

Origin of Sulfur in Diet Drives Spatial and Temporal Mercury Trends in Seabird Eggs From Pacific Canada 1968–2015

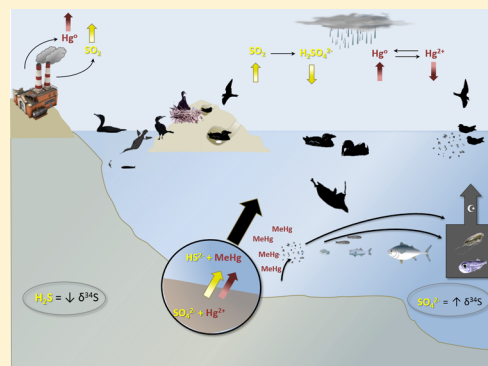
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S Supporting Information

ABSTRACT: Mercury (Hg) is a neurotoxin that can be particularly harmful to top predators because it biomagnifies through the food web. Due to variation in the food web structure, variation in Hg exposure in predators may represent variation in diet rather than Hg availability. We measured Hg in eggs from six seabird species ($N = 537$) over 47 years. In contrast to expectation, storm-petrels feeding partially on invertebrates had the highest Hg burden while herons feeding on large fish had the lowest Hg burden. A multiple regression showed that Hg correlated with $\delta^{34}\text{S}$ ($R^2 = 0.86$) rather than trophic level ($\delta^{15}\text{N}$ of “trophic” amino acids). Sulfate-rich environments (high $\delta^{34}\text{S}$) have sulfate-reducing bacteria that produce methylmercury. Variation in Hg within and among seabirds near the top of the food web was associated with variation in $\delta^{34}\text{S}$ at the base of the food web more so than trophic position within the food web. Hg levels in seabirds only changed over time for those species where $\delta^{34}\text{S}$ also varied in tandem; after accounting for diet ($\delta^{34}\text{S}$), there was no variation in Hg levels. Variation in Hg in seabirds across space and time was associated with the origin of sulfur in the diet.



INTRODUCTION

Humans are Earth’s most important ecosystem engineers, and global ecosystems are now dramatically altered by anthropogenic chemical pollution.^{1,2} Regulation has proven effective at eventually removing legacy organic pollutants from ecosystems, demonstrating that some forms of chemical pollution can be remediated.^{3–5} In contrast to organic pollutants, mercury is more difficult to cleanse globally due to its release from common industrial activities, and because mercury, as a naturally occurring element, does not degrade chemically.^{6–9} The Minamata Convention on Mercury has been ratified recently by most of the international community with the aim of reducing mercury levels in the global environment. To assess the effectiveness of the Convention, it is important to monitor the spatial and temporal trends of mercury. Top predators are useful biomonitors because they: (1) bioaccumulate high levels of contaminants leading to high signal-to-noise ratios, (2) integrate signals across space, and time, (3) often feed on prey, especially fish, at a similar trophic level to humans, and (4) often return to a central place (e.g., colonial birds) where such signals can be readily measured.^{4,10–12}

Although predator tissue can be used to monitor mercury levels in the environment, variation in diet can confound such monitoring.^{13–17} In particular, methylmercury, the organic form of mercury that is most toxic to animals, biomagnifies such that individuals foraging at high trophic levels have higher levels of methylmercury than individuals foraging at low trophic

levels.^{18–20} Stable isotope ratios measured on the same tissue as mercury can be used as biogeochemical tracers of diet to determine whether variation in contamination levels in top predators is due to diet or other environmental factors.^{13–20}

The ratio of ^{15}N to ^{14}N , represented in relative terms by $\delta^{15}\text{N}$, increases systematically with trophic position.²¹ Authors often correct measured mercury levels by $\delta^{15}\text{N}$ to account for dietary variation associated with different trophic levels^{14,15,22–24} under the assumption that mercury levels in animals are primarily associated with trophic position (trophic position hypothesis). Nonetheless, other dietary factors beyond biomagnification may cause variation in mercury.^{25–27} For example, baseline $\delta^{15}\text{N}$ varies by up to 8‰ among environments so that $\delta^{15}\text{N}$ may reflect spatial rather than trophic variation in diet.^{26,27} Whereas most attempts to account for the effect of diet on contamination have focused on $\delta^{15}\text{N}$, additional dietary tracers could refine diet reconstruction.^{28,29}

