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Perfluoroalkyl substances in polar bear mother–cub pairs: A comparative study based on plasma levels from 1998 and 2008

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ABSTRACT

Perfluoroalkyl substances (PFASs) are protein-binding blood-accumulating contaminants that may have detrimental toxicological effects on the early phases of mammalian development. To enable an evaluation of the potential health risks of PFAS exposure for polar bears (*Ursus maritimus*), an exposure assessment was made by examining plasma levels of PFASs in polar bear mothers in relation to their suckling cubs-of-the-year (~4 months old). Samples were collected at Svalbard in 1998 and 2008, and we investigated the between-year differences in levels of PFASs. Seven perfluorinated carboxylic acids ($\sum_7$PFCAs: PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA) and two perfluorinated sulfonic acids ($\sum_2$PFSAs: PFHxS and PFOS) were detected in the majority of the mothers and cubs from both years. In mothers and cubs, most PFCAs were detected in higher concentrations in 2008 than in 1998. On the contrary, levels of PFOS were lower in 2008 than in 1998, while levels of PFHxS did not differ between the two sampling years. PFOS was the dominating compound in mothers and cubs both in 1998 and in 2008. Concentration of PFHpA did not differ between mothers and cubs, while concentrations of PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFHxS, and PFOS were higher in mothers than in their cubs. Except from PFHpA, all compounds correlated significantly between mothers and their cubs. The mean cub to mother ratios ranged from 0.15 for PFNA to 1.69 for PFHpA. On average (mean ± standard error of mean), the levels of $\sum_7$PFCAs and $\sum_2$PFSAs in cubs were 0.24 ± 0.01 and 0.22 ± 0.01 times the levels in their mothers, respectively. Although maternal transfer appears to be a substantial source of exposure for the cubs, the low cub to mother ratios indicate that maternal transfer of PFASs in polar bears is relatively low in comparison with hydrophobic contaminants (e.g. PCBs). Because the level of several PFASs in mothers and cubs from both sampling years exceeded the levels associated with health effects in humans, our findings raise concern on the potential health effects of PFASs in polar bears from Svalbard. Effort should be made to examine the potential health effects of PFASs in polar bears.

1. Introduction

Perfluoroalkyl substances (PFASs) have gained increased attention in the last decades due to their widespread distribution in humans and wildlife including remote regions such as the Arctic (Giesy and Kannan, 2001). These anthropogenic contaminants have been manufactured for more than 50 years, and are widely used as additives in stain repelling agents, surfactants, lubricants, fire-fighting foams, insecticides, paint, metal plating, and cleaners (Buck et al., 2011; Prevedouros et al., 2006). The physicochemical properties of PFASs (e.g. stable carbon–fluorine [C – F] bonds and amphipathic nature [hydrophobic and lipophobic]), and thus, their behaviour in the environment and toxicokinetics differ from legacy persistent organic pollutants (POPs).

The PFASs most commonly detected in biota are divided in two groups; perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs). PFASs have the potency to bioaccumulate in biota and are considered metabolically inert (Conder et al., 2008; Houde et al., 2006). Despite their low volatility that should preclude long-range transport, they are present at all tropic levels in the arctic

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food web including polar bears (*Ursus maritimus*) (Conder et al., 2008; Houde et al., 2006). Exactly how PFASs reach arctic regions is unclear. However, transport of directly emitted PFASs by oceanic currents, and long-range atmospheric transport of more volatile PFASs precursors used commercially (e.g. perfluorinated sulfonamido alcohols and fluorotelomer alcohols [FTOHs]) and which degrade to PFCAs and PFSAs in the atmosphere, are believed to be the most important transport routes (Buck et al., 2011; Butt et al., 2010; Prevedouros et al., 2006).

PFOS is the most common PFAS in humans and wildlife (Giesy and Kannan, 2001; Houde et al., 2006). Concerns about the potential toxicological and ecotoxicological effects of PFOS and other fluorinated compounds on humans and wildlife have resulted in several regulations of production and use of PFASs (i.e. PFOA and PFOS) (3M, 2000; Buck et al., 2011; UNEP, 2009). Despite these regulations and agreements, PFASs are still used in significant amounts and for multiple industrial purposes (Buck et al., 2011; Prevedouros et al., 2006).

PFASs bind to proteins (Jones et al., 2003; Simon et al., 2011; Weiss et al., 2009). Due to their proteinophilic nature, PFASs accumulate in protein-rich tissue such as liver, blood and kidneys (Butt et al., 2010; Jones et al., 2003). PFASs have been detected in cord blood, maternal milk and suckling offspring, supporting both a prenatal and postnatal transfer of PFASs (Fromme et al., 2010; Karrman et al., 2007; Liu et al., 2011). Examining the maternal transfer of PFASs in highly exposed species such as polar bears could be of relevance for understanding maternal transfer of PFASs in humans and other mammals.

