Monitoring organic contaminants in eggs of glaucous and glaucous-winged gulls (Larus hyperboreus and Larus glaucescens) from Alaska

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Organic contaminant concentrations in Alaskan gull eggs could possibly be affecting chick growth and survival rates, but the eggs should be safe for humans to eat in small quantities.

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1. Introduction

Gulls have been used to monitor contaminants in many parts of the world. The Canadian Great Lakes herring gull monitoring program is probably the most extensive (see Hebert et al., 1999), but the German, and Norwegian efforts are also noteworthy (see Martí et al., 2000; Borgà et al., 2001; Bustnes et al., 2003; Mallory et al., 2006; Verreault et al., 2006). In Alaska, only two studies have collected information on contaminant levels in gull eggs (Ohlendorf et al., 1982; Jack and Martínez, 2003). During 1973–1976, Ohlendorf et al. (1982) collected and analyzed glaucous-winged gull eggs from 12 locations in the Gulf of Alaska, Aleutian Islands, and southeastern Bering Sea (Copper River delta; Amalik Bay; Barren, Semidi, Shumagin Hinchinbrook, Middleton, Kodiak, Ugainshak, Buldir, Bogoslof, and Shalak Islands), and Jack and Martínez (2003) collected and analyzed glaucous gull eggs from the Koteluev and Nunivak Island areas, and glaucous-winged gull eggs from the Togiak, Dutch Harbor, and Sitka vicinities in 2000.

In Alaska, glaucous gulls (Larus hyperboreus) nest coastally from the Beaufort Sea southward to St. Lawrence and Nunivak Islands and the Cape Peirce vicinity in the Bering Sea (ASIS, 2006a; Gilchrist, 2001, see Supplemental Fig. 1). Most of the Alaskan birds winter south of the pack ice in the Aleutian Islands and southern Bering Sea, but some individuals stay in open leads in ice-covered areas of the Chukchi and Bering Seas while others venture into the coastal waters of Russia as far south as the Kamchatka Peninsula (Troy Ecological Research Associates, 2004). Some birds also migrate along the North American coast as far south as Oregon and California. Glaucous-winged gulls (Larus glaucescens) breed from Cape Romanzof in western Alaska southward to Bristol Bay and the Alaska Peninsula (Verbeek, 1993). They also nest on the Pribilof and St. Matthew – Hall islands in the Bering Sea and throughout the Aleutian Islands and Gulf of Alaska. Some birds also breed on the Commander Islands in the Russian Far East and along the North American coast as far south as northeastern Oregon. Most of the Alaskan birds winter southward from the Bering Sea ice-front to the North Pacific and Gulf of Alaska, but some birds venture as far west as northern Japan and the Kurile Islands in the Russian Far East and as far south as California and the Baja Peninsula in North America (ASIS, 2006b; Verbeek, 1993; Supplemental Fig. 1).

Both gull species are surface feeders that tend to utilize nearshore environments. They are opportunistic predators and scavengers, feeding on a variety of fish and invertebrates and bird and...
mammal carcasses in both marine and terrestrial habitats. They also take bird eggs and chicks, and feed on human refuse and occasionally even seaweed and berries. Both species lay 2–3 eggs per clutch that may be replaced if lost early in the breeding season (Gilchrist, 2001; Verbeek, 1993). Seabird eggs have been used to monitor contaminants, and they are representative of the females at the time of laying (Verreault et al., 2006). Gulls and their eggs are still important in subsistence diets in many parts of rural Alaska.

The Seabird Tissue Archival and Monitoring Project (STAMP) was developed in 1999 as a long-term co-operative program among the U.S. Fish and Wildlife Service (USFWS), the U.S. Geological Survey (USGS), the Bureau of Indian Affairs (BIA), and the National Institute of Standards and Technology (NIST) to collect, cryo-genically store (on the decadal scale), and analyze seabird tissues (primarily eggs) for chemical contaminants (e.g., polychlorinated biphenyls [PCBs], organochlorine pesticides [e.g., DDTs and chlordane], polybrominated diphenyl ethers [PBDEs], and metals and organometals [e.g., mercury, methylmercury, and butyltins]). In addition to collecting glaucous and glaucous-winged gull eggs, STAMP has also collected eggs from three other seabird species based on their feeding behavior and prey species: common and thick-billed murres (Uria aalge and Uria lomvia) and black-legged kittiwakes (Rissa tridactyla).

