Organobromine, Organochlorine and Metabolically-Derived Contaminants in Norwegian Arctic Glaucous Gulls: Associations with Whole Body Constituents

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Introduction. Monitoring of organohalogens in the glaucous gull (*Larus hyperboreus*) has been given high priority in Svalbard (Norwegian Arctic). Glaucous gulls are distributed widely in the Arctic and are an important avian scavenger-predator in the marine food web. Thus far among circumpolar arctic seabirds, glaucous gulls from Svalbard are reported to accumulate some of the highest concentrations of organohalogen contaminants. These include the metabolically-derived or -associated polychlorinated biphenyls (PCBs) (e.g., methylsulfonyl ($MeSO_2$)- and hydroxyl (OH)-PCBs) (Verreault et al., 2005a), and brominated flame retardants (e.g., polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCD)) and PBDE metabolites and/or naturally-occurring compounds with similar structures (MeO- and OH-PBDEs) (Verreault et al., 2005b).

Despite comprehensive surveys of organohalogen residues in various tissues and blood/plasma of Svalbard glaucous gulls, no attention has been paid to the physico-chemical properties that can influence toxicokinetics and by extension tissue-specific accumulation of compounds. Depending on physico-chemical properties such as functional groups and molecular structure, contaminant toxicokinetics can be altered due to, e.g., the type of halogenation (e.g., chlorine and bromine substitution), and particularly the presence or absence of additional phenyl group substituents (e.g., MeO and OH groups). Such fundamental characteristics of organohalogens are suggested to have great impact on their affinity to specific body constituents or macromolecules (Hakk & Letcher, 2003; Letcher et al., 2000). Therefore, the physico-chemical properties of a compound, including whether it is chlorinated or brominated and MeO-/OH-substituted or unsubstituted, would be expected to selectively influence its partitioning and accumulation within specific body compartments (e.g., blood) and tissues (e.g., liver and adipose tissue).

To our knowledge, there has not been an avian study investigating the total body burdens and patterns of chlorinated and brominated contaminants and their metabolites and/or naturally-occurring compounds with similar or analogous physico-chemical characteristics, and their associations to parameters of whole body composition (i.e., total water, protein, lipid and mineral contents). In the present study, we investigated the concentrations, total body burdens and compositional patterns of a large suite of persistent organohalogens: PCBs, chlordanes, PBDEs, PBBs, total-HBCD, $MeSO_2$-PCBs/-*p,p*'-DDE, OH-PCBs/-PBDEs, and MeO-PBDEs in liver, blood and whole body homogenate samples of adult glaucous gulls from Svalbard. Furthermore, we examined the relationships between the distribution of these organohalogens and metabolites and the total water, protein, lipid and mineral contents in whole body homogenates, and the toxicokinetics implications of some contaminants being less affected by lipid solubility and more influenced by, among others, protein associations.

Materials and Methods. The collection of adult glaucous gull samples (n = 11 females, 8 males) was conducted in Ny-Ålesund (79°N, 19°E) in the Svalbard archipelago during June and July 2002. For the

purpose of a validation study of water flux and body composition in glaucous gulls (Shaffer et al., 2006), individuals were assigned randomly to four treatment groups [group A (no food or water), group B (food only), group C (water only) and group D (both food and water)] to reflect the natural nutritional conditions of randomly-captured glaucous gulls in the field. Further details on the field protocol can be found in Shaffer et al. (2006). A detailed description of sampling (blood, tissues) and sample processing is provided by Verreault et al. (2005a). Glaucous gull carcasses were homogenized in a food grinder with (n = 9) or without (n = 10) feathers and skin. These two distinct carcass processing methods were utilized based on the assumption they may yield different body composition, and thus enhance the inter-individual variations in proportions of whole body constituents. Body composition analysis of whole glaucous gull carcasses generated total contents of water, minerals (mainly calcium and phosphorus), lipids and proteins.

