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Mercury trends in herring gull (*Larus argentatus*) eggs from Atlantic Canada, 1972–2008: Temporal change or dietary shift?

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ABSTRACT

Mercury (Hg) is a pervasive contaminant that can adversely affect predatory wildlife. Bird eggs provide insights into breeding females' Hg burdens, and are easily collected and archived. We present data on Hg trends in herring gull (*Larus argentatus*) eggs from five sites in Atlantic Canada from 1972 to 2008. We found a significant decrease in Hg at Manawagonish Island, New Brunswick and Île du Corossol, Quebec, but after correcting Hg for dietary shifts using stable isotopes ($\delta^{15}N$), these trends disappeared. Decreasing temporal trends of stable isotopes in gull eggs were observed at four sites, suggesting shifts in gull diets. At Gull Island, Newfoundland, diet-adjusted Hg increased from 1977 to 1992, dropped sharply between 1992 and 1996, and rose again from 1996 to 2008. After adjusting Hg trends for dietary shifts of herring gulls, it appears that environmental Hg in coastal ecosystems has remained relatively constant at most sites in Atlantic Canada over the last 36 years.

1. Introduction

Mercury (Hg) is an atmospherically transported contaminant, much of which is anthropogenically generated, and deposition is increasing worldwide (Nriagu, 1989; Nriagu and Pacyna, 1988; Streets et al., 2009). As top predators in the marine environment, seabirds are used frequently as sentinel species for monitoring ecosystem contamination (Burger and Gochfeld, 2004; Goodale et al., 2008; Hebert et al., 1999; Mineau et al., 1984; Pearce et al., 1979). Their high trophic position also means that seabirds can be exposed to high concentrations of biomagnified contaminants, including Hg (Braune et al., 2005). The biologically active and toxic form, methylmercury (MeHg), is the predominant type found in seabird feathers and eggs (Bond and Diamond, 2009; Thompson and Furness, 1989). Seabirds acquire MeHg through ingestion of contaminated prey. MeHg is then deposited in body tissues, demethylated in the liver or brain, or depurated into feathers or eggs (Braune and Gaskin, 1987; Monteiro and Furness, 2001; Spalding et al., 2000).

In some marine ecosystems, Hg concentrations in seabirds have increased over time (e.g., Braune, 2007; Thompson et al., 1992). This increase could be due to two processes: first, the birds consumed a relatively constant diet over time and MeHg levels increased in that diet, or second, the birds shifted their diet over time to prey with higher Hg concentrations (see Hebert et al., 2009). The first possibility of changing Hg levels in prey could result from environmental changes, such as increased atmospheric deposition of Hg, increased bioavailability of MeHg, climatic or oceanographic changes (e.g., Aebischer et al., 1990; Drinkwater, 1996), or changes in food web structure (e.g., Carscadden et al., 2001; Montevecchi and Myers, 1996). Stable isotope analysis can be used to address the second possibility (a shift in diet) because isotope values ($^{13}C/^{12}C$, or $\delta^{13}C$, and $^{15}N/^{14}N$, or $\delta^{15}N$) will reflect the consumer's diet at the time of tissue synthesis (Hobson, 1995; Hobson and Clark, 1992). $\delta^{13}C$ can give an indication of the geographic foraging area, as inshore and more productive oceanic areas (including terrestrial sources, such as landfill sites) are enriched in ^{13}C (France, 1995; Goericke and Fry, 1994; Peterson and Fry, 1987; Popp et al., 1998), while $\delta^{15}N$ values increase 2–5‰ with each trophic level because ^{14}N is excreted preferentially in nitrogenous waste (Kelly, 2000; Minagawa and Wada, 1984; Steele and Daniel, 1978). However, analysing changes in carbon isotope values over time is potentially confounded by the Suess (1955) Effect, as the combustion of fossil fuels (naturally depleted in ^{13}C) have altered the baseline $\delta^{13}C$ value globally, including in the North Atlantic (Quay et al., 2007), but this can be taken into account

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mathematically (e.g., Farmer and Leonard, 2011). The Suess Effect is a global phenomenon affecting terrestrial, freshwater, and marine ecosystems (Keeling, 1979; Keeling et al., 1995; Quay et al., 2007; Suess, 1953, 1955).