This paper reports organic contaminant levels in gull eggs collected at seven Alaskan colonies from the initial collections to serve as baseline data for STAMP and compares them with literature values. Geographic differences are also discussed, along with information related to human and environmental safety.

2. Materials and methods

2.1. Sample collection and processing

Glaucous and glaucous-winged gull clutches (1–3 eggs) were collected at seven colonies in the Bering and Chukchi seas and Gulf of Alaska in 2005 (Fig. 1) and processed at the USGS Alaska Science Center in Anchorage, Alaska using STAMP protocols (see Roseneau et al., 2008) between 16 Jun and 21 Oct 2005. Briefly, the eggs were cleaned with Type 1 water and measured (length, width, whole egg mass) before they were cut in half under a positive pressure laminar flow hood with a custom-made titanium knife. Eggs from the same clutch were pooled (Table 1). Egg shells were rinsed with Type 1 water, dried, weighed, placed in labeled plastic bags, and shipped to the University of Alaska Museum of the North in Fairbanks, Alaska for long-term storage.

The contents from each clutch were combined in a clean glass beaker and homogenized with a stainless steel kitchen hand blender (Oster 2614, Rye, New York). The blender blades and beaker were washed with soap and rinsed with Type 1 water, methanol, acetone, and hexane before they were used to process another clutch. Aliquots of the homogenized contents were put into Teflon PFA jars (Savillex, Minnetonka, Minnesota) and cryogenic polypropylene vials (Nunc International, Rochester, New York) and frozen before being shipped to NIST in liquid nitrogen vapor dry shippers. The samples were stored at −150 °C in liquid nitrogen vapor freezers at the Marine Environmental Specimen Bank (MESB) in the Hollings Marine Laboratory in Charleston, South Carolina for future analyses.

Fig. 1. Locations and organic contaminant concentrations (medians with standard errors in ng g⁻¹ wet mass) in glaucous gull (GLGU) and glaucous-winged gull (GWGU) eggs collected at Alaskan colonies in 2005 (n = 3 clutches for each colony).
2.2. Sample preparation

Three clutch samples stored in Teflon jars in the MESB were randomly chosen from each colony (see Table 1). Approximately 2 g of material was removed from each sample, weighed on a three-place analytical balance and mixed with 8 g of diatomaceous earth that had been combusted at 650 °C for 12 h and cooled in a desiccator prior to use. The mixture was transferred to a 33 mL pressurized fluid reference material (PFM) cell held isothermally at 50 °C (ASA Dimens, Salt Lake City, Utah) and extracted as previously described by Sulsaint et al. (1997). One half (0.5 mL) of a mixed internal standard solution was added to the PFM cell using a gas-tight syringe that was weighed on a five-place analytical balance before and after dispensing the liquid into the cell. The internal standard solution contained 13C-labeled PCB congeners 28, 52, 118, 153, 180, 194, and 209; 13C-labeled BDE congeners 4 and 9; and 154, 159, and 209; 13C-labeled 4,4'-DDE in one egg from Viesokoi Rock near Sitka in the south-central Gulf of Alaska, and 209. This standard was used to identify the compounds and species that were different. To help visualize the results, a principal components analysis using a correlation matrix was also run on a lipid mass basis for the percentages of total compounds with no samples that fell below detection limits (36 PCB congeners, 14 organochlorine compounds, and 5 BDE congeners). Statistical tests were conducted using commercially available software (SAS Institute, JMP3.26, Cary, North Carolina). Because of human consumption concerns, acceptable/tolerable daily intake (ADI/TDI) values (number of eggs day−1) for a 70 kg person were calculated using the following formula: ADI/TDI for the contaminant (kg kg−1 body weight day−1) from Van Oortdam et al. (1999) × 70 kg (contaminant concentration in the egg) (μg g−1) × egg mass (g) (egg mass was averaged for eggs belonging to multiple egg clutches).

2.5. Literature comparisons

The literature was searched for persistent pollutant data on glaucous and glaucous-winged gulls. If necessary, values were converted to ng g−1 wet mass by using stated percent lipid. Data were then organized by contaminant, region, and year of collection. Information from similar regions and years were sometimes combined by taking the central tendency (means or medians as reported) multiplied by the number of samples and dividing by the total number of samples for an arithmetic mean. If not given, ranges were calculated by multiplying the standard deviation by 3 which covers 99% of the values based on a Gaussian distribution. If data were presented with 95% confidence intervals or standard errors, the values were converted to standard deviations before calculating ranges. These conversions were only made to help provide more accurate visual comparisons in larger sets of data.

