

Trace Element Concentrations in Feathers of Flesh-footed Shearwaters (*Puffinus carneipes*) from Across Their Breeding Range

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Abstract Seabirds are convenient indicators of contamination of the marine environment because feathers can be sampled non-destructively, and a great deal is known about their ecology. Flesh-footed Shearwaters (*Puffinus carneipes*) are of conservation concern in Australia and New Zealand, partly because ingestion of marine debris may be reducing breeding success at their largest colony. Because marine plastics accumulate contaminants in the ocean environment, an assessment of metal and metalloid contaminants was initiated. We sampled feathers from Kauwahaia ($n = 18$) and Lady Alice Island, New Zealand ($n = 30$), Lord Howe Island ($n = 24$) and Western Australia ($n = 33$) during the 2008 austral summer, making this the most complete assessment of metal and metalloid contamination of any shearwater. We found colony differences in all elements except lead and thallium. Samples from Western Australia had higher silver, aluminium, cadmium, and copper concentrations, while shearwaters from Lord Howe Island (eastern Australia) had elevated concentrations of mercury (mean \pm S.D., 11221 ± 5612 ppb). We conclude that mercury, and potentially arsenic and cadmium represent toxicological concerns for this declining species.

Seabirds are among the top predators in the marine ecosystem, and because of their relatively high trophic position, are at risk from the bioaccumulation of toxic chemicals from both natural and anthropogenic sources. Mercury (Hg), lead (Pb), arsenic (As) and cadmium (Cd) are non-essential elements that are distributed globally and transported atmospherically (Nriagu 1989). Seabirds can be used as indicators of the health of marine systems (Cairns 1987; Monteiro and Furness 1995; Burger and Gochfeld 2004), including contaminants (e.g., Barrett et al. 1996; Braune et al. 2005; Goodale et al. 2008). Contaminants in seabirds can be sampled non-destructively using feathers, which are grown and moulted on a regular basis (e.g., Nisbet et al. 2002; Bond and Diamond 2009a). Feathers often contain the biologically active form of metal contaminants (e.g., methylmercury, Bond and Diamond 2009b), and feather replacement is a major pathway for the elimination of contaminants from a body burden (Braune and Gaskin 1987; Monteiro and Furness 2001a).

Flesh-footed Shearwaters (*Puffinus carneipes*) are classified as Vulnerable in New South Wales, Australia (their main breeding area, Threatened Species Conservation Act 1995) and are listed as a declining species in New Zealand. They breed in dense colonies on North Island, New Zealand (8000–10,000 pairs, Baker et al. 2010), Lord Howe Island, Australia (their largest single breeding site, 17,500 pairs, Priddel et al. 2006), on numerous islands in Western Australia (100,000–200,000 pairs, Johnstone and Storr 1998), on Smith Island, South Australia (150 pairs, Robinson et al. 1986) and on l'île Saint-Paul in the Indian Ocean (500 pairs, Roux 1985). Flesh-footed Shearwaters are taken frequently as bycatch in fisheries (Baker and Wise 2005), but this has decreased in some well-managed fisheries, such as the Australian Eastern Tuna and Billfish Fishery, where bycatch decreased from 1200 to 6800 birds

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in 1999/2000 to less than 20 per year in 2004 (Tuck and Wilcox 2008), and less than 5 per year in 2006 (Trebilco et al. 2010). Current threats on Lord Howe Island now include ingestion of marine debris and habitat destruction (Priddel et al. 2006). Ingestion of plastics is correlated with contaminant burden (Ryan 1988), body condition, body mass (Connors and Smith 1982; Furness 1985a, b; Spear et al. 1995), the decision to breed (Day 1980), and chick growth and survival (Sievert and Sileo 1993). Currently, the relative threat posed by plastic ingestion to Flesh-footed Shearwaters on Lord Howe Island is unknown, although a large proportion of chicks ingest plastic on a regular basis (Hutton et al. 2008). Virgin (pre-manufacture) plastic can accumulate and magnify organic, hydrophobic contaminants found in the ocean (Mato et al. 2001), and post-manufacture plastics often contain elements of eco-toxicological interest, such as mercury, lead, cadmium, or arsenic (Saron and Felisberti 2006; Cadore et al. 2008). When seabirds ingest plastics, some of these contaminants are transferred to both the adult birds, and their chicks (to whom they often offload plastic during feeding). While the prevalence of plastic ingestion in Flesh-footed Shearwaters is unknown at other breeding sites, it is likely of concern. For example, 44% ($n = 25$) of adult birds recovered off vessels fishing in New Zealand waters during 2005–2009 contained plastic (D. Thompson, pers. comm.). Therefore, we hypothesized that Flesh-footed Shearwaters may exhibit elevated contaminant levels as compared with species less affected by marine debris.

