Environmental Research 134 (2014) 46–56

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

A geographical comparison of chlorinated, brominated and fluorinated compounds in seabirds breeding in the eastern Canadian Arctic ☆

Birgit M. Braune [a,*], Anthony J. Gaston [a], Robert J. Letcher [a], H. Grant Gilchrist [a], Mark L. Mallory [b], Jennifer F. Provencher [c]

[a] Environment Canada, National Wildlife Research Centre, Carleton University, Raven Road, Ottawa, Ontario, Canada K1A 0H3
[b] Biology Department, Acadia University, Wolfville, Nova Scotia, Canada B4P 2R6
[c] Department of Biology, Carleton University, Ottawa, Ontario, Canada K1S 5B6

ARTICLE INFO

Article history:
Received 15 May 2014
Received in revised form
19 June 2014
Accepted 20 June 2014

Keywords:
Canadian Arctic
Seabirds
Organochlorines
Polybrominated diphenyl ethers
Perfluorinated compounds
Spatial analysis

ABSTRACT

A suite of chlorinated, brominated and fluorinated organic contaminants were measured in livers of adult thick-billed murres (*Uria lomvia*) and northern fulmars (*Fulmarus glacialis*) from several locations in the eastern Canadian Arctic during 2007–2008. Thick-billed murres were collected from five colonies (Coats Island, Digges Island, Akpatok Island, Prince Leopold Island, Minarets) and northern fulmars from two colonies (Prince Leopold Island, Minarets). Legacy organochlorines (e.g. PCBs, DDT, chlorobenzenes, chlordanes) and perfluorooctane sulfonate (PFOS) dominated the compositional profiles of the measured halogenated compounds in the livers of both species at all colonies. Among the murre colonies sampled, Prince Leopold Island birds generally had the highest mean concentrations of organochlorines, whereas the highest mean concentration of sum (Σ) polybrominated diphenyl ethers (PBDEs) was found at the Minarets and the lowest at Prince Leopold Island. PBDEs were detected in only a few fulmar livers from the Minarets and in none of the fulmar livers from Prince Leopold Island. Mean PFOS concentrations were highest in both murre and fulmar livers at Prince Leopold Island. PFOS was approximately two orders of magnitude higher than the mean sum (Σ) perfluorinated carboxylate (PFCA) concentration in both species and at all colonies. The reasons for inter-colony and inter-species differences in contaminant liver levels are probably variable and complex, and likely reflect differences in contaminant transport and exposure pathways, as well as differences among colonies in their diets and overwintering areas. To our knowledge, this is the first spatial assessment of PBDEs, PFCAs and PFOS in seabirds from the Canadian Arctic.

1. Introduction

A growing number of persistent chlorinated, brominated and fluorinated organic contaminants have been shown to be ubiquitous in arctic biota including avian wildlife (Braune et al., 2005; Butt et al., 2010; de Wit et al., 2010; Letcher et al., 2010). These chemical contaminants are, for the most part, transported there by air and/or ocean currents (Macdonald et al., 2000). Air is the most important transport route to the Arctic for volatile and semi-volatile contaminants (Wania, 2003), but not for non-volatile compounds that include per- and poly-fluoroalkyl substances (PFASs) such as the perfluorinated sulfonates (PFSAs) and carboxylates (PFCAs). PFSAs and PFCAs of varying carbon chain lengths have been found in a wide variety of arctic wildlife (Butt et al., 2010; Houde et al., 2011; Letcher et al., 2010). It has been proposed that neutral, volatile precursor compounds of PFCAs and PFSAs, such as fluorotelomer alcohols (FTOHs) and sulfonamide alcohols, undergo long-range atmospheric transport and are degraded in remote regions (Ellis et al., 2004; Martin et al., 2006; Schenker et al., 2008; Young and Mabury, 2010). Alternatively, ionizable PFASs, such as the more water-soluble and less volatile PFSAs and PFCAs, could be transported directly to the arctic marine environment via ocean currents (Armitage et al., 2006; Wania, 2007).

