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Chiral Organochlorine Contaminants in Blood and Eggs of Glaucous Gulls (*Larus hyperboreus*) from the Norwegian Arctic

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Glaucous gulls (*Larus hyperboreus*) and their eggs from Svalbard (Norwegian Arctic) have been used as biomonitors of contaminants in the marine environment. In this study, the enantiomer fractions (EFs) of chiral chlordanes and atropisomeric polychlorinated biphenyl (PCB) congeners were determined in the blood plasma of adult male and female glaucous gulls from three breeding colonies in Svalbard. Plasma EFs were similar in magnitude and direction to EFs previously reported in glaucous gulls from other arctic food webs, suggesting overall similarities in the biochemical processes influencing the EFs of bioaccumulated organochlorine (OC) contaminants within the food webs at those locations. Additionally, EFs in yolk of eggs collected concurrently from within the same nesting colonies varied with location, laying date, and OC concentrations, and may be influenced by changes in the local feeding ecology between those colonies. No differences were found between the EFs for any analyte in female gulls compared to those found in egg yolk, indicating that processes involved in the maternal transfer of chlordanes and PCBs to eggs do not modulate the stereochemical ratio between enantiomers. Therefore, the use of eggs as a valuable and noninvasive means of OC biomonitoring may also extend to enantiomer compositions in glaucous gulls, and perhaps also in other seabird species from arctic regions.

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Introduction

Despite the discontinued use of many organochlorine (OC) compounds, their environmental persistence continues to result in high concentrations in biota. Of particular concern are birds and mammals feeding at the top of the food webs. Glaucous gulls (*Larus hyperboreus*) breeding in Svalbard in the Norwegian Arctic occupy an apical position in the arctic marine food web, and they accumulate some of the highest body burdens of polychlorinated biphenyls (PCBs) and other legacy OC contaminants relative to other arctic avian species and populations (1). In addition, glaucous gulls accumulate a variety of pollutants of emerging environmental concern, such as brominated flame retardants (2, 3) and fluorinated compounds (4). High concentrations of organic contaminants have been linked to a variety of potentially chemical-induced biological effects in this species (5). Over the past decade, monitoring studies in the Norwegian Arctic have utilized glaucous gull whole blood, blood plasma, and eggs to monitor environmental contamination in the Norwegian Arctic (5–8).

Some OC contaminants are chiral, and are present in the environment as pairs of enantiomers (e.g., OC pesticides) or atropisomers (e.g., PCBs, hereafter referred to as enantiomers). Despite being released into the environment as racemic mixtures, nonracemic distributions of some chiral OC compounds have been detected in tissues of a variety of organisms. Nonracemic distributions are evidence of biological processes that alter these stereochemical ratios. Thus, enantioselective analysis provides a sensitive means of detecting such processes within individuals and/or food webs. Enantiomers may also possess different toxicological properties (9–11). For example, (+)-PCB 139 is a more potent inducer of ethoxresorufin-O-deethylase activity than (–)-PCB 139 in chick embryo hepatocyte cultures (10). Due to potential enantiospecific differences in toxicity, it is important to understand the exposure of organisms to individual enantiomers, particularly when exposure occurs during sensitive life-stages, such as during avian ovogenesis and chick development.

A number of environmental monitoring programs have routinely used the eggs of avian species to assess exposure levels of adult birds to environmental contaminants (1, 12), and to investigate maternal transfer of OC contaminants to eggs. Eggs are an advantageous medium to sample as they are generally easy to collect, and egg contaminant concentrations may directly reflect concentrations in the mother at the time of laying (13). Nonracemic distributions of some chiral OC pollutants have been found in the eggs of raptors and seabirds (14–17), although why those distributions arose is not fully understood. The enrichment or depletion of one enantiomer over the other in eggs may be due to the direct transfer of nonracemic proportions of OCs from the mother to the egg. Alternatively, the enrichment may be due to stereoselective maternal transfer of contaminants to eggs, or to microbial degradation in unfertilized eggs (15). To evaluate the reliability of eggs as an option for monitoring of chiral pollutants, we must understand the mechanism by which chiral contaminants are transferred to eggs, and the degree to which the distribution of enantiomers in eggs reflects that of the overall breeding adult population.