The ratio of ^{34}S to ^{32}S , represented in relative terms by $\delta^{34}\text{S}$, may be a particularly useful dietary tracer for mercury as $\delta^{34}\text{S}$ varies little from source to consumer and is therefore unaffected by trophic level. Sulfur dissolved in the water column is primarily present as sulfates while sulfur within sediments is primarily present as sulfides due to anaerobic reduction by bacteria.^{28,30} Sulfates are more enriched with ^{34}S compared with

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sulfides, and animals living in epipelagic, marine environments are enriched in ^{34}S due to the higher proportion of sulfates present in the diet.^{28,30} At the same time, methylmercury is largely synthesized by sulfate-reducing bacteria. Methylmercury then binds to the sulfur-containing group on cysteine residues within protein, creating the primary source of methylmercury in organisms and facilitating biomagnification because of the preference for essential (e.g., cysteine) amino acids.^{31–33} The supply of sulfate, rather than the abundance of mercury, usually controls the ability of sulfate-reducing bacteria to methylate mercury.^{34–37} Thus, animals with diets enriched in ^{34}S are potentially feeding in food webs rich in sulfate and high in methylmercury,³⁸ and mercury levels in animals can be primarily associated with availability of sulfate at the base of the food web (sulfate availability hypothesis). Methylmercury levels are high in the deep waters of the oxygen minimum zone, suggesting that methylmercury is produced by anaerobic bacteria in that zone.^{39–41} However, recent studies have demonstrated methylation in surface waters and the source of methylmercury in the deep ocean remains a mystery.^{39–41} Regardless, coupled with $\delta^{15}\text{N}$, $\delta^{34}\text{S}$ could improve determination of the effect of diet on mercury trends in top predators.

Aquatic bird eggs are particularly useful for monitoring mercury because almost all mercury deposited into eggs is methylmercury.^{42,43} In Canada, mercury levels in seabird eggs over the past few decades, after accounting for trophic level, increased in the Arctic¹⁴ and varied interannually but with no clear trend in the Atlantic.¹⁵ Leach's storm-petrel (*Oceanodroma leucorhoa*) eggs from both the Pacific and Atlantic Oceans usually have the highest levels of mercury of any monitored seabird species.^{14,44–46} That is surprising because mercury increases with trophic level and is often higher in subsurface than surface fish,⁴⁶ and yet storm-petrels feed at the surface on invertebrates and small fish. An explanation for such trends may be that storm-petrels feed on deep-water, myctophid fish (Family Myctophidae) that feed at the surface at night.^{44,47–50} Mesopelagic fish, including myctophids, have high levels of methylmercury because they occur during the day at the oxygen minimum zone where anaerobic decomposition of organic matter leads to high levels of methylmercury.^{49,50}

We determined trends in mercury over up to 47 years (1968–2015) in eggs from a suite of seabirds in Pacific Canada ranging from estuarine to epipelagic habitats. Because the sulfate availability hypothesis states that mercury levels in the food chain are limited by sulfate availability rather than mercury input, we predict no increase in seabird mercury levels. Based on the trophic position and sulfate limitation hypotheses, we predicted that mercury would correlate positively across species, space and time with both $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$.

MATERIALS AND METHODS

Eggs were collected from ancient murrelets (*Synthliboramphus antiquus*; $N = 59$), rhinoceros auklets (*Cerorhinca monocerata*; $N = 147$), Leach's storm-petrels ($N = 157$), double-crested cormorants (*Phalacrocorax auritus*; $N = 58$), pelagic cormorants (*Phalacrocorax pelagicus*; $N = 106$) and great blue herons (*Ardea herodias*; $N = 10$). Collection details are reported elsewhere^{5,51} and raw data are available as an appendix. All samples were processed for mercury at Environment Canada laboratory facilities using an AMA-254 mercury analyzer and following standardized treatment protocols including quality assurance procedures.¹⁴ Recoveries of total mercury ranged from 98.7 to 105.3%. Based on 16 replicate measurements,

