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Methoxylated PBDEs (MeO-PBDEs), hydroxylated PBDEs (HO-PBDEs) and hydroxylated PCBs (HO-PCBs) in the liver of harbor seals from the northwest Atlantic

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HIGHLIGHTS

- HO-PCBs, HO-PBDEs, and MeO-PBDEs were present in Atlantic harbor seal pup liver.
- Order of importance was: HO-PCBs > MeO-PBDEs > HO-PBDEs.
- HO-PCBs and HO-PBDEs were correlated with precursor PCBs and PBDEs, respectively.
- HO-PCBs and HO-PBDEs may pose an additional stress for young harbor seals.

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ABSTRACT

Metabolites of PCBs and PBDEs are shown to influence the thyroid hormone homeostasis and therefore, could have an influence on the growth of newborn or young animals. We have investigated the occurrence of hydroxylated PCBs (HO-PCBs), hydroxylated PBDEs (HO-PBDEs), and methoxylated PBDEs (MeO-PBDEs) in the liver (48 pups; 6 adults) and blubber (4 pups; 1 adult) of harbor seals (*Phoca vitulina concolor*) from the northwest Atlantic. The sum of HO-PCBs in the liver ranged from 90 to 22,450 pg/g wet weight (ww) for pups and from 410 to 5290 pg/g ww for adults. Congener 4-HO-CB 107 was predominant in almost all samples regardless of age or gender, except in one adult male. Sum HO-PCB concentrations were highly correlated with the sum of precursor PCBs in the liver of harbor seals ($r^2 = 0.79$; $p < 0.0001$). Concentrations of sum HO-PBDEs in the liver ranged from 70 to 1850 pg/g ww for pups and from 90 to 230 pg/g ww for adults. HO-PBDEs were also correlated with PBDEs ($r^2 = 0.58$; $p < 0.0001$). Sum MeO-PBDE concentrations in the liver ranged from 20 to 1460 pg/g ww in pups and from 10 to 270 pg/g ww in adults. HO-PCBs and HO-PBDEs were not detected in the blubber. Levels of MeO-PBDEs in the blubber ranged from 1500 to 4400 pg/g ww. In all blubber samples, 6-MeO-BDE 47 was the predominant MeO-PBDE congener, followed by 2′-MeO-BDE 68 and 5-MeO-BDE 47, respectively. The presence of HO-metabolites in pup liver suggests that young harbor seals may have some, yet limited, metabolic capacity for PCBs and PBDEs, which can lead to an excessive accumulation of these chemicals in the body. Moreover, the presence of HO-PCB and HO-PBDE metabolites may pose an additional stress for young harbor seals due to their influence on the thyroid hormone system and could have consequences for the entire population.

1. Introduction

The bioaccumulative potential and toxicity of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in marine mammals has been the focus of recent research. Both groups of chemicals are associated with endocrine-disrupting, reproductive, and neurodevelopmental effects in animals (Birnbaum and Staskal, 2004; Darnerud, 2003; Crinnion, 2011; Winneke, 2011). PCBs and PBDEs enter coastal and marine waters from multiple sources and readily biomagnify in marine food webs (de Wit, 2002; Shaw et al., 2005, 2008, 2009; Shaw and Kannan, 2009). Levels and profiles of PCB and PBDE congeners in seal species suggest that these animals not only can accumulate high concentrations of the persistent and lipophilic contaminants, but also able to metabolize specific congeners (Weijs et al., 2009a; Vanden Berghe et al., 2012).

Recently, concerns have been raised about the presence and health effects of hydroxylated metabolites of PCBs and PBDEs in wildlife (Letcher et al., 2009). Effects of these metabolites are mostly related to

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disturbances of hormonal and endocrine systems as they can bind to and interact with several hormone receptors and transport proteins (Cheek et al., 1999; Birnbaum and Staskal, 2004; Shimokawa et al., 2006). As a result, these toxic interactions can have a significant adverse impact on the health condition of organisms in general. Hydroxylated metabolites are not particularly associated with lipids as are the parent compounds, but have a high affinity for plasma proteins and thus are typically found in the blood and blood-perfused tissues, such as the liver (Gebbink et al., 2008).

The present study is a follow-up of the recent studies of Shaw et al. (2012, 2014), which aimed at determining the occurrence and patterns of PBDEs and PCBs, respectively, in harbor seals (*Phoca vitulina concolor*), apex predators in the northwest Atlantic marine ecosystem. Since the concentrations of these two groups of pollutants were at the high end of levels reported elsewhere, the main objective of the present study was to investigate the concentrations and profiles of HO-PCBs, HO-PBDEs and MeO-PBDEs in the same individuals. Most of the animals investigated were pups, providing an opportunity to examine the fate of these hydroxylated and methoxylated metabolites resulting from placental and/or lactational transfer or from biotransformation of the parent PCBs and PBDEs. The information presented herein about HO-PCBs, HO-PBDEs and MeO-PBDEs is complementary to the data on PCBs and PBDEs reported elsewhere (Shaw et al., 2014; Shaw et al., 2012, respectively).