The levels of PFASs in polar bears exceed levels in most other Arctic species and humans (Dietz et al., 2008; Giesy and Kannan, 2001; Kannan et al., 2005; Kim et al., 2011a; Letcher et al., 2010; Martin et al., 2004; Needham et al., 2010; Smithwick et al., 2005). Epidemiological studies and experimental studies on rodents have associated exposure to PFASs with alterations of thyroid hormone (TH-)homeostasis, influence on brain development, neurobehavioral effects (i.e. impulsivity), alterations of lipid homeostasis and immune effects (Dallaire et al., 2009; Gump et al., 2011; Johansson et al., 2009; Lau et al., 2004; Loveless et al., 2008; Van Rafelghem et al., 1988). Although the exposure doses, sensitivity and potential effects may differ between species and between wildlife and laboratory animals, the widespread distribution of PFASs and reported effects on vulnerable processes of development raises concern about potential health consequences on humans and wildlife, and the potential long-term ecotoxicological effects of PFASs on wildlife including polar bears.

To enable an evaluation of the potential health risk associated with PFAS exposure for polar bear mothers and their cubs, an exposure assessment is necessary. Hence, the aim of the present study was to examine the plasma concentrations and mother–cub transfer of PFASs in polar bear mother–cub pairs shortly after den emergence. Concentrations of PFCAs and PFSAs were determined in plasma of live-caught polar bear mother–cub pairs from Svalbard sampled in 1998 and in 2008. Between-year differences (1998 vs. 2008) in levels, the PFAS pattern, the maternal transfer ratios of PFASs, and the effect of litter size on levels of PFASs in mothers and cubs were investigated. We also discussed the potential health risk for polar bear mothers and cubs associated with the determined plasma levels of PFAS.

2. Material and methods

2.1. Field sampling

Blood samples were collected from polar bear mothers and their approximately 4 month old cubs in the Svalbard archipelago (Norway) in April 1998 (12 mothers, 16 cubs [4 sibling pairs]) and 2008 (9 mothers, 12 cubs [3 sibling pairs]). Because blood sampling of cubs may be challenging, the mothers sampled could have several cubs ($\leq$3 cubs) than the once we managed to sample from and which thereby were available for PFASs analysis (for details, see Appendix Table A.1). Among the 14 single cubs and the 7 sibling pairs sampled, there were 25 females and 3 males. Mothers and corresponding offspring were sampled simultaneously. Blood samples were separated into plasma and cells by centrifugation (3500 rpm, 10 min), and the plasma samples were kept in cryo vials at −20 °C in the field and then at −70 °C until analysis. Capture and handling procedures followed standard protocols (Derocher and Wiig, 2002; Stirling et al., 1989) and were approved by the National Animal Research Authority (NARA, Oslo, Norway). Capture location is referred to as latitude and longitude, and capture time as capture day (1–365, with 1st of January set to 1). Routine measurements of morphometric variables of polar bears are described by Derocher et al. (2005), and the measurements used in the present paper are body condition index (BCI) for mothers and body mass (BM) for cubs. Morphometric equations used to calculate BM and thereafter BCI of mothers are described by Derocher and Wiig (2002) and Cattet et al. (2002), respectively. Plasma lipid percentage (PL%) was determined according to Brevik (1978). Detailed information on capture location, capture day, age and the morphometric measurements of mothers and cubs are listed in Table A.2

2.2. Analysis of PFASs

The chemical analysis of PFASs in the polar bear plasma included 16 PFASs, consisting of 11 PFCAs, 3 PFSAs, 6:2 fluorotelomer sulfonic acid (6:2-FTSA), and the non-ionic precursor perfluorooctane sulfonamide (PFOSA) (Table A.3). The 11 PFCAs were: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), and perfluorotetradecanoic acid (PFTeDA), and the 3 PFSAs were: perfluorobutane sulfonate (PFBA), perfluorohexane sulfonate (PFHxS), and perfluorooctane sulfonate (PFOS). All analytical and quality assurance (QA) details can be found in Appendix (Section A.1). Briefly, after the addition of internal standards (IS), 150 μL of plasma was extracted twice with methanol. After sample concentration, the extracts were analysed by liquid chromatography/negative electrospray ionisation tandem mass spectrometry (LC-ESI-MS/MS) (for details, see Ballesteros-Gomez et al., 2010). QA consisted of the use of internal standards to cover the whole procedure, syringe standards, analysis of blanks, analyses of reference samples, and assessment of recoveries. On average (all PFASs in all samples), the recovery of the internal standards were (mean ± standard error of mean [SEM]) 79 ± 3% (for details, see Appendix section A.1). Inaccuracies due to interferences of PFOS and PFHxS analysis were avoided by using an analytical column with fluorinated stationary phase (for details, see Appendix section A.1). As no blank contributions were detected, the method detection limits (LODs) were only defined by the method sensitivity. Plasma concentration of PFASs is given as ng/g wet weight (ww).

2.3. Data analysis

Data are presented as mean ± SEM unless otherwise noted, and the statistical analyses were performed using SPSS Statistical software (Version 17.0 for Windows, SPSS Inc., Chicago, IL, USA). Normality was tested by Shapiro–Wilk test as $n \leq 50$. When necessary, variables were $\log_{10}$-transformed to obtain normality before the statistical analysis. The level of statistical significance was set at $p < 0.05$.

Polar bears were divided into four groups based on age and sampling year: Mothers 1998, Mothers 2008, Cubs 1998, and Cubs 2008. 7 of 11 PFCAs and 2 of 3 PFSAs were detected in >80% of the individuals in each group and summed up to $\sum_7$PFCAs (PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA) and $\sum_2$PFSAs (PFHxS and PFOS),