Our goal was therefore to assess the contamination of adult Flesh-footed Shearwaters from across their breeding range to determine whether contaminants pose a threat to this species, and could be a factor relating to its decline on Lord Howe Island (Priddel et al. 2006). Few studies of trace elements in wildlife are as geographically comprehensive—here, we present data from Flesh-footed Shearwaters from New Zealand, Lord Howe Island, and Western Australia, encompassing the majority of the species' range. Furthermore, we consider 17 trace elements in the most comprehensive review of elemental contamination of any shearwater to date.

Two previous studies have examined metal and metalloid contaminants in Flesh-footed Shearwaters (Lock et al. 1992; Elliott 2005), but in both cases, internal tissues were sampled from dead birds, meaning that further comparisons would require sacrificing individuals. The most comprehensive of these studies utilised birds killed as bycatch in North Pacific drift net and long-line fisheries, and so their provenance is unknown (Elliott 2005).

In summary, our objectives were (1) to provide detailed trace element analysis on Flesh-footed Shearwaters from multiple breeding sites across their range, (2) to compare Hg, Pb, Cd, As concentrations in feathers among sites to

examine inter-colony differences, as these elements have been studied the most intensively in seabirds, and thus have the most complete toxicological information, and (3) to compare our results to hypothesized effect levels for marine birds and assess the potential risk that metal and metalloid contaminants pose to Flesh-footed Shearwater populations.

