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Baseline

Mercury concentrations, biomagnification and isotopic discrimination factors in two seabird species from the Humboldt Current ecosystem

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ABSTRACT

Assessing mercury (Hg) biomagnification requires the description of prey-predator relationships, for each species and ecosystem, usually based on carbon and nitrogen isotope analyses. Here, we analyzed two seabirds from the Humboldt Current ecosystem, the Guanay cormorant (*Phalacrocorax bougainvillii*) and the Peruvian booby (*Sula variegata*), as well as their main prey, the Peruvian anchovy (*Engraulis ringens*). We reported Hg concentrations, Hg biomagnification (BMF) and isotopic discrimination factors ($\Delta^{13}C$ and $\Delta^{15}N$) in seabird whole blood. BMFs and $\Delta^{13}C$ in our study (on wild birds where diet was not controlled) were similar to other piscivorous seabirds previously studied in captive settings, but $\Delta^{15}N$ were lower than most captive experiments. We observed lower Hg concentrations in Humboldt seabirds compared to other oligotrophic ecosystems, possibly due to Hg biodilution in the high biomass of the first trophic levels. This work calls for a better characterization of Hg trophic dynamics in productive upwelling ecosystems.

Mercury (Hg) is a global pollutant of natural and anthropogenic origins (Driscoll et al., 2013). Atmospheric Hg emissions have increased by 450% since the preanthropogenic times, resulting in a 230% increase in Hg concentration in the surface ocean (Outridge et al., 2018). Once deposited in marine waters, a yet unknown fraction of Hg can be naturally converted to methylmercury (MeHg), mostly by microorganisms (Podar et al., 2015). MeHg is bioaccumulated by marine organisms, which induces an increase in MeHg concentration in tissues over time (Wang and Wong, 2003). In addition, MeHg is known to biomagnify along trophic chains, resulting in increased MeHg levels with the position of consumers in the food web (Lavoie et al., 2013). Due to their long life span and high trophic position, marine top predators contain among the highest MeHg concentrations of biota (Cherel et al., 2018; McKinney et al., 2016). Human exposure to MeHg occurs mainly through the consumption of seafood (Sunderland, 2007), particularly high trophic level species (Lavoie et al., 2018). As a potent neurotoxin, MeHg poses a threat to marine predators and human populations that consume them (Ha et al., 2017; López-Berenguer et al., 2020).

Accurate estimation of Hg biomagnification in marine ecosystems remains a challenge based on methods that allow determination of trophic levels. The analysis of carbon and nitrogen isotopic ratios ($\delta^{13}C$ and $\delta^{15}N$, respectively) is to date the most used tool to assess the differences in trophic level between species (Post, 2002). Both $\delta^{13}C$ and $\delta^{15}N$ values increase with trophic position (Hussey et al., 2015). The difference between the isotopic values of a consumer and its diet is called discrimination factor or trophic enrichment (respectively $\Delta^{13}C$ and $\Delta^{15}N$ for carbon and nitrogen). While $\delta^{13}C$ is generally assumed to vary minimally through trophic transfers, a $\Delta^{15}N$ of 3–4‰ is commonly used to estimate trophic positions (Post, 2002). However, discrimination factors are known to depend on several sources of variation, such as environment, taxon, tissue and diet (Caut et al., 2009).

Hg biomagnification and discrimination factors for certain species have previously been determined in controlled studies (Bearhop et al., 2000; Cherel et al., 2005; Kim et al., 2012). However, the difficulty of keeping marine predators in captivity often leads to a modest number of sampled individuals (Ciancio et al., 2016; Giménez et al., 2016; Hussey

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et al., 2010). In addition, controlled studies fail to reflect the complexity and temporal variations of natural environments, especially in dynamic ecosystems such as upwelling zones. Conversely, the determination of these parameters in the field can be complicated by the generalist feeding of marine predators, which can consume prey with different Hg concentrations and isotopic signatures (Le Croizier et al., 2020; Tixier et al., 2019). Finally, the determination of Hg biomagnification can be biased by the confounding effect of bioaccumulation when analyzes are performed on tissues where Hg turnover is slow, such as muscle (Kwon et al., 2016).

In the present study, we focused on the northern Humboldt Current system off Peru (Pacific Ocean), a high productivity upwelling ecosystem encompassing one of the largest and shallowest oxygen minimum zones in the world (Fiedler and Talley, 2006). This ecosystem participates in the global export of Hg through marine fisheries, and human exposure to Hg via the consumption of seafood (Lavoie et al., 2018). Although low oxygen and upwelling conditions favor high MeHg production in Humboldt waters (Bowman et al., 2020), very little data are currently available on Hg concentrations in local biota (Adkesson et al., 2019). To improve our understanding of Hg biomagnification within the Humboldt food web, we conducted analyzes on emblematic species of this region. We collected muscle samples from Peruvian anchovies (*Engraulis ringens*), which constitute the highest biomass in the ecosystem (Tam et al., 2008). Blood samples from the two most abundant seabirds off the coast of Peru (Weimerskirch et al., 2012), the Guanay cormorant *Phalacrocorax bougainvillii* and the Peruvian booby *Sula variegata*, were also collected. These two predators are highly specialized on anchovies, which may represent more than 80% of their diet (Barbraud et al., 2018; Gochfeld, 1980). We analyzed $\delta^{13}C$ and $\delta^{15}N$ values, as well as Hg concentrations, in a large sample set over 5 consecutive years to overcome ecosystem temporal variability. Our study determined carbon and nitrogen isotopic discrimination factors ($\Delta^{13}C$ and $\Delta^{15}N$), as well as Hg biomagnification factor (BMF) by overcoming the effect of bioaccumulation, as blood Hg concentration reflects recent trophic exposure in seabirds (i.e. last weeks prior sampling) (Bearhop et al., 2000; Renedo et al., 2018a). We compared the $\Delta^{13}C$, $\Delta^{15}N$ and BMF values obtained here with previous studies on other seabird species, and we discussed the implications of the observed variability between species. Finally, we compared Hg concentrations in Humboldt seabirds with similar species from other oligotrophic ecosystems. We sought to explain the low Hg levels in marine predators of the Humboldt ecosystem, despite being a region particularly active for in situ methylmercury production (Bowman et al., 2020).

Seabirds (92 cormorants, 90 boobies) were sampled from 2009 to 2013 during the months of October–November on Pescadores Island, Peru (11°46′S, 77°15′W) (Fig. 1). All seabirds were breeding adults, but sex was not systematically recorded for inclusion in the data (Table S1). Blood samples were collected from a wing or tarsal vein and preserved in 70% ethanol. As the main prey of cormorants and boobies, anchovies ($n = 65$) were also sampled. From 2010 to 2013, ingested anchovies were collected and preserved similarly when the birds regurgitated spontaneously. The length of the anchovies was not measured individually, but ranged from 12 to 16 cm. No other prey species was observed. In 2009, anchovies were collected during routine acoustic surveys performed by the Peruvian Institute of the Sea (IMARPE) near Pescadores Island (11°47′S, 77°23′W). These anchovies were stored frozen and ranged from 13 to 16 cm. Prior to analyses, all samples were freeze-dried and ground to powder.