The objectives of the present study were 2-fold. The first was to determine the enantiomer distribution of chiral OC contaminants in the blood plasma of adult male and female glaucous gulls from Svalbard, and to compare these to known chiral distributions in other arctic populations. Second, enantiomer signatures were determined in the yolk of freshly

laid, unincubated eggs collected concurrently from within the same nesting colonies. These signatures were compared to those found in female glaucous gull plasma to determine whether the maternal transfer of OC contaminants occurs in a stereoselective manner, and to assess the feasibility of using eggs as a means of monitoring chiral signatures within a top predator seabird population.

Experimental Section

Sample Collection. Blood samples were collected from live-trapped adult male ($n = 19$) and female ($n = 30$) glaucous gulls from three breeding colonies less than 15 km apart on Bear Island (74°22'N, 19°05'E) in the Svalbard archipelago (Norwegian Arctic) during the nesting period between May and June 2006. Glupen, the southernmost colony, is part of the major seabird breeding colony, consisting mainly of black legged kittiwakes (*Rissa tridactyla*), northern fulmars (*Fulmarus glacialis*), and common and Brünnich's guillemots (*Uria aalge* and *Uria lomvia*., respectively). Teltvika is the northernmost breeding colony and is located furthest from the major seabird breeding colony. Kapp Harry is an intermediate site, located between Glupen and Teltvika. From each site, the third-laid egg from random three-egg clutches was collected concurrently ($n = 31$) from the same colonies shortly after laying (<3 days) and prior to any embryo development. Further details on the sampling location, animal capture, and sampling methods can be found elsewhere (2, 18).

Extraction and Cleanup. Sample extraction and cleanup was performed as described previously (5), with no modification. Briefly, plasma samples were denatured by addition of 1 mL of HCl and 3 mL of 2-propanol, and analytes were extracted by liquid-liquid extraction with 1:1 methyl-*tert*-butyl-ether/*n*-hexane. Whole eggs were separated into yolk and albumen components, and yolks were homogenized and ground with anhydrous Na₂SO₄. Egg homogenates were added to an extraction column and extracted with 45:55 dichloromethane/*n*-hexane. Lipids were removed from yolk samples by gel permeation chromatography. For yolk and plasma samples, four fractions, containing PCBs (fraction 1, F1), OC pesticides and byproducts (F2), heptachlor epoxide and dieldrin (F3), and aryl sulfones (F4), were collected by Florisil cleanup chromatography. All four fractions were quantified by achiral gas chromatography-mass spectrometry (GC-MS, see below). For stereoisomer analysis, the first three fractions were recombined and analyzed by enantioselective GC-MS.

Chemical Analysis. Achiral analyte separation and quantification was performed on an Agilent 6890 (Agilent Technologies, Palo Alto, CA) gas chromatograph-mass spectrometer (GC-MS) with electron impact (EI) ionization. Analytes were separated on a DB-5 column (30 m × 0.25 mm internal diameter, i.d. × 0.25 μm film thickness, df, J&W Scientific, Folsom, CA) as previously described (19).

