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The highest mercury concentrations ever reported in a South American bird, the Striated Caracara (Phalcoboenus australis) 3

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7 Abstract

8 Mercury is a widely available pollutant associated with negative effects on wildlife, especially top predators. Here, we AQI 9 characterized the mercury concentrations in feathers of Striated Caracara Phalcoboenus australis on Isla de los Estados 10 (Argentina). With feather mercury levels averaging 26.3 mg/kg, this population has the highest mean feather mercury ever 11 reported for a bird population in South America. We propose that the high mercury concentrations are related to the feeding habits of the species: during feather moult, they are strongly associated with a Southern Rockhopper Penguin (Eudyptes AQ2 13 chrysocome) colony known to be highly exposed to mercury contamination. Our results suggest that this Striated Caracara 14 population should be monitored for acute effects and potential impacts of mercury toxicity.

15 Keywords Hg · Exposure · Raptor · Conservation · Biomagnification · Heavy metals

Introduction 16

17 Mercury (Hg) is a widely available pollutant documented to 18 have significant adverse effects on wildlife. Direct and acute 19 effects of mercury exposure vary widely amongst species, 20 including mortality, aberrant behaviours, reduced immune 21 response and reproductive impairment (Scheuhammer 1987; 22 Scheuhammer et al. 2007; Seewagen 2010). Birds of prey 23 are at an elevated risk of exposure to toxic concentrations

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of mercury as they are long-lived predators foraging at high trophic levels (Berg et al. 1966; Becker 2003; Lourenço et al. 2011; Cristol et al. 2012).

The Striated Caracara (Phalcoboenus australis, hereafter caracara) is a near threatened raptor with a restricted distribution on islands off the coast of southern South America and in the Malvinas/Falklands islands (Ferguson-Lees and Christie 2001; IUCN 2019). During the breeding season, their diet consists mainly of eggs, chicks and carrion of seabirds and sealions (Strange 1996). As top predators and facultative scavengers, caracaras may be highly exposed to mercury accumulation. In particular, the resident population in Franklin Bay (Isla de los Estados) build their nests in close association with Southern Rockhopper penguins (Eudyptes chrysocome, hereafter rockhopper) and are the main predator of their eggs and chicks (Liljesthröm et al. 2008; Balza et al. 2017). Moreover, caracaras of all ages and breeding status depend on marine resources and particularly on penguin subsidies during breeding season (Balza et al. 2020). Rockhoppers breeding on Franklin Bay show feather mercury concentrations amongst the highest ever reported in penguins $(5.10 \pm 1.46 \text{ mg/kg}, \text{Brasso et al. 2015})$. The rockhopper penguin population in Isla de los Estados is the only South American penguin population known to exceed the documented lowest adverse effects levels based on adult feathers (5-40 mg/kg; see Ropert-Coudert et al. 2019). In this study, we provide the first report on mercury exposure

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51 of caracaras. We predict that the caracaras will be exposed to high levels of mercury contamination, and if this is a chronic 52 process, chicks should be less contaminated than adults as 53 they only have ~ 3 months of exposure when they complete 54 their first set of feathers. 55

Methods 56

Fieldwork was conducted in Franklin Bay, a~4 km² bay on 57 Isla de los Estados (Tierra del Fuego, Argentina, 54°85'30 58 S, 64°83'90 W). During December 2016 and May 2017, 59 moulted wing (n=26) and tail (n=10) feathers were col-60 lected during systematic occupancy surveys of caracara ter-61 ritories (for details see Balza et al. 2017). These samples 62 included wing feathers from three birds found dead during 63 the surveys. We also plucked two back feathers from cap-64 tured birds (n = 10). We classified feathers as from adults 65 66 (> 5 years old) or first-year juveniles (less than one year old and therefore reflecting mercury burden during chick 67 rearing; Henny and Elliot 2007) following Strange (1996). 68 Nine adult feathers were collected in nest sites (one feather/ 69 site), representing $\sim 53\%$ of the active nests in the 2016/2017 70 breeding season. The remaining samples represented $\sim 10\%$ 71 of the total estimated population (n=37 samples from 220 to 72 530 individuals, UB unpublished data). We therefore assume 73 that they are independent samples. 74

