LEAD AND CADMIUM LEVELS IN GALAPAGOS PENGUIN SPHENISCUS MENDICULUS, FLIGHTLESS CORMORANT PHALACROCORAX HARRISI, AND WAVED ALBATROSS PHOEBASTRIA IRRORATA

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> > Received 5 December 2016, accepted 17 May 2017

ABSTRACT

JIMÉNEZ-UZCÁTEGUI, G., VINUEZA, R.L., URBINA, A.S., EGAS, D.A., GARCÍA, C., COTÍN, J. & SEVILLA, C. 2017. Lead and cadmium levels in Galapagos Penguin *Spheniscus mendiculus*, Flightless Cormorant *Phalacrocorax harrisi*, and Waved Albatross *Phoebastria irrorata*. *Marine Ornithology* 45: 159–163.

Heavy metals are a threat to wildlife, and they have yet to be analyzed in seabirds from the Galápagos Archipelago. To gauge their prevalence in Galápagos seabird species, we collected and analyzed feather samples from Galapagos Penguins *Spheniscus mendiculus*, Flightless Cormorants *Phalacrocorax harrisi*, and Waved Albatross *Phoebastria irrorata* in seven different breeding areas in 2011 and 2012 as part of an ongoing mark-recapture study. The results showed that lead is higher in penguins and cormorants; cadmium was found to be below the limit for quantification in all our samples. The heavy metals recorded did not have a clear local source related to human activities, as breeding areas are not located near populated areas. Environmental media (soil, water), marine currents, and atmospheric deposition are possible sources.

Key words: Heavy metals, threats, marine birds, Galápagos Archipelago

INTRODUCTION

The bioaccumulation of metals in wildlife can result from their introduction into the environment from natural and anthropogenic sources, which can have indirect impacts that are difficult to measure (Furness & Greewood 1993, Burger & Gochfeld 2004). The idea of using organisms to monitor environmental health has been suggested since 342 BC (Furness & Greewood 1993). Marine birds are one such example. They have been used as indicators and sentinels of contamination, because they occupy different levels of the food web, are often widely distributed, and are long-lived (Furness & Greewood 1993, Burger & Gochfeld 2004, Boersma 2008, Vega *et al.* 2009, Finger *et al.* 2015).

Heavy metals have been found in penguins, cormorants, and albatross around the world, even in seemingly remote places such as the Antarctic (Hindell *et al.* 1999, Metcheva *et al.* 2006, Calle *et al.* 2014; Table 1). Given the wide prevalence of heavy metals in marine bird tissues, we thought it would be worthwhile to investigate their presence in birds of the remote Galápagos Islands. Metal levels in endemic Galapagos Penguin *Spheniscus mendiculus*, Flightless Cormorant *Phalacrocorax harrisi*, and Waved Albatross *Phoebastria irrorata* inhabiting the Galápagos Archipelago have never been evaluated.

Herein, we report on the analysis of the presence of lead (Pb) and cadmium (Cd) in the above three species.

METHODS

Study area

The Galápagos Archipelago, located on the Equator, ~960 km west of mainland Ecuador, is composed of 13 islands and more than 100 islets and rocks (Snell *et al.* 1996). Seven areas were selected to conduct our study according to the locations of the three species studied: Galapagos Penguins were assessed on Isla Isabela at Caleta Iguana (0°58.6'S, 91°26.7'W) and Puerto Pajas (0°45.3'S, 91°22.5'W), as well as on Islotes Marielas (0°35.8'S, 91°5.4'W). Flightless Cormorants were assessed on Isla Fernandina, at the Playa Escondida (0°15.7'S, 91°28.1'W) and Carlos Valle (0°15.6'S, 91°27.5'W) location, and at the Punta Albemarle I (0°9.2'N, 91°22.0'W) and Punta Albemarle II (0°9.7'N, 91°21.6'W) location on Isla Isabela. Waved Albatross, was assessed on Isla Española, at Punta Suárez (Plot A: 1°22.3'S, 89°44.4'W and Plot B: 1°22.5'S, 89°44.1'W) and at Punta Cevallos (1°23.3'S, 89°37.2'W) (Fig. 1).