For comparison with Humboldt seabirds, we added to this study blood samples ($n = 67$) of adult red-footed boobies (*Sula sula*) collected in 2015 at Surprise Island (New-Caledonia, South-West Pacific Ocean) and the Fernando de Noronha archipelago (Brazil, Central-West Atlantic Ocean). These additional samples were collected following the same protocol as for Humboldt samples.

Isotope analyses were performed as described in a previous study (Espinoza et al., 2017). Before analysis, lipid extraction was applied to anchovy muscle samples, using 20 mL of cyclohexane on powder aliquots of about 1 g. The anchovy samples were then freeze-dried again. Lipids were not removed from seabird blood samples, as the low lipid content of whole blood does not require lipid extraction prior to isotopic analysis (Cherel et al., 2005). Seabird whole blood and anchovy muscle samples were weighed (~300 μg), packed in tin containers and analyzed using an elemental analyzer (Flash EA1112, Thermo Scientific, Milan, Italy) coupled to an isotope ratio mass spectrometer (Delta V Advantage with a Conflo IV interface, Thermo Scientific, Bremen, Germany). Results were expressed according to international standards (Vienna Pee Dee Belemnite for $\delta^{13}C$ and N_2 in air for $\delta^{15}N$) following the formula: $\delta^{13}C$ or $\delta^{15}N = [(R\ sample/R\ standard) - 1] \times 10^3$ (in ‰), where R is $^{13}C/^{12}C$ or $^{15}N/^{14}N$. Reference gas calibration was done using reference materials (USGS-24, IAEA-CH6, IAEA-600 for carbon; IAEA-N1, -N2, -N3, -600 for nitrogen). Analytical precision based on isotope values of acetanilide (Thermo Scientific) was <0.15‰ both for $\delta^{13}C$ and $\delta^{15}N$ measurements. Values are means ± SD.

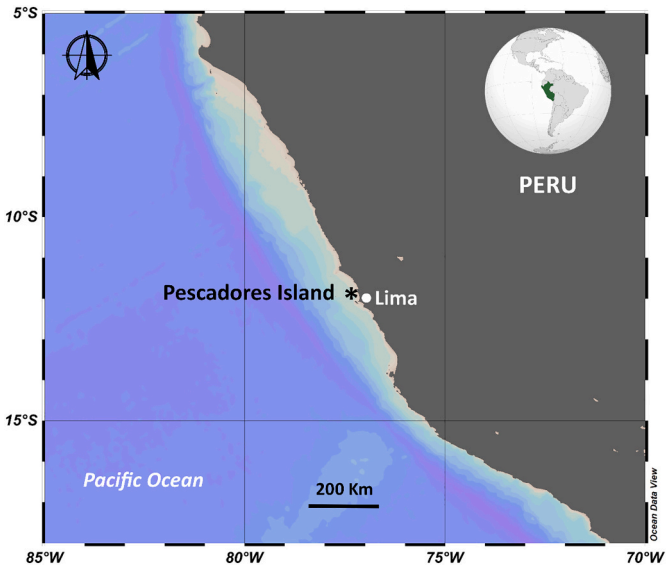

Fig. 1. Map of the coast of Peru in the southeastern Pacific Ocean. The site where seabirds and anchovies were sampled is indicated by a star symbol.

Total Hg concentrations (hereafter expressed as $\mu g \cdot g^{-1}$, dry weight: dw) were quantified in anchovy and seabird samples by using a DMA80 analyzer (Milestone, USA). The detection limit was 0.005 $\mu g \cdot g^{-1}$ dw. Three certified reference materials were analyzed for evaluation of accuracy and reproducibility of our methods: tuna fish muscle (ERM-CE-464 and IAEA-436) and lobster hepatopancreas material (TORT-3); providing a respective accuracy of 96 ± 12% ($n = 15$), 96 ± 9% ($n = 6$), and 100 ± 9% ($n = 6$) relative to recommended reference values. Internal homemade blood reference material (red blood cells, RBC-KP) was also used for validation of seabird blood analyses and provided an accuracy of 96 ± 6% ($n = 3$) relative to previously published values, as detailed elsewhere (Renedo et al., 2018a).

To compare variables ($\delta^{13}C$, $\delta^{15}N$ and Hg concentration) between species, data were first checked for normality (Shapiro–Wilk tests) and homogeneity of variances (Bartlett tests). One-way analyses of variance were applied when these conditions were met, followed by Tukey's HSD tests. Otherwise, non-parametric analogues were used, i.e. Kruskal–Wallis tests, followed by Conover–Iman multiple comparison tests with Bonferroni's adjustment. Hg biomagnification factor (BMF) was calculated as the ratio of Hg concentration in seabird (cormorant or booby) blood to Hg concentration in anchovy muscle. Carbon and nitrogen discrimination factors ($\Delta^{13}C$ and $\Delta^{15}N$, respectively), were calculated as the difference between the isotopic value ($\delta^{13}C$ or $\delta^{15}N$) in seabird blood and the isotopic signature of anchovy muscle.

The entire dataset (n = 247, Table S1) encompassing all years is presented as a 3D scatter plot in Fig. 2. The two seabird species were distinguished from anchovies by higher values for all variables ($\delta^{13}C$, $\delta^{15}N$ and Hg concentration) ($p < 0.001$). Among seabirds, the Peruvian booby was characterized by higher $\delta^{13}C$ than the Guanay cormorant, which displayed higher values for $\delta^{15}N$ and Hg concentration ($p < 0.001$). These patterns integrating 5 consecutive years were also observed on an annual scale (Fig. 3). Each year, the values of the measured variables followed the same trends: anchovy < cormorant < booby for $\delta^{13}C$, anchovy < booby < cormorant for $\delta^{15}N$ and anchovy < booby < cormorant for Hg concentration. These observed interannual isotopic variations can be explained by changes in environmental conditions caused by El Niño Southern Oscillations (ENSO) which are known to shift isotopic baselines in the Humboldt food web (Renedo et al., 2021). The higher isotope values and Hg concentrations found in seabirds compared to anchovies reflect the well-documented isotopic fractionation and Hg biomagnification between prey and predators (Kim et al., 2012; Seco et al., 2021). Differences between cormorants and boobies could be first explained by differences in foraging habitat or diet, which are known to influence isotopic values and Hg concentrations in seabirds (Renedo et al., 2018b; Thébault et al., 2021). A previous tracking study observed similar foraging areas for both species, despite a slightly higher diving depth for cormorants (i.e. mean maximum depth of 2 and 6 m for boobies and cormorants, respectively) (Weimerskirch et al., 2012). Moreover, both species are thought to feed mainly on anchovies (Gochfeld, 1980), which is consistent with the absence of other regurgitated prey during this study. Both species displayed a similar proportion of anchovies in their diet (e.g., 81–96% for cormorants and 80–93% for boobies) (Barbraud et al., 2018), and no significant difference was found for any variable ($\delta^{13}C$, $\delta^{15}N$, Hg) between anchovies regurgitated by cormorants and boobies in the same year ($p > 0.05$). Alternatively, controlled studies have previously demonstrated that diet-to-blood discrimination factor can vary between different seabird species fed the same diet (Jenkins et al., 2020). In addition, Hg trophic transfer from diet to consumer may differ depending on the assimilation efficiency of each consumer species (Pouil et al., 2018). Although fine differences in trophic niche may be involved, the absence of obvious dietary segregation suggests that the variations ($\delta^{13}C$, $\delta^{15}N$, Hg) observed between seabirds may relate to species-specific physiological characteristics. For instance, as MeHg is mostly complexed to proteins in fish muscle (Médieu et al., 2021), and isotopic compositions vary between lipids and proteins or among amino acids and fatty acids (McMahon et al., 2015; Sweeting et al., 2006; Twining et al., 2020), differences related to the assimilation of amino and/or fatty acids could explain the differences in $\delta^{13}C$, $\delta^{15}N$ and Hg observed in two species fed the same diet.