Enantiomer analysis of PCB congeners was carried out on an Agilent 5890 GC-MS with EI ionization and selected ion-monitoring (20). A Chirasil-Dex column (25 m × 0.25 mm i.d. × 0.25 μm df, Varian, Walnut Creek, CA) was used for the separation of PCBs 95 and 149. A BGB-172 column (30 m × 0.25 mm i.d. × 0.18 μm df, Analytik, Adiswil, Switzerland) was used for the separation of PCB 183. All columns were calibrated with standard solutions containing all 209 PCB congeners to ensure that there were no interferences with coeluting homologous congeners (21). Furthermore, results of the enantiomer separation of PCBs 95 and 149 were confirmed with a Cyclosil-B column (30 m × 0.25 mm i.d. × 0.25 μm df, J&W Scientific, Folsom, CA). Data points with enantiomer fractions (see below) not in agreement between the two columns within ±0.03 were removed from the data set. All OC pesticides were analyzed

on an Agilent 6890 GC-MS in electron capture negative ionization mode (22), using methane as the reagent gas at a flowrate of 40 mL/min. Separation of oxychlordane and heptachlor epoxide was achieved on a BGB-172. *trans*-Chlordane and *cis*-chlordane were separated on a Betadex-120 column (30 m × 0.25 mm i.d. × 0.25 μm df, Supelco, Oakville, ON, Canada).

Data Analysis. Due to the partial coelution of some enantiomers, model-fitting software (PeakFit v.4.0, Systat, San Jose, CA) was used for peak integrations and the deconvolution of partially coeluting peaks as previously described (23–25). Enantiomer fractions (EFs) were used to quantify stereoisomer distributions (26). For compounds with unknown enantiomer elution order (PCB 95 on Chirasil-Dex and PCB 183 on BGB-172) (23), the EF is defined as the peak area of the first-eluted enantiomer (E1) divided by the sum area of both enantiomers (equation 1):

$$EF = \frac{E1}{E1 + E2} \quad (1)$$

For all other analytes (PCB 149, oxychlordane, heptachlor epoxide, *cis*- and *trans*-chlordane) the EF was determined using the peak areas of the (+) and (−) enantiomers (eq 2) (22, 27):

$$EF = \frac{(+)}{(+)+(-)} \quad (2)$$

Enantiomer fractions are presented as mean ±1 standard error unless otherwise noted. Racemic mixtures have a theoretical EF of 0.5, and mean measured EFs of all racemic standards ranged from 0.492 to 0.504, depending on the analyte (Table 1). Nonracemic distributions of analytes were determined by comparing median EFs of samples to that of standards (Mann–Whitney test). Nonparametric tests were used for this comparison only, due to the significant differences in the variances between the samples and standards. A one-way analysis of variance (ANOVA) with Tukey honestly significant-difference posthoc test was used to determine differences in EFs among categories (e.g., male plasma, female plasma, and yolk). For all statistical analyses, the level of significance was set at 0.05.

Results and Discussion

Achiral Analysis. A comprehensive discussion of the concentrations and congener/compound profiles of the present plasma samples is found in Verreault et al. (19). Concentrations of Σ₅₈PCB (58 congeners; PCB 31/28, 33/20, 52, 49, 47/48, 44, 42, 64/41, 74, 70/76, 95, 66, 56/60, 92, 101/90, 99, 97, 87, 85, 110, 151, 149, 118, 114, 146, 153, 105, 179, 141, 130, 176, 137, 138, 158, 178, 187, 183, 128, 167, 174, 177, 202, 171, 156, 200, 157, 172, 180, 170/190, 189, 199, 196/203, 208, 195, 207, 194, and 206) and Σ₆chlordane (oxychlordane, heptachlor epoxide, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, and *cis*-nonachlor) in plasma and yolk (Figure 1) were comparable to those previously reported in glaucous gull plasma and eggs from Svalbard (3, 18, 28, 29). Furthermore, consistent with previous studies in which samples also were collected shortly after egg laying (i.e., within three days following clutch completion), Σ₅₈PCB and Σ₆chlordane concentrations in female plasma were lower than those found in males. This concentration difference between sexes is evidence that females have transferred a portion of their OC contaminant body burden to their eggs (5, 28). All females in the present study had laid three eggs; therefore, the maternal transfer effect was consistent for all female birds. Lipid-normalized concentrations of Σ₅₈PCB and Σ₆chlordane were lower in yolk than in female plasma, which was consistent with previous studies (28).

