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Unusually high Deca-BDE concentrations and new flame retardants in a Canadian Arctic top predator, the glaucous gull

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HIGHLIGHTS

- Arctic wildlife is exposed to numerous long-range transported pollutants.
- We investigated emerging flame retardants in Canadian Arctic glaucous gulls.
- Unusually high levels of BDE-209 were found in liver of males and females.
- Organophosphate esters were found at greater levels in female gulls.
- Correlations were found between contaminants and stable isotopes in tissues.

GRAPHICAL ABSTRACT

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ABSTRACT

Despite a sustained effort in surveying flame retardants (FRs) in wildlife from industrialized regions, their occurrence in birds or any other wildlife species spanning the Arctic regions, particularly in North America, has received limited attention. This study investigated in the top predator glaucous gull (*Larus hyperboreus*) breeding in the Eastern Canadian Arctic (Cape Dorset, Nunavut) a comprehensive suite of FRs including unstudied halogenated and non-halogenated FRs of potential health concern, along with legacy organochlorines and mercury. The influence of diet acquired locally and in wintering areas on the tissue contaminant profiles was also investigated using $\delta^{15}N$ and $\delta^{13}C$ signatures in liver and feathers. The principal constituent in the Deca-brominated diphenyl ether (BDE) mixture, BDE-209, was remarkably the most concentrated PBDE congener determined in liver samples of Eastern Canadian Arctic glaucous gulls. This suggests dietary exposure from the local marine food web and perhaps also from nearby community landfills. Moreover, this study revealed for the first time the presence of 16 emerging halogenated and non-halogenated FRs in glaucous gulls from this Arctic region including HBB, DDC-CO (*anti* and *syn* isomers), PBEB, EHTBB, BEHTBP as well as a series of organophosphate esters (OPEs) (TCEP, TCIPP, TPP, TDCIPP, TDBPP, TBNP, TBOEP, TBEP, TCrP, EHDPP, and TEHP). With the exception of BDE-209, concentrations of other halogenated FRs and organochlorines were found to be in the lower range in liver of Eastern Canadian Arctic glaucous gulls compared to individuals from other circumpolar populations (Svalbard and Greenland). Mercury and methylmercury concentrations, however, were greater than reported elsewhere for glaucous gull populations.

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1. Introduction

Flame retardants (FRs) are chemicals used in consumer products (e.g., upholstered furniture, electric and electronic devices, vehicles, etc.) to meet fire safety standards. These compounds have received notorious attention worldwide due to their widespread distribution in the environment and the inherent risks this may pose to wildlife and human health. Among the most widely used additive halogen-containing FRs, polybrominated diphenyl ethers (PBDEs) have been detected globally in nearly all ecosystems, including the Arctic and Antarctic regions (AMAP, 2016). A bulk of studies suggest that several biological systems (e.g., mainly endocrine, immune, and reproductive) of chronically-exposed wildlife species to PBDEs can be adversely affected, including birds (Guigueno and Fernie, 2017). The cumulative evidence on the persistence, bioaccumulation propensity, and toxicity of PBDEs have led to their inclusion in 2009 (Penta- and Octa-BDE mixtures) in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs) (Stockholm Convention, 2009). Recently, Deca-BDE (composed of >97% BDE-209) was regulated in Canada (Canada Gazette, 2015), in the European Union (European Chemicals Agency, 2014), and listed under the Stockholm Convention on POPs (Stockholm Convention, 2017).

In response to international regulations on PBDE mixtures, emerging FR classes are being used by the chemical industry as replacement products in a wide range of commercial applications. Examples of emerging halogenated and non-halogenated FRs of potential environmental concern include decabromodiphenyl ethane (DBDPE), 1,2 bis (2,4,6 tribromophenoxy)ethane (BTBPE), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), bis(2 ethylhexyl) tetrabromo phthalate (BEHTBP), 2 ethylhexyl 2,3,4,5 tetrabromobenzoate (EHTBB), Dechlorane Plus (DDC-CO), and a suite of organophosphate esters (OPEs) used as FRs and plasticizers in a variety of products (Covaci et al., 2011; Sverko et al., 2011; Bergman et al., 2012; van der Veen and de Boer, 2012; Greaves and Letcher, 2017). Some of these emerging FRs (including OPEs) have been reported, among others, in eggs of Great Lakes herring gulls (*Larus argentatus*) (Greaves et al., 2016; Su et al., 2015), eggs of European starlings (*Sturnus vulgaris*) collected from various Canadian sites (Lu et al., 2017; Chen et al., 2013), as well as in tissues of ring-billed gulls (*Larus delawarensis*) breeding in the Montreal area (QC, Canada) (Gentes et al., 2012).

