Persistent Organic Pollutants (POPs) in Harbor Seals (Phoca vitulina concolor) from the Northwestern Atlantic Coast

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Introduction
Harbor seals (*Phoca vitulina*) are widely distributed in the temperate nearshore waters of the northern hemisphere and are useful sentinels of food chain contamination because they occupy a high trophic level, are long-lived, and accumulate high concentrations of persistent organic pollutants (POPs). Concern has focused on the polychlorinated biphenyls (PCBs), dioxins and furans (PCDD/Fs), and chlorinated pesticides (DDT, chlordane) because of their physiochemical properties and their documented immune- and endocrine-disrupting potential in marine wildlife and humans[1,2]. The sensitivity of harbor seals to the effects of these compounds was previously demonstrated by a semi-field study in which immune and endocrine functions were reduced in seals fed POP-contaminated fish from the Baltic Sea[3].

Since the 1970s, very little research has been conducted on levels and potential effects of POPs in harbor seals inhabiting the northwestern Atlantic coast. During 1979-1980, an outbreak of type A influenza virus occurred among these seals, spreading northward from Cape Cod into the Gulf of Maine and ultimately resulting in the deaths of more than 500 animals[4]. A decade later, during the winter of 1991-1992, a morbillivirus epizootic of unknown magnitude was reported among harbor seals found stranded from southern Maine to Long Island, New York[5]. A possible role of environmental chemicals (*e.g.*, PCBs) in these outbreaks was not investigated, although data from the 1970s indicated that their PCBs and DDT burdens were approaching the 100 ppm range[6]. The estimated threshold value for adverse effects in harbor seals including effects on immune function is ~17µg PCB/g lw in blubber[7]. At present, there are an estimated 99,340 harbor seals (*Phoca vitulina concolor*) inhabiting New England waters from the Gulf of Maine along the Atlantic coast to New Jersey[8]. Isolated from the deeper waters of the northeast Atlantic Ocean by Georges and Brown Banks and Nantucket Shoals, the northern portion of their range is a semi-enclosed sea with a principally estuarine circulation pattern receiving significant riverine, urban, agricultural, and industrial pollutant inputs from population centers in the Northeast as well as via long-range atmospheric transport. The harbor seal population has steadily increased since the early 1980s, although in recent years, pup production has sharply declined in southern and mid-coast Maine for reasons that are poorly understood[9]. Here we report results of the first comprehensive analysis of organohalogen compounds in harbor seals along the northwestern Atlantic coast.

Methods and Materials

Samples. During 2001 and 2002, blubber samples were collected *postmortem* from 31 harbor seals (6 adults, 17 yearlings, 5 pups, and 3 fetuses) that had stranded at locations in the Gulf of Maine (n=25, 12 males, 11 females, 2 of unknown gender) and south from Cape Cod (n=6, 3 males, 3 females) along the mid-Atlantic coast to the eastern shore of Long Island, NY (Fig. 1). Data on the 3 fetal samples were used in age comparisons but were otherwise excluded from the analysis. Seals were weighed, and standard length and axillary girth were measured. Age was estimated based on body size. Body condition was assessed by calculating condition indices (axillary girth/standard length X 100)[10]. Blubber samples were stored in a freezer at -40°C until analysis.

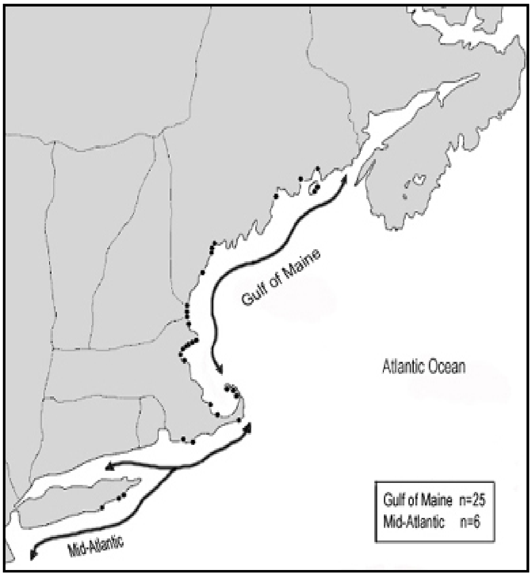


Figure 1. Stranding locations of harbor seals along the northwestern Atlantic coast. Lines and arrows represent possible seasonal movements of the population.