Carbon discrimination factor ($\Delta^{13}C$) varied among years: from 0.1 to 0.9‰ for cormorants and from 0.4 to 1.1‰ for boobies (Table 1). Nitrogen discrimination factor ($\Delta^{15}N$) also showed inter-annual variations: from 0.4 to 1.1‰ for cormorants and from 0.4 to 2.1‰ for boobies. By averaging the discrimination factors over 5 years in order to consider the inter-annual variability, mean $\Delta^{13}C$ values of 0.5 ± 0.3 and 0.7 ± 0.3‰ were obtained for cormorants and boobies, respectively (Table 1). Similarly, mean $\Delta^{15}N$ values of 1.7 ± 0.6 and 1.3 ± 0.7‰ were respectively found for cormorants and boobies. We compared the isotopic discrimination factors estimated during this study with values derived from previous studies, for other seabird species experimentally fed on a fish diet (Bearhop et al., 2002; Cherel et al., 2005; Ciancio et al., 2016; Craig et al., 2015; Hobson and Clark, 1992; Micklem et al., 2021). The $\Delta^{13}C$ values we obtained for boobies and cormorants fall in the middle of the range reported in the literature (Fig. 4A). By contrast, our $\Delta^{15}N$ values were among the lowest described in other seabirds (Fig. 4B). Isotopic discrimination factors may vary for the same tissue according to several factors, such as habitat, species and diet (Caut et al., 2009). Since we found close $\Delta^{13}C$ and $\Delta^{15}N$ values in the whole blood of boobies and cormorants sharing similar habitat and diet, differences in isotopic discrimination factors compared to other species (Fig. 4A and B) suggest that large-scale $\Delta^{13}C$ and $\Delta^{15}N$ variations among seabirds may be primarily caused by discrepancies in environmental conditions. Mixing models based on isotopic signatures represent an increasingly used tool to estimate the contribution of different prey to the diet of predators (van den Berg et al., 2021; Skinner et al., 2021). However, recent Bayesian models are highly sensitive to variation in discrimination factors and require accurate $\Delta^{13}C$ and $\Delta^{15}N$ values to correctly reconstruct the diet of the species studied (Bond and Diamond, 2011; Swan et al., 2020). Meeting this condition is particularly important for piscivorous seabirds, as the published discrimination factors appear highly variable between species (e.g., −1.1 to 1.6 for $\Delta^{13}C$ and 1.2 to 3.1 for $\Delta^{15}N$ in the selected studies, Fig. 4A and B). Here, we present the first assessment of discrimination factors for the Guanay cormorant and the Peruvian booby. The values obtained differed from other piscivorous seabirds, highlighting the need for species-specific estimates. Our values, based on a large number of individuals and encompassing several years, can be used for future studies using mixing models on these species or on other related seabirds.

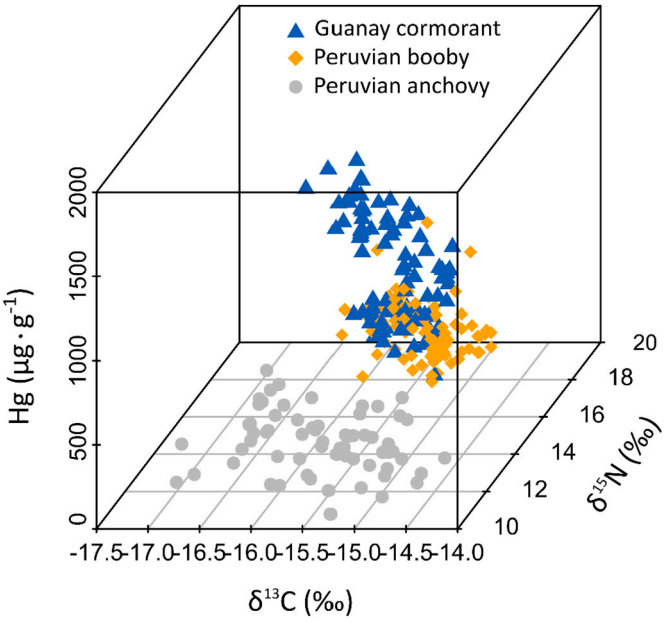

Fig. 2. Three-dimensional scatter plot of $\delta^{13}C$ and $\delta^{15}N$ values, as well as Hg concentrations, in the muscle of Peruvian anchovies and in the whole blood of Guanay cormorants and Peruvian boobies.

Hg biomagnification factor (BMF) varied annually from 6 to 28 for cormorants and from 3 to 15 for boobies (Table 1). The mean BMF for boobies was 9, which falls in the middle of the range reported for whole blood in other seabird species (Fig. 4C). The Guanay cormorant displayed a higher mean BMF of 16, which however matches the BMF observed in other anchovy consumers such as the little penguin (Finger et al., 2017). MeHg is characterized by a strong affinity to the thiol groups of amino acids such as cysteine, and MeHg-cysteine (MeHg-Cyst) complexes have been shown to constitute the predominant form of Hg in seabird blood (Manceau et al., 2021). Although these complexes may be formed in vivo, part of the dietary Hg is believed to be assimilated in the digestive tract as MeHg-Cyst (Varian-Ramos et al., 2017). Thus, we hypothesize that differences in BMF among seabird species could be partially explained by differences in the assimilation of amino acids such as cysteine (e.g., higher assimilation and BMF in cormorants than in boobies). A proper estimate of biomagnification is essential because this phenomenon, alongside bioaccumulation, conditions the concentration of toxic Hg in marine predators. Tissues incorporating Hg exposure over several months, such as feathers and muscle (Kwon et al., 2016; Renedo et al., 2018a), are commonly used for Hg analysis in marine predators.