Sampling

Feather collection is the most common non-destructive and non-invasive sampling protocol used to assess the presence of heavy metals in birds (Burger 1993). Our sampling took place in 2011 and 2012 in the breeding areas of the three species. Each sample was individually preserved in an envelope along with pertinent information (date, island, place, species, and identification number). The effort was part of an ongoing mark-recapture study, in which biological and clinical data are taken before marking each individual. All samples collected in this research were taken from live individuals prior to marking and releasing. Secondary feathers were collected from the wings of cormorants and albatross, while tail feathers were sampled from penguins. The same methodology was applied to both juveniles and adults.

Laboratory analysis

The analyses were performed in the laboratory of the Department of Chemical Engineering at Universidad San Francisco de Quito (USFQ), Quito, Ecuador, using the US EPA (United States Environmental Protection Agency 2007) method 7000B. Each feather was cut into small pieces of approximately 1 cm \times 1 cm and labeled according to species and the place where they were collected (Table 1). Samples were weighed in a beaker. Nitric acid (HNO₃, 50%) was added to the seven samples according to their weight (Table 1) and heated for digestion for ~25 min (Niazi & Littlejohn 1993, Barbieri *et al.* 2010). As a control measure, the cadmium analysis was performed twice. In the second analysis, we used a smaller amount of each sample (Table 1).

Calibrations were performed by successively diluting a base solution of lead (995 ppm, Inorganic Ventures, Christiansburg VA) and cadmium (1000 ppm, AccuStandard, New Haven CT). These calibrations were also conducted to achieve a final concentration of 5% nitric acid.

The concentrations of these elements were determined using an atomic absorption spectrophotometer (Buck Scientific, model 210 VGP, Norwalk CT) equipped with an air/acetylene flame. The primary wavelengths of the hollow-cathode lead and cadmium lamps were 283.3 nm and 228.9 nm, respectively. The detection ranges were 0.08–20.00 ppm for lead and 0.01–2.00 ppm for cadmium. The calibration curve was obtained with triplicate measurements for each standard, yielding a calibration curve of y = 0.0146x + 0.0026 ($R^2 = 0.9990$) for lead and y = 0.171x + 0.0047 ($R^2 = 0.9995$) for cadmium.

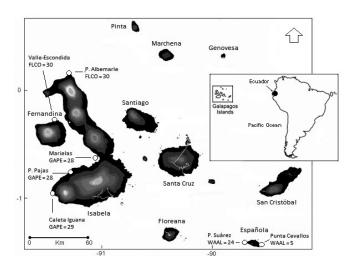


Fig. 1. Galapagos Penguins (GAPE), Flightless Cormorants (FLCO), and Waved Albatross (WAAL) breeding colonies sampled in 2011 and 2012 in the Galápagos Archipelago; GAPE, FLCO, WAAL = number of individuals captured.

RESULTS AND DISCUSSION

By using the calibration curve obtained for lead, as well as the dilution factor and the mass of the feathers in the sample, it was possible to determine the lead concentration in the Galapagos Penguin and Flightless Cormorant in five different areas. The lead results for Waved Albatross in Punta Cevallos and Punta Suárez were below the limit of detection of the calibration curve (Table 1).

Our results showed that the lead concentrations recorded in Galapagos Penguins were higher than in other penguin species, but mid-range compared with cormorants (Table 1). It was surprising that the results from less frequently visited areas, such as Islotes Marielas (penguins), Puerto Pajas (penguins), and Punta Albemarle (cormorants) produced the highest concentrations of this metal. In albatross, places with higher boat-traffic, such as Punta Suárez, produced values below the limit of detection (LOD). Therefore, to analyze the sources of lead, we tracked the movement and foraging distance of the three species.