measurement precision for mercury was estimated to be 1.84% (± 2.60 SE). Stable isotope analysis for $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, and $^{34}\text{S}/^{32}\text{S}$ isotopes was carried out using the same egg homogenate as used for chemical analyses and described elsewhere.^{5,51} The $\delta^{13}\text{C}$ values were lipid normalized.⁵² The Suess effect—the systematic decline in $\delta^{13}\text{C}$ over time due to the increased release of fossil fuels—could potentially confound our results. However, given the relatively short time period of our study, the variability of the Suess effect in marine systems^{53,54} and the absence of change in $\delta^{13}\text{C}$ values in several forage fish species within the Salish Sea over the past century,⁵³ we did not correct for the Suess effect. Because of the large spatial scale of our sampling, we were concerned that variation in baseline $\delta^{15}\text{N}$ could confound our estimates of trophic level. Therefore, we sent subsamples for $\delta^{15}\text{N}$ analysis of phenylalanine and glutamate. Phenylalanine provides baseline $\delta^{15}\text{N}$, whereas glutamate increases systematically with trophic level.²⁶ Thus, the difference between $\delta^{15}\text{N}$ of glutamate and phenylalanine ($\delta^{15}\text{N}_{\text{glu-phe}}$) provides an index of trophic level independent of baseline.²⁶ Details on sample collections and mercury and stable isotope analyses appear in the [Supporting Information](#). Statistical analyses were conducted using general linear models in R 3.2.1 with mercury (dry weight basis, log-transformed) as the dependent variable and species, moisture, site, year and isotope values as the independent variables.

RESULTS

Total mercury across all species and locations correlated with $\delta^{34}\text{S}$, not $\delta^{15}\text{N}$ or $\delta^{13}\text{C}$ (GLM, $\delta^{34}\text{S}$: $t_{10} = 7.45$, $P < 0.0001$; $\delta^{15}\text{N}$: $t_{10} = 1.03$, $P = 0.33$; $\delta^{13}\text{C}$: $t_{10} = 0.09$, $P = 0.93$; [Figure 1](#)

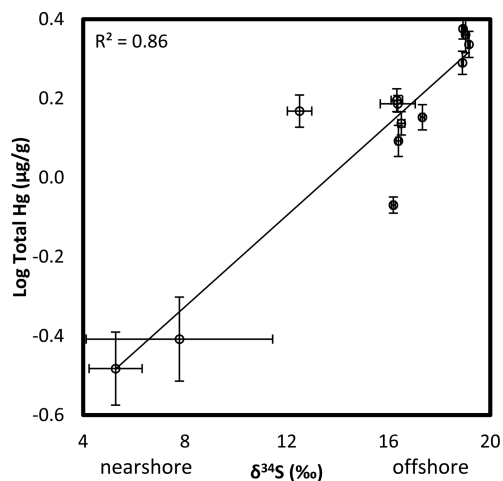


Figure 1. Geometric mean total mercury (dry weight) in eggs increases with $\delta^{34}\text{S}$ across six seabird species (13 colonies) from the Pacific coast of Canada.

and [Figure S3](#)). For the subsample of individuals with amino acid-specific data, mercury increased with $\delta^{34}\text{S}$ but not $\delta^{15}\text{N}_{\text{glu-phe}}$ (GLM, $\delta^{34}\text{S}$: $t_8 = 5.06$, $P = 0.001$; $\delta^{15}\text{N}_{\text{glu-phe}}$: $t_8 = 0.46$, $P = 0.66$). Within species, mercury increased with $\delta^{34}\text{S}$ (both cormorants) and $\delta^{15}\text{N}$ (double-crested cormorant and Leach's storm-petrel; [Table S1](#); [Figure 2](#)). Average $\delta^{15}\text{N}$ across species did not correlate with $\delta^{34}\text{S}$ ($t_{11} = -0.42$, $P = 0.68$) or $\delta^{13}\text{C}$ ($t_{11} = 1.16$, $P = 0.14$), but $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ were nonlinearly correlated with one another (linear term: $t_{10} = -3.14$, $P = 0.01$;