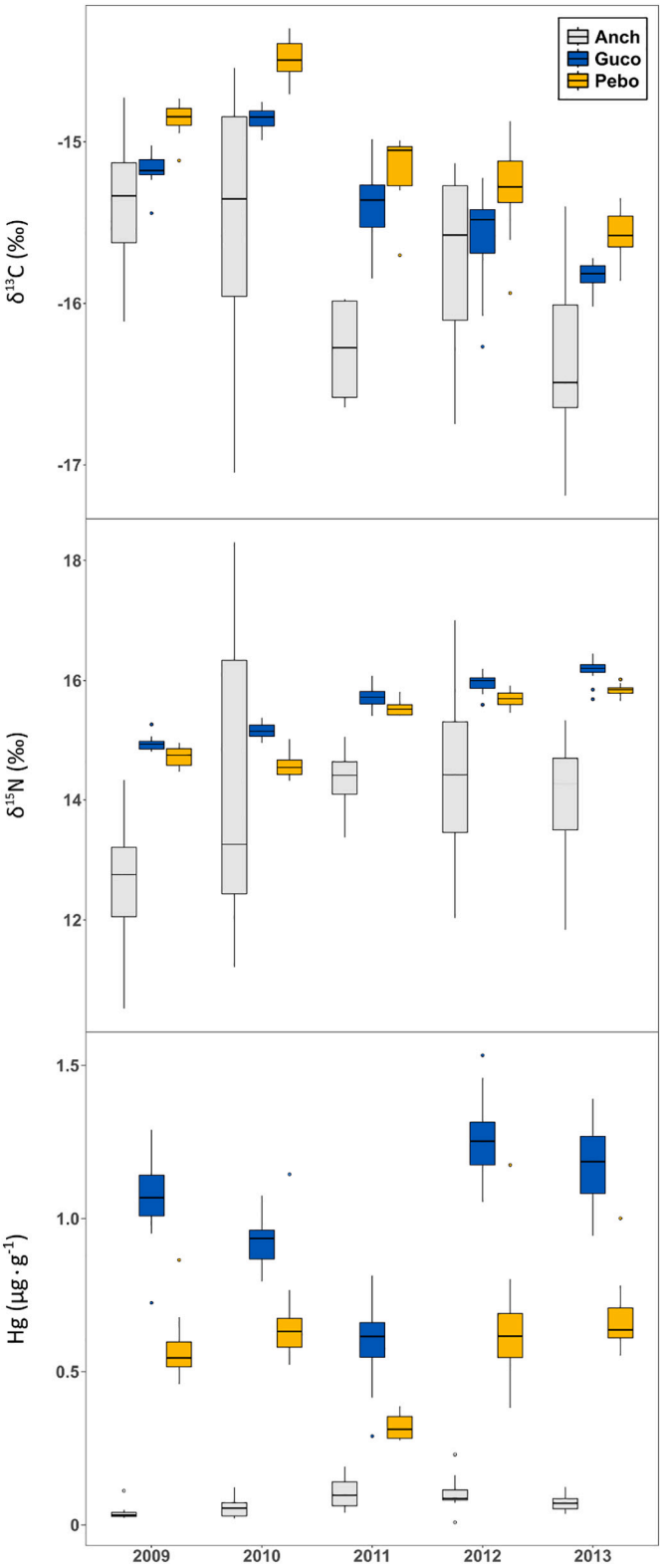

Fig. 3. Boxplots of $\delta^{13}C$ and $\delta^{15}N$ values, as well as Hg concentrations, in the muscle of Peruvian anchovies (Anch) and in the whole blood of Guanay cormorants (Guco) and Peruvian boobies (Pebo). The median value is shown by the horizontal line in the box. The lower and upper bounds of the box indicate the 25% and 75% quartiles. The whisker lines extend to the maximum and minimum values and outliers are represented by dots.

Table 1
Carbon ($\Delta^{13}C$) and nitrogen ($\Delta^{15}N$) discrimination factors, blood Hg concentration and Hg biomagnification factor (BMF) for Guanay cormorants and Peruvian boobies collected over five consecutive years. Values encompassing all years are means ± standard deviation. N: sample size for each year.

Species	N	Year	$\Delta^{13}C$ (‰)	$\Delta^{15}N$ (‰)	Hg ($\mu g \cdot g^{-1}$)	BMF
Guanay cormorant (*Phalacrocorax bougainvillii*)	11	2009	0.2	2.4	1.1	28
	12	2010	0.6	1.0	0.9	16
	38	2011	0.9	1.4	0.6	6
	11	2012	0.1	1.5	1.3	12
	20	2013	0.5	2.2	1.2	17
		Mean	**0.5 ± 0.3**	**1.7 ± 0.6**	**1.0 ± 0.3**	**16 ± 8**
Peruvian booby (*Sula variegata*)	21	2009	0.5	2.1	0.6	15
	16	2010	1.0	0.4	0.7	12
	7	2011	1.1	1.2	0.3	3
	29	2012	0.4	1.2	0.6	6
	17	2013	0.7	1.8	0.7	10
		Mean	**0.7 ± 0.3**	**1.3 ± 0.7**	**0.6 ± 0.1**	**9 ± 5**

Blood analysis, which reflects recent exposure to Hg (Bearhop et al., 2000), eliminates the confounding effect of bioaccumulation and thus better assesses the increase in Hg concentration from prey to predator. Despite similar BMFs to other species, Hg concentrations in the blood of seabirds from the Humboldt Current were lower than in species of the same genus from different ecosystems (Fig. 4C). By averaging the 5 years of sampling, the mean Hg concentration was 0.6 ± 0.1 $\mu g \cdot g^{-1}$ in boobies and 1.0 ± 0.3 $\mu g \cdot g^{-1}$ in cormorants (Table 1), which are among the lowest values observed for different species of boobies and cormorants from other regions (Fig. 4D). Moreover, Humboldt seabirds showed Hg concentrations similar to red-footed boobies from remote sites, isolated from any human activity (Surprise Island in New Caledonia, South-West Pacific Ocean). Interestingly, boobies from the coastal eastern Pacific (the Peruvian booby from the Humboldt Current and the blue-footed booby from the Gulf of California, Mexico) were less contaminated (Hg concentrations up to 3 to 4 times lower) than species from the central Pacific (e.g., masked and red-footed booby from Hawaii) and the western Atlantic (red-footed booby from Brazil) (Fig. 4D). The Humboldt Current and the Gulf of California are located within the two most important oxygen-minimum zones, which are thought to favor the production of MeHg by anaerobic bacteria (Blum et al., 2013; Bowman et al., 2020). Despite a high Hg bioavailability in eastern Pacific waters (Bowman et al., 2016), productive upwelling ecosystems such as the Humboldt Current contain large biomasses of phytoplankton, zooplankton and forage fish (Salvatteci et al., 2018; Tam et al., 2008), which could reduce the Hg concentration in seabird prey through the biodilution effect (i.e. "dilution" of the available Hg by the important biomass of the first trophic levels) (Chouvelon et al., 2018). This hypothesis is supported by the lower Hg concentration found in Peruvian anchovies from the Humboldt Current (0.075 ± 0.029 $\mu g \cdot g^{-1}$, this study) compared to European anchovies from the Mediterranean Sea (0.268 ± 0.067 $\mu g \cdot g^{-1}$) (Chouvelon et al., 2019), despite similar seawater Hg concentrations in both regions (Bowman et al., 2016; Cossa et al., 1997).