Enantiomers in Adult Plasma. With the exception of *trans*-chlordane, all analytes quantified in plasma (*cis*-

TABLE 1. Mean Enantiomer Fractions of Analytes (± 1 Standard Error) in Racemic Standards, and Egg Yolk and Plasma Samples from Svalbard Glaucous Gulls^a

	standard	egg yolk	female plasma	male plasma	NOW
PCB 95	0.492 \pm 0.001 (n = 3)	0.523 \pm 0.059 (n = 3)	nd	nd	0.609 \pm 0.177 ^b
PCB 149	0.500 \pm 0.001 (n = 4)	0.226 \pm 0.009 (n = 31)	nd	nd	0.227 \pm 0.052 ^b
PCB 183	0.498 \pm 0.002 (n = 5)	0.451 \pm 0.010 (n = 30)	0.439 \pm 0.014 (n = 8)	0.434 \pm 0.028 (n = 6)	0.443 ^b
<i>trans</i> -chlordane	0.491 \pm 0.001 (n = 6)	0.581 \pm 0.013 (n = 20)	0.513 \pm 0.019 (n = 6)	0.557 \pm 0.073 (n = 2)	0.23 \pm 0.04 ^{c,d}
<i>cis</i> -chlordane	0.493 \pm 0.001 (n = 6)	0.255 \pm 0.009 (n = 28)	0.350 \pm 0.009 (n = 3)	0.267 \pm 0.042 (n = 2)	0.30 \pm 0.04 ^{c,d} 0.26 \pm 0.04 ^{c,e}
oxychlordane	0.504 \pm 0.001 (n = 6)	0.630 \pm 0.009 (n = 29)	0.634 \pm 0.012 (n = 19)	0.626 \pm 0.011 (n = 13)	0.63 \pm 0.01 ^{c,d} 0.65 \pm 0.03 ^{c,e}
heptachlor epoxide	0.502 \pm 0.002 (n = 5)	0.650 \pm 0.009 (n = 28)	0.680 \pm 0.012 (n = 10)	0.693 \pm 0.014 (n = 10)	0.62 \pm 0.01 ^{c,d} 0.61 \pm 0.07 ^{c,e}

^a Sample sizes are given in parenthesis. Mean ($\pm\sigma$) of EFs found in glaucous gull liver and muscle samples from the Canadian Arctic Northwater Polynya (NOW) are given for comparison. ^b Data obtained from Warner et al. (30). ^c Data obtained from Fisk et al. (14). ^d Enantiomer fractions found in liver samples. ^e Enantiomer fractions found in muscle samples.

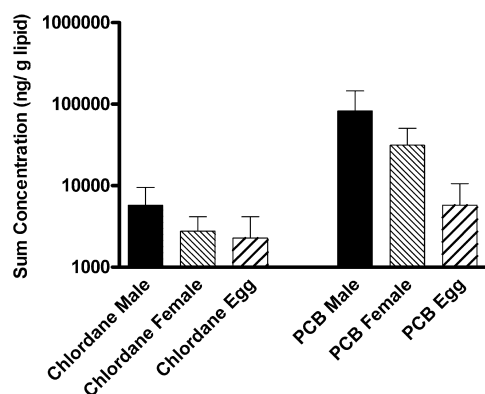


FIGURE 1. Mean ± 1 standard error of Σ_{58} PCB (58 congeners) and Σ_6 chlordane (six compounds) concentrations (ng/g lipid weight) in male plasma, female plasma, and egg yolk samples of glaucous gulls from Svalbard, Norwegian Arctic.

chlordane, *trans*-chlordane, oxychlordane, heptachlor *exo*-epoxide, and PCB 183, Table 1) had nonracemic EFs (EF \neq 0.5) (Figure 2). Plasma EFs of all analytes were not correlated either to extractable lipid percentage, breeding colony, or achiral Σ_{58} PCB or Σ_6 chlordane concentrations.