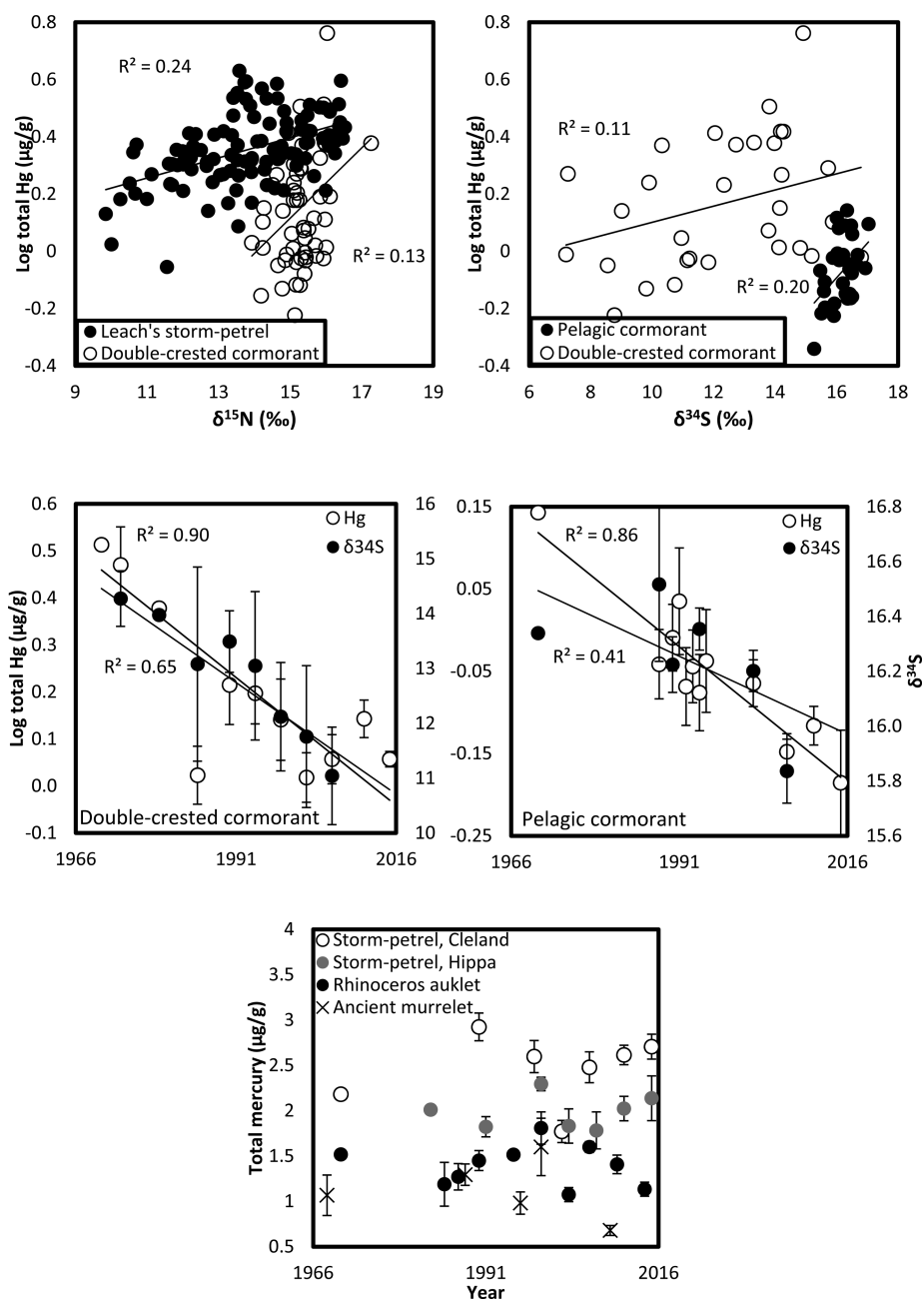


Figure 2. Mercury (dry weight) increased with (a) $\delta^{15}\text{N}$ and (b) $\delta^{34}\text{S}$ in seabird eggs collected from the Pacific coast of Canada. Mercury (dry weight) and $\delta^{34}\text{S}$ declined between 1968 and 2015 in eggs for (a) double-crested and (b) pelagic cormorants with (c) no significant trend for three other species.

quadratic term: $t_{10} = -3.29$, $P = 0.008$; Figures 3, S2). Total mercury was also independent of percent sulfur (Figure S2).

We included data from the five species (six colonies) that spanned at least two decades: ancient murrelets, pelagic cormorants, double-crested cormorants, Leach's storm-petrel (Cleland and Hippan colonies) and rhinoceros auklet. The time trends in carbon and nitrogen isotopes for all species but murrelets showed no significant change with time, although $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were depleted in cormorants during the 1994 El Niño.⁵⁴ For murrelets, $\delta^{13}\text{C}$ ($t_{33} = -3.24$, $P = 0.003$), but not $\delta^{15}\text{N}$ ($t_{33} = -1.35$, $P = 0.18$) or $\delta^{34}\text{S}$ ($t_8 = 0.58$, $P = 0.58$), declined with year. Mercury levels declined with year in murrelets ($t_{56} = -4.06$, $P = 0.0002$), double-crested cormorants ($t_{57} = -3.64$, $P = 0.0006$) and pelagic cormorants ($t_{56} = 227.2$,

