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Declining trends of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and non-*ortho* PCBs in Canadian Arctic seabirds☆

Birgit M. Braune [a, *], Mark L. Mallory [b]

[a] Environment and Climate Change Canada, National Wildlife Research Centre, Carleton University, Raven Road, Ottawa, Ontario, K1A 0H3, Canada
[b] Biology Department, Acadia University, Wolfville, Nova Scotia, B4P 2R6, Canada

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ABSTRACT

Polychorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs) such as the non-*ortho* PCBs (nPCBs) persist in the environment despite international measures to ban their emissions. We determined congener patterns and temporal trends for PCDDs, PCDFs, nPCBs as well as their toxic equivalents (TEQs) in eggs of thick-billed murres (*Uria lomvia*) and northern fulmars (*Fulmarus glacialis*) sampled from Prince Leopold Island in the Canadian Arctic between 1975 and 2014. The dominant PCDD congeners were 1,2,3,7,8-PnCDD, 2,3,7,8-TCDD and 1,2,3,6,7,8-HxCDD, and the dominant PCDF congener was 2,3,4,7,8-PnCDF. The nPCB profile was dominated by PCB-126. The TEQ profile in the murre eggs was dominated by nPCB-TEQ whereas in the fulmar eggs, the PCDF-TEQ contribution to ΣTEQ was slightly greater than that of nPCB-TEQ. Concentrations of ΣPCDD, ΣPCDF, ΣnPCB and ΣTEQ declined between 1975 and 2014 in both murre and fulmar eggs. Based on TEQ thresholds in the literature for other species, and taking into account the trend towards declining TEQ levels, it is unlikely that current levels of PCDDs, PCDFs or nPCBs are affecting the reproductive success of thick-billed murres or northern fulmars in the Canadian Arctic.

1. Introduction

Polychorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are persistent organic pollutants which have been found in wildlife around the world, including the Arctic (Addison et al., 2005; Braune and Simon, 2003; Braune et al., 2005; de March et al., 1998). PCDDs and PCDFs enter the environment as by-products of industrial processes such as the combustion of chlorine-containing waste, especially plastics, wood burning and other combustion, metal production and, more historically, manufacturing of chlorophenol-based biocides and chlorine bleach pulping of wood (de March et al., 1998; Fiedler, 2007; Zook and Rappe, 1994). PCBs were used in various industrial materials such as transformer and capacitor oils, hydraulic and heat exchange fluids, lubricating oils, and plasticizers (de March et al., 1998; Rice et al., 2003). The use of PCBs was phased out nationally and regionally during the 1970–90s (de March et al., 1998), and in 2004, PCBs, PCDDs and PCDFs were globally banned under the Stockholm Convention on Persistent Organic Pollutants (http://www.pops.int). However, despite being regulated, these compounds continue to persist in the environment (Breivik et al., 2004, 2007; Schiavon et al., 2016).

PCBs, PCDDs and PCDFs are semivolatile, hydrophobic compounds which can undergo long-range atmospheric transport to remote regions such as the Arctic (Wania, 2003; Wania and Su, 2004). Given their chemically stable and lipophilic characteristics, these compounds tend to bioaccumulate in wildlife and biomagnify in food chains. Bioaccumulation and toxicity of PCDDs and PCDFs is related to structure and, in birds, is generally associated with a 2,3,7,8-chlorine substitution pattern (Braune and Norstrom, 1989; Rice et al., 2003; Van den Berg et al., 1994). For PCBs, bioaccumulation and toxicity is also structure-dependent with the non-*ortho*-substituted coplanar PCBs, which are structurally similar to the 2,3,7,8-substituted PCDDs and PCDFs, being the most toxic (Giesy and Kannan, 1998; Rice et al., 2003). PCDDs, PCDFs and non-*ortho* PCBs (nPCBs) have a similar mechanism of toxicity mediated by the AhR receptor and, in birds, toxicological effects may range from adverse effects on reproduction and development to immunotoxicity and hepatotoxicity, although sensitivity appears to vary among species (Augspurger et al., 2008; Harris and Elliott, 2011;