Enantiomer distributions of PCBs and chlordanes have previously been determined in liver and muscle tissue samples of glaucous gulls from the Northwater (NOW) polynya (14, 30) in northern Baffin Bay (Canadian Arctic). With the exception of *trans*-chlordane, the enantiomer distributions of all analytes from the present study were similar to those from the NOW, both in the magnitude and direction of the enantiomer enrichment (Table 1). The strong similarity in EFs between these two locations suggests overall similarities in the biochemical processes influencing the EFs of bioaccumulated OC contaminants within the food webs at those two locations, despite possible differences in age class, feeding ecologies, and reproductive status between the NOW birds and those of the present study. Nonracemic EFs in glaucous gulls may arise due to *in vivo* stereoselective biotransformation of the compounds (30, 31), and/or the uptake of food containing nonracemic distributions of these compounds (32). The biochemical pathways mediating the biotransformation of chiral OC compounds are assumed to

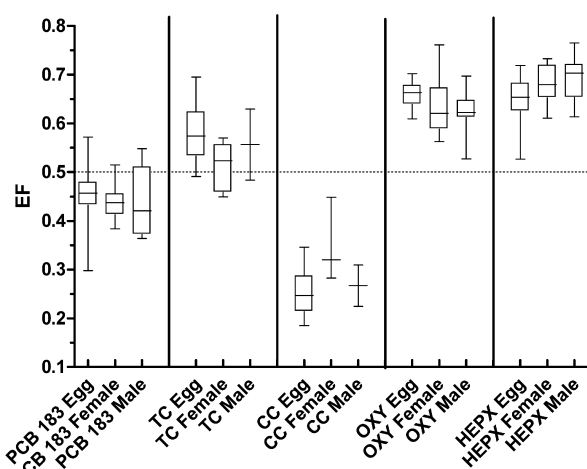


FIGURE 2. Enantiomer fractions (EF) of organochlorine compounds in egg yolk and plasma of glaucous gulls from Svalbard, Norwegian Arctic. Box plots are defined as follows: Center line, median; boxplot edges, 25th and 75th percentile; whiskers, range of data values. Dotted line represents racemic EF of 0.5. OXY, oxychlordane; TC, *trans*-chlordane; CC, *cis*-chlordane; HEPX, heptachlor epoxide.

be the same between individuals within a given species, and therefore the extent of biotransformation of chiral compounds between two populations of glaucous gulls is likely to be similar. The EFs observed in adult glaucous gull plasma were most likely steady-state EFs, as OC concentrations in blood of this species have been reported to reach steady-state levels after the first year of breeding (33). Previous studies have determined that wild mummichogs (*Fundulus* sp.) maintained near-constant EFs by continually taking up contaminants with enantiomer distributions which were closer to racemic (34). Therefore, in order for similar steady-state EFs to occur between these two populations, the birds must have a regular consumption of prey containing analogous enantiomer distributions of chiral compounds. It has been shown that glaucous gulls from Svalbard and the NOW polynya in the Canadian Arctic feed at similar trophic levels (35), although their opportunistic diets may include a wide variety of food items that may differ between these two

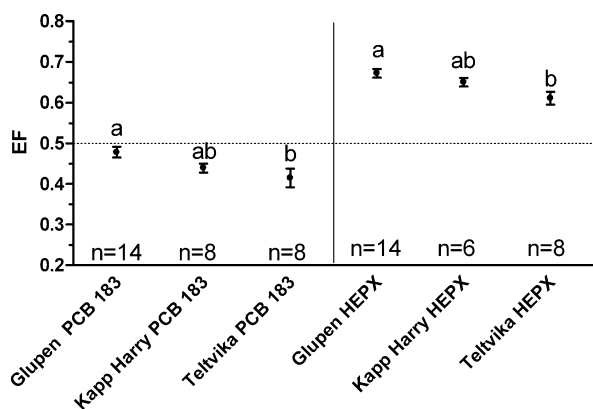


FIGURE 3. Enantiomer fractions (EFs) for organochlorine compounds in the egg yolk at the three breeding sites investigated in this study. Points indicate mean value, and error bars indicate standard error. EF distributions sharing a letter designation (a, b) are not statistically different. HEPX, heptachlor epoxide. Dotted line represents theoretical racemic EF (EF = 0.5).