Chemical Analysis. Blubber samples were extracted in an accelerated solvent extraction (ASE) cell with methylene chloride. Surrogate, internal standard and matrix spiking solutions were added to the cell prior to extraction. Samples were cleaned up using silicagel columns and gel permeation chromatography (GPC). Extracts were passed across a Florasil cartridge for final clean-up. Samples were reduced in volume using high purity nitrogen. Identification and quantification of PCBs and OCs was performed using HRGC (Agilent 6890), with dual microelectron capture detectiors (GC/uECD) by NOAA Method ORCA 130[11]. GC separation was carried out by two 60-m long x 0.25-mm I.D. fused silica capillary columns, DB-XLB and DB-5ms, using helium as a carrier gas. Final concentrations were not corrected for internal standard or surrogate recovery. A method blank, a lab control spike sample and a MS/MSD pair was processed with each sample preparation batch or every 20 samples.

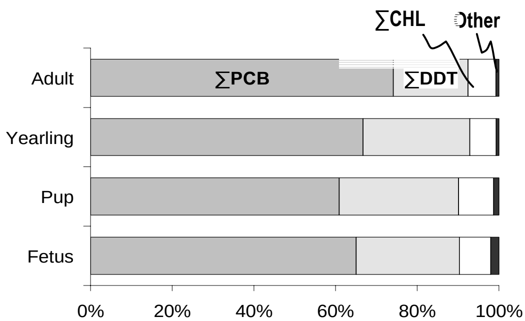


Figure 2. Contribution of POPs to the total OC load in harbor seals by age

Results and Discussion

PCBs, DDT, and chlordane-related compounds (CHL) were the major persistent POPs in harbor seals relative to other groups (Figure 2). The sum of PCB_{soc20} and DDT concentrations contributed up to 95% of the total POPs measured. PCBs were the predominant contaminant, followed by DDT, CHLs, mirex, HCHs, and dieldrin. Ten PCB congeners (52, 101, 105, 118, 128, 138, 153, 170, 180, and 187) accounted for the majority (98%) of total PCBs in seal blubber. *p,p'*-DDE was the major DDT residue in all samples. Although ratios of *p,p'*-DDE/ ∑DDT were similar for seals in all age groups, the pups had the highest *p,p'*-DDE/ ∑DDT ratios, averaging 0.90 ± 0.03.

Mean blubber concentrations of ∑PCB and ∑DDT were relatively high (33.9 and 12.9 µg/g, lw, respectively) (Table 1). The PCB burdens in these seals were two-fold higher than the proposed threshold level of 17µg PCB/g lw in blubber for adverse effects on immune function in the species[7].