The analytical procedures employed for the determination of non-polar and phenolic chlorinated and brominated compounds in glaucous gull samples were based on methods by Verreault et al. (2005a, b). Quantification of analytes was carried out using a GC-MS, and separation was performed using a fused silica DB-5 capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness). GC-MS(electron capture negative ionization (ECNI)) was used for all analytes except the PCBs and chlordanes, which where quantified using GC-MS(electron impact (EI)). GC-MS(ECNI) utilized methane as a buffer gas. GC-MS(ECNI) and GC-MS(EI) analyte determinations were accomplished in the selected ion-monitoring (SIM) mode.

Results and Discussion. The mean (±1 standard error) total burden of organohalogens and metabolites in present adult glaucous gull males and females (mean body mass: 1.49 ± 0.05 kg), calculated from the combined organohalogen concentrations in whole blood aliquots, liver and body homogenates, was 13.3 ± 1.98 mg (range: 3.3 – 33.0 mg). Based on the wide annual distribution and population size of Svalbard glaucous gulls, this is indicative of the relative importance of breeding glaucous gulls as biological vectors of organohalogen compounds within the Norwegian Arctic marine environment.

The contaminant patterns among glaucous gull samples were compared by examining the structure in the relationships between the proportions of major analyte classes and individual compounds to the total organohalogen concentration using the first two principal components (PC 1 and PC 2) in principal component analysis. Compound class distribution showed the relative proportions of sum (Σ) OH-PCB and ΣOH-PBDE to the total organohalogen concentrations were significantly highest in blood. Conversely, the Σchlordane and ΣPCB showed generally more pronounced accumulation in liver and whole body homogenates (Figure 1). No significant difference in the compositional patterns of individual congeners/compounds was found among tissues/blood, with the exception of the class comprised of neutral brominated compounds (PBDEs, PBBs and total-HBCD). Total-HBCD had significantly ($p \leq 0.001$) higher proportions in whole homogenate samples with and without feathers compared to blood and liver. In contrast, proportions of BDE47 and BDE99 were significantly ($p \leq 0.02$) greater in blood and liver comparatively to the two whole homogenate types.

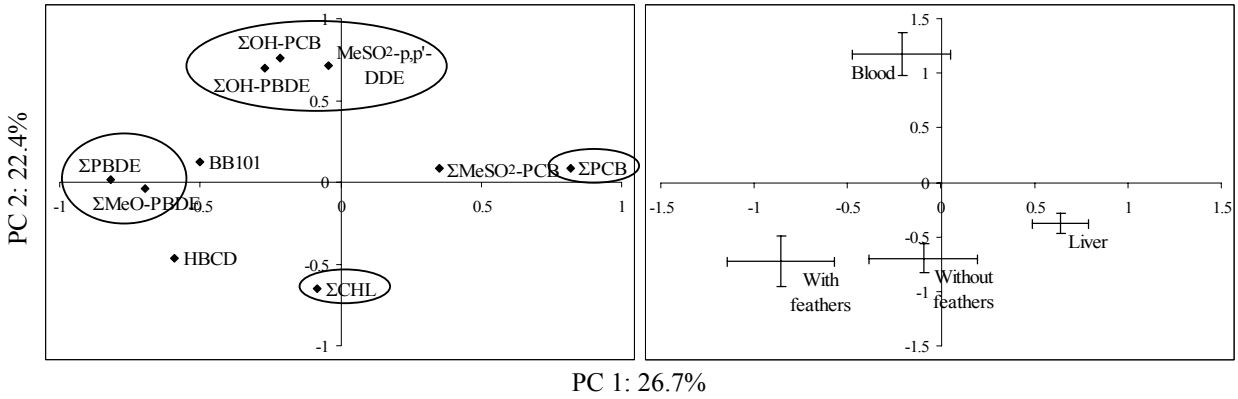

Figure 1. Proportions of ten major chlorinated and brominated contaminant classes or individual compounds to the total organohalogen concentrations plotted using the two first principal components (PCs), PC 1 and PC 2. Mean (± 1 standard error) factor scores (right biplot) are showed for blood, liver and whole body homogenate samples (with or without feathers) of Svalbard glaucous gulls. Compounds with significant factor loadings (i.e., ≥ ± 0.65) on PC 1 or PC 2 are encircled.

