(RE)EMERGING PERSISTENT ORGANIC POLLUTANTS (POPS), EXPOSURE, FATE AND TEMPORAL CHANGES IN POLAR BEARS (*URSUS MARITIMUS*) FROM A POP HOTSPOT IN THE CANADIAN ARCTIC, HUDSON BAY

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Introduction

There is a growing array of chlorinated, brominated and fluorinated persistent organic pollutants (POPs) that have been shown to be transported to the Arctic and bioaccumulate in biota and wildlife[1,2]. (Re)emerging POPs include the polybrominated diphenyl ether (PBDE) congener BDE-209 and other flame retardants (FRs) including polychlorinated *n*-alkanes known as chlorinated paraffins (CPs; and especially $C_{10} - C_{13}$ short chain chlorinated paraffins (SCCPs)), as well as polychlorinated naphthalenes (PCNs), and per-/poly-fluoroalkyl substances (PFASs). The polar bear (*Ursus maritimus*) is the apex predator of the arctic marine ecosystem and food web[1]. "New" POPs such as PentaBDE and OctaBDE derived PBDE congeners and bioaccumulative PFASs such as PFOS and perfluorinated carboxylic acids (PFCAs) are now well-known in Arctic biota including in the tissues of bears from circumpolar subpopulations including those from the Arctic POP hotspots Hudson Bay (Canada) and East Greenland[2-6].

There are several high priority POPs under consideration by or nominated for addition to annexes of the Stockholm Convention on POPs, and that have recently or are currently being reviewed by the POP Review Committee (POPRC), and for which there is a dearth of data for Arctic wildlife including polar bears. For example, POPs currently under POPRC review are DecaBDE (BDE-209), SCCPs, pentachlorophenol (PCP; and transformation product pentachloroanisole (PCA)), PCNs and hexabromocyclododecane (HBCDD; recently added to Annex A in November 2014). Data on other non-PBDE FRs including organophosphate FRs (OPFRs) and new PFASs such as perfluorooctane-4ethylcyclohexane sulfonic acid (PFEtCHxS; PFOS replacement) remains non-existent for polar bears. POPs such as CPs are still produced in countries such as the United States and China according to a 2012 Revised Draft Risk Profile for SCCPs from United Nations Environment Program[7].

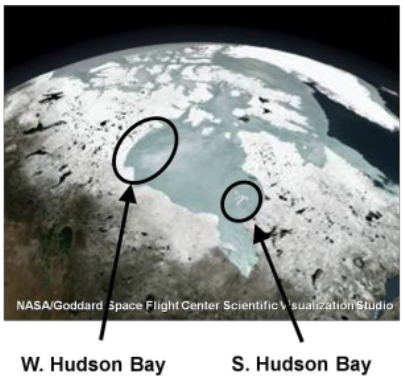

Figure 1. Polar bear subpopulation locations in Hudson Bay, Canada.

The known and unknown complexity of POP exposure poses an increase in health risks to polar bears, especially for bears from Hudson Bay and East Greenland, which have been shown to be `hot spots` with respect to high and /or changing tissue levels of POPs, and/or greater temperature changes due to Arctic warming[1,5,8,9]. We presently report on (re)emerged, targeted and newer POPs of regulatory priority in the tissues of polar bears harvested from western and southern Hudson Bay subpopulations, and where possible, temporal trends (over the last decade) are discussed and in comparison with legacy POPs such as PCBs, CHLs and DDTs.

Materials and Methods

Via the Nunavut Department of Environment (NDE), Nunavut Wildlife Research Permits (NWRPs) were obtained on an annual basis over the last decade to allow for polar bear sample collections during harvests by communities in western and southern Hudson Bay in Canada (Figure 1). As per the valid and approved NWRPs, community hunters annually collected polar bear adipose (fat), muscle and liver sample sets. For the recent late 2013/early 2014 harvests, sample sets were obtained from n=17 western Hudson Bay (14 males and 3 females) and n=24 southern Hudson Bay (15 males and 9 females) bears.

Adipose or liver samples were analyzed at NWRC (Ottawa, Canada), NLET or ALS Life Sciences (Burlington, Canada) or OME (Toronto, Canada). All of the Hudson bear fat samples were analyzed by GC-MS-based methods for the 46 PBDE congeners, 22 other FRs, SCCPs, PCNs as well as all PCB congener (74 congeners) and 25 organochlorine (pesticides) including HCBD, α-endosulfan, β-endosulfan and endosulfan sulfate[3,4,5]. LC-MS-based methods were employed to determine OPFRs[9] and PFASs[6]. Quality assurance/quality control (QA/QC) measures were high for all labs.