Herring gulls (*Larus argentatus*) are a common predator in the northwest Atlantic Ocean, and are found throughout Atlantic Canada (Pierotti and Good, 1994). As income breeders, herring gulls incorporate nutrients from local breeding grounds into their eggs (Drent and Daan, 1980; Hobson et al., 2000). Herring gulls have also been identified as useful biomonitors of biomagnifying contaminants, such as Hg, because they are top predators, often forage in urbanized areas, are long-lived, widely distributed, and egg samples are easy to collect (Golden and Rattner, 2003; Hebert et al., 1999). Hg concentrations in herring gulls have been studied in the Great Lakes region (Koster et al., 1996; Weseloh et al., 1990, 2011), northeastern United States (Burger and Gochfeld, 1995), Gulf of St. Lawrence (Lavoie et al., 2010a) and in Europe (Lewis et al., 1993; Rüdel et al., 2010). However, because herring gulls are opportunistic inshore predators and scavengers, they commonly shift their diet to take advantage of changes in prey availability (Pierotti and Annett, 1991; Pierotti and Good, 1994). While their diet is primarily marine fish, invertebrates and seabirds, they can also forage at garbage dumps and sewage outfalls (Pierotti and Annett, 1991; Pierotti and Good, 1994). Shifts in diet have been linked to changes in contaminant levels in herring gull eggs (Hebert et al., 2000, 2009). As a result, recent analyses of temporal trends of contaminant concentrations in herring gull eggs have adjusted for diet shifts using stable isotope data (Hebert and Weseloh, 2006; Weseloh et al., 2011).

Our objectives were to: 1) assess changes in Hg concentrations over the last 36 years in the eggs of an abundant marine predator, the herring gull, 2) examine concurrent changes in stable isotope values to detect any possible trophic shifts that might be related to simultaneous changes in Hg concentrations, and 3) to adjust the temporal changes in egg Hg concentrations for any trophic shifts observed, to yield a more accurate indicator of Hg trends in the marine ecosystems studied.

2. Methods

2.1. Sample collection

Eggs were collected from five colonies in Atlantic Canada. Colony locations were diverse and included one site in the northern Gulf of St. Lawrence (Île du Corossol, Québec, 50°05′N, 66°23′W), two in the Bay of Fundy (Kent Island, New Brunswick, 44°34′N, 66°44′W, and Manawagonish Island, New Brunswick, 45°12′N, 66°06′W), an offshore site 300 km off the coast of Nova Scotia (Sable Island, Nova Scotia, 43°56′N, 59°54′W), and a coastal site open to the Grand Banks (Gull Island, Newfoundland 47°13′N, 52°47′W; Fig. S-1). Eggs were sampled at each colony beginning in 1972 (Corossol, Manawagonish), 1976 (Kent, Sable) or 1977 (Gull), continuing at irregular intervals until 1980, after which eggs were sampled every four years until 2008 (Table S-1). From 1972 to 1988 we collected one egg from five nests in each colony, and from 1992 to 2008 we collected one egg from 15 nests in each colony. The change in sampling design in 1992 was done to increase our ability to detect changes in contaminant levels, based on power analysis (Hebert and Weseloh, 2003). Eggs were stored in foam-lined toolboxes at 4 °C within 24 h of collection and then were shipped by overnight courier to Environment Canada's National Wildlife Research Centre (NWRC; Ottawa, ON), where egg contents were stored at −40 °C in chemically cleaned glass jars prior to analysis.

To ensure comparable Hg data, archived egg samples from 1972 to 1996 were retrieved from the National Wildlife Specimen Bank at NWRC for Hg analysis. These archived samples were frozen at −40 °C since their collection.

2.2. Total mercury analysis

The five eggs collected at each colony prior to 1992 were analysed individually for total Hg. The 15 eggs collected at each colony in 1992–2008 were analysed as three composite (pooled) samples of five eggs each. We used two methods to analyse total Hg in herring gull eggs. Samples collected in 2000 were analysed using cold vapour atomic absorption spectrophotometry (CVAAS) using a Perkin–Elmer 3030b, AAS (Waltham, MA, USA) and Varian VGA-76 vapour generation accessory (Agilent Technologies, Mississauga, Ontario). Detailed methods were described by Scheuhammer and Bond (1991) and Neugebauer et al. (2000). All other egg samples were analysed using an Advanced Mercury Analyser 254 (AMA-254; Altec Ltd., Prague, Czech Republic), which is a direct system, using EPA Method 7473 (U.S. EPA, 1998) as described by Weseloh et al. (2011).

Frozen egg samples were thawed at 4 °C, and individual samples were homogenized using an electric mixer. For samples collected from 1992 to 2008, aliquots of equal volume were pooled in sterile Teflon vials and mixed thoroughly. Pools were generally 5 individual eggs, except in the few cases where an individual egg broke during transport to NWRC. Samples analysed using CVAAS were first freeze-dried, and then digested overnight in 70% nitric acid, followed by digestion with 95% sulphuric acid and 37% hydrochloric acid (Neugebauer et al., 2000).

Samples analysed using direct mercury analyser AMA-254 were placed in nickel boats for direct measurement of Hg, and Hg concentrations were converted to dry weight after % moisture determination. Detection limits using CVAAS were 0.02 μg/g for the analysed dry sample, and 0.006 μg/g in the dry sample for the AMA-254. The difference in detection limits was not a concern since all egg samples had Hg concentrations well above the higher detection limit.