3. Results and discussion

3.1. Contaminant concentrations

Contaminant concentrations in the eggs varied from below detection limits (0.1 ng g−1 wet mass) to 322 ng g−1 wet mass for 4,4′-DDE in one egg from Viesokoi Rock near Sitka in the south-central Gulf of Alaska (the mean relative standard deviation within a colony was 45.6%; see Fig. 1 and Supplemental Tables 1–3). All contaminant concentrations were based on a persistent pollutant data on gulls. If necessary, values were converted to ng g−1 wet mass by using stated percent lipid. Data were then organized by contaminant, region, and year of collection. Information from similar regions and years were sometimes combined by taking the central tendency (means or medians as reported) multiplied by the number of samples and dividing by the total number of samples for an arithmetic mean. If not given, ranges were calculated by multiplying the standard deviation by 3 which covers 99% of the values based on a Gaussian distribution. If data were presented with 95% confidence intervals or standard errors, the values were converted to standard deviations before calculating ranges. These conversions were only made to help provide more accurate visual comparisons in larger sets of data.

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Contaminant concentrations (medians in ng g⁻¹ lipid mass with ranges shown in parentheses) in glaucous gull (GLGU) and glaucous-winged gull (GWGU) eggs from Alaska (n = 3 clutches for each colony). ANOVA F ratios and probabilities are shown following significant MANOVAs (Wilks’ λ = 0.0326, approximate F₁,226.9 = 2.25, P = 0.0212). Groups with different letters were significantly different based on Tukey-Kramer HSD post-hoc tests (e.g., for 2HCHs. Chukchi Sea GLGU eggs (A) were significantly different than Gulf of Alaska GWGU eggs (B), but Bering Sea eggs (AB) were not different from either colony). Percent lipid values and statistics are shown for reference only.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chuckchi Sea</th>
<th>Bering Sea</th>
<th>Gulf of Alaska</th>
<th>F Ratio</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent</td>
<td>7.96</td>
<td>8.02</td>
<td>7.13</td>
<td>7.70</td>
<td>0.640</td>
</tr>
<tr>
<td>Lipid</td>
<td>(7.24-8.34)</td>
<td>(5.90-10.2)</td>
<td>(5.70-8.23)</td>
<td>(7.00-8.84)</td>
<td>0.60</td>
</tr>
<tr>
<td>2BDEs</td>
<td>76.8</td>
<td>92.8</td>
<td>61.4</td>
<td>348</td>
<td>2.49</td>
</tr>
<tr>
<td>ΣCHLs</td>
<td>(59.5-470)</td>
<td>(511-142)</td>
<td>(472-99.2)</td>
<td>(243-4130)</td>
<td>0.096</td>
</tr>
<tr>
<td>ΣDDTs</td>
<td>330</td>
<td>287</td>
<td>308</td>
<td>180</td>
<td>2.62</td>
</tr>
<tr>
<td>ΣHCHs</td>
<td>(279-408)</td>
<td>(253-452)</td>
<td>(225-530)</td>
<td>(96.2-325)</td>
<td>0.084</td>
</tr>
<tr>
<td>2PCBs</td>
<td>1470</td>
<td>1590</td>
<td>1060</td>
<td>1960</td>
<td>0.357</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>(1280-1910)</td>
<td>(1040-2020)</td>
<td>(893-3780)</td>
<td>(594-3700)</td>
<td>0.79</td>
</tr>
<tr>
<td>HCB</td>
<td>278^a</td>
<td>215^AB</td>
<td>184^ab</td>
<td>116^a</td>
<td>3.40</td>
</tr>
<tr>
<td>Epoxide</td>
<td>(194-313)</td>
<td>(98.3-274)</td>
<td>(85.6-243)</td>
<td>(33.0-221)</td>
<td>0.0418*</td>
</tr>
<tr>
<td>Mirex</td>
<td>1720</td>
<td>1690</td>
<td>1400</td>
<td>1710</td>
<td>0.0345</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>(1620-2500)</td>
<td>(1580-2280)</td>
<td>(1130-3870)</td>
<td>(700-2920)</td>
<td>0.99</td>
</tr>
<tr>
<td>HCB</td>
<td>104</td>
<td>115</td>
<td>118</td>
<td>134</td>
<td>0.443</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>524^a</td>
<td>588^A</td>
<td>547^A</td>
<td>216^A</td>
<td>8.49</td>
</tr>
<tr>
<td>Epoxide</td>
<td>(433-585)</td>
<td>(342-758)</td>
<td>(326-622)</td>
<td>(133-388)</td>
<td>0.0011*</td>
</tr>
<tr>
<td>Mirex</td>
<td>36.2</td>
<td>38.4</td>
<td>33.3</td>
<td>14.8</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Values fell within the range reported for murre eggs from the same regions (Roseneau et al., 2008; Vander Pol et al., 2004), and lipids ranged from 5.7% to 10.2% and did not differ among colonies (Table 2 and Supplemental Table 8). To meet normality assumptions, all tests were run on a lipid mass basis. The values generated on the reference materials fell within previously reported ranges indicating that the analyses were in control.

