TEMPORAL TRENDS OF PERFLUORINATED SULFONATE AND CARBOXYLATE COMPOUNDS IN SEABIRD EGGS FROM THE CANADIAN ARCTIC

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Introduction

Poly- and per-fluorinated alkyl substances (PFASs) are ubiquitous in the Arctic environment[1]. The major fluorinated compounds which have been measured are the perfluorinated sulfonates (PFSAs) - e.g. perfluorooctane sulfonate (PFOS) - and the perfluorinated carboxylates (PFCAs) which include perfluorooctanoate (PFOA). PFASs can biomagnify through the food web[2,3] and have been found in arctic biota including seabirds and their eggs[1]. Unlike lipophilic halogenated organic contaminants, which are transferred along with fat to the eggs at the time of egg formation, perfluoroalkyl acids such as PFCAs and PFSAs bind to proteins rather than partitioning into lipid[1]. Nonetheless, PFCAs and PFSAs, and other PFASs are transferred to bird eggs and eggs have been used in a number of studies to monitor PFASs[4-6]. Braune and Letcher[7] examined temporal trends of PFOS and PFCAs (C_6-C_{15} chain lengths: PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA and PFPA, respectively) in eggs of two seabird species, the thick-billed murre (*Uria lomvia*) and northern fulmar (*Fulmarus glacialis*), sampled from the Canadian Arctic during 1975-2011. Here we provide an update on the PFOS and PFCA trends reported by Braune and Letcher[7] and discuss reasons for changes in trends.

Materials and methods

From 1975 to 2012, eggs of northern fulmars and thick-billed murres were collected from Prince Leopold Island (74°02'N, 90°05'W) in Lancaster Sound, Nunavut, Canada. Six to 15 eggs were sampled per species per year and egg homogenates were analyzed as pooled (composite) samples consisting of three eggs. The PFAS extraction, cleanup and analysis have been described elsewhere[6,8]. Briefly, approximately 1 g of egg 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 fluorotelomer alcohols (FTOHs) and perfluorosulfonamides (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 coupled to a Waters Quattro Ultima triple quadrupole mass spectrometer. 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. All solvents used were HPLC grade. Where no labeled standards were available, labeled internal standards with the closest retention time were used. Since an isotope dilution quantification approach was used, concentrations were inherently recovery-corrected. For every block of 6-12 samples, a blank sample and an in-house reference material was analyzed.

Eggs were also individually analyzed for stable isotopes of nitrogen ($^{15}N/^{14}N$). Egg homogenates were freeze-dried and powdered. Lipids were removed using a 2:1 chloroform:methanol rinse. Stable-nitrogen isotope assays were performed on 1 mg subsamples of homogenized material loaded into tin cups. Samples were analyzed on a Europa 20:20 continuous-flow isotope ratio mass spectrometer (CFIRMS) interfaced with a Robo-Prep elemental analyzer. Within each analytical run, five unknowns were separated by two laboratory standards. Measurements are reported in standard δ notation in parts per thousand ($^o/_{oo}$) relative to the AIR international standard. Replicate measurements of internal laboratory standards indicate a measurement error of $\pm 0.3^o/_{oo}$.

Since PFASs such as PFCAs and PFSAs bind to proteins rather than partition into lipid, concentrations were not lipid-normalized. Statistical tests were performed using Statistica for Windows Version 7.0 with a significance level of $p < 0.05$. Temporal trends were analyzed by backward stepwise regression analysis, with year and $\delta^{15}N$ as regressors.

Results and discussion

PFOS was the major PFSA measured and was detected in all northern fulmar and thick-billed murre eggs sampled from 1975 to 2012. FOSA was detected at very low concentrations (<0.7 ng g^{-1} ww) in only a few samples and *N*-Me-FOSA was not detected in any of the samples (<0.2 ng g^{-1} ww). No FTOHs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) were detected (<0.6 ng g^{-1} ww, <0.6 ng g^{-1} ww and <0.5 ng g^{-1} ww, respectively) in any of the samples, and FTUCAs (6:2 FTUCA, 8:2 FTUCA,10:2 FTUCA) were detected in a few samples but could not be quantified (<0.1 ng g^{-1} ww).