$P < 0.0001$), but not storm-petrels ($t_{112} = -1.01$, $P = 0.31$; colony covariate: $t_{112} = -2.03$, $P = 0.048$) or auklets ($t_{57} = 1.02$, $P = 0.31$; Figure 2). Likewise, $\delta^{34}\text{S}$ declined with year in double-crested cormorants ($t_{30} = -2.56$, $P = 0.02$) and pelagic cormorants ($t_{31} = -2.61$, $P = 0.01$), but was constant in storm-petrels ($t_{45} = -1.25$, $P = 0.21$) and auklets ($t_{11} = -1.62$, $P = 0.13$; Figure 2).

DISCUSSION

Interspecies Relationships: Links between Mercury and Sulfur Across Space. In support of the sulfate availability hypothesis, across species and within two species, mercury levels increased with $\delta^{34}\text{S}$. Similarly, previous authors observed that individuals and species feeding on mesopelagic fish,

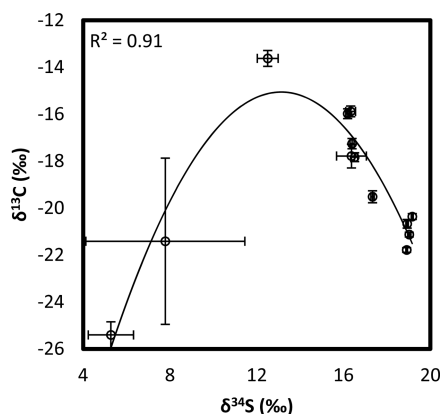


Figure 3. Relationship between $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ among eggs of bird species from the Pacific coast of Canada.

especially myctophids, have high levels of mercury.^{11,44,50} Myctophids spend the daytime in the methylmercury-rich³⁹ oxygen minimum zone. There, anaerobic conditions, decomposition of organic material descending from the surface and high sulfate levels provide ideal conditions for sulfate-reducing bacteria to produce methylmercury that then biomagnifies through the food web. We extend those observations beyond the deep sea to suggest that $\delta^{34}\text{S}$ is a strong index of those processes across marine ecosystems (Figure 4). Associations with habitats high in sulfate-reducing bacteria may also explain why surface-feeding albatrosses at fairly low trophic level have exceptionally high levels of mercury.^{9,55,56} Relationships with $\delta^{34}\text{S}$ break down in freshwater environments where barriers to dispersal of mercury mean that local deposition and physiographic factors play a stronger role than sulfate abundance.^{25,57–59} Furthermore, in estuarine environments, high levels of mercury sulfide, which reduces the availability of mercury and ultimately decreases methylmercury levels, further

confounds relationships.⁶⁰ Nonetheless, $\delta^{34}\text{S}$ might predict mercury levels in predators foraging within a single estuary or freshwater body.

Our explanation assumes that methylmercury is produced by anaerobic bacteria in the deep waters of the oxygen minimum zone, where methylmercury levels are highest.³⁹ Recent studies have challenged that assumption, showing significant levels of methylation in surface waters, where some mesopelagic fish, such as myctophids, actually feed.^{39–41} Indeed, iron- and carbon dioxide-reducing bacteria, rather than sulfate-reducing bacteria, can play significant roles in methylmercury production.⁴¹ The variation across environments in the importance of sulfate-reducing bacteria to the production of methylmercury explains why some studies have found positive relationships (e.g., smallmouth bass *Micropterus dolomieu*; crayfish *Orconectes* spp.; fish in San Francisco Bay, cormorants, gulls), and others have found negative (e.g., hog sucker *Hypentelium nigricans*) or no relationships (e.g., Asian clam *Corbicula fluminea*; yellow perch; pumpkinseed sunfish *Lepomis gibbosus*) between $\delta^{34}\text{S}$ and mercury.^{25,38,62–66} Although some tropical oceans had little evidence for methylation genes in sulfate-reducing bacteria, implying that sulfate-reducing bacteria were not important methylators in tropical oceans, a site (Saanich Inlet) near where the eggs in the current study were collected had high levels of methylation genes in sulfate-reducing bacteria, implying that sulfate-reducing bacteria likely play a strong role as methylators in our system.⁴¹ Regardless of the exact source of methylmercury in the deep ocean, the correlation between mercury levels in top predators and $\delta^{34}\text{S}$ imply that mercury concentrations are associated with the origin of sulfur at the base of the food web. We urge researchers to collect $\delta^{34}\text{S}$ alongside mercury levels for other organisms and ecosystems to help elucidate the underlying mechanisms.

