use grid cells for any of the three pelican
270 colonies, including the Edisto River, St. Helena Island, Cooper River, Bulls Bay, and Stono River
271 watersheds. Of these, the most highly urbanized watershed was the Cooper River (17.3% developed
272 land), which also contained nearly 4 times the number of NPDES-registered facilities (68) as the next
273 nearest watershed (Table 2). All remaining watersheds contained < 10% developed land cover, and < 20
274 NPDES facilities. Pelicans from Castle Pinckney used the Cooper River watershed the most frequently
275 (58.8% overlap), while use by individuals from Bird Key Stono was infrequent (8.9%) and use by
276 individuals from Deveaux Bank was absent (Table 2). Individuals from Bird Key Stono instead used all five
277 watersheds at relatively similar levels (range = 8.9 – 28.3%), while over half of the high-use grid cells for
278 individuals from Deveaux Bank occurred within the Edisto River watershed.

279 **3.2 Potential Sub-lethal Effects**

280 Brown pelican eggs from the Charleston region displayed relatively elevated levels of Σ PFAS ($175.4 \pm$
281 120.1 ng/g w wt) compared to published values of Σ PFAS from eggs of other seabirds (Table S2). These
282 high concentrations were driven in large part by PFOS loads in individual eggs. Exposure to PFAS may
283 precipitate reproductive impacts for seabirds, including pelicans. Critically, it remains unclear exactly
284 which PFAS analytes or mixtures of analytes may induce reproductive impairment and at what
285 concentrations these effects begin to manifest (Custer 2021). Research examining reproductive impacts

286 to wild populations in field setting is especially limited (Custer 2021). Tree swallows (*Tachycineta*
287 *bicolor*) at a contaminated location experienced a detectable reduction in hatching success when PFOS
288 levels in eggs were as low as 148 ng/g w wt, and a 50% reduction in hatching success compared to the
289 average rate throughout the USA with PFOS levels of 494 ng/g w wt (Custer et al. 2014). In the current
290 study, 5 of 36 pelican eggs were above the 148 ng/g value and 2 of 36 were above the 494 ng/g value.
291 Tartu et al. (2014) reported a correlation between plasma PFDoA concentrations and reduced hatching
292 success in black-legged kittiwakes (*Rissa tridactyla*) from the Arctic. Additional research on tree
293 swallows as well as great tits (*Parus major*) has suggested a possible association between reduced
294 hatching success and elevated levels of PFDA at concentrations similar to those found in pelican eggs
295 from this study (Groffen et al. 2019, Custer 2021). Taken together, these results suggest that further
296 study of hatchability in relation to concentrations of PFAS may be warranted at pelican colonies in the
297 region.

298 **3.3 FOSA Contamination and Recent Exposure**

299 The concentrations of the semi-volatile precursor compound FOSA measured in brown pelican
300 eggs (mean = 1.0 ± 0.1 , range = 0 – 3 ng/g w wt) suggest relatively recent inputs of PFAS into the
301 Charleston system extending beyond the phase-out period for this compound (Robuck et al. 2020). As
302 avian consumers may have the capacity to biotransform FOSA *in vivo* to more stable compounds (e.g.
303 PFOS; Gebbink et al. 2009), significant concentrations of precursor compounds may indicate that the
304 metabolic capacity for transformation has been exceeded as a result of continued, elevated exposure to
305 FOSA or other FOSA-precursors (Gebbink et al. 2016, Robuck et al. 2020). For example, over the period
306 1990-2010, Gebbink et al. (2011) were unable to detect FOSA in herring gull (*Larus argentatus*) eggs
307 from the Great Lakes after 2006 which is consistent with industrial PFAS phase-outs during that same
308 time period. Importantly, FOSA generally declined throughout the two decades of study, with
309 concentrations never exceeding 1.7 ng/g w wt (Gebbink et al. 2011). A follow-up study also was unable

310 to detect FOSA and other precursor compounds from eggs of herring gulls in the same area (Letcher et
311 al. 2015). These patterns suggest that the occurrence of FOSA in our samples may be due to continued
312 exposure and not to historic exposure, particularly given that we found brown pelican eggs with
313 maximum concentrations of FOSA approaching 3 ng/g w wt (Table 1).