Results and Discussion:

Figure 2 illustrates an overall comparison of recent data on legacy and (re)emerging POPs (including newly screened POPs, e.g. ΣSCCPs, ΣPCNs, ΣOPFRs and α-endosulfan) in the tissues of polar bears (fat or liver) from Hudson Bay subpopulations, and collected in the most recent 2014 monitoring year. The overall view of the legacy and emerging POPs in both southern and western Hudson Bay bears shows that with the exception of the major PFASs (ΣPFCA and PFOS in liver), ΣSCCPs, ΣPCNs, ΣPBDEs and BB-153, all other recently screened POPs (e.g. ΣOPFRs, α-endosulfan, HBCDD and ΣDP-like substances) were generally at much lower concentrations in adipose tissue compared with the legacy POPs (ΣPCB, ΣCHL, ΣHCH, ΣDDT and ΣClBz). Also, some priority POPs that were screened in the same adipose samples collected in 2013 and 2014 were not detectable with any frequency e.g. HCBD, BDE-209, β-endosulfan and endosulfan sulfate.

Western Hudson Bay adipose samples collected in 2012-2013 had also been screened for several Dechlorane Plus (DP)-like, norbornene derivatives, as well as for *syn*- and *anti*-DP FRs and structurally related Mirex (Dechlorane) and Photomirex (Photo-Dechlorane). *Syn*- and *anti*-DP were not detectable in any of these samples. However, DP-602 and DP-603 were quantifiable and at levels of 2.5 ± 2.4 and 0.3 ± 0.2 ng•g^{-1} lipid weight (lw), respectively.