### 3.2. Geographical and literature comparisons

The MANOVA comparing regions and species was significantly different (Wilks’ λ = 0.0326, approximate F₁,226.9 = 2.25, P = 0.0212). Eggs from glaucous-winged gull colonies in the Gulf of Alaska contained lower levels of 2HCHs, HCB, and heptachlor epoxide (Table 2) than eggs from the Bering Sea, which was...
consistent with what is known about global organic contaminant transport (Shen and Wania, 2005; Wania and Dugani, 2003; Wania, 2006). The other compounds were not significantly different (Table 2). Murre eggs collected in the same regions only followed this pattern for HCB. The concentration levels of DDE and ΣPCBs in the murre eggs were higher in the Gulf of Alaska than in the Bering Sea (see Table 2 and Vander Pol et al., 2004).

The principal components analysis did not reveal any differences in contaminant patterns based on species (Fig. 2). However, the Middleton Island glaucous-winged gull eggs were distinct from the other colonies because of their higher proportions of BDEs and higher chlorinated PCBs. Also, the eggs from Viesoki Rock near Sitka showed a slight amount of separation (see Fig. 2), something that was also noted in murre eggs from this same region (Vander Pol et al., 2004; Roseneau et al., 2008). This suggests a possible difference in regional contaminant levels. In comparison, a Norwegian gull study concluded that geographical contaminant patterns were more dependent on biomagnification than on global distillation/fractionation theory (Steffen et al., 2006). A stable isotope study of the Alaska gull eggs is underway that will help determine if there are trophic differences among individuals and colonies.

More data are needed to explain the variations in BDE levels found in the Middleton Island gull eggs (Fig. 1 and Supplemental Table 3). The congener patterns of BDEs within the eggs were also variable (Fig. 3 and Supplemental Table 3), with BDE 47 standing out as the predominant congener. The exceptions were glaucous-winged gull eggs from Shaiak Island near the entrance to Bristol Bay in the Bering Sea where BDE 154 was the dominate substance, and egg 619 from Hooper Bay in western Alaska where BDE 100 comprised 57.7% of the total BDEs. BDE 47 was also the major flame retardant (44.7% of the total) found in Norwegian glaucous gull eggs (Verreault et al., 2007). However the order of the other BDEs reported in the Norwegian study was congeners 100, 154 (with co-elution of polybrominated biphenyl [BB] congener 153), 99, and 153 (5–10% each) compared to the importance of the congeners found in this study (congeners 99 [5–40%], 154 [2–27%], 100 [7–58%], and 99 [0.2–21%]; see Fig. 3 and Verreault et al., 2007). The large range in the percentages of the major BDEs found during this study demonstrated that the pattern in congeners was highly variable among both the colonies and individuals with a mean relative standard deviation (RSD) of 52.1% for the compounds found at the colonies (glaucous gull eggs from the Penny River delta had consistent BDE congener patterns with a mean RSD of
7.2%; see Fig. 3). Because gulls are opportunistic predators and scavengers, their diet includes a broad range of items that vary from berries and fish to invertebrates, marine mammal carcasses and human refuse in landfills, which markedly increases their exposure to BDEs. Feeding on refuse in dumps may help explain the high variation in BDE concentrations and congener patterns. ΣBDE levels at Middleton Island were 162, 21, and 302 ng g\(^{-1}\) wet mass in eggs 664, 666, 669, respectively, compared to 3.3–34 ng g\(^{-1}\) wet mass in all of the other eggs analyzed during this study. Middleton Island supported an active Civil Aeronautics Authority (CAA) and Federal
Aviation Agency (FAA) Flight Service Station during the 1940s–1970s (the CAA was renamed the FAA in 1958). It also supported an active U.S. Air Force Aerospace Control and Warning Site (ACWS) from 1958 to 1963 and an active White Alice Communications Site (WACS) from 1956 to 1985. Since the mid-1980s, an automated National Weather Service weather radar and FAA flight service facility has been located on the island that is intermittently maintained by personnel that commute to the site from Anchorage. A small team of USGS scientists has also visited the island almost every summer since the late 1970s to study seabirds. Although current anthropogenic influences are minimal, some of the historical operations may still play roles in exposure to some types of contaminants (e.g., BDEs and PCBS leaching out of old dump sites) and a recent study has shown the impacts of research stations and BDE contamination of the local ecosystem in Antarctica (Hale et al., 2008).