There is abundant information supporting the trophic position hypothesis,^{17–20} and it is unsurprising that $\delta^{15}\text{N}$ correlated with mercury in two species in our own study. More

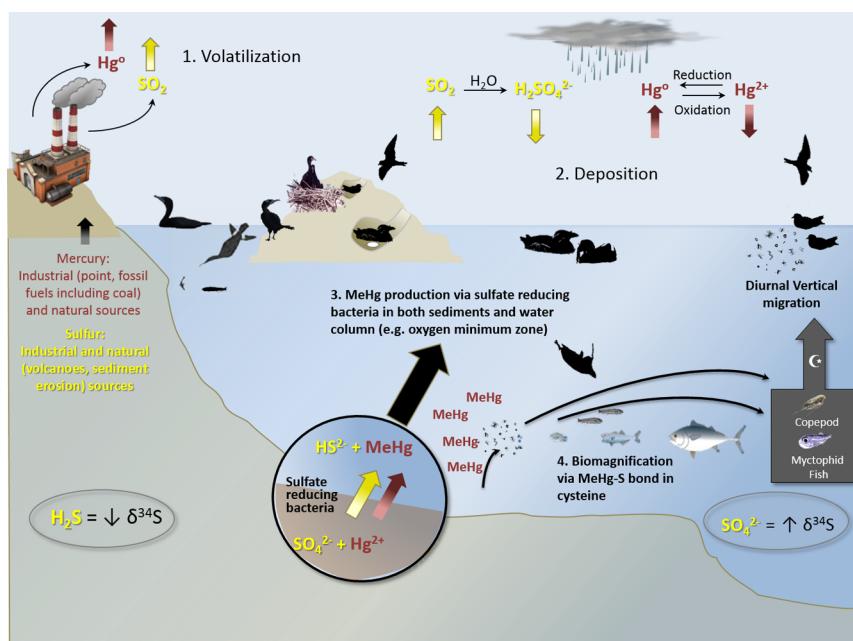


Figure 4. Schematic overlaying simplified mercury and sulfur cycles. Figure shows mercury (1) production and volatilization, (2) deposition via rain in marine habitats, (3) methylation by sulfate-reducing bacteria in sulfate-rich anaerobic regions (e.g., sediments, oxygen minimum zone), and (4) biomagnification through the food web with eventual uptake by marine birds via oceanic food chains.

surprising was the absence of a relationship between mercury and $\delta^{15}\text{N}$ across species, with most of the species feeding on large fish (herons and cormorants) having lower levels of mercury than partial planktivores (storm-petrels and murrelets). The absence of a relationship was not simply because of confounding spatial variation in baseline $\delta^{15}\text{N}$ as there was no relationship even after accounting for baseline variation using amino acid-specific $\delta^{15}\text{N}$ measurements of phenylalanine. Likewise, there was no relationship between $\delta^{15}\text{N}$ and mercury in auklets and their prey.⁶¹ Given that other factors overwhelmed any variation in mercury due to $\delta^{15}\text{N}$ at the level of inter- and intraspecific variation in $\delta^{15}\text{N}$ observed within our study, we urge caution in use of $\delta^{15}\text{N}$ alone²² to correct for variation in diet.

We recommend that researchers examine both sulfur and nitrogen isotopes when considering sources of variation for mercury. Indeed, the main predictors of whether there were significant associations between mercury and $\delta^{34}\text{S}$ or $\delta^{15}\text{N}$ was the amount of variance in the isotope (i.e., SE bars in Figure 2) and a sample size of greater than ten. Virtually all mercury in eggs is methylmercury (e.g., ~80–120% of total mercury^{42,43}) and it is methylmercury—produced largely by sulfate-reducing bacteria—that biomagnifies. Consequently, relationships between mercury and $\delta^{34}\text{S}$ or $\delta^{15}\text{N}$ are likely to be particularly strong in eggs. Future research could test the prediction that $\delta^{34}\text{S}$ or $\delta^{15}\text{N}$ should correlate primarily with methylmercury rather than inorganic mercury by studying tissues, such as muscle or liver, with measurable inorganic mercury. Importantly, associations with isotopes occurred in both migratory (Leach's storm-petrel) and resident (cormorant) species while nonassociations occurred only in migratory (auklets, murrelets) species, and the lack of an association could be because isotopic signatures represent the previous 2 weeks whereas mercury levels reflect sources from overwintering grounds.