Upon reaching the Arctic, most persistent pollutants biomagnify through food webs making those species feeding at higher trophic levels more vulnerable to exposure via their diet (Borgå et

☆*Funding sources*: Financial support was provided by International Polar Year 2007–2009, Aboriginal Affairs and Northern Development Canada (Northern Contaminants Program and Northern Scientific Training Program), the Arctic Institute of North America (Grant-in-Aid Program), Natural Sciences and Engineering Research Council of Canada (NSERC), and the Nasivvik Centre for Inuit Health and Changing Environments which is supported by Université Laval and Trent University.

Research approval: collections were made in accordance with guidelines from the Canadian Council on Animal Care, and under appropriate territorial and federal research permits.

* Corresponding author. Fax: +1 613 998 0458.
E-mail address: birgit.braune@ec.gc.ca (B.M. Braune).

http://dx.doi.org/10.1016/j.envres.2014.06.019
0013-9351/

al., 2004; Braune et al., 2005; Butt et al., 2010; de Wit et al., 2010; Hop et al., 2002; Houde et al., 2011; Vorkamp et al., 2004; Wolkers et al., 2004). Seabirds such as thick-billed murres (*Uria lomvia*) and northern fulmars (*Fulmarus glacialis*) feed at relatively high trophic positions in arctic marine food webs (Hobson et al., 2002; Hop et al., 2002) making them ideal sentinel species for a spatial analysis of persistent organohalogens.

A spatial survey of contaminants in Canadian Arctic seabirds was carried out in 1993 and included thick-billed murres from four locations: two in the Canadian high Arctic, and two in northern Hudson Bay. Concentrations of many of the legacy persistent organic pollutants (POPs), such as PCBs and DDT, differed significantly in eggs of murres between one of the high Arctic colonies and the other colonies sampled (Braune et al., 2002). To our knowledge, no spatial data have been reported for PFASs or brominated compounds in Canadian Arctic seabirds.

As part of a recent study assessing changes in diets of arctic marine birds (Mallory et al., 2010; Provencher et al., 2012), adult thick-billed murres and northern fulmars were collected from several locations in the eastern Canadian Arctic during 2007–2008. In this paper, we present data on contaminants in livers from those birds to: (i) determine recent spatial patterns for a range of known and persistent organochlorines, and (ii) examine spatial patterns for suites of more recently discovered contaminants such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and PFASs in seabirds.

2. Materials and methods

2.1. Sample collection

During 2007–2008, adult thick-billed murres were collected from waters adjacent to five colonies in the eastern Canadian Arctic: Coats Island (62°98′N, 82°00′W), Digges Island (62°33′N, 77°35′W), Akpatok Island (60°58′N, 68°08′W), Prince Leopold Island (74°02′N, 90°00′W), and Akpait (also known as the "Minarets") (67°00′N, 61°80′W) on eastern Baffin Island (Fig. 1). Adult northern fulmars were collected from two areas: Prince Leopold Island and waters adjacent to the breeding colonies at the Minarets and Cape Searle (67°15′N, 62°35′W), about 30 km apart. Sampling details can be found in Provencher et al. (2009, 2012) and Mallory et al. (2010). The murres from Coats Island and the Minarets were collected in late July–early August 2007, and the rest of the birds were collected in August 2008. All female birds were assumed to be breeding birds based on the presence of brood patches.

Livers of five male and five female birds from each species and sampling location (except Coats Island) were removed and stored in acetone-hexane rinsed glass vials for subsequent organohalogen analysis. At Coats Island, only female murres were sampled in adequate numbers ($n=5$ females). Liver samples were shipped to the National Wildlife Research Centre (NWRC) in Ottawa, Ontario, where they were homogenized and stored at −40 °C. All birds were taken under appropriate research and collection permits.

