LEGACY ORGANOCHLORINES, MERCURY, PBDEs, AND EMERGING HALOGENATED FLAME RETARDANTS IN GLAUCOUS GULLS FROM EASTERN NUNAVUT

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KEY MESSAGES

- ✓ Stable isotope profiles of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in liver and two feather types of breeding glaucous gulls from Cape Dorset, Eastern Nunavut, suggest that birds feed higher up in the food chain during the winter compared to the breeding period. Alternatively, this may suggest that winter and summer ranges differ in isoscapes.
- ✓ Concentrations of PCBs, organochlorine pesticides, and PBDEs determined in Cape Dorset glaucous gull liver were lower than those reported elsewhere in glaucous gull populations (e.g., Svalbard). Exposure to Hg and MeHg, however, appears to be higher in this particular area of the Canadian Arctic.
- ✓ BDE-209, the principal component in the deca-BDE mixture, was remarkably the most abundant PBDE congener determined in most liver samples of Cape Dorset glaucous gulls. BDE-209 was positively correlated with $\delta^{15}N$ in liver of males, thus pointing out to a more recent dietary input and accumulation of this compound in the local food wed.
- ✓ This study revealed for the first time the presence of six emerging halogenated flame retardants (HFRs) in liver of glaucous gulls from the Canadian Arctic including HBB, DP (*anfi* and *syn* isomers), PBEB, EHTBB, and BEHTBP. Some of these emerging HFRs are suggested replacement products for the recently banned PBDE mixtures.

BACKGROUND

Large gulls in the Arctic are predominantly omnivorous and occupy high trophic levels in the marine food web. As a consequence, they are chronically exposed to a wide array and occasionally elevated concentrations of trace elements and organic contaminants (Letcher et al., 2010, Sci. Total Environ. 408:2995–3043). These include Hg, legacy organochlorines (e.g., PCBs, DDTs, chlordanes, etc.), and PBDEs, but also an increasingly more complex "cocktail" of emerging contaminants. These comprise the alternative or replacement HFR compounds to the banned PBDE mixtures (penta- and octa-BDE) in consumer products to achieve fire safety standards, in which many may fulfill the criteria of persistence, propensity for bioaccumulation, and toxicity (Covaci et al., 2011, Environ. Int. 37:532–556). Examples of emerging HFRs of growing environmental concern are: hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), pentabromoethylbenzene (PBEB), bis(2-ethylhexyl)-tetrabromophthalate (BEHTBP), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), Dechlorane Plus (DP), and decabromodiphenyl ethane (DBDPE). The occurrence of emerging HFRs in birds from the Canadian Arctic regions has as yet not been the subject of any studies.

OBJECTIVE

The objective of the present project was twofold:

1) Screen for a comprehensive suite of legacy and emerging halogenated organic contaminants and Hg in glaucous gulls (*Larus hyperboreus*) breeding off Cape Dorset, Eastern Nunavut, and
2) investigate the influence of diet on the concentrations of these contaminants based on stable isotope signature ($\delta^{13}C$ and $\delta^{15}N$).

METHODS

Sample Collection

Fig. 1: Map of the Canadian Arctic showing the study site. Samples (liver and feathers) of breeding male and female glaucous gulls (n = 31) were collected in June-July 2012 from colonies located on islands off the community of Cape Dorset (Kinngait), Eastern Nunavut.

Stable Isotope Analysis

Stable carbon (^{13}C) and nitrogen (^{15}N) isotope analyses were conducted at the GEOTOP research center, University of Quebec in Montreal, according to methods described by Caron-Beaudoin et al. (Can. J. Zool., available online Aug. 1st, 2013). Isotopic measurements were performed using a continuous flow isotope ratio mass spectrometer (MS) coupled to an elementary analyzer.

Hg Analysis

Total Hg and MeHg analyses were conducted at the GEOTOP research center, University of Quebec in Montreal, using methods by Pichet et al. (Springer, Berlin, 1999, pp. 41–52). Concentrations were determined using atomic fluorescence.

Organochlorine Analysis

Organochlorines were analyzed at the Great Lakes Institute for Environmental Research (GLIER), University of Windsor. Chemical extraction, clean-up, and analysis of PCBs and organochlorine pesticides and by-products followed the procedures of Lazar et al. (Chemosphere 1992, 25:493–504). Analysis was performed using a gas chromatograph with mass selective detector (GC-MSD) operated in the electron impact (EI) mode, and using selected ion monitoring (SIM) mode.

PBDEs and Emerging HFR Analysis

Analysis of PBDEs and eight emerging HFRs was carried out at the University of Quebec in Montreal. Analysis of PBDEs/HFRs was performed using a GC-MS operating in the electron capture negative ionization mode (ECNI) following methods by Gentes et al. (Environ. Sci. Technol. 2012, 46:9735–9744). Quantification of PBDEs/HFRs was achieved using SIM mode.

RESULTS

Stable Isotope Profiles

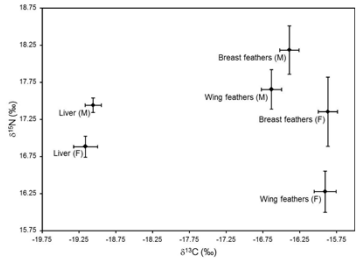


Fig. 2: Mean (± SE) $\delta^{13}C$ and $\delta^{15}N$ (‰) in breast and wing feathers, and liver of female (F) and male (M) glaucous gulls breeding off Cape Dorset, Eastern Nunavut. Two feather types and liver were selected to investigate dietary component assimilation over short time frames: post-breeding period (secondary wing feathers: October-November, 2011), winter (breast feathers: January-March 2012), and breeding period (liver: June-July 2012).