Also, contaminant patterns may have varied among first-, second-, and third-laid eggs (see Verreault et al., 2006), and this factor may help explain some of the Middleton Island variation because two of the samples were from single eggs belonging to three-egg clutches (see Figs. 2 and 3 and Table 1). However, if this factor played a role, greater variation should have occurred at several of the other colonies where only single eggs from multi-egg clutches were analyzed (the other eggs belonging to these clutches were broken in transit).

PCB, DDT, and mirex levels in the eggs were generally lower than those found in the literature (Fig. 4). HCB was generally higher than the literature values with the exception of the Canadian gull eggs. Other contaminant concentrations were similar to reported levels, including those found during the most recent Alaskan gull study (Jack and Martinez, 2003).

3.3. Human consumption and environmental safety

In general, the gull eggs are safe for daily consumption based on the levels of organic contaminants observed in this study (Fig. 5). Schiordanes are of the most concern because in most cases a 70 kg person can only eat one to two eggs per day (range 1.5–4.7) before they exceed the recommended Canadian Acceptable/ Tolerable Daily Intake level (see Van Oostdam et al., 1999). Based on these same standards, a 70 kg person can consume at least 4 eggs per day before they exceed the recommended levels for the other contaminant groups. In comparison to other potential marine subsistence foods in Alaska, gull eggs are at least an order of magnitude greater in concentration than salmon (Oncorhynchus spp.; ADEC, 2008), similar to two times greater than walleye pollock (Theragra chalcogramma; de Brito et al., 2002), and similar to an order of magnitude lower than walrus (Odobenus rosmarus) and ringed seal (Phoca hispida) blubber (Kucklick et al., 2006).

Estimating environmentally safe consumption for individuals, populations, and predators is always difficult for contaminants. Few toxicological data exist for most species and contaminants are usually tested alone or in combination with only a few others in spite of the possible synergistic effects of large mixtures. Bustnes et al. (2003) conducted a three-year glaucous gull study that correlated male and female blood contaminant levels with survival and fitness endpoints. Using this data, egg burdens were estimated by multiplying the ratio of the egg concentrations to the male or female plasma concentrations (after converting them to wet mass based on the percent lipids) reported from the same colonies by Verreault et al. (2005) and these values were compared with the current results (see Supplemental Table 4). Given that laying dates appear to be negatively correlated with HCB, β-HCH, oxychlordane, DDE, and persistent PCBs (see Bustnes et al., 2003), the body mass and survival of the chicks, if they had been allowed to live, might have been lower than normal.

4. Conclusions

Contaminant levels in the gull eggs analyzed during this study were similar to murre egg values reported from these same regions,
and based on this information, they appear to be safe for humans to eat in small quantities, and the local public health authorities may be contacted for more personalized assessments. It is possible that chick growth and survival rates may have been affected by the contaminant concentrations. Some geographical separation was evident between the Chukchi/Bering sea and Gulf of Alaska colonies. More information is needed to help understand the large variations in contaminant levels found in the gull eggs from Middleton Island. STAMP plans to continue collecting and banking eggs from both gull species to monitor long-term trends and conduct retrospective analyses.

5. Disclaimer

Any mention of commercial products is for information only; it does not imply recommendation or endorsement by NIST.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.envpol.2008.11.026.

References