Galapagos Penguins remain near their breeding areas, traveling 1-24 km from their nest site on a daily basis (Steinfurth et al. 2008); during non-breeding periods, they have been found 27-59 km away from their nests (Boersma et al. 2013). Flightless Cormorants also travel locally, being found within a 53 km range of their nesting areas (Larrea 2007). In contrast, Waved Albatross occur widely in the waters of the Humboldt Current, from at least El Chocó (Colombia) southward to northern Chile (Awkerman et al. 2014). Regarding the results found for lead, we expected that albatross would have the highest concentration of the species we studied, because they have more anthropogenic interactions, spending most of their lives in the productive waters off the west coast of South America, where there are industrial, semi-industrial, and artisanal fishing boats (Jiménez-Uzcátegui et al. 2006) and other sources of lead. However, the concentrations of lead found in albatross were below the LOD. We are at a loss as to why the highest levels of lead were found in penguins and cormorants, compared with albatross; also, we cannot explain why the levels of lead among Galapagos Penguins were higher than those found in other penguin species to date. In some way, food must be a source of both remote (e.g., Sun & Xie 2001) and local contamination, since it has been recorded in volcanic material (Teasdale et al. 2005).

Regarding cadmium, we found that the concentrations in Galapagos Penguins, Flightless Cormorants, and Waved Albatross were lower than in other seabird species studied to date (Table 1), i.e., the different assays provided absorbance values below the LOD. That was somewhat surprising, given that cadmium is found in the ocean, at levels that vary, depending on the region, the currents, and the upwellings (Delaney *et al.* 1993, Abouchami *et al.* 2014), and upwellings occur close to Galápagos (Hayes & Baker 1989). Cadmium has been found in Galápagos corals at lower concentrations in deeper areas (Abouchami *et al.* 2014). To better interpret our results, further research is needed on both cadmium and lead levels in penguin and cormorant prey species of the Galápagos Islands.

In conclusion, our results provide the first data on metal concentrations in feathers of Galapagos Penguins, Flightless Cormorants, and Waved Albatross. In our study, the concentrations of lead seemed to derive not from local human sources but from natural sources, or from distant human sources carried to the area by marine currents or atmospheric deposition (Duce *et al.* 1991, Delaney *et al.* 1993, Sun & Xie 2001). The levels of these metals

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TABLE 1 Samples, methodology, and lead (Pb) and cadmium (Cd) concentrations in feathers of Galapagos Penguins, Flightless Cormorants, and Waved Albatross in the Galápagos (GPS) archipelago compared with results from other studies

