Science of the Total Environment 646 (2019) 551–563

Contents lists available at ScienceDirect

Science of the Total Environment

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

Temporal trends of legacy organochlorines in eggs of Canadian Arctic seabirds monitored over four decades

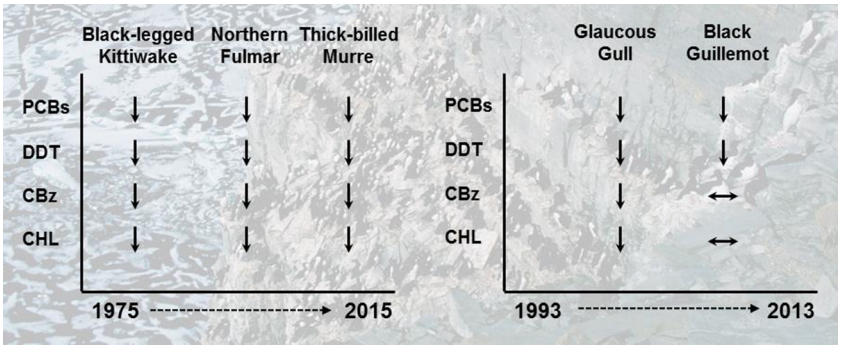
Birgit M. Braune [a,*], Anthony J. Gaston [a,1], Mark L. Mallory [b,c]

[a] Environment and Climate Change 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] Canada Fulbright Chair in Arctic Studies, University of Washington, Box 353650, Seattle, WA, USA, 98195-3650

HIGHLIGHTS

- The major organochlorines found in seabird eggs were Σ_{35}PCB, ΣDDT, ΣCBz and ΣCHL.
- Most legacy organochlorines declined since 1975 in Canadian Arctic seabird eggs.
- Most of the declines occurred during the 1970s to 1990s.
- β-HCH continues to increase in eggs of most Canadian Arctic seabird species.
- Glaucous gulls generally had the highest organochlorine concentrations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 June 2018
Received in revised form 19 July 2018
Accepted 20 July 2018
Available online 21 July 2018

Editor: D. Barcelo

Keywords:
Canadian Arctic
Seabird eggs
Organochlorine pesticides
PCBs
Temporal trends

ABSTRACT

We compared temporal trends of legacy organochlorine pesticides and PCBs in eggs of five seabird species breeding at Prince Leopold Island in the Canadian high Arctic. Concentrations of most of the major organochlorine groups/compounds have either declined (e.g. Σ_{35}PCB, ΣDDT, ΣCBz, ΣCHL, octachlorostyrene) or shown no consistent directional change (e.g. heptachlor epoxide) since 1975 in eggs of thick-billed murres (*Uria lomvia*), northern fulmars (*Fulmarus glacialis*) and black-legged kittiwakes (*Rissa tridactyla*). Aside from β-HCH, which increased in most species, the major organochlorine compounds either declined or showed no trend between 1993 and 2013 in eggs of five seabird species (thick-billed murre, northern fulmar, black-legged kittiwake, black guillemot *Cepphus grylle*, glaucous gull *Larus hyperboreus*). Most of the declines occurred during the 1970s to 1990s followed by little change during the 2000s. Glaucous gull eggs had the highest concentrations of almost all organochlorines in the five years compared (1993, 1998, 2003/04, 2008, 2013), and murre eggs generally had among the lowest concentrations. The primary organochlorines found in eggs of all five species were Σ_{35}PCB, ΣDDT (mainly *p,p′*-DDE), ΣCBz (mainly hexachlorobenzene) and ΣCHL (mainly oxychlordane) although proportions varied by species and year. The major PCB congeners found in eggs of all five species were CB-153, -138, -118 and -180. The penta-, hexa- and heptachlorobiphenyl homologs comprised the largest proportion of Σ_{35}PCB in all five species. Although levels of most legacy organochlorines have declined since 1975, the potential for climate change to alter chemical transport pathways as well as exposure pathways in the biotic environment could affect temporal trends. Therefore, it is important to continue to monitor these legacy contaminants in order to determine how these changes will affect the temporal trends observed to date.