populations. In general, the few studies investigating EFs in lower trophic level organisms from both Svalbard and the NOW polynya found that they contained EFs of most OC compounds which were closer to racemic than EFs measured in glaucous gulls from these arctic locations (30, 36–38). However, *trans*-chlordane was racemic or slightly enriched in the (+)-enantiomer in plasma and egg yolk, in contrast to enrichment of the (–)-enantiomer observed in the NOW polynya birds (14). While the reasons for this observation are unclear, it is possible this is a result of uptake of dietary items already enriched in the (+)-enantiomer. In the Svalbard region, chiral signatures of *trans*-chlordane were near racemic in whole Atlantic cod (*Gadus morhua*) (38) and marine invertebrates (39), while (–)-*trans*-chlordane was slightly enriched in muscle and blubber of ringed seals (*Pusa hispida*) from the NOW polynya (36), similar to what was also observed in glaucous gulls from this region. It is difficult to draw firm conclusions based on the data in this study, but clearly, further work needs to be done to understand the relative contributions of diet and of food web structure on the resulting EFs observed in upper trophic level predators.

Enantiomers in Eggs. For OC pesticides and metabolites, an enrichment of (–)-*cis*-chlordane was observed in yolk, while for *trans*-chlordane, heptachlor epoxide, and oxychlordane the (+)-enantiomer was enriched (Figure 2). Enantiomer fractions of only three PCB congeners (PCB 95, 149, and 183) were quantifiable in yolk; PCB 95 was racemic, while the PCBs 149 and 183 were nonracemic (Table 1).

There were significant differences in PCB 183 and heptachlor epoxide EFs between the Glupen and Teltvika breeding sites. Heptachlor epoxide EFs were more racemic, whereas EFs of PCB 183 deviated more from racemic at Teltvika compared to Glupen (Figure 3). The EFs of both analytes in the egg yolks from Kapp Harry fell in between and were not significantly different from EFs from the other sites. To our knowledge, this is the first time that local differences in EFs in any species of biota has been shown. In addition, this finding contrasts previous studies in ringed seals, which found no differences in chlordane EFs between nearby sample locations in the NOW polynya (36). PCB 183 and heptachlor epoxide EFs were also correlated with egg laying date and with total PCB and chlordane concentrations. With respect to egg laying date, EF signatures of heptachlor epoxide in eggs laid later in the breeding season deviated less from racemic ($p < 0.004$, $r^2 = 0.27$) than those laid earlier in the breeding season, while EFs of PCB 183 became less racemic as the breeding season progressed ($p < 0.002$, $r^2 = 0.32$) (Figure 4a). This observation may partially explain the

