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Polychlorinated biphenyls still pose significant health risks to northwest Atlantic harbor seals

Susan D. Shaw [a,b,*], Michelle L. Berger [a], Liesbeth Weijs [c,d], Olaf Päpke [e], Adrian Covaci [c,d]

[a] Marine Environmental Research Institute, Center for Marine Studies, P.O. Box 1652, Blue Hill, ME 04614, USA
[b] Department of Environmental Health Sciences, School of Public Health, State University of New York at Albany, P.O. Box 509, Albany, NY 12201-0509, USA
[c] Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
[d] Systemic Physiological and Ecotoxicological Research (SPHERE), Department of Biology, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium
[e] Eurofins-ERGO, Neuländerkamp 1, 21079 Hamburg, Germany

HIGHLIGHTS

- $\sum_{30}$PCB concentrations in liver exceeded those in blubber and varied by age and gender.
- Accumulation of lighter PCBs in pup blubber may be strongly influenced by log K_{ow}.
- PCA loadings suggest heavier PCBs are transferred to pup liver during late lactation.
- PCBs were highly biomagnified from prey fish to tissues of adult harbor seals.
- Current PCB burdens in these seals likely diminish their fitness and survivability.

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ABSTRACT

Polychlorinated biphenyls (PCBs) have been detected at relatively high concentrations in harbor seals, apex predators in the northwest Atlantic. As part of an ongoing assessment of the effects of PCBs on population health, we analyzed tri- to deca-PCBs in the liver of 56 harbor seals (6 adult males, 50 pups) and in 11 blubber samples (4 adult males, 7 pups) and examined tissue-specific accumulation patterns, biomagnification potential, and toxic implications of current PCB concentrations. Hepatic $\sum_{30}$PCB concentrations (overall mean ± standard deviation: 76,860 ± 111,800 ng/g lipid weight, lw) were higher than blubber concentrations (48,180 ± 69,420 ng/g lw). Regional trends were suggestive of fresh PCB inputs from the industrialized, densely populated southern coast of New England versus the rural north. The lack of temporal trends confirmed that tissue concentrations of PCBs have plateaued since the early 1990s. Tissue distribution of PCBs varied significantly by age and, surprisingly by gender among the pups. Principal Component Analysis (PCA) revealed that lighter PCBs are selectively transferred from mother to pup blubber in relation to lipid solubility (log K_{ow}), but heavier PCBs may be efficiently transferred during late lactation from mother to pup liver. Biomagnification factors (BMFs) for $\sum_{6}$PCBs from prey fish to adult male seals ranged from 90 to 547 in the liver and 88 to 532 in the blubber, and suggested that molecular structure and metabolic capacity were more important influences than log K_{ow} on the retention of PCBs. Blubber concentrations of $\sum_{30}$PCBs in 87% of the pups were an order of magnitude higher than recent toxic reference values (TRVs) calculated for $\sum_{154}$PCBs in nursing harbor seals, suggesting that the pups are at risk for PCB-mediated toxicity at a vulnerable stage of development. Given the recurring pattern of epizootics in these seals, the health of the population is of concern.

1. Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) of priority concern for long-lived, high-trophic level wildlife such as marine mammals (Dorneles et al., 2013; Giesy and Kannan, 2001; Johnson-Restrepo et al., 2005; Letcher et al., 2009; Mos et al., 2010; Roos et al., 2010). Although emerging contaminants such as the polybrominated diphenyl ethers (PBDEs) and perfluorinated chemicals (PFCs) have been steadily increasing since the 1980s (Hites, 2004; Shaw and Kannan, 2009; Giesy and Kannan, 2001), PCBs remain the predominant POP in lipid tissues and pose the greatest health risks to many populations (Dorneles et al., 2013; Letcher et al., 2009; Mos et al., 2010).

* Corresponding author at: Marine Environmental Research Institute, Center for Marine Studies, P.O. Box 1652, Blue Hill, ME 04614, USA. Tel.: +1 207 374 2135; fax: +1 207 374 2931.
E-mail address: sshaw@meriresearch.org (S.D. Shaw).