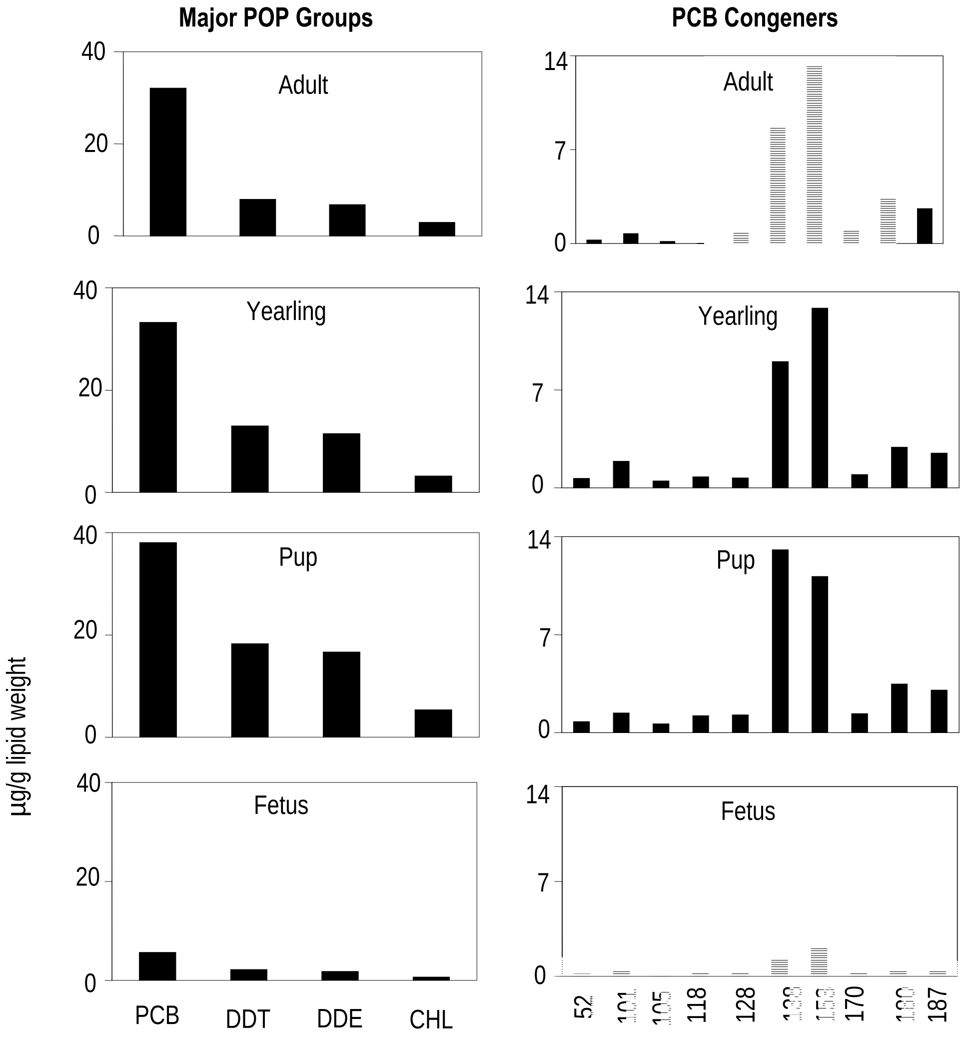
Table 1. POP concentrations (ng/g, lw) in blubber of harbor seals from the northwestern Atlantic coast

Sample Date	∑PCB	∑DDT	p,p'- DDE	∑CHL	Mirex	∑HCH	Dieldrin
2001	33,865 ± 35,969 5,668 – 150,501 (28)	12,855 ± 13,819 1,388 – 57,541 (28)	11,411 ± 12,423 1,231 – 50,386 (28)	3,551 ± 4,242 317 – 17,570 (28)	123 ± 164 3.2-605 (28)	121 ± 96 22-425 (28)	92 ± 201 3-1,064 (28)
1991	28,344 ± 17,607 14,229-48.075 (3)	11,386 ± 7,605 4,685-19,652 (3)	10,074 ± 6,503 4,179-17,050 (3)	2,728 ± 2.102 1,119-5,106 (3)	110 ± 61 40-155 (3)	118 ± 82 68-212 (3)	64 ± 24 44-91 (3)

Values given are mean ± standard deviation

Influence of gender, age, and condition. The lack of significant POP-gender relationships observed in these samples is likely due to the fact that 81% of the animals were one year of age or less. The highest POP concentrations were found in the pups (mean 38, 18.3, and 5.4 µg/g, lw, for ∑PCB, ∑DDT, and ∑CHL, respectively), followed by yearlings, adults, and fetuses (Figure 3). Elevated levels in the pups reflect the importance of perinatal exposure, and are of concern because their PCB levels are 2-fold higher than the estimated threshold level for adverse effects in adult harbor seals[7], and because these levels are an order of magnitude higher than those associated with reduced immune responses and thyroid hormone levels reported in stranded harbor seal pups from the central California coast[12]. With the exception of DDT, blubber levels of the major POPs were significantly higher in the pups than in fetal samples, reflecting the greater accumulation of lipophilic POPs through lactational versus placental transfer.