Methods

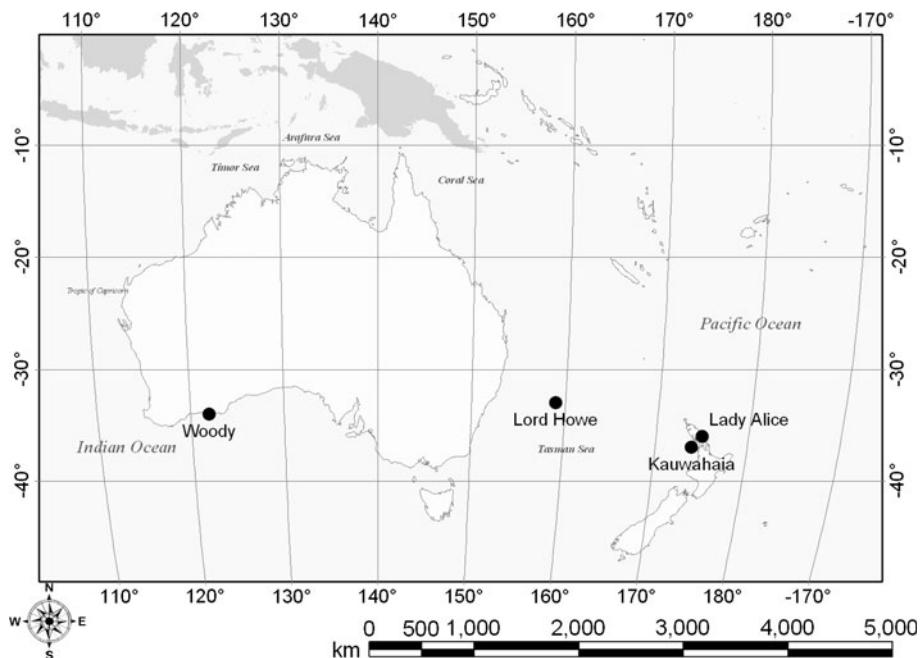
Sample Collection

Four breast feathers were collected from breeding adults on Kauwahaia Island (36.54°S, 174.26°E, $n = 18$) and Lady Alice Island, New Zealand (35.89°S, 174.71°E, $n = 30$), Lord Howe Island, Australia (32.53°S, 159.08°E, $n = 24$), from birds caught as bycatch in the King George Sound pilchard fishery in Western Australia during the breeding season (approx. 35.05°S, 118.03°E, $n = 30$), and breeding birds from Woody Island, Western Australia (33.87°S, 121.89°E, $n = 3$; see Fig. 1). Birds from the King George Sound fishery were caught inshore, so were grouped with samples from nearby Woody Island, and assumed to be from Western Australia (Powell 2009). Breast feathers were selected because they are the best indicator of whole-body metal burdens (Furness et al. 1986). In addition, Flesh-footed Shearwaters replace their breast feathers during the latter half of the breeding season (February–April, Onley and Scofield 2007), so it is likely that the contaminants deposited into breast feathers were accumulated, at least in part, on the breeding grounds, as wing feathers are moulted on the wintering grounds (Onley and Scofield 2007). Feathers were stored in sterile polyethylene bags or paper envelopes and stored at –20°C prior to analysis.

Analytical Methods

Feathers were washed in 0.25 M NaOH to remove external contamination (Bearhop et al. 2000; Bond and Diamond 2009a). Two feathers per bird, or approximately 15–25 mg, were weighed accurately into clean Savillex 15 ml Teflon screw-cap vessels. We analysed two feathers per sample, as individual feathers can be highly variable in metal concentrations (Bond and Diamond 2008). About 1 mL of 8 M HNO₃ (Fisher Scientific, Ottawa, ON, 16 M, distilled in-house using Teflon stills) was added, the vessel capped tight, and placed on a hotplate at 70°C. When the feathers were wet, after 60 min., an additional 1 mL of 8 M HNO₃ was added and the feathers were pushed down with clean disposable plastic pipettes until submerged fully in the acid. After 24 h, the hotplate was cooled to 50°C, then 1 mL of

Fig. 1 Flesh-footed Shearwater breeding colonies from which feathers were sampled. Individuals from the King George Sound pilchard fishery were caught within 300 km of Woody Island, Western Australia



H_2O_2 (Fisher Scientific, Ottawa, ON, 30% certified, American Chemical Society) was added and the vessel caps removed. When most of the reaction had taken place, the vessels were recapped and left on hotplate for 3 h more at 70°C. Solutions were then transferred to clean, sealed containers, and taken up to volume with distilled, deionised water to dilute the sample 500×. For inductively coupled plasma mass spectrometry (ICP-MS) analysis, 1 mL of the sample solution was pipetted into clean 10-mL tubes, and 4 mL distilled, deionised water added to make a final tube dilution of approximately 2500×.

Trace element concentrations were measured in a PerkinElmer ELAN DRCII ICP-MS (Rf power: 1200 W, ICP-MS plasma gas flow: 15 L/min, auxiliary gas flow: 1 L/min, nebulizer gas flow: 1 L/min, sample uptake rate: 3.055 ml/min). Data acquisition was by peak-hopping mode, and each analyte mass was measured for 6 s. The protocol used was based on Friel et al. (1990). Procedural blanks and secondary reference materials were included for every 15–20 samples. The secondary materials used were certified human hair samples 6H-09 and 7H-09 from the Centre de Toxicologie du Québec, Institut National de Santé Publique du Québec. Secondary reference materials were certified for concentrations of ^9Be , ^{27}Al , ^{51}V , ^{53}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{77}Se , ^{98}Mo , ^{107}Ag , ^{111}Cd , ^{118}Sn , ^{121}Sb , ^{137}Ba , ^{201}Hg , ^{205}Tl , ^{208}Pb , and ^{238}U , and we restricted our statistical analysis to those elements that could be analysed reliably as assessed by the recovery of reference materials. We therefore excluded Be, Cr, Se, and Sn from our analysis, leaving 17 elements. Recovery of the secondary reference material ranged from 85 to 129% among all remaining elements for all runs. Values were