Despite a sustained effort in surveying FRs in birds (mainly gulls) from industrialized regions in North America, their occurrence in birds or any other wildlife species spanning the North American Arctic regions has received limited attention (AMAP, 2017; Letcher et al., 2010). Reports on OPEs in arctic biota and wildlife are extremely scarce, especially for birds. Among the limited number of reports in arctic wildlife, in Hudson Bay and East Greenland polar bears (*Ursus maritimus*) (fat), OPEs were recently reported at very low and mostly non-detectable levels (Letcher et al., 2018; Strobel et al., 2018). Generally low to moderate levels of nine OPEs were also reported in samples collected from 2007 to 2010 in Svalbard (Norwegian Arctic), and including the liver of arctic fox (*Vulpes lagopus*) and kittiwakes (*Rissa tridactyla*), blood of polar bear and harbour seal (*Phoca vitulina*), blubber of ringed seal (*Pusa hispida*), and eggs of Brünnich's guillemot (*Uria lomvia*) and glaucous gull (*Larus hyperboreus*) (Hallanger et al., 2015). In another study on OPEs in birds, Eulaers et al. (2014) reported mean concentrations six OPEs (4–110 ng/g ww) in the feathers and sub-ng/g ww levels in the plasma of white-tailed sea eagle nestlings (*Haliaeetus albicilla*) from central Norway. The exposure-related biological effects of emerging FRs, and including OPEs, especially in avian wildlife are to date largely unstudied (Chen and Hale, 2010; Covaci et al., 2011; Sverko et al., 2011; Marteinson et al., 2012; Greaves and Letcher, 2017; Guigueno and Fernie, 2017), thus warranting investigations in the most susceptible species from temperate and Arctic regions.

Large gulls in the Arctic occupy high trophic positions in the marine food web, and thus are chronically exposed to a wide array and occasionally elevated concentrations of trace elements and organic contaminants. As such, the top predator glaucous gull has served as an ideal sentinel of temporal and spatial distribution as well as exposure-related effects of contaminants in several Arctic regions, mainly in the Norwegian Arctic (Svalbard) (Verreault et al., 2010; Letcher et al., 2010). PBDEs (including BDE-209), HBB, BTBPE, PBEB and pentabromotoluene (PBT) were detected at low levels in plasma and eggs of glaucous gulls collected in 2006 from this Norwegian Arctic region (Verreault et al., 2007a). Canadian Arctic glaucous gulls were also reported to accumulate mercury, organochlorines (e.g., PCBs, DDT, chlordanes, etc.) (Peck et al., 2016) and PBDEs (Braune et al., 2015), although at concentrations several-fold lower than those reported in Norwegian Arctic glaucous gulls. There is currently no study that has investigated the accumulation of current-use FRs (e.g., emerging FRs including OPEs) in glaucous gulls or any other seabirds from the Canadian Arctic (AMAP, 2017; Letcher et al., 2010).

The objective of the present study was to determine a comprehensive suite of established (PBDEs) and current-use halogenated and non-halogenated FRs (including OPEs) in glaucous gulls breeding in Nunavut (Eastern Canadian Arctic). A second objective was to investigate in this top predator species the accumulation of mercury and selected legacy organochlorines (e.g., PCBs, DDT, chlordanes, etc.) for which data are lacking in the Eastern part of the Canadian Arctic for any wildlife species. The influence of diet on the accumulation profiles of these contaminants was investigated using stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in two tissues (feathers and liver) that provided information on nutrient assimilation in different periods of the year, including the wintering and nesting periods (Kelly, 2000; Post, 2002).

2. Materials and methods

2.1. Sample collection

Liver samples and feathers of breeding glaucous gulls (n = 14 females and 17 males) were collected in June–July 2012 from colonies located on islands off the community of Cape Dorset (NU, Eastern Canadian Arctic; 64°13′54″ N, 76°32′25″ W) (Fig. S1). Based on knowledge of feather molting sequence in glaucous gulls (Gaston A., Environment and Climate Change Canada, pers. comm.), two feather types (wing and breast) were collected for dietary assessment during the previous year using stable isotope profiles (Section 2.6). Specifically, wing feathers (secondaries) were used to represent nutrient assimilation during the post-breeding period (October–November 2011), while those from the breast represented the winter period (January–March 2012). Liver stable isotope profiles provided dietary information at the regional scale one month prior to sampling and during the sample collection period (May–July 2012). Liver was also used for chemical analysis (Sections 2.2, 2.3, 2.4, and 2.5). Liver samples and feathers were transported on ice in the dark while in the field, and kept thereafter in a −30 °C freezer until laboratory analyses.

Capture and handling methods were approved by the Institutional Committee on Animal Care (CIPA) of the Université du Québec à Montréal (permit no. 771), which complies with the guidelines issued by the Canadian Council on Animal Care (Ottawa, ON, Canada). Permits to collect glaucous gulls were issued by the Canadian Wildlife Service (Environment and Climate Change Canada; Ottawa, ON, Canada), Government of Nunavut (Iqaluit, NU, Canada) and Nunavut Impact Review Board (Cambridge Bay, NU, Canada).

2.2. PBDE and halogenated FR analysis

Glaucous gull liver samples were analyzed for 38 PBDE congeners and eight emerging halogenated FRs (see full compound list in Table 1) at the Université du Québec à Montréal following methods described by Houde et al. (2014) with minor modifications. Briefly, liver samples (~1 g) were homogenized with diatomaceous earth, spiked