314 FOSA was also one of four compounds with significant differences in concentrations among
315 colonies, and was most elevated in eggs from Castle Pinckney. Foraging pelicans from this urban colony
316 consistently showed frequent use of the Cooper and Ashley Rivers during the breeding season compared
317 to pelicans from Bird Key Stono and Deveaux Bank, which both had relatively low overlap of high-use
318 areas with the Cooper River watershed (Table 2). Together with the ability of FOSA to be
319 biotransformed, and therefore the increased likelihood of relatively recent exposure, the spatial
320 segregation of daily breeding-season movements found here suggest that differences in habitat used for
321 foraging during reproduction may at least partially contribute to the loads of this precursor compound.
322 Establishing interannual trends of FOSA concentrations from urban colonies such as Castle Pinckney may
323 therefore assist efforts to determine changes in regional production or use that may drive changes in
324 FOSA or FOSA precursor concentrations in the environment.

325 **3.4 Other Differences in Analytes**

326 While FOSA is likely influenced primarily by recent inputs of FOSA or its precursors into the local
327 environment, observed differences in PFNA, PFPeA, and PFOA concentrations between colonies are
328 likely influenced not only by freshwater industrial sources of these perfluorocarboxylic acids (PFCA).
329 Most likely, the latent transport, oxidation, and accumulation of PFCA precursors will have contributed
330 to the observed PFCA in the marine environments and biota (Ellis et al. 2004, Thackray et al. 2020). For
331 example, Zhang et al. (2019) observed higher than expected bioaccumulation of PFPeA in marine
332 plankton off the northeastern Atlantic coast of the United States, and attributed this to the *in situ*
333 biotransformation of precursors. Several studies have implied that the consumption of marine prey is

334 causing a PFAS profile enriched in longer-chain PFCAs, including PFNA (Dassuncao et al. 2017, Robuck et
335 al. 2020). Indeed, longer chain PFCAs have been increasing linearly with time in seabird eggs globally
336 (Gebbinck et al. 2011, Miller et al. 2015, Pereira et al. 2021), perhaps as a result of an increased
337 bioaccumulation ability of longer-chain compounds or an increase in their anthropogenic use. Pelican
338 eggs from the current study contained high concentrations of several long-chain PFCAs (e.g. PFDA and
339 PFUnDA) compared to shorter-chain analytes, and this may be a result of their highly marine diet.

340 **3.5 Similarities in Contamination Profiles Among Colonies**

341 A thorough assessment of contaminant profiles within an ecosystem is possible only when
342 multiple species and temporal points are considered. For example, Adams et al. (2008) examined PFAS
343 contamination in plasma of bottlenose dolphins from the Charleston region and suggested a positive
344 relationship between contaminant concentrations and urban habitat use immediately following
345 industrial PFAS phaseouts, which was consistent with our initial prediction. While the overall pattern of
346 analyte abundance in the plasma of dolphins was similar to that found in pelican eggs during our study
347 (PFOS > PFDA > PFUnDA > PFNA > PFOA), dolphins residing primarily in or near the harbor exhibited
348 significantly higher concentrations of PFOS, PFDA, and PFUnDA compared to those living in a less
349 urbanized environment (i.e., the Stono River estuary; Adams et al. 2008). No differences were found
350 spatially for PFOA and PFNA (Adams et al. 2008). In contrast, we found no differences in levels of PFOS,
351 PFDA, or PFUnDA among pelican colonies based on the same land cover and watershed classifications,
352 while reporting significant differences for PFOA and PFNA (Fig. 3). Of note is that pelicans from Deveaux
353 Bank, which primarily used the Edisto River watershed, had the highest concentrations of PFOA and
354 PFNA in sampled eggs. Two non-exclusive hypotheses explaining the spatial structuring found in Adams
355 et al. (2008) compared to our results are that (i) the dolphin study reflected the direct release of PFAS
356 from local point sources before industrial phaseouts in comparison to our study that occurred after
357 phaseouts were implemented or that (ii) dolphins in the region may have displayed a higher degree of

358 fidelity to specific locations compared to pelicans, especially across the annual cycle (i.e. a lack of
359 migration in dolphins). The contrast between our results and those of Adams et al. (2008) highlights the
360 need to examine multiple apex predators with different life histories and at different temporal points
361 when investigating contaminant profiles for a given region.