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

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Karchner et al., 2006; Rice et al., 2003). In order to quantify these dioxin-like effects, toxic equivalency factors (TEFs) were developed to express the relative toxic potency of PCDD, PCDF and PCB congeners against 2,3,7,8-TCDD, considered the most potent congener within these groups of compounds (Van den Berg et al., 1998), although recent studies suggest that some PCDFs (i.e. TCDF, PeCDF) may have a higher potency than TCDD in some avian species (Cohen-Barnhouse et al., 2011; Farmahin et al., 2012; Hervé et al., 2010; Yang et al., 2010). Toxic equivalent concentrations (TEQs) have been widely used to evaluate the toxicity of these groups of compounds.

Temporal trends have been reported for many of the legacy persistent organic pollutants in Arctic biota (Rigét et al., 2010). However, available time series data for PCDDs and PCDFs in Arctic biota are limited (Muir and de Wit, 2010). Seabird eggs have been used to monitor contamination in the marine environment of the Canadian Arctic since 1975 (Braune, 2007; Braune et al., 2005, 2015). Concentrations of PCDDs, PCDFs and nPCBs have been reported in eggs of ivory gulls (*Pagophila eburnea*) collected in 1976, 1987 and 2004 from Seymour Island in the central Canadian Arctic (Braune et al., 2007), and the presence of PCDDs, PCDFs and nPCBs have been reported for seabird eggs and livers sampled in 1975 and 1993 from Prince Leopold Island in the Canadian high Arctic (Braune and Simon, 2003). In this study, we examine compositional profiles and temporal trends of PCDDs, PCDFs and nPCBs in eggs of two seabird species, the thick-billed murre (*Uria lomvia*) and northern fulmar (*Fulmarus glacialis*), from Prince Leopold Island.

2. Methods

2.1. Collection of samples

Collections of thick-billed murre and northern fulmar eggs were made from Prince Leopold Island (74°02′N, 90°05′W), Nunavut, Canada (Fig. S1), from 1975 to 2014 (1975, 1987, 1988 (murres only), 1993, 1998, 2003, annually 2005–2014). As both species lay a single egg, independence among samples was ensured. To be consistent over years, sampling occurred at the same time each year. Collection and research permits were obtained prior to sampling each year.

Eggs were processed at the National Wildlife Research Centre (NWRC) in Ottawa, Canada. Homogenized egg contents were aliquoted into chemically-cleaned glass vials and stored frozen at −40 °C. Archived samples from 1975 to 1998 were analyzed retrospectively, whereas analyses of samples from 2003 to 2014 occurred within six months of collection. Samples were analyzed for PCDDs, PCDFs and nPCBs, as well as stable isotopes of nitrogen.