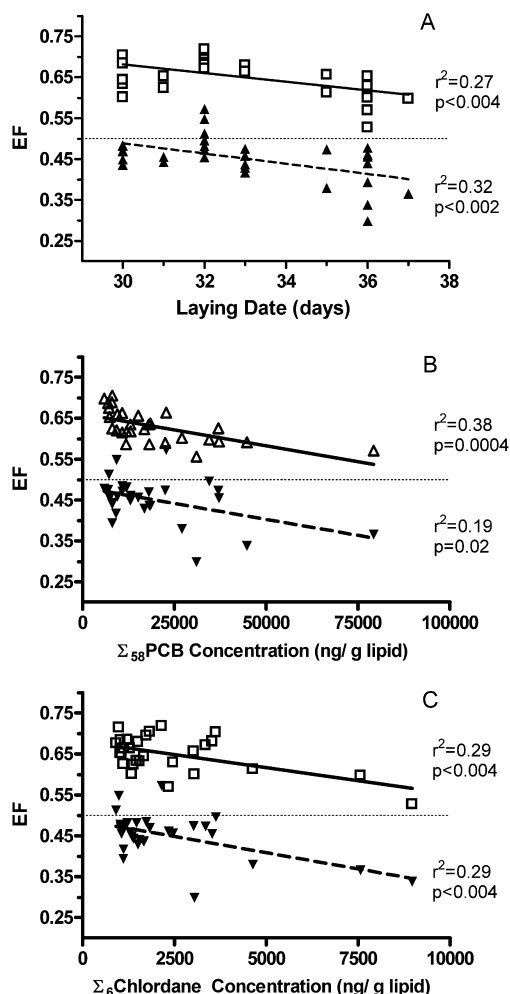


FIGURE 4. Linear regression of enantiomer fractions (EF) versus (A) laying date, expressed as days after May 1, 2006, (B) Σ_{58} PCB and (C) Σ_6 chlordane concentrations in glaucous gull egg yolk. ▼ PCB 183; □ Heptachlor Epoxide; Δ Oxychlordane (not shown in subfigure C for simplicity). Dotted line represents theoretical racemic EF (EF = 0.5).

differences in EFs between sites, as laying dates also varied between sites, with birds from Glupen laying eggs earlier than Teltvika, and birds from Kapp Harry having an intermediate laying date (40). Furthermore, EFs of PCB 183, oxychlordane, and heptachlor epoxide in eggs were correlated with egg Σ_6 chlordane concentrations (Figure 4c, $p < 0.004$, $r^2 = 0.29$, 0.28, and 0.29, respectively), while PCB 183 ($p = 0.02$ and $r^2 = 0.19$) and oxychlordane ($p = 0.0004$ and $r^2 = 0.38$) EFs in eggs were also correlated with egg Σ_{58} PCB concentrations (Figure 4b). At higher Σ_6 chlordane or Σ_{58} PCB concentrations, PCB 183 deviated more from racemic, whereas oxychlordane and heptachlor epoxide became more racemic. This trend was similar to what was found for location and laying date. However, there were no significant differences in concentrations of PCBs or chlordanes between nesting sites (40), although eggs laid later in the breeding season had higher concentrations of these two compound classes. Therefore, based on the present small sample size, it is unclear whether location or laying date had a greater effect on EFs, suggesting that other factors may be responsible.

The variation in EFs among locations and throughout the breeding period may be due to differences in the feeding ecologies between birds at the three nesting sites. In addition to contaminants in eggs only being derived from a long-term accumulation in the mothers (endogenous resources) and subsequent transfer to eggs, Verreault et al. (28) suggested

that a portion of the contaminant burden in glaucous gull eggs might originate from the transfer of recently ingested contaminants during the process of ovogenesis. If this is the case, then subtle changes in the diet of birds in different colonies or throughout the egg-laying period may impact the EF distribution in eggs, if those dietary items contained enantiomer compositions varying from those of the female gull. Variation in feeding ecology in relation to OC concentrations has been documented among neighboring nesting colonies of glaucous gulls from Bear Island (41). Glaucous gulls breeding near large seabird colonies, such as those from Glupen, supplement their diet with seabird eggs, chicks, and occasionally adult individuals. Thus, glaucous gulls from these colonies feed at a higher trophic level and are more contaminated than those breeding at sites farther from large aggregates of seabirds, which tend to feed more on lower trophic level organisms such as fish and crustaceans (40). Additionally, glaucous gulls may change their dietary preferences as the breeding season progresses, possibly to correspond with the egg laying of other seabirds (40). The concentrations and relative proportions of several organic pollutants in egg yolks from this study varied with location and laying date, indicating that location and/or feeding ecology may have significant impacts on the contaminants to which the gulls were exposed (40). These variations in feeding ecology and foraging strategies may lead to the uptake of dietary items containing contaminants of varying EF signatures, leading to differences in the EFs between sites and throughout the breeding season.