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From 1929 until their prohibition in 1979, PCBs were in widespread use in North America as closed systems and heat transfer fluids, hydraulic fluids and lubricants, plasticizers, and fire retardants (US EPA, 2003). Over five decades, the U.S. was responsible for approximately half of the world's production of PCBs and imported 50% of the PCBs produced by other countries (UNEP Chemicals, 1999). Under current regulations, PCBs are still authorized for use in many applications (US EPA, 2003). Primary "new" sources of PCBs include in-service electrical equipment, transformers, machinery, manufacturing sites, building materials, landfills and scrap yards, and waste and recycling operations, many of which are located in densely populated urban/industrial centers (ATSDR, 2014; US EPA, 2003). It was estimated by the late 1980s that only about 1% of all PCBs had reached the oceans, while about 30% had accumulated in dumpsites and sediments of rivers, coastal zones, and estuaries (Marquenie and Reijnders, 1989).

Harbor seals (*Phoca vitulina concolor*) inhabiting the northwestern Atlantic (from eastern Canada to New York) have been shown to be highly contaminated by POPs, with PCBs dominating their tissue profiles in the order: PCBs > DDTs > PBDEs > chlordanes (CHLs) > PFCs > mirex > hexachlorocyclohexanes (HCHs) > dieldrin > hexachlorobenzene (HCB) (Shaw et al., 2005, 2007, 2008, 2009a,b, 2012). $\sum$PCB concentrations in harbor seal blubber were four times higher than $\sum$DDT concentrations, and contributed 61–75% of the total organochlorine content (Shaw et al., 2005). This contamination pattern reflects significant riverine, urban, and industrial pollutant discharges from industrialized areas of the US Northeast region as well as inputs via long-range atmospheric transport (Hameedi et al., 2002). In the southern portion of the range, coastal urban development has produced some of the densest concentrations of human populations in North America, and PCB contamination has been a concern since the 1950s (O'Connor, 1990).

The northwest Atlantic harbor seal population has been increasing since the 1970s and is currently estimated to comprise 99,000 seals (Gilbert et al., 2005). Similar to harbor seals from Europe, this population appears to be susceptible to disease outbreaks, as evidenced by a recurrence of epizootics since the late 1970s. In 1979–80 and again in 1991–92, viral epizootics resulted in the deaths of approximately 1000 harbor seals from Maine to New York (Geraci et al., 1982; Duignan et al., 1993; 1995). Between 2004 and 2009, approximately 2000 harbor seals died of unknown causes during "Unusual Mortality Events" (UMEs) along the New England coast (Garron and McNulty 2008). The possible contributory role of POPs in these events cannot be ruled out, since the PCB burdens alone in these seals exceed the estimated threshold levels for POP-mediated reproductive and immune system effects in the species (Kannan et al., 2000; Shaw et al., 2005).

High levels of PCBs have been implicated in reproductive failure in ringed seals (*Phoca hispida*), harbor seals (*Phoca vitulina*), and gray seals (*Halichoerus grypus*) (Helle et al., 1976; Hutchinson and Simmonds, 1994; Reijnders, 1986), skull deformations, bone lesions, and immunotoxicity in Baltic gray seals (Bergman et al., 1992; Mortensen et al., 1992; Sørmo et al., 2009), reduced immune functions (De Swart et al., 1994; Ross et al., 1995) and altered thyroid hormone levels (Brouwer et al., 1989) in harbor seals, and a high prevalence of neoplasms and carcinoma, causing mortality in California sea lions, *Zalophus californianus* (Ylitalo et al., 2005). Recent biomarker studies (Mos et al., 2006, 2007, 2010; Simms et al., 2000; Tabuchi et al., 2006) suggest that adverse endocrine and immune system effects in young harbor seals may occur at much lower exposure concentrations than previously demonstrated in adults.