2.2. Chemical analysis

Egg homogenates were analyzed for PCDDs, PCDFs and nPCBs as pooled (composite) samples with each pool consisting of equal aliquots of five individual egg samples (see Tables S1 and S2). The nPCBs (i.e. PCB-77, −126 and −169), were of particular interest due to their structural similarity to 2,3,7,8-TCDD and were identified by their IUPAC numbers (Ballschmiter et al., 1992). Analyses of the samples from 1975, 1987, 1993, 1998 and 2006 were carried out at NWRC, Ottawa, Canada. Samples from 1988 and 2003 were carried out by Axys Analytical Services Ltd. (Sidney, BC, Canada), and samples from 2005 and 2007–2014 were carried out by the Research and Productivity Council (RPC; Fredericton, NB, Canada). All of the analytical laboratories used the HRGC/HRMS Selected Ion Monitoring (SIM) procedure which is based on the US EPA Method 1613 (Simon and Wakeford, 2000; US EPA Method 1613, Revision B, 1997). Samples were ground with anhydrous sodium sulfate followed by neutral extraction (NWRC) or Soxhlet extraction (Axys, RPC) with dichloromethane:hexane (1:1). Extract clean-up and fractionation was done by gel permeation chromatography and alumina column clean-up followed by carbon/glass fibre column separation (NWRC, Axys) or acid-basic silica column followed by alumina column clean-up and carbon column separation (RPC). Florisil column chromatography was used to further separate the PCDDs and PCDFs from the nPCBs (NWRC, Axys). All samples were spiked with $^{13}C_{12}$-labelled internal and external standards prior to extraction and analysis. Internal standard recoveries were generally over 80%. Sample analysis was by VG AutoSpec high-resolution mass spectrometer (HRMS) interfaced with a high-resolution gas chromatograph (HRGC) operating at 7000–10000 resolution for nPCBs and 10000 resolution for PCDDs and PCDFs. Blanks, duplicates and in-house reference material (HGQA) (Wakeford and Turle, 1997) were run for quality control by all three laboratories (NWRC, Axys, RPC). Results from Axys for the HGQA sample ($n = 1$) were within ±2 standard deviations of the NWRC mean ($n = 60$ replicate sample runs) for 81% of the PCDD/PCDF/nPCB congeners, and 92% of the results from RPC over nine replicate sample runs for all congeners were within ±2 standard deviations of the NWRC mean ($n = 60$). Additional certified reference materials were also run by Axys (NIST SRM 1614) and RPC (WMF01 - Freeze-dried Fish Certified Reference Material from Wellington Laboratories; CIL-EDF-2525 - Fish Certified Reference Material from Cambridge Isotope Laboratories). Four egg samples analyzed by both NWRC and Axys for values above the detection limit (paired t-test; $n = 8, 7, 7, 9$) showed no significant inter-laboratory differences ($p > 0.05$). All reported residue levels were corrected for internal standard recoveries. The Method Detection Limit (MDL) was defined as 3:1 signal-to-noise and varied among analytes and samples. See Tables S1 and S2 for details.

2.3. Stable-nitrogen isotope analysis

Egg homogenates from 1975 to 2005 were analyzed for stable isotopes of nitrogen ($^{15}N/^{14}N$, expressed $\delta^{15}N$) in composite samples of three eggs each. The eggs from 2006 to 2014 were analyzed individually for $\delta^{15}N$. The Department of Soil Science, University of Saskatchewan, Saskatoon, Canada, analyzed the samples from 1975 to 2011 and the G.G. Hatch Stable Isotope Laboratory, University of Ottawa, Ottawa, Canada, analyzed the samples from 2012 to 2014 as described in Braune et al. (2015).

2.4. Data treatment

Egg $\delta^{15}N$ values were used as a measure of relative trophic position, reflecting the diet of the female during or just prior to egg-laying (Hebert et al., 1999; Hobson, 1995). To allow statistical comparisons with related PCDD/PCDF/nPCB data, samples from 2006 to 2014, which were individually analyzed for $\delta^{15}N$, were averaged for groups of the same five eggs that were pooled for the PCDD/PCDF/nPCB analyses. Likewise, as eggs of thick-billed murres and northern fulmars from 1975 to 2005 were analyzed for $\delta^{15}N$ in pools of three eggs, those values were calculated to represent the five-egg pools analyzed for PCDD/PCDF/nPCBs by proportional weighting of the $\delta^{15}N$ values. For example, having identified which three or five individual samples comprised each sample pool for $\delta^{15}N$ and PCDD/PCDF/nPCB analyses, we assigned the pool value for $\delta^{15}N$ to each sample in the pool, calculated the sum for the five eggs that comprised the sample pool for PCDD/PCDF/nPCB, and divided by five to arrive at an average $\delta^{15}N$ value to match the five-egg pool (e.g. for 15 eggs analyzed as three five-egg pools for PCDD/PCDF/nPCBs and five three-egg pools for $\delta^{15}N$, we can make the following calculation: $([3 \times \delta^{15}N_{pool1}] + [2 \times \delta^{15}N_{pool2}])/5$;

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