corrected for background levels using procedural blanks, and for recovery using values from secondary reference materials within each run. Approximately 12% of samples were run in duplicate, and mean coefficients of variation ($(\text{S.D.}/\text{mean}) \times 100$) of elemental concentrations ranged from 4.4 to 25.7. For values below detection levels, we used one half of the detection level to calculate means and associated statistical error.

Statistical Methods

Concentrations were log-transformed to meet the normality assumptions of our statistical analyses, which were conducted in SPSS 16 (SPSS Inc, Chicago, IL, USA). To test for differences among colonies in elemental concentrations, we used analysis of variance (ANOVA) with Ryan's Q post-hoc tests (Ryan 1959, 1960; Day and Quinn 1989) and homogeneity of variance was assessed using Levene's test (Levene 1960). We also examined the covariation among elements using Pearson correlations. In all cases, differences were considered significant when $p < 0.05$. All concentrations are expressed as parts-per-billion (ppb, ng/g) on a fresh weight basis.

Results

A summary of elemental concentrations in each colony is presented in Table 1. There were significant differences in concentrations among colonies for all elements except Tl and Pb (Table 1). There were three broad patterns in the inter-colony differences: (1) a trend from east to west in

Table 1 Trace element concentrations from Flesh-footed Shearwater breast feathers from four breeding regions

	Kauwahaia (<i>n</i> = 18)	Lady Alice (<i>n</i> = 30)	Lord Howe (<i>n</i> = 18)	W. Australia (<i>n</i> = 33)
Aluminum (Al)	90439 ± 45529 ^a	97952 ± 96673 ^a	63260 ± 34520 ^a	222454 ± 195798 ^b
Vanadium (V)	491 ± 396 ^{ab}	214 ± 114 ^a	662 ± 417 ^{bc}	921 ± 450 ^c
Manganese (Mn)	10191 ± 5753 ^c	1499 ± 639 ^a	2341 ± 1050 ^b	2189 ± 1336 ^b
Cobalt (Co)	104 ± 93 ^b	23 ± 21 ^a	178 ± 12 ^c	257 ± 102 ^c
Nickel (Ni)	2025 ± 725 ^c	1113 ± 656 ^b	1063 ± 2316 ^a	2649 ± 3593 ^{bc}
Copper (Cu)	14796 ± 4330 ^b	13330 ± 2433 ^b	9628 ± 1406 ^a	18382 ± 3053 ^c
Zinc (Zn)	104291 ± 31540 ^b	87932 ± 14786 ^{ab}	8588 ± 24059 ^a	92244 ± 33945 ^{ab}
Arsenic (As)	1229 ± 1454 ^b	3629 ± 4724 ^c	241 ± 162 ^a	3089 ± 8572 ^{ab}
Molybdenum (Mo)	243 ± 160 ^{ab}	333 ± 166 ^b	293 ± 125 ^b	213 ± 137 ^a
Silver (Ag)	36 ± 20 ^a	41 ± 66 ^a	206 ± 224 ^b	820 ± 947 ^c
Cadmium (Cd)	71 ± 41 ^a	59 ± 27 ^a	89 ± 100 ^a	288 ± 816 ^b
Antimony (Sb)	89 ± 37 ^{bc}	128 ± 65 ^c	30 ± 29 ^a	71 ± 73 ^b
Barium (Ba)	20037 ± 14977 ^c	13724 ± 7241 ^{bc}	2430 ± 4141 ^a	11494 ± 7532 ^b
Mercury (Hg)	7466 ± 2360 ^{ab}	8007 ± 3641 ^b	11221 ± 5612 ^c	6038 ± 3998 ^a
Thallium (Tl)	10 ± 3 ^a	9 ± 6 ^a	10 ± 4 ^a	9 ± 4 ^a
Lead (Pb)	347 ± 176 ^a	492 ± 257 ^a	471 ± 291 ^a	515 ± 367 ^a
Uranium (U)	23 ± 9 ^{ab}	17 ± 13 ^a	42 ± 31 ^a	24 ± 20 ^b