* Corresponding author.
E-mail address: birgit.braune@canada.ca (B.M. Braune).
[1] Retired.

https://doi.org/10.1016/j.scitotenv.2018.07.291
0048-9697/

1. Introduction

The presence of persistent organic pollutants (POPs) has been monitored in the Arctic environment since the early 1970s (AMAP, 2016; NCP, 2013; Rigét et al., 2010). Those POPs which have been banned or regulated under international conventions, such as the Stockholm Convention on POPs (http://chm.pops.int) and the United Nations Economic Commission for Europe (UN ECE) Convention on Long-range Transboundary Air Pollution (LRTAP) Protocol on POPs (http://www.unece.org/env/lrtap/pops_h1.html), are often referred to as "legacy" POPs because present day contamination or re-emissions are primarily related to a "legacy" of past releases (Rigét et al., 2010). As a result of national and international efforts to reduce emissions, legacy POPs, such as organochlorine pesticides (e.g. DDT) and PCBs, have generally declined in the Arctic environment (AMAP, 2016; NCP, 2013). Declining trends of legacy POPs observed in Arctic biota are consistent with decreasing trends in Arctic air which reflect the historic decreases in emissions (AMAP, 2016; Rigét et al., 2010). However, there is renewed interest in legacy POPs due to the potential for climate change to alter chemical transport pathways as well as exposure pathways in the biotic environment (Borgå et al., 2010; Ma et al., 2011) which could affect temporal trends.

The statistical power of a time-series to detect a trend increases with the number of years of sampling data (Fryer and Nicholson, 1993). For most Arctic time-series, the statistical power to detect a trend of the magnitude typically observed for Arctic biota is rather low (AMAP, 2016; Rigét et al., 2010). Contaminant time-series for seabird eggs sampled from the Canadian high Arctic have provided the highest power and among the lowest detectable trends for Arctic biota (AMAP, 2016). At the time of egg formation, lipophilic organochlorine compounds are transferred along with lipids to the eggs thus reflecting the relative contaminant burden of the various POPs in the female at the time of laying (Braune and Norstrom, 1989; Verboven et al., 2009). Therefore, eggs are an ideal and relatively non-intrusive sampling medium.

Eggs of thick-billed murres (*Uria lomvia*), northern fulmars (*Fulmarus glacialis*) and black-legged kittiwakes (*Rissa tridactyla*) have been monitored for environmental contaminants at Prince Leopold Island, Nunavut, in the Canadian high Arctic since 1975 (Braune, 2007). As of 1993, eggs of black guillemots (*Cepphus grylle*) and glaucous gulls (*Larus hyperboreus*) have also been monitored for contaminants at that location. Four of those species, the thick-billed murre (a.k.a. Brünnich's guillemot), northern fulmar, black-legged kittiwake and black guillemot, feed in the marine environment (Bradstreet, 1980; Butler and Buckley, 2002; Hatch et al., 2009; Mallory et al., 2012; Matley et al., 2012; Provencher et al., 2012), while the glaucous gull feeds in both marine and terrestrial environments (Weiser and Gilchrist, 2012), although the gulls at Prince Leopold Island probably feed principally on marine prey during the breeding season (Matley et al., 2012; Nettleship et al., 1990). Despite the fact that they all have a marine-based diet during the breeding season, their trophic positions vary considerably (Braune et al., 2016), thus influencing their exposure to contaminants.

The objectives of this study were to: (i) compare concentrations of legacy organochlorine contaminants as well as PCB congener patterns in eggs of five seabird species breeding in the Canadian high Arctic, (ii) examine temporal trends of legacy organochlorines in eggs of those same five seabird species to determine if the trends among species are similar over a given time period, and (iii) extend the time-series data for organochlorines in eggs of three of those seabird species previously reported by Braune (2007).