To test the comparability of CVAAS and AMA-254 results, 24 common loon egg samples were analysed for total Hg using both methods (Bond, 2008). The mean Hg concentrations were not significantly different (Wilcoxon Sign Rank test, $p = 0.2$). Average variability of the paired Hg data was 8.4 ± 7.1% (mean relative standard deviation (r_{sd}) ± S.D.) Regression analysis showed a strong association between the CVAAS vs. AMA-254 data (CVAAS = 0.98 * AMA + 0.12, $R^2 = 0.86$).

Of the 185 total samples, 100 (54%) were analysed in duplicate or triplicate. Average variability (r_{sd} ± S.D.) of these replicate samples was 1.86 ± 2.69%. Within each analytical run, Hg concentrations were corrected for recoveries of certified reference materials (mean ± S.D. recovery among all analytical runs, certified concentration): DOLT-2 (dogfish liver, 104 ± 7% recovery, certified concentration: 2.14 μg/g, $n = 13$), DOLT-3 (dogfish liver, 103 ± 11% recovery, certified concentration: 3.37 μg/g, $n = 8$), DORM-2 (dogfish muscle, 100 ± 3% recovery, certified concentration: 4.64 μg/g, $n = 5$), OT-1566b (oyster tissue, 89 ± 9% recovery, certified concentration: 0.037 μg/g, $n = 14$), and TORT-2 (lobster hepatopancreas, 103 ± 7% recovery, certified concentration: 0.270 μg/g, $n = 24$). Oyster tissue was used in all analytical runs, along with one of the other four reference materials. Hg concentrations measured in the herring gull eggs were within the range of concentrations of the certified reference materials.

2.3. Stable isotope analysis

Stable nitrogen and carbon isotope analyses were conducted at the University of Ottawa's G.G. Hatch Stable Isotope Laboratory using 1 mg (±0.2 mg) of freeze-dried egg tissue encapsulated in tin. Isotope analysis was completed using a VarioEL III Elemental Analyser (Elementar, Hanau, Germany) followed by trap and purge separation and on-line analysis by continuous-flow with a DeltaPlus Advantage isotope ratio mass spectrometer (Thermo Scientific, Waltham, USA) coupled with a ConFlo II. Data were normalized using international standards for calibration (IAEA-CH-6, IAEA-NBS22, IAEA-N1, IAEA-N2, USGS-40, USGS-41) and quality control was maintained through sample duplicates. Stable isotope values were reported in delta notation in parts per thousand (‰, per mil) relative to the above standards, and mean values are reported for samples taken in duplicate. Analytical precision of both $\delta^{13}C$ and $\delta^{15}N$, based on repeat measures of a standard (C-55), was ±0.2‰.

Lipids are naturally depleted in ^{13}C, and because individual eggs vary in lipid content, lipids must be removed or adjusted for mathematically to interpret carbon isotope values (Bond and Jones, 2009; Kojadinovic et al., 2008; Logan et al., 2008; Post et al., 2007). We assumed that, as income breeders, all macronutrients incorporated into eggs would be from the breeding grounds (Oppel et al., 2010), so we adjusted for eggs' variable lipid content mathematically using methods described in Post et al. (2007: 186) for aquatic organisms, where

$$\delta^{13}C_{normalized} = \delta^{13}C_{uncorrected} - 3.32 + 0.99 \times C:N \quad (1)$$

Herring gull C:N in our samples ranged from 5.74 to 10.89 (mean ± SD: 7.5 ± 0.5), and the equation in Post et al. (2007) was derived for C:N 3.0–7.0. Since only 11% of our eggs had C:N > 8.0 and the relationship described by Post et al. (2007) is strongly linear, we assumed that this approach was valid.

Following lipid adjustment, we used the approach of Farmer and Leonard (2011: 126) to adjust $\delta^{13}C$ values for the Suess Effect using the post-1950 portion of their Eq. (2):

$$\delta^{13}C_{corrected_i} = \delta^{13}C_{normalized_i} - b_{his} \times (1950 - t_i) - b_{mod} \times (t_i - 1950) \quad (2)$$

where $\delta^{13}C_{normalized}$ is the $\delta^{13}C$ value normalized for lipid content, b_{his} is the historical annual decline in $\delta^{13}C$ (0.007‰; Tagliabue and Bopp, 2008), and b_{mod} is the modelled annual decline in $\delta^{13}C$ in North Atlantic surface waters between 1950 and 1993 (0.026‰; Körtzinger and Quay, 2003). We used a Suess correction based on the marine environment as a majority of herring gulls in Atlantic Canada consume marine prey (Pierotti and Annett, 1991), and the Suess effect in the world's oceans is of a similar magnitude to that in the atmosphere (Gruber et al., 1999; Keeling et al.,