Values are expressed as parts per billion (ng/g) and we present means ± SD. Colonies sharing the same letter for a given element are not significantly different based on Ryan's Q post-hoc tests

either increasing or decreasing concentrations (Ag, Cd, Co, V); (2) no significant difference in concentrations between the two New Zealand colonies (Silver (Ag), Barium (Ba), Cd, Copper (Cu), Hg, Molybdenum (Mo), Antimony (Sb), Uranium (U), Vanadium (V), Zinc (Zn)); and 3) the highest concentrations were found in feathers from birds from Western Australia (Ag, Al, Cd, Cu). Several concentrations were correlated significantly among all colonies (Table 2), and Co and Ba were correlated with the largest number of other elements (13). Tl was not correlated significantly with any other elements.

Discussion

Our study represents the most comprehensive examination of trace element concentrations in any shearwater to date. We found significant intercolony differences in all but two trace elements (lead and thallium), and among those elements, distinct patterns emerged. In four cases, we found a significant geographic trend where shearwater feathers had increasing concentrations of Ag, Cd, Co, and V moving east to west. Flesh-footed Shearwaters breeding in New Zealand and eastern Australia migrate into the North Pacific, whereas those breeding in Western Australia migrate into the Indian Ocean (Powell 2009). Thus, differing oceanographic regimes between the two oceans and variation in the behaviour of elements in ocean water likely

play a considerable role in the acquisition of contaminants by shearwaters. However, as the pharmacokinetics of trace elements in feathers are poorly studied, their source is unknown.

We also found that, in general, Lord Howe Island had the lowest elemental concentrations, while Kauwahaia Island and Western Australia had the highest. The notable exception to this pattern was Hg, where Flesh-footed Shearwaters from Lord Howe Island exhibited the highest concentrations. We have limited the subsequent discussion to elements of toxicological significance—As, Cd, Hg, and Pb—for the sake of brevity, because of the lack of substantive toxicological information on other metals, and the biological significance of their concentrations in feathers. We present data on all elements measured, however, in the hope that future ecotoxicological investigations may shed light on the patterns in, or significance of, the feather concentrations of less-studied elements.

Only two previous studies have examined trace elements in Flesh-footed Shearwaters, although using internal tissues (liver, kidney; Lock et al. 1992; Elliott 2005). The timing of sampling in relation to moult confounds comparisons of concentrations from internal tissues and feathers. Contaminants are excreted from an internal body burden into growing feathers, and thus with the progress of moult, concentrations in internal tissues and in feathers replaced later in the same moult cycle would decrease with time (Braune and Gaskin 1987; Monteiro and Furness 2001a, b).

Table 2 Pearson correlations among trace element concentrations in Flesh-footed Shearwater breast feathers