2. Materials & methods

2.1. Samples

Liver samples were collected between 2001 and 2006 from 54 harbor seals (6 adult males, 20 male pups, and 28 female pups) that were stranded along the northwest Atlantic coast from the eastern coast of Maine to Long Island, New York (Fig. 1). In addition, matched blubber samples (4 pups, 1 adult) of 5 animals out of those 54 were analyzed as well. Seals were weighed, and standard length and axillary girth were measured. Age was estimated based on body size. Liver and blubber samples were stored in a freezer at −20 °C until analysis.

2.2. Sample preparation

Seal liver (about 2 g) and blubber (about 0.2 g) were mixed with sodium sulfate and spiked with internal standards which included 4-HO-CB 159 (for the quantification of HO-PCBs and HO-PBDEs) and BDE 77 (for the quantification of MeO-PBDEs). Samples were extracted by hot Soxhlet (Buchi, Switzerland) for 2 h with a mixture of acetone/hexane (1/3, v/v). The extract cleaned-up on 8 g of acid silica (H_2SO_4, 44%), from which pollutants were eluted with 20 ml hexane and 15 ml DCM in one fraction (Voorspoels et al., 2003; Covaci et al., 2008). Minor adaptations were required as to separate different groups of pollutants. The cleaned extract after acid silica clean-up was evaporated to dryness, re-dissolved in 0.5 ml hexane and loaded onto a prepacked and silica cartridge (Bond-Elut Si, 500 mg, 3 ml, Agilent Technologies) pre-washed with 6 ml hexane. PBDEs and PCBs were eluted with 6 ml hexane (fraction 1), while MeO-PBDEs, HO-PBDEs, HO-PCBs, and hexabromocyclododecanes (HBCDs) were eluted with 6 ml DCM (fraction 2). Both fractions were evaporated to dryness and re-dissolved in 100 μl iso-octane (fraction 1) or methanol (fraction 2), respectively. Fraction 2 was first analyzed for HBCDs by LC–MS/MS (Shaw et al., 2012), after which methanol was evaporated to dryness and the extract was resolubilized in iso-octane and analyzed by GC/MS (see further).

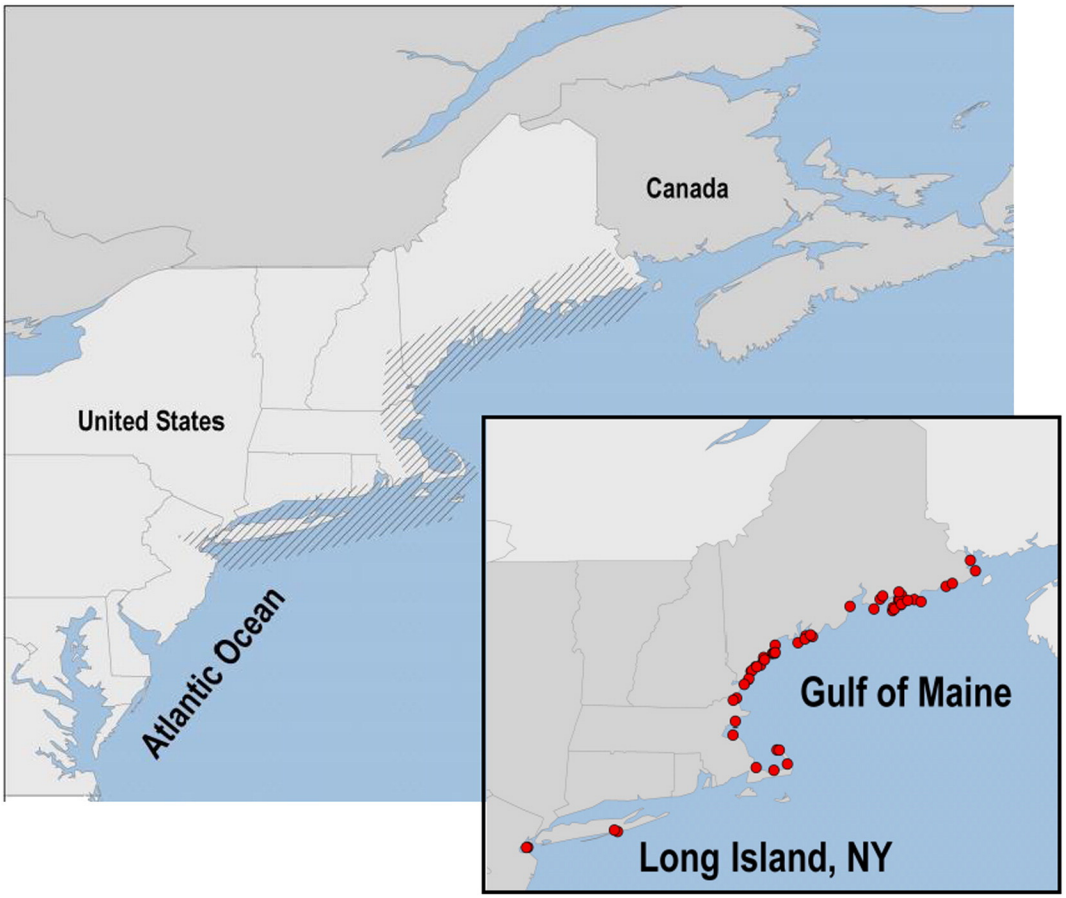

Fig. 1. Map of the northwest Atlantic showing stranding locations of harbor seals.