While it is clear that local differences existed in the egg EFs, due to the large number of potentially confounding variables in this study, it is unclear exactly how egg yolk EFs were impacted by ecological factors, such as laying date and foraging behavior. In addition, the effect of dietary composition on egg EFs cannot be fully ascertained, as there have been no studies to date investigating the EFs in lower trophic level prey species from Bear Island. This is the first time that EFs in eggs have been related to any ecological variables, and makes clear the need for further study on how feeding strategies and food web structures impact egg EFs.

Maternal Transfer. It has been hypothesized that nonracemic EFs of chiral contaminants in eggs may be the result of either stereoselective microbial degradation in unfertilized or abandoned eggs (16), stereoselective chemical transfer from the female to the eggs (15), or direct transfer of nonracemic distributions of chiral compounds from the female to the eggs (an achiral process). To distinguish among these hypotheses, we examined the EFs of several chiral contaminants in female glaucous gull plasma, and compared those to the EFs in freshly laid eggs collected from the same breeding colony. Because eggs were collected within three days of clutch completion, no microbial or metabolic degradation had likely taken place. For all analytes, no differences were observed between EFs in female plasma and in eggs, indicating that the transfer of the studied chemicals to eggs occurred nonstereoselectively.

Maternal OC residues are generally associated with lipidoidal material, and the contaminant residues which are transferred to the egg are predominantly derived from these endogenous stores, with an unknown portion from dietary intake (13). At the onset of ovogenesis, endogenous lipid stores are mobilized and transported by the bloodstream to the growing oocyte via lipoproteins (42). Previous studies have found that OC contaminants are associated with several different lipoproteins in blood, including low-density lipoproteins and very low-density lipoproteins, both of which constitute a large proportion of lipoproteins in the blood of laying hens and in the resulting yolk (42–44). This association with lipoproteins does not appear to be a stereoselective process, as the enantiomer distribution of several OC

compounds in plasma was similar to that in other tissues, including the liver (25, 45). The lipoproteins, containing both lipids and associated contaminants, are then taken by active transport across the cell membranes of the ovarian follicle. This active transport of proteins across the cell membranes is unlikely to be a process that is stereoselective for OC contaminants, as they are associated with achiral lipids, and are transported across the membrane in conjunction with these lipids. Therefore, the overall process should result in an enantiomer distribution in the eggs mirroring that found in the female. The results of our study are in agreement with this postulated mechanism.

Implications for Biomonitoring. The finding that chiral OC contaminants are transferred to eggs (based on the yolk fraction) nonenantioselectively, and that EFs in eggs are representative of those in female glaucous gull plasma, suggests that egg yolk may be used for biomonitoring of the enantiomeric distribution of chiral OCs in birds. Furthermore, there were no significant differences in EFs in both male and female plasma to EFs in egg yolk (ANOVA, $p > 0.05$). This observation suggests that egg EFs may be representative of the entire glaucous gull breeding population on Bear Island, rather than of females alone. It should be noted, however, that our results are for egg yolk homogenates. Analysis of whole egg homogenates, including the protein-rich albumen, may yield different results. Furthermore, we should point out that all eggs from this study were collected shortly after laying, and that the use of unfertilized or degraded eggs may yield different results due to possible microbial degradation of the analytes.

An understanding of the enantiomer distribution in avian top predators will allow for insight into the biochemical processing occurring within the food web, and the identification of atypical EFs may help identify disturbances or differences within the given food web (34). Furthermore, with an increased knowledge of enantiomer specific toxicity, the determination of the enantiomer distribution in eggs will allow for more accurate risk assessments in birds, by taking into account enantiomer-specific exposure. Given the information that can be gleaned from enantioselective analysis, we advocate its inclusion into biomonitoring programs.

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