Mercury and Organochlorines

Table 1. Lipid content (%), moisture (%) and concentrations of mercury (Hg and MeHg; µg/g dry weight), PCBs and organochlorines (ng/g wet weight) in liver of female and male glaucous gulls breeding off Cape Dorset, Eastern Nunavut.

	Females (n = 14)			Males (n = 17)		
	Samples >MLOD	Mean ± SE	Range	Samples >MLOD	Mean ± SE	Range
Lipid %	-	5.38 ± 0.65	2.99 – 11.1	-	4.12 ± 0.27	1.79 – 5.78
Moisture %	-	67.3 ± 0.36	64.3 – 68.9	-	69.7 ± 1.34	64.7 – 90.3
Total Hg	100%	7.04 ± 0.63	2.80 – 11.6	100%	9.74 ± 1.09	3.55 – 20.0
MeHg	100%	1.19 ± 0.72	0.23 – 4.08	100%	0.98 ± 0.20	0.45 – 1.33
ΣCBz	100%	56.2 ± 4.99	26.3 – 88.4	100%	87.8 ± 7.99	52.9 – 157
OCS	100%	0.44 ± 0.1	0.24 – 0.88	100%	0.62 ± 0.1	0.38 – 1.17
Mirex	100%	7.07 ± 0.84	2.22 – 13.8	100%	15.1 ± 1.24	6.29 – 23.9
ΣHCH	100%	10.4 ± 1.46	5.13 – 26.2	100%	16.5 ± 1.73	8.3 – 29.7
ΣDDT	100%	233 ± 33.2	85.7 – 433	100%	519 ± 45.9	244 – 891
ΣCHL	100%	128 ± 13.4	65.5 – 267	100%	250 ± 21.2	127 – 413
Dieldrin	100%	35.6 ± 3.45	18.7 – 68.6	100%	53.8 ± 5.09	24.4 – 112
ΣPCB	100%	346 ± 63.9	118 – 951	100%	716 ± 59.5	302 – 1,175

PBDEs and Emerging HFRs

Table 2. Lipid content (%) and concentrations of PBDEs and emerging HFRs (ng/g wet weight) in liver of female and male glaucous gulls breeding off Cape Dorset, Eastern Nunavut. Means were computed only if at least 50% of the samples had concentrations above the analyte-specific method limit of detection (MLOD).

	Females (n = 14)			Males (n = 17)		
	Samples >MLOD	Mean ± SE	Range	Samples >MLOD	Mean ± SE	Range
Lipid %	-	6.22 ± 0.64	4.33 – 13.4	-	±	-
ΣPBDE	93%	7.24 ± 3.07	<MLOD – 34.6	94%	24.5 ± 5.46	<MLOD – 66.3
DBDPE	0%	-	<MLOD	0%	-	<MLOD
PBEB	29%	-	<MLOD – 0.01	47%	-	<MLOD – 0.01
HBB	29%	-	<MLOD – 0.53	59%	0.07 ± 0.02	<MLOD – 0.32
BTBPE	0%	-	<MLOD	0%	-	<MLOD
EHTBB	36%	-	<MLOD – 0.92	47%	-	<MLOD – 0.85
BEHTBP	21%	-	<MLOD – 2.05	12%	-	<MLOD – 2.58
syn-DP	21%	-	<MLOD – 0.30	65%	0.18 ± 0.06	<MLOD – 0.71
anti-DP	21%	-	<MLOD – 0.42	59%	0.16 ± 0.05	<MLOD – 0.77

RESULTS

Fig. 3: Mean (± SE) concentrations (ng/g wet weight) of 17 PBDE congeners detected in at least 50% of the liver samples of male glaucous gulls breeding off Cape Dorset, Eastern Nunavut.

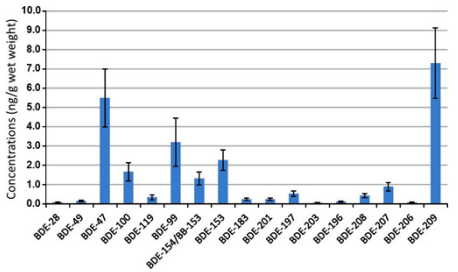
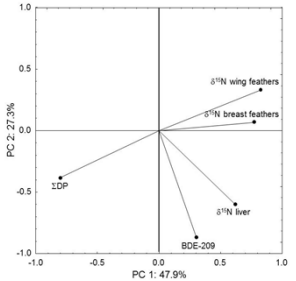


Fig. 4: Ordination diagram based on principal components analysis on the correlation matrix of ΣDP (sum of *anti* and *syn* isomers) and BDE-209 liver concentrations (ng/g wet weight) as well as $\delta^{15}N$ (‰) determined in liver and breast and wing feathers of male glaucous gulls breeding off Cape Dorset, Eastern Nunavut. The relative percentage of the total variance explained by each of the principal components (PCs) is provided.



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