Although working in the natural environment implies that food sources could not be completely controlled, unlike experiments on captive birds, this baseline study reports for the first time an estimate of the diet-to-blood Hg biomagnification and isotopic discrimination factors ($\Delta^{13}C$ and $\Delta^{15}N$) for the Guanay cormorant and the Peruvian booby in the Humboldt Current system. Our contribution helps to refine the characterization of Hg transfer in upwelling ecosystems and provides new isotopic discrimination factors that can be used in future studies on cormorant and booby species. The use of stable sulfur isotopes would be of interest in future similar studies, as this tracer is increasingly identified as a reliable predictor of Hg levels in marine food webs (Elliott et al.,

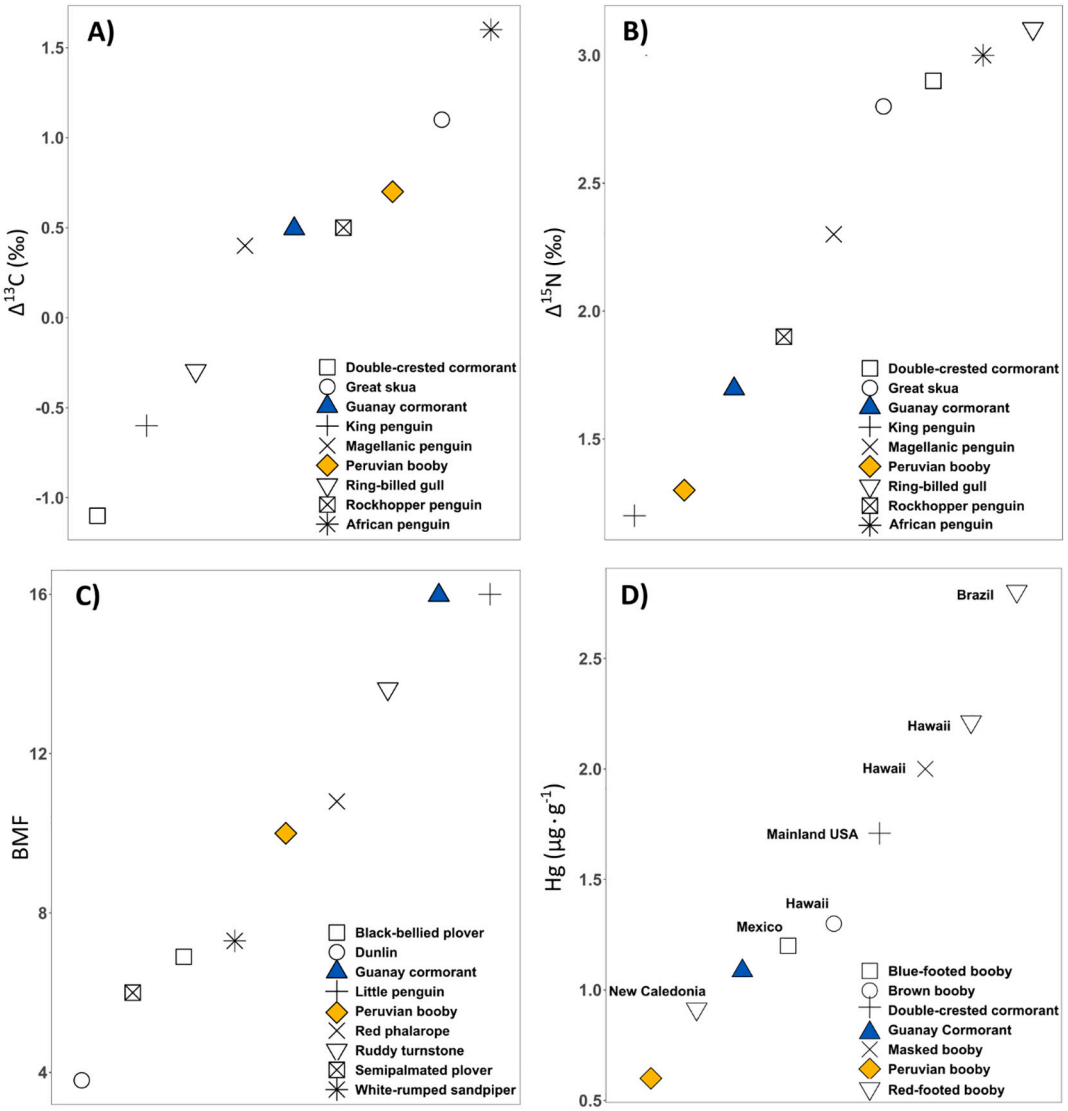

Fig. 4. Comparison of Guanay cormorants and Peruvian boobies with other seabirds for carbon ($\Delta^{13}C$) and nitrogen ($\Delta^{15}N$) discrimination factors, Hg biomagnification factor (BMF) and Hg concentration. Discrimination factors were obtained between lipid-extracted fish muscle and seabird whole blood (Bearhop et al., 2002; Cherel et al., 2005; Ciancio et al., 2016; Craig et al., 2015; Hobson and Clark, 1992; Micklem et al., 2021). BMFs were calculated for the whole blood of seabirds and their prey (Finger et al., 2017; Hargreaves et al., 2011). Hg concentrations are reported in the whole blood of different species of cormorants and boobies. Values were obtained from previous studies (Caldwell et al., 1999; Gilmour et al., 2019; Lerma et al., 2016), except for red-footed boobies from Brazil and New Caledonia (this study, Table S1). Literature Hg values were converted to dry weight considering a 79% moisture content (Eagles-Smith et al., 2008). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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CRediT authorship contribution statement

Gaël Le Croizier: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **David Point:** Resources, Writing – review & editing, Supervision, Funding acquisition. **Marina Renedo:** Formal analysis, Writing – review & editing. **Jean-Marie Munaron:** Formal analysis, Writing – review & editing. **Pepe Espinoza:** Resources, Writing – review & editing. **Felipe Amezcua-Martinez:** Writing – review & editing. **Sophie Lanco Bertrand:** Resources, Writing – review & editing, Supervision, Funding acquisition. **Anne Lorrain:** Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Adkesson, M.J., Levengood, J.M., Scott, J.W., Schaeffer, D.J., Panno, B., Langan, J.N., Cárdenas-Alayza, S., James-Yi, S., 2019. Analysis of toxic and essential elements in the blood and feathers of Humboldt penguins (Spheniscus humboldti) at Punta San Juan, Peru. J. Wildl. Dis. 55, 438–443. https://doi.org/10.7589/2018-03-081.

Barbraud, C., Bertrand, A., Bouchón, M., Chaigneau, A., Delord, K., Demarcq, H., Gimenez, O., Torero, M.G., Gutiérrez, D., Oliveros-Ramos, R., Passuni, G., Tremblay, Y., Bertrand, S., 2018. Density dependence, prey accessibility and prey depletion by fisheries drive Peruvian seabird population dynamics. Ecography 41, 1092–1102. https://doi.org/10.1111/ecog.02485.