362 Indeed, the relatively broad similarities in concentrations of the majority of PFAS analytes
363 among the three pelican colonies in our study suggest that the frequency of using highly urbanized
364 watersheds by foraging adults cannot reliably predict PFAS concentrations in eggs of brown pelicans.
365 Lamb et al. (2020) made a similar conclusion when assessing concentrations of polycyclic aromatic
366 hydrocarbons (PAHs) in blood samples of adult brown pelicans from the northern Gulf of Mexico. There,
367 it was expected that PAHs would differ among regions of the Gulf based on differing background levels
368 of oil and gas activity but the data did not consistently support that supposition. Lamb et al. (2020)
369 posited that other inputs unrelated to the level of oil and gas activity and extensive ranging patterns in
370 individuals may have contributed to the lack of consistent regional differences. Similarly, Newtoff &
371 Emslie (2017) were unable to find differences in methylmercury concentrations in pelican eggs between
372 two estuarine complexes with differing intensities of anthropogenic influence, contrary to expectations.
373 While some tissues (e.g. blood) reflect relatively local contamination due to their high turnover times,
374 and therefore tend to minimize the influence of migratory and non-breeding areas in determining
375 source locations (Miller et al. 2020 but see Leat et al. 2013), eggs primarily reflect the contamination
376 levels of the nutrient sources that were used to create them (Bond & Diamond 2010). Individuals may
377 mobilize nutrients for egg production from energy reserves acquired while on migratory or non-
378 breeding areas (*capital* strategy) or through the rapid conversion of local resources obtained at the
379 breeding grounds (*income* strategy) (Drent & Daan 1980). Capital and income strategies are best
380 represented, however, not as dichotomous alternatives but as two endpoints on a spectrum containing
381 many intermediates (Meijer & Drent 1999). While the balance of endogenous versus exogenous

382 nutrients involved in egg deposition in brown pelicans remains unclear, it is likely to be a combination of
383 sources rather than one or the other in totality.

384 According to traditional life-history theory, species with large body sizes or those undertaking
385 relatively short migrations are likely to favor a capital breeding strategy (Klaassen et al. 2006). Brown
386 pelicans are one of the largest avian species in North America and exhibit a facultative partial migration
387 that can range from completely sedentary to highly migratory (Lamb et al. 2017b). However, brown
388 pelicans also lay relatively small eggs compared to other seabirds and a full clutch may comprise < 8 %
389 body mass of an average adult (Bartholomew & Goldstein 1984). Pelicans may therefore pay a relatively
390 low energetic cost for producing eggs, suggesting a reduced need to build energetic reserves for this
391 purpose. The local estuarine systems inhabited by pre-breeding pelicans are also likely relatively
392 productive, unlike more temperate or polar systems favored by capital breeders that may not be as
393 predictably productive during pre-breeding for individuals returning from wintering areas (Schelske &
394 Odum 1962, Hahn et al. 2011, Hupp et al. 2018). Results from Geary et al. (2020) indicated that adult
395 pelicans begin the reproductive cycle foraging in suboptimal habitats relative to the surrounding
396 environment, foraging in optimal habitats only as chicks age and energetic costs rise. This suggests that
397 local productivity is not a limiting factor when considering resource acquisition immediately following
398 egg laying, and that pre-breeding conditions are likely capable of providing the energy necessary for egg
399 formation as well.

400 If brown pelicans are therefore capable of using local resources for egg production, their
401 reliance on foraging habitats at the interface of actively dynamic and complex estuarine systems near
402 Charleston may pose a significant risk for PFAS contamination, as the potential for the release,
403 transport, and accumulation of harmful anthropogenic compounds appears high. Prior investigations
404 into both abiotic and biotic PFAS concentrations centered on the estuarine regions of Charleston suggest
405 that the surrounding aquatic environment, particularly the Cooper River watershed, may indeed be