Species	,		8	Digestion 1		Digestion 2	Mean ± SD (ppm)		
	Location	No. feathers (individuals)		HNO ₃ Vol 50% (mL) ^a	weight 2 $(\alpha)^{a}$	HNO ₃ Vol 50% (mL) ^a	Pb	Cd	Source
Galapagos Penguin Spheniscus mendiculus	Caleta Iguana, GPS, Ecuador	64 (29)	0.1645	20	0.0366	20	55.5 ± 27.80	LOD ^b	
	Puerto Pajas, GPS, Ecuador	54 (28)	0.1281	20	0.0303	20	71.3 ± 35.60	LOD	This study
	Marielas, GPS, Ecuador	53 (28)	0.0946	20	0.0438	20	193.0 ± 48.30	LOD	
Little Penguin Eudyptula minor	St. Kilda, Victoria, Australia						0.42 ± 0.20	0.04 ± 0.02	Finger <i>et al.</i> 2015
	Phillip Island, Victoria, Australia						0.08 ± 0.03	0.04 ± 0.03	Finger <i>et al.</i> 2015
	Notch Island, Victoria, Australia						0.10 ± 0.05	0.06 ± 0.02	Finger <i>et al.</i> 2015
African Penguin S. demersus	Biopark Zoom, Torino, Italy							0.152 ± 0.080 0.192 ± 0.056	1
Adelie Penguin Pygoscelis adeliae	East Antarctica						0.28 ± 0.07	0.20 ± 0.09	Honda <i>et al</i> . 1986
	Avian Island, Antarctica						0.14 ± 0.21	0.04 ± 0.02	Jerez <i>et al.</i> 2011
Gentoo Penguin P. papua	King George Island, Antarctica						0.51 ± 0.46	-	Jerez <i>et al.</i> 2011
	King George Island, Antarctica						-	0.03 ± 0.03	Brasso <i>et al.</i> 2013
Chinstrap Penguin P. antarctica	Ronge Island, Antarctica						0.14 ± 0.09	0.10 ± 0.05	Jerez <i>et al.</i> 2011
Flightless Cormorant Phalacrocorax harrisi	Valle-Escondida, GPS, Ecuador	47 (30)	0.8046	30	0.0586	30	17.00 ± 8.51	LOD	—This study
	Punta Albemarle, GPS, Ecuador	47 (30)	10.719	40	0.1094	30	42.60 ± 8.52	LOD	
Double-crested Cormorant Ph. auritus	Agassiz Wildlife Refuge, MN, USA						1930 ± 310	957 ± 167	Burger & Gochfeld 1994
Great Cormorant Ph. carbo	Fish Farm, Serbia						29.92 ± 0.00	-	Skoric <i>et al</i> . 2012
Waved Albatross Phoebastria irrorata	Punta Cevallos, GPS, Ecuador	5 (5)	0.1331	20	0.0198	20	LOD	LOD	This study
	Punta Suárez, GPS, Ecuador	31 (24)	12.384	50	0.004	20	LOD	LOD	
Black-footed Albatross Phoebastria nigripes	Midway Atoll, North Pacific						0.973	0.152	Burger & Gochfeld 2000
Wandering Albatross Diomedea exulans	Bird Island, South Georgia						LOD	0.317	Anderson <i>et al.</i> 2010
Grey-headed Albatross Thalassarche chrysostoma	Bird Island, South Georgia						LOD	0.196	Anderson <i>et al.</i> 2010
Black-browed Albatross	Bird Island, South Georgia						LOD	0.578	Anderson <i>et al.</i> 2010
	Patagonian Shield, Argentina						4.31	0.2	Seco Pon <i>et al.</i> 2011

^a Numerals 1 and 2 refer to the first and second Cd analysis for control (weight of feathers [g] and digestion [mL]), because the results (ppm) were LOD; confirmed from both analyses.

^b LOD = below the limit of detection.

in tissues of the studied species were low; thus, this issue currently is not critical to the well-being of these populations. However, the occasional monitoring for these metals is warranted, as the planet undergoes rapid environmental change during the Anthropocene.

ACKNOWLEDGMENTS

We would like to thank the Galápagos National Park Directorate and the Charles Darwin Foundation. We would also like to thank the donors to the Galapagos Conservation Trust, The Truell Charitable Foundation, the Penguin Fund of Japan, and Mr. Seishi Sakamoto. We are grateful to our collaborators and the more than 60 assistants and volunteers who helped with the research from 2009 to 2015, mainly Manuel Masaquisa, Freddy Villalva, Franklin Gil, Wilman Valle, Patricio Carrera, Ainoa Nieto, and Alba Costales. We also thank Inti Keith for correcting the grammar of an earlier version of this article. Thanks to the reviewers, especially to R. Furness and D. Ainley, for their helpful comments on this manuscript. This publication is the contribution number 2 163 of the Charles Darwin Foundation for the Galápagos Islands.

