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Legacy and new halogenated persistent organic pollutants in polar bears from a contamination hotspot in the Arctic, Hudson Bay Canada

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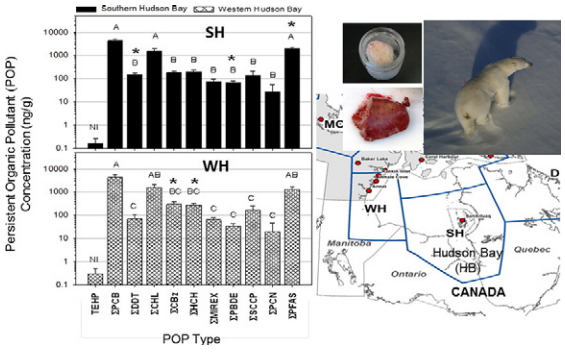
HIGHLIGHTS

- 210 out of 295 legacy and new POPs were present in Hudson Bay (HB) polar bears.
- ΣPCBs, ΣCHLs and PFOS were the dominant POPs in fat or liver samples.
- Some POPs (e.g. ΣPFASs and ΣCHLs) were influenced by age, sex and/or subpopulation.
- Some new POP concentrations were comparable (ΣSCCPs) and some lower (ΣPCNs) to legacy POPs.

GRAPHICAL ABSTRACT



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ABSTRACT

A large and complex suite of 295 legacy and new halogenated persistent organic pollutants (POPs) were investigated in fat or liver tissue samples of polar bears collected in 2013–2014 from Southern (SHB) and Western (WHB) subpopulations of the Canadian Arctic contaminants hotspot of Hudson Bay. A total of 210 POPs were detected and/or quantifiable with some frequency in all fat or liver samples. POP profile and concentration differences were investigated both within (e.g. age and sex) and between the two subpopulations. Two time-point comparisons were made relative to POPs reported for Hudson Bay polar bears harvested in 2007–2008. ΣPolychlorinated biphenyl (PCB) concentrations at both time points were the most concentrated of the POP groups, and were spatially uniform with no detectable influence of sex or age, as were concentrations of the dominant congener CB153. ΣChlordanes (ΣCHLs, 74–79% oxychlordane) and the Σperfluoroalkyl substances (ΣPFASs, ≈60% perfluorooctane sulfonate (PFOS)) had the second greatest POP group concentrations in SHB and WHB respectively, with ΣPFASs and ΣCHLs being significantly influenced by age and/or sex. ΣCHLs were spatially uniform but ΣPFASs were greater in the SHB bears, as were e.g. some flame retardants, due to e.g. local contamination and/or changes in bear behavior and diet. Endosulfans and hexabromocyclododecane were detectable in samples from 2007–2008 but not from 2013–2014, which is consistent with their global POP regulations. ΣPolychlorinated naphthalenes (ΣPCNs) were consistently detected at relatively high concentrations compared to other arctic wildlife, however these concentrations were low relative to legacy POPs. ΣShort-chain chlorinated paraffins (ΣSCCPs) were major contributors to the overall POPs burden with concentrations comparable to other legacy POPs, though there was no significant difference between or within subpopulations

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for PCNs or SCCPs. Except for octachlorostyrene, POPs concentrations were generally lower in female and male bears from SHB in 2013–2014 relative to 2007–2008, however those of WHB males were greater over the same timeframe for almost all POPs.

1. Introduction

Persistent organic pollutants (POPs) are contaminants of global interest, found in environmental matrices and wildlife from the Arctic to the Antarctic (Muir et al., 2013a; Nash, 2011). Contaminants are assessed for toxicity, persistence, long range transport (LRT), and bioaccumulation potential under the Stockholm Convention on POPs (SC-POPs) and are regulated by the 180 member parties if reclassified (United Nations Environment Programme, 2017). The initial 12 (legacy) POPs under the SC-POPs were all organochlorine compounds (OCs) that included the organochlorine pesticides (OCPs, 9 pesticides), polychlorinated biphenyls (PCBs) and industrial by-products (United Nations Environment Programme, 2017). Fourteen new and more structurally diverse POPs have been listed since 2009 including seven halogenated (Cl, Br or F) industrial compounds or flame retardants, and seven additional OCPs.

By definition POPs are capable of LRT through atmospheric or ocean currents, allowing them to reach the Arctic (Wania and Mackay, 1995). Once they are taken up into the food chain, the lipophilic properties of most POPs render them a concern for polar bears (*Ursus maritimus*) and other top predators in the complex arctic marine food web, which can biomagnify the levels of POPs in tissues hundreds of times as a result of their lipid-rich diets (Kelly et al., 2007, 2008; Norstrom et al., 1998; Letcher et al., 2009, 2010). Perfluoroalkyl substances (PFASs) are unique among POPs, as they have limited lipophilicity and bioaccumulate primarily in the liver, yet can still exhibit biomagnification (e.g. perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs)) between consumers and their diets (Martin et al., 2004; Greaves et al., 2012). Some older and/or new POPs such as tetra- to heptabromodiphenyl ethers (PBDEs) and endosulfan bioaccumulate but remain at low (low to sub parts per billion) concentrations in marine mammals relative to legacy POPs (Kelly et al., 2008; Letcher et al., 2009, 2010; Morris et al., 2016). Other new or more recently emerged POPs such as flame retardants and perfluorooctane sulfonate (PFOS) and other PFASs biomagnify to greater extents, and can reach concentrations comparable to some recalcitrant PCB congeners in wildlife (Dietz et al., 2013a; Martin et al., 2004; Letcher et al., 2009, 2010, 2014a; Verreault et al., 2005a, 2005b).