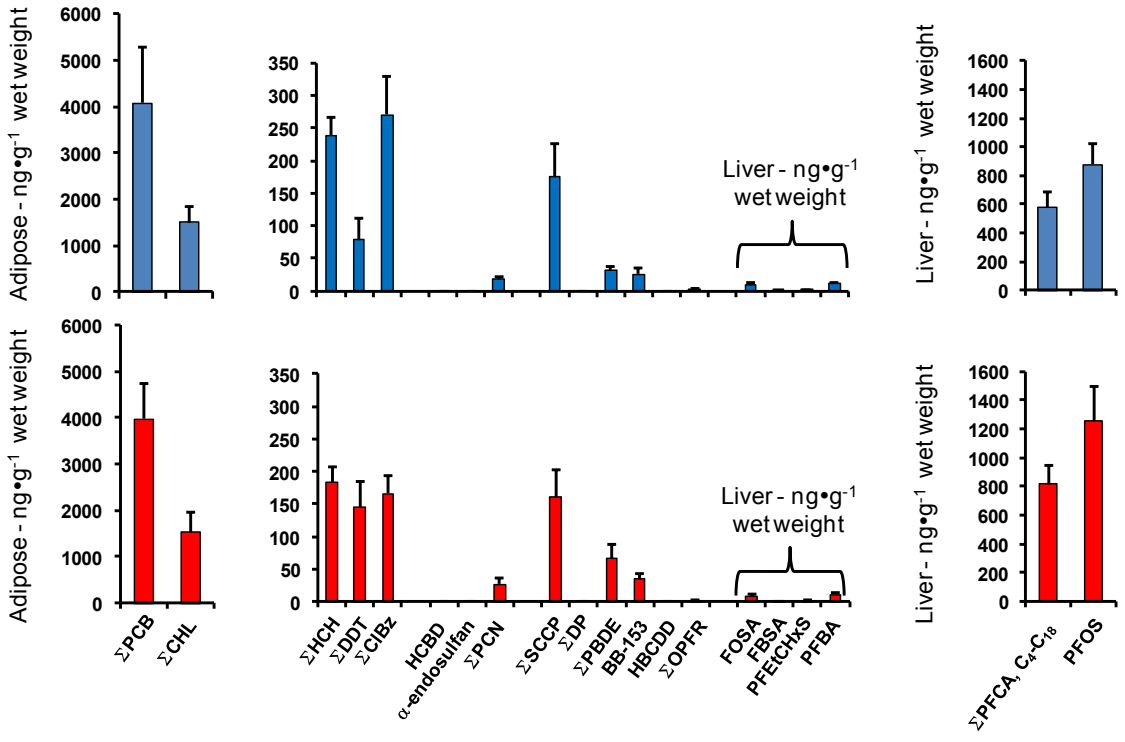

Figure 2. Geometric mean concentrations of individual and Σ-groups of major legacy and emerging POPs measured in 2013-2014 liver or fat samples of polar bears from western Hudson Bay (top, blue; n=17 individuals (except for ΣPCNs, n=5)) and southern Hudson Bay (bottom, red; n=24 individuals (except for ΣPCNs, n=5)). Error bars are SDs. Data not corrected for sex, age or diet.

In 2013 and 2014 collected adipose samples, low- to sub-ppb (ww) concentrations of the OPFRs tris(2-chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl)phosphate (TCIPP), tributyl phosphate (TNBP), triphenyl phosphate (TPHP) and/or tris(2-butoxyethyl)phosphate (TBOEP) were found. For both western and southern

Hudson Bay bears, TCIPP and TBOEP were at the highest levels at 1.2 ± 0.7 and 3.8 ± 2.1 ng•g^{-1} wet weight (ww), respectively. Regardless, for all Hudson Bay bears the mean ΣOPFRs in adipose has been consistently very low compared to other emerging POPs, and exceedingly low compared to legacy POPs (Figure 2). The suite of 24 SCCP congeners screened for in adipose samples were of chain lengths of C_{10}-C_{13}, and for each chain length SCCP grouping they contained 5 to 10 chlorines. There was 100% frequency of detection for all the quantifiable SCCPs. The mean Σ_{24}SCCP concentrations in the 2014 samples were 175 ± 100 ng•g^{-1} ww and 160 ± 84 ng•g^{-1} ww for western and southern Hudson Bay bears, respectively, and were among the most concentrated POPs for bears from both subpopulations (Figure 2). A suite of 50 mono- to hepta-chloro-PCN congeners were determined in bear adipose samples from 2014. There was a very high frequency percentage of detection for 27 of the PCN congeners in the sub-sets of n=5 adult male and female bears from each of the two subpopulations. The mean Σ_{27}PCN concentrations in the 2014 samples were 17.6 ± 8.5 ng•g^{-1} ww and 27.1 ± 17 ng•g^{-1} ww for western and southern Hudson Bay bears, respectively, and comparable to ΣPBDEs and BB-153 (Figure 2). Tetra- to hexa-chlorinated congeners accounted for >95% of the Σ_{27}PCN concentrations, and with penta-chlorinated congeners accounting for >80% of the Σ_{27}PCN concentrations.

In the 2014-collected liver samples the PFCAs were mostly C_9-C_{11} congeners with the PFNA (C_9) dominating. In addition to PFOS, the C_6 PFSA and several "Pre-FOS" precursors were quantifiable e.g. N-EtFOSA and FOSA at low levels, which are ultimate precursors to PFOS. Also, to our knowledge, the (low ppb concentration) detection of C_4 perfluorobutane sulfonamide (FBSA) in polar bear liver is a first for any Arctic wildlife sample (Figure 1), although no corresponding perfluorobutane sulfonic acid (PFBS) was detectable in any liver sample. Perfluorobutane carboxylic acid (PFBA) was measureable at low ppb levels with almost 100% frequency in all western and southern Hudson Bay bear livers (Figure 2). Furthermore, the cyclic analogue of PFOS, PFEtCHxS was quantifiable in all Hudson Bay bear liver samples. To our knowledge this is the first report detecting PFEtCHxS or FBSA in any Arctic sample[2].

With respect to temporal trends, and although uncorrected for e.g. age, sex and diet, from 1991 to 2014 the most concentrated BFRs, ΣPBDEs (mostly PentaBDE congeners), concentrations increased up until 2009 and then began a general decline progressing to 2014 in western Hudson Bay bears (Figure 3). The same downward trend occurred between 2007 and 2014 in southern Hudson Bay bears (Figure 3). This is consistent with the PentaBDE and OctaBDE production phase out in the early 2000s and addition of these formulations to Annex A of the Stockholm Convention in 2009[1].