2.2. Chemical analyses

2.2.1. Organochlorines

Liver homogenates were individually analyzed for organochlorines (OCs) including chlorobenzenes (ΣCBz = 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene), hexachlorocyclohexanes (ΣHCH = α-, β- and γ-hexachlorocyclohexane), chlordane-related compounds (ΣCHL = oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and heptachlor epoxide), DDT and its metabolites (ΣDDT = *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT), octachlorostyrene (OCS), mirex, dieldrin and PCB congeners (ΣPCB). Measurements for 71 PCB congeners, as identified according to IUPAC numbers (Ballschmiter et al., 1992), were reported: 16/32, 17, 18, 22, 28, 31, 33/20, 42, 44, 47/48, 49, 52, 56/60, 64/41, 66, 70/76, 74, 85, 87, 92, 95, 97, 99, 101/90, 105, 110, 114, 118, 128, 130, 137, 138, 141, 146, 149, 151, 153, 156, 157, 158, 167, 170/190, 171, 172, 174, 176, 177, 178, 179, 180, 183, 187, 189, 194, 195, 196/203, 199, 200, 202, 206, 207, and 208. However, only 59 congeners were detected: 28, 31, 44, 47/48, 49, 52, 56/60, 64/41, 66, 70/76, 74, 85, 87, 92, 95, 99, 101/90, 105, 110, 114, 118, 128, 130, 137, 138, 141, 146, 149, 151, 153, 156, 157, 158, 167, 170/190, 171, 172, 177, 178, 179, 180, 183, 187, 189, 194, 195, 196/203, 199, 200, 206, 207, and 208. Congeners that are separated above by a slash chromatographically co-eluted during the separation process and are therefore reported together.

Samples were analyzed for organochlorines by gas chromatography using a mass selective detector (GC/MSD) and lipids were determined by gravimetric methods. Chemical extraction and cleanup of PCBs and organochlorine pesticides followed the procedures of Lazar et al. (1992). Briefly, tissue homogenates were ground with anhydrous sodium sulfate, spiked with labeled ^{13}C-OC/PCB quantification standards and extracted with dichloromethane:hexane (50:50% v/v). Sample clean-up was performed by gel permeation chromatography followed by activated Florisil chromatography. Chemical analysis was performed using a capillary gas chromatograph (Agilent 6890N) coupled with a mass selective detector (Agilent 5973N) operated in electron impact (EI) mode. The column was a 30 m × 0.25 mm × 0.25 μm DB-5 column. PCBs and organochlorine pesticides were determined using an external quantification approach as described by Drouillard and Norstrom (2003). Three duplicate extractions, one duplicate injection, two method blanks and four in-house reference materials (DCCO Reference Egg Pools DCCOQA-2008-12 and DCCOQA-2009-01, HERG Reference Egg Pools HERGQA-2008-20 and HERGQA-2009-01) were run for quality control. Internal standard recoveries averaged 93 ± 1.4% (mean ± SE). Therefore, residues were not corrected for internal standard recoveries. The nominal detection limit was 0.1 ng g^{-1} wet weight (ww).

2.2.2. Brominated contaminants

Liver homogenates were analyzed for PBDEs, two polybrominated biphenyls (PBBs) and total-(α)-HBCDD. Sample extraction and clean-up were the same as for the organochlorines except that tissue homogenates were spiked with an internal standard (BDE-30). Using this method, it has been shown the BDE-30 is a representative internal standard for the PBDEs, PBBs and HBCDD (Chen et al., 2012). Chemical analysis for 13 BDE congeners (BDE-17, -28, -47, -49, -66, -85, -99, -100, -138, -153, -154 (co-elution with BB-153), -183 and -190), BB-101 and total-(α)-HBCDD was performed using an Agilent 6890 gas chromatograph (GC) equipped with a 5973 quadrupole mass spectrometer (MS) detector run in electron capture negative ionization (ECNI) mode. The GC column was a 15 m × 0.25 mm × 0.1 μm DB-5HT capillary column. The determination of α-HBCDD by GC–MS is representative of total-HBCDD, as low levels of β- and γ-HBCDD isomer residues are thermally isomerized to α-HBCDD in the injection port at temperatures exceeding 160 °C (Chen et al., 2012).