Polar bears have been shown to bioaccumulate a broad array of POPs classified as organohalogen contaminants (OHCs) in their fat or liver, but also have a high capacity to metabolize OHCs. Metabolism can detoxify some contaminants and facilitate depuration but may also result in persistent and/or bioaccumulative and possibly toxic metabolites such as oxychlordane and *p,p′*-bis(4-chlorophenyl)-1,1-dichloroethylene (*p,p′*-DDE) (Letcher et al., 2009, 2010; McKinney et al., 2011a, 2011b). Polar bears from different Hudson Bay subpopulations have been reported, in some cases, to have significantly different concentrations and patterns of OHCs (McKinney et al., 2011b). For example, the sum (Σ) PCB concentrations were shown to be essentially constant in the Western Hudson Bay (WHB) or slowly decreasing in the Southern Hudson Bay (SHB) subpopulations, respectively, between 1989 and 2008 (McKinney et al., 2011b). In the same study the ΣOCP concentrations were variable as well; sum chlordanes (ΣCHL) followed the same trend as ΣPCBs, while *p,p′*-DDE decreased in both subpopulations. Increasing tissue residues of regulated OHCs are due to their persistence/recalcitrance, likely coupled with both seasonal and climate-related emissions from melting multiyear sea-ice and permafrost, as well as volatilization from land, seawater and lakes (among other potential effects) (Ma et al., 2011; Macdonald et al., 2005).

Relative to other circumpolar regions, Hudson Bay, East Greenland and Svalbard are hot spots in terms of POP exposure and levels in the tissues of polar bears from these subpopulations (Letcher et al., 2010). An objective of the present study was to investigate a broad suite of legacy and new OHCs in liver or fat tissues of polar bears that were recently collected in 2013–2014 from the SHB and WHB subpopulations, and included the screening and determination of new POP contaminants of interest. Thus, for the first time since 2007–2008, the profiles and levels of legacy, but also older, understudied and new OHCs, were investigated in polar bears from Hudson Bay and thus showing the increasing complexity of OHC exposure in these subpopulations (Letcher et al., 1995a; McKinney et al., 2011b; Muir et al., 2006). The suite included new POPs such as PFOS, PBDEs and polychlorinated naphthalenes (PCNs), candidate POPs such as short-chain chlorinated paraffins (SCCPs) and decabromodiphenyl ether (decaBDE/BDE209), and other relatively unregulated contaminants including organophosphate ester (OPE) flame retardants and plasticizers and alternative halogenated flame retardants (HFRs; including Dechlorane Plus (DDC-CO) isomers and the DDC-CO-like compounds Dec602 and Dec603) (regulatory status of these OHCs are summarized in Table S1). Reports of both SCCPs, PCNs, DDC-COs and DDC-CO-like compounds in top predators from the Canadian Arctic are relatively rare and few contemporary measurements exist, though they do meet the criteria for classification as POPs as a function of their environmental and physical-chemical properties, e.g. log*K*ow values and atmospheric half-lives (Bidleman et al., 2010; Helm et al., 2002; Strid et al., 2013; Tomy et al., 1999, 2000). Other study objectives were to better understand the sources/exposure pathways, temporal changes, age-sex differences, influence of climate change, etc., of legacy and new POPs in polar bears from Hudson Bay. Where possible, tissue concentrations of OHC classes in the present 2013–2014 bears were also compared to previously reported OHC data in Hudson Bay bear samples collected in 2007–2008.

2. Experimental section

2.1. Sample collection

Tissue samples (liver and subcutaneous fat) were collected in 2013–2014 from polar bears of different sexes and ages from the WHB ($n = 17$) and SHB ($n = 24$) subpopulations, where the harvests and sampling were carried out by participating local hunters and the Government of Nunavut (Igloolik, NU) (Fig. S1, Table S2) (Morris et al., Accepted for publication). Samples were excised, double-wrapped tightly in chemically rinsed (acetone and then hexanes) aluminum foil, and then placed inside a sterile Whirlpak bag and frozen to −20°C until subsampling and analysis at the Letcher Labs/Organic Contaminants Research Laboratory in the National Wildlife Research Centre [NWRC; Environment and Climate Change Canada (ECCC), Ottawa, ON]. When the samples were received at NWRC, they were completely frozen and with no indication of cross-contamination of the samples via contact with the Whirlpak bags. Furthermore, while the received fat samples were partially frozen, sub-samples of fat were taken from the inner core of the received fat samples, and thus from a section where no POP cross-contamination could have penetrated. After this sub-sampling step, remaining tissue aliquots were archived in ECCC's National Wildlife Specimen Bank located in the NWRC.