2. Materials and methods

2.1. Sample collection and preparation

During 1975–2015, eggs of thick-billed murres, northern fulmars, black-legged kittiwakes, black guillemots, and glaucous gulls were collected from the Prince Leopold Island Migratory Bird Sanctuary (74°02′N, 90°05′W) in Lancaster Sound, Nunavut, Canada (Fig. S1). Murre and fulmar eggs were sampled in 1975, 1976, 1977, 1987, 1988 (murre eggs only), 1993, 1998, 2003, annually from 2005 to 2014, and in 2015 (fulmar eggs only). Kittiwake eggs were sampled in 1975, 1976, 1987, 1993, 1998, 2003, 2008, and 2013; black guillemot eggs in 1993, 1998, 2004, 2008, and 2013; and glaucous gull eggs in 1993, 1998, 2003, 2008, and 2013. Thick-billed murres and northern fulmars lay a single egg, whereas black-legged kittiwakes and glaucous gulls may lay up to three eggs (Gaston et al., 2005). Black guillemots generally lay one or two eggs (Butler and Buckley, 2002). Eggs were sampled randomly on the basis of one egg per nest as soon after laying as was possible. Eggs were collected by hand or using a small cup attached to the end of an extension pole. All eggs were taken under appropriate annual research and collection permits.

Eggs were kept cool in the field and shipped to the National Wildlife Research Centre (NWRC), Ottawa, Ontario, for processing and chemical analyses. Egg contents were homogenized and stored frozen (−40 °C) in acetone-hexane rinsed glass vials for subsequent organochlorine analysis. The validity of this storage method has been previously discussed (see Braune, 2007).

Three to 15 eggs per species per year were analyzed (see Tables S1–S5 for sample sizes). Egg homogenates from 1975 to 2005 were analyzed for organochlorines and $\delta^{15}N$ as pooled (composite) samples with each pool comprising equal aliquots of three individual eggs, with the exception of glaucous gull eggs sampled in 1993, which were analyzed as pools of two eggs each. Eggs sampled during 2006–2015 were also analyzed for organochlorines as pooled samples but were individually analyzed for $\delta^{15}N$.

2.2. Organochlorine analysis

Organochlorine analyses were carried out at NWRC. Archived samples collected prior to 1998 were retrieved from the National Wildlife Specimen Bank at NWRC and analyzed retrospectively in 1998–99 in order to standardize pooling and analytical protocols which varied over earlier years of sampling. Archived eggs of black guillemots and glaucous gulls collected in 1993 were re-analyzed in 2006 for the same reasons. Samples collected from 1998 to 2015 were analyzed within six months of collection. Pooled egg homogenates were 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), heptachlor epoxide (HE), chlordane-related compounds (ΣCHL = oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor and *cis*-nonachlor), DDT and its metabolites (ΣDDT = *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT), octachlorostyrene (OCS), mirex (ΣMirex = photomirex and mirex), dieldrin and PCB congeners (ΣPCB). ΣPCB was standardized to 35 congeners identified according to IUPAC numbers (Ballschmiter et al., 1992): 18, 17 (or 18/17), 31/28, 33 (or 33/20), 52, 49, 44, 74, 70 (or 70/76), 95, 101 (or 101/90), 99, 87, 110, 151, 149, 118, 153, 105, 158, 138, 187, 183, 128 (or 128/167), 177, 171, 156, 180, 170 (or 170/190), 199, 208, 195, 194, 206. Congeners separated by a slash co-eluted during the chromatography process and were therefore reported together.

Samples were analyzed for organochlorines by capillary gas chromatograph coupled with a mass selective detector (GC/MSD) operated in selected ion monitoring electron impact mode and lipids were determined by gravimetric methods. Chemical extraction and cleanup of PCBs and organochlorine pesticides in samples from 1975 to 2014 followed the procedures of Lazar et al. (1992). Tissue homogenates were ground with anhydrous sodium sulfate, spiked with labeled ^{13}C-OC/PCB internal standards and extracted with dichloromethane:hexane (50:50% v/v). Sample clean-up was performed by gel permeation chromatography followed by activated Florisil® column chromatography. Samples analyzed in 2015 were homogenized with diatomaceous