Bearhop, S., Ruxton, G.D., Furness, R.W., 2000. Dynamics of mercury in blood and feathers of great skuas. Environ. Toxicol. Chem. 19, 1638–1643. https://doi.org/10.1002/etc.5620190622.

Bearhop, S., Waldron, S., Votier, S.C., Furness, R.W., 2002. Factors that influence assimilation rates and fractionation of nitrogen and carbon stable isotopes in avian blood and feathers. Physiol. Biochem. Zool. 75, 451–458. https://doi.org/10.1086/342800.

van den Berg, G.L., Vermeulen, E., Valenzuela, L.O., Bérubé, M., Ganswindt, A., Gröcke, D.R., Hall, G., Hulva, P., Neveceralova, P., Palsbøll, P.J., Carroll, E.L., 2021. Decadal shift in foraging strategy of a migratory southern ocean predator. Glob. Chang. Biol. 27, 1052–1067. https://doi.org/10.1111/gcb.15465.

Blum, J.D., Popp, B.N., Drazen, J.C., Anela Choy, C., Johnson, M.W., 2013. Methylmercury production below the mixed layer in the North Pacific Ocean. Nat. Geosci. 6, 879–884. https://doi.org/10.1038/ngeo1918.

Bond, A.L., Diamond, A.W., 2011. Recent Bayesian stable-isotope mixing models are highly sensitive to variation in discrimination factors. Ecol. Appl. 21, 1017–1023. https://doi.org/10.1890/09-2409.1.

Bowman, K.L., Hammerschmidt, C.R., Lamborg, C.H., Swarr, G.J., Agather, A.M., 2016. Distribution of mercury species across a zonal section of the eastern tropical South Pacific Ocean (U.S. GEOTRACES GP16). Mar. Chem. 186, 156–166. https://doi.org/10.1016/j.marchem.2016.09.005.

Bowman, K.L., Lamborg, C.H., Agather, A.M., 2020. A global perspective on mercury cycling in the ocean. Sci. Total Environ. 710, 136166 https://doi.org/10.1016/j.scitotenv.2019.136166.

Caldwell, C.A., Arnold, M.A., Gould, W.R., 1999. Mercury distribution in blood, tissues, and feathers of double-crested cormorant nestlings from arid-lands reservoirs in South Central New Mexico. Arch. Environ. Contam. Toxicol. 36, 456–461. https://doi.org/10.1007/PL00006618.

Caut, S., Angulo, E., Courchamp, F., 2009. Variation in discrimination factors (Δ15N and Δ13C): the effect of diet isotopic values and applications for diet reconstruction. J. Appl. Ecol. 46, 443–453. https://doi.org/10.1111/j.1365-2664.2009.01620.x.

Cherel, Y., Hobson, K.A., Hassani, S., 2005. Isotopic discrimination between food and blood and feathers of captive penguins: implications for dietary studies in the wild. Physiol. Biochem. Zool. 78, 106–115. https://doi.org/10.1086/425202.

Cherel, Y., Barbraud, C., Lahournat, M., Jaeger, A., Jaquemet, S., Wanless, R.M., Phillips, R.A., Thompson, D.R., Bustamante, P., 2018. Accumulate or eliminate? Seasonal mercury dynamics in albatrosses, the most contaminated family of birds. Environ. Pollut. 241, 124–135. https://doi.org/10.1016/j.envpol.2018.05.048.

Chouvelon, T., Cresson, P., Bouchoucha, M., Brach-Papa, C., Bustamante, P., Crochet, S., Marco-Miralles, F., Thomas, B., Knoery, J., 2018. Oligotrophy as a major driver of mercury bioaccumulation in medium-to high-trophic level consumers: a marine ecosystem-comparative study. Environ. Pollut. 233, 844–854. https://doi.org/10.1016/j.envpol.2017.11.015.

Chouvelon, T., Strady, E., Harmelin-Vivien, M., Radakovitch, O., Brach-Papa, C., Crochet, S., Knoery, J., Rozuel, E., Thomas, B., Tronczynski, J., Chiffoleau, J.-F., 2019. Patterns of trace metal bioaccumulation and trophic transfer in a phytoplankton-zooplankton-small pelagic fish marine food web. Mar. Pollut. Bull. 146, 1013–1030. https://doi.org/10.1016/j.marpolbul.2019.07.047.

Ciancio, J.E., Righi, C., Faiella, A., Frere, E., 2016. Blood-specific isotopic discrimination factors in the Magellanic penguin (Spheniscus magellanicus). Rapid Commun. Mass Spectrom. 30, 1865–1869. https://doi.org/10.1002/rcm.7661.

Cossa, D., Martin, J.-M., Takayanagi, K., Sanjuan, J., 1997. The distribution and cycling of mercury species in the western Mediterranean. Deep-Sea Res. II Top. Stud. Oceanogr. 44, 721–740. https://doi.org/10.1016/S0967-0645(96)00097-5.

Craig, E.C., Dorr, B.S., Hanson-Dorr, K.C., Sparks, J.P., Curtis, P.D., 2015. Isotopic discrimination in the double-crested cormorant (Phalacrocorax auritus). PLOS ONE 10, e0140946. https://doi.org/10.1371/journal.pone.0140946.

Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 47, 4967–4983. https://doi.org/10.1021/es305071v.

Eagles-Smith, C.A., Ackerman, J.T., Adelsbach, T.L., Takekawa, J.Y., Miles, A.K., Keister, R.A., 2008. Mercury correlations among six tissues for four waterbird species breeding in San Francisco Bay, California, USA. Environ. Toxicol. Chem. 27, 2136–2153. https://doi.org/10.1897/08-038.1.

Elliott, K.H., Braune, B.M., Elliott, J.E., 2021. Beyond bulk δ15N: combining a suite of stable isotopic measures improves the resolution of the food webs mediating contaminant signals across space, time and communities. Environ. Int. 148, 106370 https://doi.org/10.1016/j.envint.2020.106370.

Espinoza, P., Lorrain, A., Ménard, F., Cherel, Y., Tremblay-Boyer, L., Argüelles, J., Tafur, R., Bertrand, S., Tremblay, Y., Ayón, P., Munaron, J.-M., Richard, P., Bertrand, A., 2017. Trophic structure in the northern Humboldt Current system: new perspectives from stable isotope analysis. Mar. Biol. 164, 86. https://doi.org/10.1007/s00227-017-3119-8.

Fiedler, P.C., Talley, L.D., 2006. Hydrography of the eastern tropical Pacific: a review. In: Progress in Oceanography, A Review of Eastern Tropical Pacific Oceanography, 69, pp. 143–180. https://doi.org/10.1016/j.pocean.2006.03.008.

Finger, A., Lavers, J.L., Dann, P., Kowalczyk, N.D., Scarpaci, C., Nugegoda, D., Orbell, J. D., 2017. Metals and metalloids in Little Penguin (Eudyptula minor) prey, blood and faeces. Environ. Pollut. 223, 567–574. https://doi.org/10.1016/j.envpol.2017.01.059.