75 As feather moult is the primary mechanism through which birds can excrete mercury (e.g. Renedo et al. 2021), 76 recently moulted feathers can provide insights into mercury 77 78 exposure in the previous year. Annual moult occurs during the spring and summer (September to March) in this 79 population (UB, NAL and ARR unpublished). Therefore, the 80 mercury signal in moulted feathers would represent accu-81 mulation since the previous moult with higher influence of 82 recent dietary exposure during the period of feather growth 83 (Bearhop et al. 2000; Bond and Diamond 2009), which in 84 our case would correspond to when rockhopper penguins are 85 present at the colony. 86

Feathers were cleaned in a series of deionized water 87 and acetone baths to remove any exogenously deposited 88 contaminants, air dried at room temperature for 24-48 h 89 90 and stored in sealed plastic centrifuge tubes until analysed. A central part of the feather vane (in moulted feathers) 91 or three whole back feathers (in captured birds) from 92 93 each individual were cut into fine pieces using a pair of sterilized stainless-steel scissors to create a homog-94 enous mixture. We subsampled ~ 10 g of feathers of each 95 individual to analyse for total mercury using a Nippon 96 MA-3000 Direct Mercury Analyzer at Weber State Univer-97 sity (Ogden, UT, USA). Each set of 20 samples analysed 98 was preceded and followed by two samples of a standard 99 reference material (TORT-3, National Resource Council 100

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Canada). Mean percent recovery for the standard reference 101 material was 98.5% (n=8) with relative significant dif-102 ferences in mercury concentration of 2.6%. Mercury con-103 centrations in feathers are reported as mg/kg fresh weight. 104

Intra-individual variation has been found amongst 105 feather types due to moulting sequence and timing (Dauwe 106 et al. 2003; Cristol et al. 2012), but we were not able to 107 design a sampling with more than one feather per indi-108 vidual. Therefore, to account for this possible effect, we 109 modelled variation in mercury concentration as an additive 110 function of both age and feather type. We use generalized 111 linear models (GLM) with gamma error distribution and 112 rank all possible models according to Akaike criterion cor-113 rected for small sample size (AICc) using MuMIn package 114 in R software (Barton 2015; R Core Team 2018). Since 115 only one best model was retained (see Results), we used 116 the coefficients of the best model to estimate 95% confi-117 dence intervals for the mean value of mercury for each age 118 group. We also used the coefficient of the null model to 119 estimate 95% confidence intervals for the mean value of 120 the whole population. 121

Results

We analysed 39 feather samples from adults and seven from juveniles. We detected mercury in all samples, and 124 the average estimated mercury concentration for the whole 125 population was 26.34 mg/kg (95% CI 22.11-31.72 mg/kg, 126 range 0.79-85.46 mg/kg). Model selection using Akaike 127 criterion retained the best model containing age as the only explanatory variable (Table 1), with more than two AICc values between it and the next model suggesting a single best model fit (Burnham and Anderson 2002). The best model explained 22% of the variability of mercury in feathers. Predicted mean values for Hg concentration in feathers were 29.19 mg/kg for adults (95% CI 24.86-35.35 mg/kg) and 10.47 mg/kg for juveniles (95% 135 CI 7.42-17.79 mg/kg). 136

Table 1 Additive GLM models of mercury concentration in feathers of striated Caracara (Phalcoboenus australis) ranked by Akaike criterion corrected for small sample size (AICc)

Model	df	LogLik	AICc	Delta AICc	Weight
Age	3	- 183.95	374.5	0.0	0.90
Age+feather type	5	- 183.76	379.0	4.5	0.09
Null	2	- 189.98	384.2	9.7	0.01
Feather type	4	-188.88	386.7	12.2	0.00