	V	Mn	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Sb	Ba	Hg	Tl	Pb	U	
Al	0.276**	0.312**	0.272**	0.327***	0.482***	0.175	-0.106	-0.204*	0.375***	0.464***	-0.076	0.337***	-0.148	-0.018	0.132	-0.087	
V	0.095	0.596***	0.104	0.196*	0.022	-0.298**	-0.128	0.502***	0.295**	-0.298**	-0.141	-0.069	0.032	0.021	0.011		
Mn	0.225*	0.0293**	0.091	0.293**	-0.107	-0.106	-0.087	0.047	-0.019	0.219*	0.069	0.191	-0.117	0.116			
Co	0.062	0.165	-0.021	-0.596***	-0.288**	0.639***	0.411***	-0.478***	-0.335***	-0.335***	-0.087	0.079	-0.099	0.215*			
Ni	0.386***	0.181	0.012	-0.046	0.128	0.217*	0.194*	0.194*	0.388***	-0.212*	0.083	0.09	-0.048				
Cu	0.295**	0.036	-0.237*	0.332**	0.351***	0.201*	0.201*	0.502***	0.502***	-0.329**	-0.069	0.065	-0.125				
Zn	0.049	-0.217*	-0.18	0.18	0.118	0.118	0.263***	0.263***	-0.079	0.001	0.001	-0.495***					
As		0.278**	-0.573***	-0.083	0.609***	0.496***	0.496***	0.496***	0.496***	0.075	-0.108	0.179	-0.156				
Mo			-0.175	-0.181	0.158	-0.044	-0.044	-0.044	-0.044	0.332**	-0.033	0.242*	0.253*				
Ag				0.208*	-0.391***	-0.265**	-0.265**	-0.265**	-0.265**	-0.149	-0.007	0.133	0.177				
Cd					-0.102	0.12	-0.123	-0.123	-0.123	-0.038	0.198*	-0.011					
Sb						0.517***	-0.128	-0.128	-0.128	-0.076	0.154	-0.146					
Ba							-0.260**	-0.260**	-0.260**	-0.004	0.064	-0.295**					
Hg								0.037	0.037	0.045	0.045	0.239*					
Tl									0.009	0.009	0.029	0.029	0.154				
Pb																	

Levels of significance: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

Arsenic (As)

Arsenic is both a teratogen and carcinogen that can cause behavioural and physical defects in birds. Marine organisms often have elevated concentrations of As because of their acquisition of As via seawater (Maher and Butler 1988). With the exception of Flesh-footed Shearwaters from Lord Howe Island, all other populations had the highest recorded feather As values for any bird (Goede 1985; Burger and Gochfeld 2000b; Burger et al. 2007; Burger et al. 2008; Burger and Gochfeld 2009; Anderson et al. 2010). Arsenic was also highly variable, and in three of the four colonies, the S.D. exceeded the mean estimate (Table 1). While As has been measured in a variety of seabird studies, its toxicology and chemistry in marine birds is poorly known as compared with elements such as Hg or Pb (Burger et al. 2007). As a consequence, there is currently no theoretical effects threshold for As in feathers.

The largest source of arsenic is in continental shelf sediments rather than atmospheric transport (Maher and Butler 1988), although the majority of As in the Australian environment is likely anthropogenic (Nriagu 1989; Smith et al. 2003). Caution must be used when interpreting As concentrations in keratinous materials, however, as external contamination is likely to occur, and feathers can magnify the concentrations in surrounding liquid media (Smith and Hendry 1934; Goede and de Bruin 1984; Smith et al. 2008).

Arsenic also comes in a variety of forms (Kunito et al. 2008), and among three species of passerine birds, arsenate, arsenic(III)-glutathione ($\text{As}(\text{GS})_3$), arsenite, monomethylarsonic acid (MMA), and dimethylarsonic acid (DMA) were the predominating chemical species, although among marine birds, feathers had the lowest concentration of As of any tissue (Fujihara et al. 2004). Of the predominant feather As species, $\text{As}(\text{GS})_3$ is a binding of As to three sulphur-containing groups, and would be expected to be the main form of As in sulphur-rich keratin of seabird feathers (Crewther et al. 1965). Given the high concentrations of As in Flesh-footed Shearwater feathers (the highest reported in the literature), and the unknown toxicological significance, we identified As contamination as a potential concern that requires further investigation.

Cadmium (Cd)

In general, less than 30% of birds' cadmium body burden is in feathers (Honda et al. 1985; Burger 1993), much less than for Hg or Pb. Cd levels in feathers are often low, but concentrations that are observed are likely endogenous in origin (Burger 1993; Pilastro et al. 1993). The Cd concentrations observed in Flesh-footed Shearwaters in this study (Table 1) fall within the known range of Cd

concentrations from bird feathers, and two-thirds (70/105) were below the hypothesized effect level of 100–2000 ppb (Burger 1993; Burger and Gochfeld 2000b). Greater knowledge about the effects of Cd, and relationships between adverse effect levels and Cd concentrations observed in feathers are required before a sound conclusion can be drawn regarding the toxicological risk posed to Flesh-footed Shearwaters (Scheuhammer 1987).