Gilmour, M.E., Hudson, S.A.T., Lamborg, C., Fleishman, A.B., Young, H.S., Shaffer, S.A., 2019. Tropical seabirds sample broadscale patterns of marine contaminants. Sci. Total Environ. 691, 631–643. https://doi.org/10.1016/j.scitotenv.2019.07.147.

Giménez, J., Ramírez, F., Almunia, J., G. Forero, M., de Stephanis, R., 2016. From the pool to the sea: applicable isotope turnover rates and diet to skin discrimination factors for bottlenose dolphins (Tursiops truncatus). J. Exp. Mar. Biol. Ecol. 475, 54–61. https://doi.org/10.1016/j.jembe.2015.11.001.

Gochfeld, M., 1980. Mercury levels in some seabirds of the Humboldt Current, Peru. Environ. Pollut. Ser. A Ecol. Biol. 22, 197–205. https://doi.org/10.1016/0143-1471(80)90014-8.

Ha, E., Basu, N., Bose-O'Reilly, S., Dórea, J.G., McSorley, E., Sakamoto, M., Chan, H.M., 2017. Current progress on understanding the impact of mercury on human health. Environ. Res. 152, 419–433. https://doi.org/10.1016/j.envres.2016.06.042.

Hargreaves, A.L., Whiteside, D.P., Gilchrist, G., 2011. Concentrations of 17 elements, including mercury, in the tissues, food and abiotic environment of Arctic shorebirds. Sci. Total Environ. 409, 3757–3770. https://doi.org/10.1016/j.scitotenv.2011.06.043.

Hobson, K.A., Clark, R.G., 1992. Assessing avian diets using stable isotopes II: factors influencing diet-tissue fractionation. Condor 94, 189–197. https://doi.org/10.2307/1368808.

Hussey, N.E., Brush, J., McCarthy, I.D., Fisk, A.T., 2010. δ15N and δ13C diet–tissue discrimination factors for large sharks under semi-controlled conditions. In: Comparative Biochemistry and Physiology Part A: Molecular & Integrative Physiology, Special Issue of Papers Derived From a Presentation at the Session Entitled 'Biology of Elasmobranchs: From Genes to Ecophysiology and Behaviour' at the Society for Experimental Biology's Annual Main Meeting, Glasgow, UK, 28 June–1 July, 2009, 155, pp. 445–453. https://doi.org/10.1016/j.cbpa.2009.09.023.

Hussey, N.E., MacNeil, M.A., Siple, M.C., Popp, B.N., Dudley, S.F.J., Fisk, A.T., 2015. Expanded trophic complexity among large sharks. Food Webs 4, 1–7. https://doi.org/10.1016/j.fooweb.2015.04.002.

Jenkins, E., Gulka, J., Yurkowski, D.J., François, N.R.L., Wong, E., Davoren, G.K., 2020. Isotopic discrimination (δ15N, δ13C) in captive and wild common murres (Uria aalge) and Atlantic Puffins (Fratercula arctica). Physiol. Biochem. Zool. https://doi.org/10.1086/709460.

Kim, S.L., Casper, D.R., Galván-Magaña, F., Ochoa-Díaz, R., Hernández-Aguilar, S.B., Koch, P.L., 2012. Carbon and nitrogen discrimination factors for elasmobranch soft tissues based on a long-term controlled feeding study. Environ. Biol. Fish 95, 37–52. https://doi.org/10.1007/s10641-011-9919-7.

Kwon, S.Y., Blum, J.D., Madigan, D.J., Block, B.A., Popp, B.N., 2016. Quantifying mercury isotope dynamics in captive Pacific bluefin tuna (Thunnus orientalis). Elem. Sci. Anth. 4, 000088 https://doi.org/10.12952/journal.elementa.000088.

Lavoie, R.A., Jardine, T.D., Chumchal, M.M., Kidd, K.A., Campbell, L.M., 2013. Biomagnification of mercury in aquatic food webs: a worldwide meta-analysis. Environ. Sci. Technol. 47, 13385–13394. https://doi.org/10.1021/es403103t.

Lavoie, R.A., Bouffard, A., Maranger, R., Amyot, M., 2018. Mercury transport and human exposure from global marine fisheries. Sci. Rep. 8, 6705. https://doi.org/10.1038/s41598-018-24938-3.

Le Croizier, G., Lorrain, A., Sonke, J.E., Hoyos-Padilla, E.M., Galván-Magaña, F., Santana-Morales, O., Aquino-Baleytó, M., Becerril-García, E.E., Muntaner-López, G., Ketchum, J., Block, B., Carlisle, A., Jorgensen, S.J., Besnard, L., Jung, A., Schaal, G., Point, D., 2020. The twilight zone as a major foraging habitat and mercury source for the great white shark. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.0c05621.

Lerma, M., Castillo-Guerrero, J.A., Ruelas-Inzunza, J., Fernández, G., 2016. Lead, cadmium and mercury in the blood of the blue-footed booby (Sula nebouxii) from the coast of Sinaloa, Gulf of California, Mexico. Mar. Pollut. Bull. 110, 293–298. https://doi.org/10.1016/j.marpolbul.2016.06.049.

López-Berenguer, G., Peñalver, J., Martínez-López, E., 2020. A critical review about neurotoxic effects in marine mammals of mercury and other trace elements. Chemosphere 246, 125688. https://doi.org/10.1016/j.chemosphere.2019.125688.

Manceau, A., Gaillot, A.-C., Glatzel, P., Cherel, Y., Bustamante, P., 2021. In vivo formation of HgSe nanoparticles and Hg–tetraselenolate complex from methylmercury in seabirds—implications for the Hg–Se antagonism. Environ. Sci. Technol. 55, 1515–1526. https://doi.org/10.1021/acs.est.0c06269.

McKinney, M.A., Dean, K., Hussey, N.E., Cliff, G., Wintner, S.P., Dudley, S.F.J., Zungu, M. P., Fisk, A.T., 2016. Global versus local causes and health implications of high mercury concentrations in sharks from the east coast of South Africa. Sci. Total Environ. 541, 176–183. https://doi.org/10.1016/j.scitotenv.2015.09.074.

McMahon, K.W., Polito, M.J., Abel, S., McCarthy, M.D., Thorrold, S.R., 2015. Carbon and nitrogen isotope fractionation of amino acids in an avian marine predator, the gentoo penguin (Pygoscelis papua). Ecol. Evol. 5, 1278–1290. https://doi.org/10.1002/ece3.1437.

Médieu, A., Sardenne, F., Lorrain, A., Bodin, N., Pazart, C., Le Delliou, H., Point, D., 2021. Lipid-free tuna muscle samples are suitable for total mercury analysis. Mar. Environ. Res. 169, 105385 https://doi.org/10.1016/j.marenvres.2021.105385.

Micklem, I.A., Connan, M., Stander, N., McQuaid, C.D., 2021. Influence of ontogeny on stable isotope ratios and trophic discrimination factors of African penguin (Spheniscus demersus) tissues. Mar. Biol. 168, 96. https://doi.org/10.1007/s00227-021-03877-0.