REFERENCES

- ABOUCHAMI, W., GALER, S.J.G., DE BAAR, H.J.W., ET AL. 2014. Biogeochemical cycling of cadmium isotopes in the Southern Ocean along the Zero Meridian. *Geochimica et Cosmochimica Acta* 127: 348-367. doi:10.1016/j. gca.2013.10.022
- ANDERSON, O.R.J., PHILLIPS, R.A., SHORE, R.F., MCGILL, R.A.R., MCDONALD, R.A. & BEARHOP, S. 2010. Element patterns in albatrosses and petrels: influence of trophic position, foraging range, and prey type. *Environmental Pollution* 158: 98-107. doi:10.1016/j.envpol.2009.07.040
- AWKERMAN, J.A., CRUZ, S., PROAÑO, C., ET AL. 2014. Small range and distinct distribution in a satellite breeding colony of the critically endangered waved albatross. *Journal* of Ornithology 155: 367-378. doi:10.1007/s10336-013-1013-9
- BARBIERI, E., PASSOS, E.A., FILIPPINI, A., DOS SANTOS, I.S. & GARCIA, C.A.B. 2010. Assessment of trace metal concentration in feathers of seabirds (*Larus dominicans*) sampled in the Florianapolis, SC, Brazilian coast. *Environmental Monitoring and Assessment* 169: 631-638. doi:10.1007/s10661-009-1202-4
- BRASSO, R.L., DRUMMOND, B.E., BORRETT, S.R., CHIARADIA, A., POLITO, M.J. & REY, A.R. 2013. Unique pattern of molt leads to low intraindividual variation in feather mercury concentrations in penguins. *Environmental Toxicology* and Chemistry 32: 2331-2334. doi:10.1002/etc.2303
- BOERSMA, P.D., STEINFURTH, A., MERLEN, G., JIMÉNEZ-UZCÁTEGUI, G., VARGAS, F.H. & PARKER, P.G. 2013. Galapagos Penguin (*Spheniscus mendiculus*). In: GARCIA BORBOROGLU, P. & BOERSMA, P.D. (Eds.) *Penguins: Natural History and Conservation*. Seattle, WA: University of Washington Press.
- BOERSMA, P.D. 2008. Penguins as marine sentinel. *BioScience* 58: 597-607 doi:10.1641/B580707.
- BURGER, J. 1993. Metals in avian feathers: bioindicators of environmental pollution. *Reviews Environmental Toxicology* 5: 203-311.
- BURGER, J. & GOCHFELD, M. 2004. Marine birds as sentinels of environmental pollution. *EcoHealth* 1: 263-274. doi:10.1007/ s10393-004-0096-4

- BURGER, J. & GOCHFELD, M. 2000. Metals in albatross feathers from Midway Atoll. *Environmental Research* 82: 207-221.
- BURGER, J. & GOCHFELD, M. 1994. Heavy metal and selenium levels in birds at Agassiz National Wildlife refuge, Minnesota: Food Chain difference. *Environmental Monitoring and Assessment* 43: 267-282. doi:10.1007/BF00394454
- CALLE, P., ALVARADO, O., MONSERRATE, L., CEVALLOS, J.M., CALLE, N. & ALAVA, J.J. 2014. Mercury accumulation in sediments and seabird feathers from the Antarctic Peninsula. *Marine Pollution Bulletin* 91: 410-417. doi:10.1016/j. marpolbul.2014.10.009
- DUCE, R.A., LISS, P.S., MERRILL, J.T., ET AL. 1991. The atmospheric input of trace species to the World Ocean. *Global biogeochemical cycles* 5: 193-259. doi:10.1029/91GB01778
- DELANEY, M.L., LINN, L.J. & DRUFFEL, E.R.M. 1993. Seasonal cycles of manganese and cadmium in coral from Galápagos Islands. *Geochimica et Cosmochimica Acta* 57: 347-354.
- FURNESS, R.W. & GREENWOOD, J.J.D. (Eds.). 1993. Birds as Monitors of Environmental Change. London, UK: Chapman and Hall.
- FINGER, A., LAVERS, J.L., DANN, P., ET AL. 2015. The Little Penguin (*Eudyptula minor*) as an indicator of coastal trace metal pollution. *Environmental Pollution* 205: 365-377. doi:10.1016/j. envpol.2015.06.022
- HAYES, F.E. & BAKER, W.S. 1989. Seabird distribution at sea in the Galapagos Islands: Environmental correlations and associations with upwelled Water. *Colonial Waterbirds* 12: 60-66.
- HINDELL, M.A., BROTHERS, N. & GALES, R. 1999. Mercury and cadmium concentrations in the tissues of three species of southern albatross. *Polar Biology* 22: 102-108.
- HONDA, K., YAMAMOTO, Y., HIDAKA, H. & TATSUKAWA, R. 1986. Heavy metal accumulations in Adelie penguin, *Pygoscelis adeliae*, and their variations with the reproductive processes. Tokyo, Japan: Memoirs of National Institute Polar Research. 40: 443-453.
- JEREZ, S., MOTAS, M., PALACIOS, M.J., VALERA, F., CUERVO, J.J. & BARBOSA, A. 2011. Concentration of trace elements in feathers of three Antarctic penguins: geographical and interspecific differences. *Environmental Pollution* 159: 2412-2419. doi:10.1016/j.envpol.2011.06.036
- JIMÉNEZ-UZCÁTEGUI, G., MANGEL, J., ALFARO-SHIGUETO, J. & ANDERSON, D.J. 2006. Fishery bycatch of the waved albatross *P. irrorata*, a need for implementation of agreements. *Galapagos Research* 64: 7-9.
- LARREA, C. 2007. Movimiento, dispersión y éxito reproductive del comorán no volador Phalacrocorax harrisi, en las islas Galápagos. Biology undergraduate thesis. Quito, Ecuador: Pontificia Universidad Católica del Ecuador.
- METCHEVA, R., YURUKOVA, L., TEODORAVA, S. & NIKOLOVA, E. 2006. The penguin feathers as bioindicator of Antarctica environmental state. *Science of Total Environmental* 362: 259-265. doi:10.1016/j.scitotenv.2005.05.008
- NIAZI, S.B. & LITTLEJOHN, D. 1993. Rapid partial digestion of biological tissues with nitric acid for the determination of trace elements by atomic spectrometry. *Analyst* 118: 821-825. doi:10.1039/AN9931800821
- SECO PON, J.P., BELTRAMEC, O., MARCOVECCHIO, J., FAVERO, M. & GANDINI, P. 2011. Trace metals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) in feathers of Black-browed Albatross *Thalassarche melanophrys* attending the Patagonian Shelf. *Marine Environmental Research* 72: 40-45. doi:10.1016/j. marenvres.2011.04.004