406 more heavily contaminated than other comparable urbanized estuaries (White et al. 2015, Fair & Houde
407 2018, Fair et al. 2019). Identifying specific source inputs of PFAS in the Charleston region, however, is
408 difficult. Candidate sources include PFOS-contaminated groundwater associated with relatively recent
409 releases of aqueous film-forming foams (AFFF) from Joint Charleston Air Force Base near the Ashley
410 River (U.S. Army Corps of Engineers 2018), as well as older AFFF events from the former Charleston Navy
411 Base on the Cooper River (operational from 1901-1996) (White et al. 2015). Wastewater treatment
412 plants (WWTP) discharging effluent into Charleston Harbor have also been identified as potential
413 sources, with tested effluent containing relatively large amounts of both PFOS and PFOA (Houde et al.
414 2006b). Other suggested point sources include commercial container ships entering the Port of
415 Charleston as well as various anthropogenic activities along freshwater inputs, especially the Cooper
416 River, which aggregates discharge from numerous industrial facilities indicated by NPDES permit
417 registries (White et al. 2015, Leads & Weinstein 2019) (Figure 1). Importantly, increasing concentrations
418 from 2004-2012 of some compounds in estuarine sediments from the Charleston area suggest
419 continuing inputs into the system despite widespread production bans in the early 2000s (White et al.
420 2015). Although the Cooper River watershed contained the highest levels of urban development as well
421 as the most NPDES facilities, no watersheds examined were completely free of development or
422 discharge facilities, indicating the widespread potential for PFAS exposure throughout the entirety of the
423 study area.

424 However, if egg production is reliant instead on resources acquired during the non-breeding
425 season or while migrating, local point sources of PFAS in urban Charleston may have a reduced impact
426 on observed egg concentrations. Linking overwintering areas with contaminant exposure in brown
427 pelicans is difficult and compounded by the relatively broad range occupied at the population level,
428 driven by variation in post-breeding movements at the level of the individual (Poli 2015). For example,
429 pelicans from colonies in the northern Gulf of Mexico did not exhibit uniform migratory strategies

430 among individuals but instead displayed a range of behaviors from complete sedentarism to long-
431 distance migrations (e.g., ~1500 km; Lamb et al. 2017b). Preliminary observations of GPS-tracked
432 pelicans from our study colonies in South Carolina, as well as earlier tracking work by Poli (2015),
433 suggest that high-use areas during the non-breeding season occur in coastal Georgia, Florida Bay, and
434 Cuba, as well as along the central and southern coast of South Carolina (i.e., our study area). Each of the
435 aforementioned regions is likely to have a discrete contaminant profile based on anthropogenic activity,
436 local abiotic factors, and regional transport mechanisms (O’Connell et al. 2010, Robuck et al. 2020). The
437 highly variable nature of pelican migratory destinations, both within and between individuals, may
438 therefore have homogenized contaminant exposure between breeding colonies over relatively long
439 temporal scales. This study highlights the need to resolve the relative importance of endogenous versus
440 exogenous resources in eggs when examining contaminants in avian species for making assessments
441 about where contamination may occur during the annual cycle.

442 A limitation of the current study was that we were unable to assess local habitat use for the
443 same individual pelicans from which eggs were collected, due to logistical difficulties, instead relying on
444 colony-level assessments of both movement and contaminant levels. The conclusions made are
445 therefore applicable at the level of the colony, and may not reflect how individual-specific habitat use
446 and movement patterns contributes to PFAS levels. Future studies may better resolve potential
447 associations between habitat use and PFAS contamination by tracking and assaying the same individual.

448 **4.1 Conclusion**

449 Our results indicate that potentially impactful Σ PFAS concentrations exist in brown pelican eggs
450 from the Charleston region. Taken together with previous studies as well as known releases of PFAS in
451 the region (i.e. AFFF exposure from military installations), it appears that Charleston may act as a
452 significant source for these contaminants in the nearshore environment. Impacts of this contamination
453 remain unclear but the potential for reproductive or physiological impairment at current exposure levels

454 appears to be possible based on previous avifaunal studies (Custer 2021). Contrary to expectations, we
455 were unable to find a relationship between PFAS contamination and use of urbanized habitats for the
456 majority of analytes studied. We therefore suggest that proximity to likely point sources for
457 environmental contaminants may not always act as a reliable proxy for exposure when both stressor
458 and organism are capable of transboundary movement, and that individuals even relatively distant from
459 likely sources may still show elevated risk. Given that brown pelicans were previously listed under the
460 Endangered Species Act largely as a result of interactions with anthropogenic contaminants (Wilkinson
461 et al. 1994), continued monitoring of this species for PFAS contamination may be particularly valuable
462 (Vander Pol et al. 2012).

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