Body condition was positively correlated with age (R=0.673, p=0.008), with mean condition indices (CIs) ranging from 56.4 ± 7.1 in pups to 67.9 ± 2 in the adults. As expected, condition indices in these seals were lower than those recently reported for free-ranging harbor seals[13], and could reflect the older ages of the wild seals as well as the influence of stranding in the present study. Condition indices were not significantly correlated with POP concentrations in these samples, which is likely due to the fact that these are age-related markers of growth rather than markers of nutritive status. The total lipid content (% lipid) in blubber was positively correlated with condition (p=0.001), and negatively correlated with the major POPs. The lipid content of four samples (two pups, two yearlings) was extremely low (< 34%) and the POP concentrations in these samples were 3-4 fold higher than the others (mean ∑PCB 77.4 versus 24.3 µg/g, lw), which suggests that these individuals were mobilizing their lipid reserves, and subsequently concentrated POPs in the remaining lipid. However, the mean ∑PCB concentrations in the other seals were still high enough to place them at risk for POP-related immune suppression and other adverse effects.


Major POP Groups
PCB Congeners
Adult
Yearling
Pup
Fetus
µg/g lipid weight
40
20
0
14
7
0
PCB
DDT
DDE
CHL
52
101
105
118
128
138
153
170
180
187

Regional variability. Two isolated harbour seal colonies have been proposed in this region with distinct seasonal patterns of movement (Figure 1) and some exchange occurring between colonies, one inhabiting the Gulf of Maine (north of Cape Cod, MA) and the other inhabiting the southern, mid-Atlantic region (south of Cape Cod to the New Jersey coast) (Waring, pers. comm.) Levels and patterns of POPs in seals from the two regions were compared to determine possible differences that might contribute to the identification of discrete harbor seal colonies, but regional differences were not significant (data not shown). Because levels were found to vary by age, POP levels were compared in seals of the same age class (yearlings) from the Gulf of Maine and the southern region, but no significant differences were found. Further research is needed to clarify possible spatial variation in POP accumulation in these seals.

Temporal variability. While temporal comparisons must be viewed with caution because sampling locations are not identical and analytical methods have changed, PCB and DDE burdens in blubber of harbor seals in the present study were considerably lower than the extremely high 1972 levels (mean PCB 92.5 and *p,p'*-DDE 35-53 µg/g, ww) [6], which is consistent with a general decline of these compounds in the environment. Compared with data reported on a wet weight basis by Lake and co-workers (1995) [14] on stranded harbor seals from this region in 1980 and 1990-92, the mean PCB concentrations in the present study (13.7 µg/g, ww) were similar to levels in the 1980 samples (12 µg/g, ww) but 2-fold higher than levels in the 1990-92 samples (6.7 µg/g, ww). Levels of *p,p'*-DDE in this study (5.3 µg/g, ww) were lower than those reported in the 1980 samples (10.9 µg/g, ww), but similar to the levels in 1990-92 samples (4.12 µg/g, ww).

For comparison purposes, we analyzed POPs in archival blubber samples obtained from three yearling harbor seals found in the same area in 1991 (Table 1). Mean levels in the 1991 samples were slightly lower but in similar concentration ranges (28.3 and 10.1 µg/g, lw, for PCBs and *p,p'*-DDE, respectively) as those detected in our 2001-2002 samples (33.9 and 11.4 µg/g, lw). Moreover, blubber concentrations of PCBs found in the present study are in the same ranges as those recently reported in adult male harbor seals from the St. Lawrence estuary[15]. These data suggest that POPs may not be declining further in the northwestern Atlantic ecosystem.

Figure 3. Mean concentrations (µg/g, lw) of major POP groups and the 10 predominant PCB congeners in blubber of harbor seals from the northwestern Atlantic coast

These ar[illegible] his region i[illegible] ine pesticides, the data suggest that harbor seals inhabiting the northwestern Atlantic coast may accumulate levels of organohalogen compounds that place them at risk for adverse health effects including effects on immune and endocrine function. Levels in the pups resulting from perinatal exposure are of special concern given that young seals appear to be vulnerable to immune- and endocrine-disrupting effects of PCBs and *p,p'*-DDE when levels are an order of magnitude lower[12]. In view of the past vulnerability of these seals to viral epizootics, the data show a clear need for long-term monitoring of POP exposure in conjunction with assessment of health status in the population.

Acknowledgments
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