Lead (Pb)

There is a substantial body of literature describing the effects of Pb contamination on seabird behaviour and physiology (reviewed in Burger and Gochfeld 2000a). Pb is an anthropogenic contaminant that has no biological function and can be transported great distances atmospherically (Nriagu 1989; Burger 1993). In general, feather Pb levels above 4000 ppb are thought to cause sublethal effects in marine birds (Burger 1993). Pb concentrations in Flesh-footed Shearwater feathers are among the lowest reported for marine birds (470 ppb, Table 1; Burger 1993; Burger and Gochfeld 2000b), although a variety of seabird species from the South Atlantic had feather Pb concentrations <237 ppb (Anderson et al. 2010). There was no difference in Pb concentrations in Flesh-footed Shearwater feathers among colonies in this study. As the majority of Pb body burden is allocated to feathers (Honda et al. 1985), and feather Pb concentrations are often correlated significantly with Pb concentrations of internal tissues, feathers are reliable indicators of Pb contamination in the marine environment (Burger 1993). Feathers can accumulate exogenous Pb contamination (Goede and de Bruin 1984), so this further suggests that Flesh-footed Shearwaters are not at any immediate risk from Pb contamination.

Mercury (Hg)

Most Hg is anthropogenic, and is transported atmospherically before being incorporated into biota (Furness et al. 1986; Nriagu and Pacyna 1988). Global Hg emissions are predicted to increase by 2050 (Streets et al. 2009). Hg is one of the most commonly studied heavy metals in seabirds (Burger 1993), and there is a significant amount of information on its toxicology and effects on wildlife. Feather replacement is the major excretory pathway of Hg, usually in the form of the toxic methyl Hg (Thompson and Furness 1989; Monteiro and Furness 2001a; Bond and Diamond 2009b). The Hg excreted in feathers originates in a body pool, or reservoir of Hg accumulated during the period between successive feather moulting events. Seabirds can apparently tolerate higher Hg concentrations because of their ability to demethylate methyl Hg in the liver and store it as inorganic Hg (Burger and Gochfeld 2002). Feather Hg

is representative of Hg concentrations in internal tissues, making feathers an excellent biomonitoring tool for Hg in the marine environment (Agusa et al. 2005). Burger (1993) hypothesized an effect level of 5000 ppb in feathers of marine birds; all four regions of Flesh-footed Shearwaters in our study had means above this level, including one individual from Lord Howe Island with feather Hg concentrations above 30 000 ppb. Only 20 individuals (19% of all individuals sampled in this study) had feather Hg concentrations below 5000 ppb. Many Procellariiformes (albatrosses, shearwaters, and petrels) have elevated Hg as compared with other marine birds (Burger and Gochfeld 2000b; Anderson et al. 2009; Bond and Diamond 2009a), and this could be potentially related to their lengthy moulting duration, lasting several months (Stewart et al. 1999). We therefore conclude that Flesh-footed Shearwaters, particularly those at Lord Howe Island, could be potentially exposed to harmful, sublethal concentrations of Hg, and a more detailed investigation is warranted. Although caution should be exercised when comparing feather Hg concentrations to this hypothesized and untested effect level, some Flesh-footed Shearwaters from Lord Howe Island have feather Hg concentrations that are among the highest recorded for seabirds in general, and we therefore feel that our precautionary conclusion is warranted.

Correlations Among Trace Elements

We found statistically significant correlations between many of pairs of trace elements (Table 2). Cd was correlated with seven other elements, excluding Mn, which is in contrast to previously published studies (Burger et al. 1993; Burger et al. 1994). Pb was correlated with only Cd and Mo, and in both cases, the correlation was weakly positive. Other studies have reported a relationship between Pb and Mn, although we did not detect it in Flesh-footed Shearwaters (Burger et al. 1994). Hg was positively correlated with Mo and U, and negatively correlated with Ni and Cu in our study, mirroring the mixed results of other studies (Burger 1993; Burger et al. 2008).