PBDEs, HBCDD and PBBs were identified on the basis of their retention times on the DB-5HT GC columns relative to authentic standards. Three duplicate extractions, one duplicate injection, two method blanks and the same four in-house reference materials identified for the organochlorine analysis were run for quality control. Quantification of the brominated compounds was performed using an internal standard method based on the relative ECNI response factor of the ^{79}Br + ^{81}Br anions of BDE-30 and to that of authentic congener standards in the neutral fractions. The method limit of quantification (MLOQ) was 0.1 ng g^{-1} ww for all PBDE and PBB congeners, and for HBCDD, the MLOQ was 1 ng g^{-1} ww. The recovery efficiency of BDE-30 averaged 104 ± 2.1% (mean ± SE). All reported residue levels were inherently corrected for recovery as the internal standard quantification approach was used.

BDE-153 and BDE-154 have very similar physical–chemical characteristics (Tittlemier et al., 2002) and published data for biota show that BDE-154 generally occurs at lower or similar concentrations to BDE-153 (e.g., Elliott et al., 2005; Hites, 2004; McKinney et al., 2011; Norstrom et al., 2002). Given that BDE-153 was detected in only 11% of our samples compared with 60% for BDE-154/BB-153, and where both were quantified, concentrations of BDE-153 were consistently lower than for BDE-154/BB-153, we concluded that BDE-154/BB-153 was likely comprised of over 90% BB-153 and, therefore, was not included in the calculation of ΣPBDE concentrations. ΣPBDE was standardized to the sum of BDE-17, -28, -49, -47, -66, -100, -99, -85, -153, -138, -183 and -190.

2.2.3. Per- and poly-fluoroalkyl substances (PFASs)

The PFAS extraction, cleanup and analysis have been described elsewhere (Gebbink and Letcher, 2012; Greaves et al., 2012). Briefly, approximately 1 g of liver homogenate was spiked with labeled internal standards and extracted with 10 mM KOH acetonitrile/water. The cleanup and fractionation of the overall PFAS extract was performed using Waters Oasis WAX solid phase extraction (SPE) cartridges. The first fraction contained FTOHs and FOSAs; the second fraction contained PFSAs, PFCAs and fluorotelomer unsaturated acids (FTUCAs). The separation of the target compounds in both fractions was carried out on a Waters 2695 HPLC equipped with an ACE 3 C_{18} analytical column (50 mm × 2.1 mm I.D., 3 μm particle size, Advance Chromatography Technologies, Aberdeen, UK) coupled to a Waters Quattro Ultima triple quadrupole mass spectrometer (Waters, Milford, MA, USA). Analysis of PFCAs, PFSAs and FTUCAs was done using negative electrospray ionization (ESI^{-}), and the FTOHs and FOSAs were analyzed by negative atmospheric pressure photoionization (APPI^{-}). Quantification was performed using an internal standard approach. Standards for the PFSAs [C_4 (PFBS), C_6 (PFHxS), C_8 (PFOS), C_{10} (PFDS)], PFCAs (C_6–C_{15} chain lengths: PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA and PFPA, respectively), 6:2, 8:2 and 10:2 FTUCAs, 6:2, 8:2 and 10:2 FTOHs, and two FOSAs [perfluorooctanesulfonamide (PFOSA), methylated perfluorooctanesulfonamide (N-Me-FOSA)] as well as all internal labeled standards were obtained from Wellington Laboratories (Guelph, ON, Canada). See Table S1 for a complete listing of all of the above PFASs as well as the ^{13}C- or ^{18}O-enriched internal standards used. All solvents used were HPLC grade and purchased