- SKORIC, S., VISNJIC-JEFTIC, Z., JARIC, I., ET AL. 2012. Accumulation of 20 elements in great cormorant (*Phalacrocorax carbo*) and its main prey, common carp (*Cyprinus carpio*) and Prussian carp (*Carassius gibelio*). *Ecotoxicology and Environmental Safety* 80: 244-251. doi:10.1016/j.ecoenv.2012.03.004
- SNELL, H.M., STONE, P.A. & SNELL, H.L. 1996. A summary of geographical characteristics of the Galápagos Island. *Journal of Biogeography* 23: 619-624.
- SQUADRONE, S., ABETE, M.C., BRIZIO, P., ET AL. 2016. Sex- and age-related variation in metal content of penguin feathers. *Ecotoxicology* 25: 431-438. doi:10.1007/s10646-015-1593-7
- STEINFURTH, A., VARGAS, F.H., WILSON, R.P., SPINDLER, M. & MACDONALD, D.W. 2008. Space use by foraging Galapagos penguins during chick rearing. *Endangered Species Research* 4: 105-112. doi:10.3354/esr00046

- SUN, I. & XIE, Z. 2001. Changes in lead concentration in Antarctic penguin droppings during the past 3,000 years. *Environmental Geology* 40: 1205-1208. doi:10.1007/s002540100346
- TEASDALE, R., GEIST, D., KURTZ, M. & HARPP, K. 2005. 1998 Eruption at Volcán Cerro Azul, Galápagos Islands: I. Syn-Eruptive Petrogenesis. *Bulletin of Volcanology* 67: 170-185. doi:10.1007/s00445-004-0371-9
- US ENVIRONMENTAL PROTECTION AGENCY (EPA). 2007. W-846 Test Method 7000B: Flame atomic absorption spectrophotometry. [Available online at: https://www.epa. gov/hw-sw846/sw-846-test-method-7000b-flame-atomicabsorption-spectrophotometry. Accessed 28 Jan 2016].
- VEGA, C.M., SICILIANO, S., BARROCAS, P.R.G., ET AL. 2010. Levels of cadmium, mercury, and lead in Magellanic Penguins (*Spheniscus magellanicus*) stranded on the Brazilian coast. *Archives of Environmental Contamination and Toxicology* 58: 460-468. doi:10.1007/s00244-009-9349-0