Columns represent degrees of freedom (df), logarithm of likelihood (LogLik), differences in AICc respect to the best model (Delta AICc) and the relative importance of each model (weight)

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Fig. 1 A Striated Caracara (*Phalcoboenus australis*) adult female showing rigidity and overgrown claws in her right talon, with over 85 mg/kg feather mercury concentration

137 Discussion

This is the first report of mercury concentrations in Stri-138 ated Caracaras and documents the highest mean values ever 139 recorded for a bird population in South America. Overall, 140 96% of the samples in this study exceeded the documented 141 5 mg/kg lowest observable adverse effects threshold for bird 142 feathers (Burger and Gochfeld 2000) and 17% were above 143 40 mg/kg (i.e. adverse effects documented in common loons, 144 Evers et al. 2008). Raptor-specific adverse effects levels are 145 unknown. Similar to other raptor studies, we found juve-146 niles to have lower feather mercury concentrations than 147 adults (Becker et al. 1994; Bowerman et al. 1994; Cahill 148 et al. 1998; Carravieri et al. 2017). This could be explained 149 by chronic exposure of adults that are at least five years 150 old (Strange 1996). However, several other factors could 151 be responsible for the unexplained variation in our model, 152 including differences in physiology or foraging ecology 153 between age groups (Balza et al. 2020). 154

The only suggestion of a potential effect that we found 155 was that the bird with the highest mercury concentration AQ3 in our study (85.46 mg/kg) was an adult female with over-157 grown talons and lack of motion in one of her claws (Fig. 1). 158 Excretion of mercury through keratin production is a major 159 pathway for decreasing the body burden of mercury in birds 160 (Furness et al. 1986; Honda et al. 1986; Bearhop et al. 2000). 161 It is possible that mercury eliminated into growing talons 162 disrupted the availability of sulphur and/or cystine needed 163 for keratin production leading to observable changes in the 164 talon structure; however, we are not aware of evidence in the 165 literature to support this pathway in birds. Feather mercury 166 found in the present study exceeded concentrations reported 167 in other caracara species in Brazil and northern Patagonia 168 (Rapôso de Silva et al. 2017; Di Marzio et al. 2018). 169

170 Caracaras on Isla de los Estados feed on a restricted diet171 of mainly marine foragers (Balza et al. 2020), and their

mercury concentrations were similar to those detected in 172 other raptor species in North America commonly associ-173 ated with aquatic prey (Bowerman et al. 1994; Hughes et al. 174 1997; Cahill et al. 1998; Bechard et al. 2009). Moreover, in 175 the Southern Hemisphere, only marine top predators, like 176 albatrosses, show similar mercury exposure (Carravieri et al. 177 2017; Cherel et al. 2018). We propose that at this site, rock-178 hoppers serve as an environmental link importing marine 179 pollutants to terrestrial food webs. If this is the case, not only 180 would caracaras have elevated mercury reflecting previous 181 patterns detected in sympatrically breeding rockhoppers, 182 but their levels would be higher as a result of biomagnifica-183 tion. As a species of conservation concern, the high levels of 184 mercury concentration reported in this study call for a long-185 term monitoring of this population of caracaras, including 186 the possible implications on physiological and reproductive 187 success. 188

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Author contributions UB, NAL and ARR conceived and designed197research; UB and NAL conducted fieldwork; RB conducted mercury198analysis; UB analysed data; UB wrote the first version of the manu-199script; KP and ARR retrieved funds; all authors contributed with writing, discussion and editing various versions of the manuscript.200

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Data availability Raw feather mercury data and scripts to reproduce 205 the analysis in R can be found inhttps://github.com/ulisesbalza/Mercu 206 ry_caracaras. 207

Declarations 208

Conflict of interest The authors declare no conflict of interest regard-209 ing this article. 210

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