Whereas the blubber is the most commonly analyzed tissue in marine mammals, recent studies highlight the importance of the liver as a target tissue for the accumulation of PCBs and other POPs (Raach et al., 2011; Shaw et al., 2012). The liver is a large, perfused tissue that plays an active role in lipid and protein metabolism and the biotransformation of contaminants into more excretable metabolites (e.g., OH-PCBs). The blubber, having a more metabolically active inner layer and an outer layer that acts as a major reservoir, integrates historical accumulation of POPs, whereas the liver is considered to be a better indicator of recent exposure to POPs and toxicity (Raach et al., 2011).

The aim of this study was to characterize the current concentrations and patterns of PCBs in the tissues of northwest Atlantic harbor seals as part of an ongoing assessment of the effects of POPs on population health. PCBs were measured in harbor seal liver samples (n = 56) and in a subset of blubber samples (n = 11) to enable tissue comparisons. PCB concentrations previously measured in harbor seal prey fishes were compared with the tissue concentrations in adult male seals to estimate the biomagnification potential of PCBs in this marine food web. Most of the study animals were nursing or recently weaned pups, providing an opportunity to examine tissue-specific accumulation of PCBs resulting from maternal transfer. Potential PCB-related health effects of the current concentrations in the pups were assessed by applying the most recent toxicity reference values (TRVs) for sublethal effects of PCBs in nursing harbor seals (Mos et al., 2010).

2. Material and methods

2.1. Harbor seal samples

Liver samples were collected from 56 harbor seals (6 adult males, 28 female pups, 22 male pups) that were stranded along the northwest Atlantic coast between 2001 and 2006 (Fig. SI-1). Blubber samples were collected from 11 seals (4 adult males, 6 female pups, 1 male pup) to enable tissue comparisons. Samples were collected from adult male seals between March and October, and from pups between May and November. The majority of the samples (77%, 44 of 57) were collected from pups that were stranded during the months of June, July and August. Liver samples were code 2 (fresh dead) with the exception of seven samples from code 3 (moderate decomposition) animals. Blubber samples were collected from code 2, 3, and 4 (advanced decomposition) animals. Five paired liver–blubber samples were collected from four pups and one adult male. Seals were weighed, and standard length and axillary girth were measured. Age class was estimated based on body size. Samples were stored in a freezer at −20 °C until analysis.

2.2. Fish samples

Eighty seven (87) prey-sized individual fish (<35 cm) representing seven species known to be harbor seal prey were collected from Maine coastal waters by the State of Maine Department of Marine Resources during the June 2006 Gulf of Maine Trawl Survey of commercial groundfish stocks. Species included silver hake (*Merluccius bilinearis*, n = 10), white hake (*Urophycis tenuis*, n = 17), Atlantic herring (*Clupea harengus*, n = 20), American plaice (*Hippoglossoides platessoides*, n = 10), alewife (*Alosa pseudoharengus*, n = 10), and winter flounder (*Pseudopleuronectes americanus*, n = 10). Atlantic mackerel (*Scomber scombrus*, n = 10) were caught by hook and line from the same area during June 2006. Whole fish were directly placed on ice and transported to the laboratory where standard length and weight were recorded, then frozen and stored at −40 °C prior to shipment to the analytical laboratory. Details of the fish sample preparation for analysis are reported elsewhere (Shaw et al., 2009a).

2.2.1. Chemical analysis in seal tissues

In liver and blubber samples, target analytes included 30 PCB congeners (IUPAC numbers: 18, 28, 31, 44, 49, 52, 74, 87, 95, 99, 101, 105, 110, 118, 128, 138, 149, 151, 153, 156, 170, 177, 180, 183, 187, 194, 195, 199, 206, and 209). CB-143 was used as a surrogate internal standard for the quantification and 12,3,4-tetrachloronaphthalene (TCN) was used as injection (recovery) standard for the calculation of recoveries for CB-143. All individual PCB standards and TCN were obtained from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). All