Concentrations of PFOS have not changed significantly (p<0.05) in eggs of either species from 1975 to 2012 although levels have shown significant declines since 2009 in the fulmars (n=20, r=-0.73, p<0.001) and since 2008 in the murres (n=25, r=-0.82, p<0.001 (Figure 1). The recent declines in PFOS concentrations may represent variability in the temporal trend data set, or they may indicate a delayed response to the manufacturing phase-out of PFOS by the 3M Company between 2000 and 2002[1]. Other studies from the Arctic and elsewhere have also shown recent declines in PFOS levels in response to the phase-out[1,9]. The variability in PFOS data may also be due to annual differences in the contribution of the degradation PFOS precursors to PFOS. PFOS precursors such as *N*-Et-FOSA can be dealkylated to FOSA, which in turn can be degraded to PFOS, as has been reported *in vitro* in liver microsomal studies with Arctic polar bears and ringed seals[10]. The PFOS to FOSA concentration ratio for the present seabird eggs are extremely high, in cases where FOSA could be detected, which is also consistent with such ratios for polar bears and ringed seals[1,9]. There still remain many exemptions for PFOS under the Stockholm Convention resulting in PFOS and related compounds remaining in global commerce, and continued production of PFOS in China and Brazil[11]. Therefore, it is not inconceivable that the recent declines of PFOS levels in our Arctic seabird data sets are merely an artefact of data variability. Continued monitoring will determine whether or not the recent declines in PFOS concentrations in the Arctic seabird eggs constitute a real downward trend.

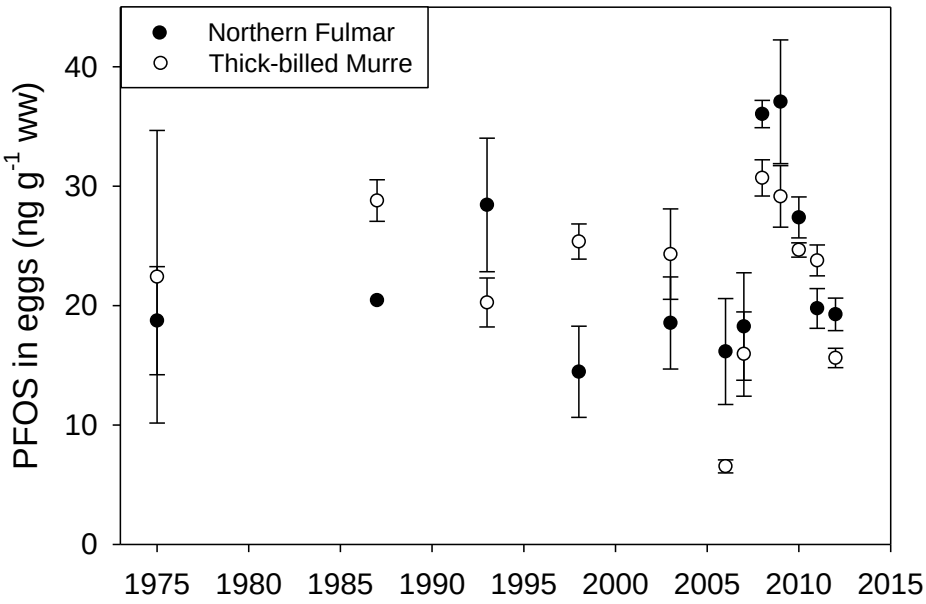

Figure 1. Mean annual concentrations (± standard error) of PFOS in eggs of northern fulmars and thick-billed murres from Prince Leopold Island, Nunavut, Canada, 1975-2012.

Concentrations of ΣPFCA increased significantly from 1975 to 2008 in northern fulmar eggs (n=37, r=0.89, p<0.001) and from 1975 to 2010 in thick-billed murre eggs (n=45, r=0.89, p<0.001) followed by significant decreases in both species to 2012 (p<0.001 for both species; $n_{fulmars}$=25, n_{murres}=15) (Figure 2). Significant increases in concentrations of all longer-chained PFCAs (C_9–C_{15}) contributed to the increase in ΣPFCA in the murres and the fulmars. PFUnA (C_{11}) and PFTrA (C_{13}) were the predominant PFCAs measured in eggs of both species (Figure 3). These two PFCAs together constituted >60% of ΣPFCA in all years, with PFTrA dominating

the fulmar PFCA profile and PFUnA dominating the murre PFCA profile. PFOA (C_8) has been detected in eggs of both species only since 2008 and comprises <3% of the PFCA profile.