Plastics as a Source of Contamination

Plastics in marine environments accumulate and magnify persistent organic pollutants, specifically hydrophobic, non-polar compounds (Carpenter et al. 1972; Mato et al. 2001; Endo et al. 2005; Rios et al. 2007). Methylmercury (monomethylmercuric cation) is the most abundant form of Hg in feathers, and the toxic form of the element (Weiner et al. 2003; Bond and Diamond 2009b). In the ocean, it can form monomethylmercuric chloride, which is also toxic to wildlife, and is non-polar (Fimreite and Karstad 1971;

Segall and Wood 1974). Cd and Zn would likely react similarly as they are in the same periodic group as Hg, and Zn is a common component of boat antifouling paint that can enter the marine environment during vessel cleaning or maintenance (Turner 2010). Pb forms compounds with chloride easily, including with tetraethyl lead, the additive once used in gasoline (Seyferth 2003), resulting in a non-polar molecule that could be taken up by plastics. Most organoarsenic compounds, however, are polar, including those consisting of As(III) and As(V). As(GS)₃, however, contains a large organic (and non-polar) portion that could associate with plastics in the ocean (Yambushhev and Savin 1979).

Household plastics, such as those ingested by Flesh-footed Shearwaters on Lord Howe Island (see Hutton et al. 2008), contain significant concentrations of heavy metals, some of which are used as colourants (Landsberger and Chichester 1995; Ritter et al. 2004; Cadore et al. 2008). In particular, Pb, Cd, and Hg are used to add colours during the manufacturing process (Saron and Felisberti 2006; Cadore et al. 2008). We therefore hypothesize that Hg, Pb, Cd, and As could be transported by plastic marine debris, and these contaminants could then be transferred to birds. Given the high incidence of plastic ingestion among Flesh-footed Shearwaters on Lord Howe Island (Hutton et al. 2008), the record of plastics ingested by New Zealand birds in recent years (see above), and the chemical and physical properties of plastic marine debris, we suggest that plastic ingestion and the associated contamination could represent a conservation concern for Flesh-footed Shearwaters globally.

Microplastics are plastic particles in the marine environment that, when ingested, pass through a bird's digestive system (Moore 2008). The stomach conditions—pH of 3–4, and temperature of around 38°C (Cheah and Hansen 1970; Whittow et al. 1987)—would likely be sufficient to remove the outer layer from plastics that contains marine-acquired contaminants, and so the absence of plastic found in the gut of a seabird does not imply that it is not affected by plastics-derived contaminants (Bond et al. 2010).

The relative contribution of debris-associated contaminants to shearwaters' overall contaminant burden is at present unknown. Contaminants, such as Hg, are transported atmospherically (Nriagu 1989) and largely acquired from prey (Monteiro and Furness 2001a). A variety of factors also affect the biomagnification and bioaccumulation of contaminants, and not all metals and metalloids are biomagnified. Marine plastic is an unexplored vector for contamination in marine birds that are affected heavily by debris ingestion, such as North Pacific albatrosses (Sileo et al. 1990; Auman et al. 1997), and likely Flesh-footed Shearwaters, although its magnitude in relation to other sources (seawater or prey) remains unknown.

Conclusions

We examined a variety of metals and metalloids in the feathers of Flesh-footed Shearwaters from across their breeding range in Australia and New Zealand—the most complete toxicological assessment of this species to date. In general, shearwaters are not at great risk from current feather contaminant levels, although our toxicological knowledge regarding many elements is insufficient to draw firm conclusions. Flesh-footed Shearwaters do exhibit high concentrations of Hg, especially individuals from Lord Howe Island. Further research is needed to determine the contribution of plastics-derived contaminants (both metals and organics) to the overall burden of seabirds, and to better relate contaminant concentrations and plastic burden to demographic parameters.

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