Sulfur isotopes provided a strong index of marine input, with sulfur isotopes clearly indicating where organisms foraged in the marine environment.^{29,60} Herons foraged in estuaries, double-crested cormorants in nearshore waters, pelagic cormorants in deeper waters, auklets and murrelets on the continental shelf and storm-petrels off the shelf; $\delta^{34}\text{S}$ mirrored that trend precisely. Due to cost and logistics, previous researchers have used $\delta^{13}\text{C}$ as an index of marine input.^{61,67} However, $\delta^{13}\text{C}$ was low both in the offshore ($^{13}\text{CO}_2$ is used preferentially by nearshore algae compared with offshore phytoplankton) and estuarine ($^{13}\text{CO}_2$ dissolves better in saltwater than freshwater) environments²⁸ (Figure S2). Clearly, $\delta^{13}\text{C}$ has limited value as an index of marine input over large scales. Furthermore, as observed in many studies, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ correlated with one another because carbon also fractionates during assimilation from source to consumer. In contrast, $\delta^{34}\text{S}$ did not correlate with $\delta^{15}\text{N}$. Across 19 studies, fractionation of $\delta^{34}\text{S}$ averaged 0‰ compared with 4–5‰ for $\delta^{15}\text{N}$.³² Thus, we provide additional evidence that sulfur does not fractionate greatly during assimilation, and that $\delta^{34}\text{S}$ is a strong indicator of habitat uninfluenced by trophic position.

Temporal Trends: Mercury Constant Across 47 Years except When Diet Changed. After accounting for cases where diet ($\delta^{34}\text{S}$) changed in tandem, mercury levels in Pacific seabird eggs were stable over the past 50 years (Figure 2). Likewise, mercury trends in marine mammals or fish in the Pacific were relatively stable over the past 50 years,⁶⁹ with an exception that may reflect a dietary shift.⁷⁰ High interannual variation with no clear trend was also present in eggs from

Atlantic Canada, after accounting for diet.¹⁵ Given that our dietary variation was inferred from sulfur rather than nitrogen isotopes, we urge more complex interpretation of food web structure as part of monitoring programs.^{13,29} Significant differences in mercury across time occurred in both resident (cormorant) and migratory (murrelet) species. Because time trends paralleled the trends in isotopic signatures (which reflect the diet over the previous 2 weeks, when all species were near their breeding grounds), we argue that time trends represent local trends in mercury rather than trends derived from the wintering grounds.

Mercury concentrations in the environment, including the oceans, increased dramatically through the Industrial Revolution. Seabird feather and eggshell mercury increased over that time period as accelerating levels of mercury bioaccumulated in top marine predators.^{9,71} Although mercury deposition rates in the Pacific Ocean have increased 3–5 fold since the Industrial Revolution,⁷² levels in seabirds have increased by less than 2-fold over that period,⁹ implying that there is a dampening effect of the food web on levels in top predators. More recently, while global mercury primary production and levels in the Atlantic have declined, mercury levels in Pacific surface water have increased because of coal burning in Asia.^{6,7,63–74} The lack of a trend in our data set may be because methylmercury in top predators is partially limited by sulfate availability rather than entirely by mercury availability.

Cormorant egg $\delta^{34}\text{S}$ declined with time. A similar decline in $\delta^{34}\text{S}$ was observed in gull feathers from the Salish Sea⁷⁶, which was interpreted as a switch from marine to terrestrial food webs. Similar trends across three species hint at a unifying underlying mechanism. Overfishing of forage fish may have caused a switch to benthic fish (possibly via discards for gulls) or to nonmarine food webs.⁷⁵ Alternatively, anthropogenic sources can alter $\delta^{34}\text{S}$ and industrial inputs, such as alterations in pulp mill effluent, may have played a role.²⁸ Regardless, all three species are currently declining in the Salish Sea due to increased eagle predation⁷⁷; perhaps changing diet also plays a role.⁷⁵

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05458.

Detailed Methods and Figures S1–S3 and Tables S1–S3 (PDF)

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Notes

The authors declare no competing financial interest.

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