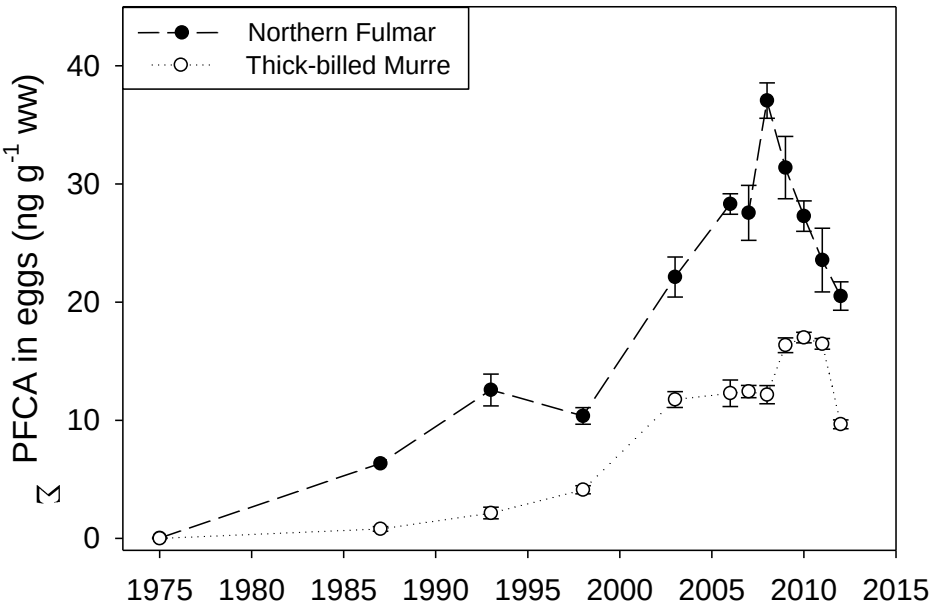

Figure 2. Mean annual concentrations (± standard error) of ΣPFCA in eggs of northern fulmars and thick-billed murres from Prince Leopold Island, Nunavut, Canada, 1975-2012. ΣPFCA = sum of PFHxA (C_6), PFHpA (C_7), PFOA (C_8), PFNA (C_9), PFDA (C_{10}), PFUnA (C_{11}), PFDoA (C_{12}), PFTrA (C_{13}), PFTeA (C_{14}) and PFPA (C_{15}).

The increase in ΣPFCA concentrations in both murre and fulmar eggs up to 2008-2010 is consistent with observed increases in other arctic species monitored into the early 2000's, including herring gull eggs from northern Norway[12], polar bears from Alaska and Baffin Island[13], ringed seals from the Canadian Arctic[14] and beluga whales from Alaska[15]. Perfluorinated carboxylates are not regulated under the Stockholm Convention. However, the United Nations Environment Program Strategic Approach for International Chemicals Management includes an initiative to reduce emissions, particularly of the long-chain PFCAs (i.e. carbon chain lengths C_8 or higher)[11]. The recently observed declines in concentrations of ΣPFCA in the fulmar and murre eggs may be a reflection of this recent UNEP initiative.

Figure 3. Mean percent contributions (± standard error) averaged for 2010-2012 of PFHxA (C_6), PFHpA (C_7), PFOA (C_8), PFNA (C_9), PFDA (C_{10}), PFUnA (C_{11}), PFDoA (C_{12}), PFTrA (C_{13}), PFTeA (C_{14}) and PFPA (C_{15}) to ΣPFCA in eggs of northern fulmars and thick-billed murres from Prince Leopold Island, Nunavut, Canada.

It has long been recognized that seabirds are good monitors of contaminants in the marine environment. Their rapid response to changes in emission patterns of contaminants such as the PFASs further endorses their utility as effective biomonitors.

Acknowledgements
We thank D. Nettleship, A. Gaston, M. Mallory and their respective field crews for sampling the eggs over the years. Sample processing was carried out by Laboratory Services personnel at the National Wildlife Research Centre (NWRC) in Ottawa, Canada. Chemical analyses were performed by S. Chu and D. Blair at NWRC. Stable isotope analyses were carried out through the Environment Canada lab in Saskatoon with isotopic measurements made at the Department of Soil Science, University of Saskatchewan, Saskatoon. Funding was provided by Environment Canada and the Northern Contaminants Program of Aboriginal Affairs and Northern Development Canada. Logistical support out of Resolute Bay was provided by the Polar Continental Shelf Project, Natural Resources Canada.

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