Outridge, P.M., Mason, R.P., Wang, F., Guerrero, S., Heimbürger-Boavida, L.E., 2018. Updated global and oceanic mercury budgets for the United Nations Global Mercury Assessment 2018. Environ. Sci. Technol. 52, 11466–11477. https://doi.org/10.1021/acs.est.8b01246.

Podar, M., Gilmour, C.C., Brandt, C.C., Soren, A., Brown, S.D., Crable, B.R., Palumbo, A. V., Somenahally, A.C., Elias, D.A., 2015. Global prevalence and distribution of genes and microorganisms involved in mercury methylation. Sci. Adv. 1, e1500675 https://doi.org/10.1126/sciadv.1500675.

Post, D.M., 2002. Using stable isotopes to estimate trophic position: models, methods, and assumptions. Ecology 83, 703–718. https://doi.org/10.1890/0012-9658(2002)083[0703, USITET]2.0.CO;2.

Pouil, S., Bustamante, P., Warnau, M., Metian, M., 2018. Overview of trace element trophic transfer in fish through the concept of assimilation efficiency. Mar. Ecol. Prog. Ser. 588, 243–254. https://doi.org/10.3354/meps12452.

Renedo, M., Amouroux, D., Duval, B., Carravieri, A., Tessier, E., Barre, J., Bérail, S., Pedrero, Z., Cherel, Y., Bustamante, P., 2018a. Seabird tissues as efficient biomonitoring tools for Hg isotopic investigations: implications of using blood and feathers from chicks and adults. Environ. Sci. Technol. 52, 4227–4234. https://doi.org/10.1021/acs.est.8b00422.

Renedo, M., Amouroux, D., Pedrero, Z., Bustamante, P., Cherel, Y., 2018b. Identification of sources and bioaccumulation pathways of MeHg in subantarctic penguins: a stable isotopic investigation. Sci. Rep. 8, 8865. https://doi.org/10.1038/s41598-018-27079-9.

Renedo, M., Point, D., Sonke, J.E., Lorrain, A., Demarcq, H., Graco, M., Grados, D., Gutiérrez, D., Médieu, A., Munaron, J.M., Pietri, A., Colas, F., Tremblay, Y., Roy, A., Bertrand, A., Bertrand, S.L., 2021. ENSO climate forcing of the marine mercury cycle in the Peruvian upwelling zone does not affect methylmercury levels of marine avian top predators. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.1c03861.

Salvatteci, R., Field, D., Gutiérrez, D., Baumgartner, T., Ferreira, V., Ortlieb, L., Sifeddine, A., Grados, D., Bertrand, A., 2018. Multifarious anchovy and sardine regimes in the Humboldt Current System during the last 150 years. Glob. Chang. Biol. 24, 1055–1068. https://doi.org/10.1111/gcb.13991.

Seco, J., Aparício, S., Brierley, A.S., Bustamante, P., Ceia, F.R., Coelho, J.P., Philips, R.A., Saunders, R.A., Fielding, S., Gregory, S., Matias, R., Pardal, M.A., Pereira, E., Stowasser, G., Tarling, G.A., Xavier, J.C., 2021. Mercury biomagnification in a Southern Ocean food web. Environ. Pollut. 275, 116620 https://doi.org/10.1016/j.envpol.2021.116620.

Skinner, C., Mill, A.C., Fox, M.D., Newman, S.P., Zhu, Y., Kuhl, A., Polunin, N.V.C., 2021. Offshore pelagic subsidies dominate carbon inputs to coral reef predators. ScienceAdvances 7, eabf3792. https://doi.org/10.1126/sciadv.abf3792.

Sunderland, E.M., 2007. Mercury Exposure from Domestic and Imported Estuarine and Marine Fish in the U.S.Seafood Market. Environ. Health Perspect. 115, 235–242. https://doi.org/10.1289/ehp.9377.

Swan, G.J.F., Bearhop, S., Redpath, S.M., Silk, M.J., Goodwin, C.E.D., Inger, R., McDonald, R.A., 2020. Evaluating Bayesian stable isotope mixing models of wild animal diet and the effects of trophic discrimination factors and informative priors. Methods Ecol. Evol. 11, 139–149. https://doi.org/10.1111/2041-210X.13311.

Sweeting, C.J., Polunin, N.V.C., Jennings, S., 2006. Effects of chemical lipid extraction and arithmetic lipid correction on stable isotope ratios of fish tissues. Rapid Commun. Mass Spectrom. 20, 595–601. https://doi.org/10.1002/rcm.2347.

Tam, J., Taylor, M.H., Blaskovic, V., Espinoza, P., Michael Ballón, R., Díaz, E., Wosnitza-Mendo, C., Argüelles, J., Purca, S., Ayón, P., Quipuzcoa, L., Gutiérrez, D., Goya, E., Ochoa, N., Wolff, M., 2008. Trophic modeling of the Northern Humboldt Current Ecosystem, Part I: comparing trophic linkages under La Niña and El Niño conditions. In: Progress in Oceanography, The Northern Humboldt Current System: Ocean Dynamics, Ecosystem Processes, and Fisheries, 79, pp. 352–365. https://doi.org/10.1016/j.pocean.2008.10.007.

Thébault, J., Bustamante, P., Massaro, M., Taylor, G., Quillfeldt, P., 2021. Influence of species-specific feeding ecology on mercury concentrations in seabirds breeding on the Chatham Islands, New Zealand. Environ. Toxicol. Chem. 40, 454–472. https://doi.org/10.1002/etc.4933.

Tixier, P., Giménez, J., Reisinger, R.R., Méndez-Fernandez, P., Arnould, J.P.Y., Cherel, Y., Guinet, C., 2019. Importance of toothfish in the diet of generalist subantarctic killer whales: implications for fisheries interactions. Mar. Ecol. Prog. Ser. 613, 197–210. https://doi.org/10.3354/meps12894.

Twining, C.W., Taipale, S.J., Ruess, L., Bec, A., Martin-Creuzburg, D., Kainz, M.J., 2020. Stable isotopes of fatty acids: current and future perspectives for advancing trophic ecology. Philos. Trans. R. Soc., B 375, 20190641. https://doi.org/10.1098/rstb.2019.0641.

Varian-Ramos, C.W., Whitney, M., Rice, G.W., Cristol, D.A., 2017. Form of dietary methylmercury does not affect total mercury accumulation in the tissues of zebra finch. Bull. Environ. Contam. Toxicol. 99, 1–8. https://doi.org/10.1007/s00128-017-2104-8.

Wang, W.-X., Wong, R.S.K., 2003. Bioaccumulation kinetics and exposure pathways of inorganic mercury and methylmercury in a marine fish, the sweetlips Plectorhinchus gibbosus. Mar. Ecol. Prog. Ser. 261, 257–268. https://doi.org/10.3354/meps261257.

Weimerskirch, H., Bertrand, S., Silva, J., Bost, C., Peraltilla, S., 2012. Foraging in Guanay cormorant and Peruvian booby, the major guano-producing seabirds in the Humboldt Current System. Mar. Ecol. Prog. Ser. 458, 231–245. https://doi.org/10.3354/meps09752.