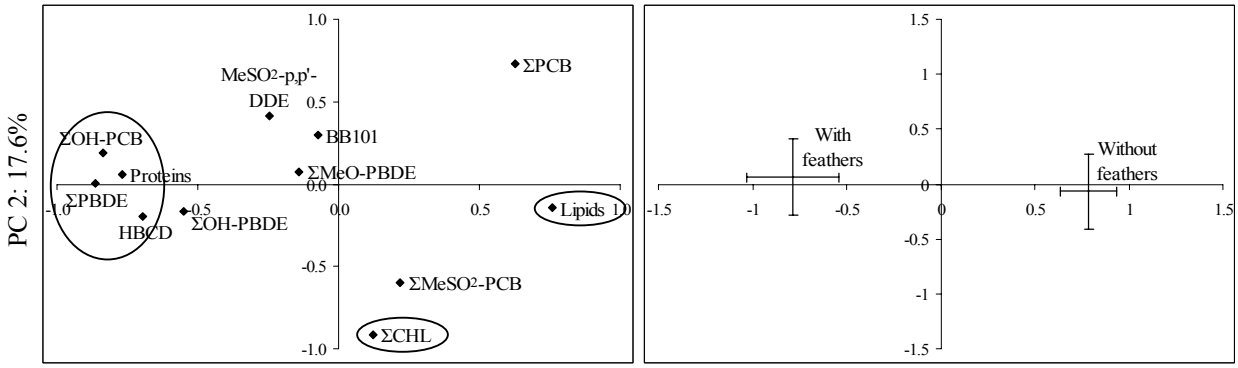

Figure 2. Proportions of ten major chlorinated and brominated contaminant classes or individual compounds to the total organohalogen concentrations, as well as proportions of lipid and protein contents to the total body composition, plotted using the two first principal components (PCs), PC 1 and PC 2. Mean (± 1 standard error) factor scores (right biplot) are showed for whole body homogenates processed with or without feathers in Svalbard glaucous gulls. Compounds with significant factor loadings (i.e., ≥ ± 0.65) on PC 1 or PC 2 are encircled.

Compound patterns in whole glaucous gull carcasses (homogenized with or without plumage) with known body composition were investigated using a similar PC approach as described in the previous section. Total proteins isolated from the whole body homogenates of glaucous gulls were significantly associated to the proportions of ΣOH-PCB and ΣPBDE (Figure 2). Hence, contents of proteins in whole carcasses correlated positively with proportions of ΣOH-PCB ($r^2 = 0.36$; $p = 0.008$) and ΣPBDE concentrations ($r^2 = 0.41$; $p = 0.004$). A consistent, but non-significant tendency was found for the total-HBCD and ΣOH-

PBDE proportions. A non-significant association was found between total lipids and the ΣPCB proportions.

The present study of glaucous gulls supports generally enhanced protein (e.g., albumin, transthyretin) association for selected major PCB and PBDE compounds with phenyl group substituents (i.e., OH) that modify physico-chemical characteristic such as polarity, but also PBDEs and total-HBCD. However, substances typically shown as having lipophilic properties such as PCBs, chlordanes and to some extent PBDEs and $MeSO_2$-PCBs/-*p,p*-DDE, did not show clear association with the bulk lipid content isolated from homogenized glaucous gull carcasses. The present study suggests that tissue-specific protein and lipid contents play an important role, together with numerous other biochemical processes, in the toxicokinetics and fate of chlorinated and brominated contaminants and metabolic and natural products. An enhanced, selective retention of certain of these organohalogen classes in given tissues/body compartments may thus lead to site-specific toxicological actions and adverse effects in the highly-contaminated Svalbard glaucous gulls. Further studies are warranted to investigate the mechanisms of macromolecule binding interactions and organohalogen accumulation in avian species.

References.

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