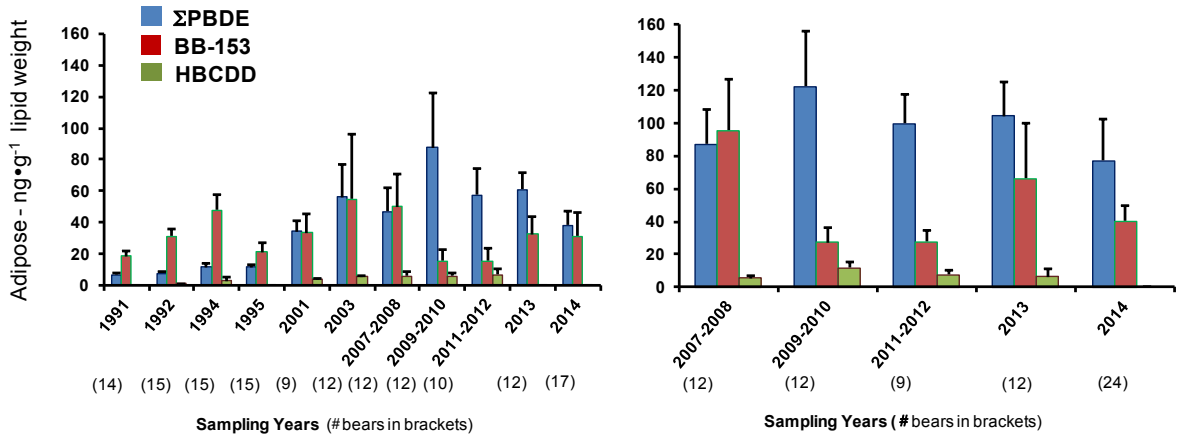

Figure 3. Temporal trends of geometric mean concentrations of major brominated FRs in western Hudson Bay bears (left panel, 1991-2007, McKinney et al., 2010; 2008-2014, unpublished) and southern Hudson Bay bears (right panel, 2008 – 2014, unpublished). Error bars are SDs. Data not corrected for sex, age or diet.

Starting in 2007 and until 2013, analysis of adipose samples from Hudson Bay bears showed that BDE-209 and 22 non-PBDE replacement FRs were not detectable at all or with any frequency, whereas HBCDD and BB-153 were quantifiable in all years (Figure 3). However, in 2014 samples HBCDD was not detectable in any southern or western Hudson Bay adipose sample (Figures 2 and 3). BDE-47, -99, -100 and -153 consistently accounted for 90% of the ΣPBDE concentration. The lack of BDE-209 is likely due to a combination of low exposure and uptake in the polar bear via the diet and to rapid metabolism and debromination. Polar bears possess a high

ability (compared to other Arctic mammalian and avian wildlife) to bio-transform compounds via liver enzymatic processes including the debromination of BDE-209 and decabromodiphenyl ethane (DBDPE)[10].

Even though the concentrations were uncorrected for e.g. age, sex and diet, between 2007 and 2014 the mean concentrations of ΣPFCAs and PFOS in Hudson Bay polar bear liver was continually very high and comparable to ΣPCB and ΣCHL concentrations in adipose tissue as exemplified for 2014 bear samples (Figure 2). However, PFOS and ΣPFCA levels appeared to be neither increasing nor decreasing and there was no clear trend for the period of 2007-2014 (data not shown), and despite C8 chemistry phase-out around 2002[2]. This stresses the importance of PFCA and PFOS precursors as sources, which are transported to the Arctic and/or degraded in bears and/or their prey/food web. It has been shown that Canadian ringed seal and Icelandic polar bear, but not Canadian beluga whale, can rapidly dealkylate N-EtFOSA to FOSA *in vitro* in liver microsomes from these Arctic species[11].

Clearly, POP exposure to Hudson Bay polar bears continues to increase in complexity, which is also being shown to be true for other circumpolar subpopulations such as for bears from East Greenland[1]. Several high priority POPs under consideration for addition to the POPs Stockholm Convention annexes (being reviewed by the POPRC that recommends POPs for addition to the Stockholm Convention Annexes) are being detected and/or are quantifiable (in some cases at high levels) in tissue from recently harvested Hudson Bay polar bears, e.g. SCCPs, PCNs and PFASs including replacements such as shorter chain perfluoroalkyl acids and sulfonamide precursors. These new emerging POPs require further annual monitoring and selective retrospective temporal examination to understand longer-term trends, sources, fate and exposure to polar bears.

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