Seals as Sentinels Research

Perfluorinated Compounds (PFCs) in Northwest Atlantic Harbor Seals

Abstract
Concentrations of perfluorochemicals (PFCs) including perfluoroalkylsulfonates (PFSAs), and perfluoroalkylcarboxylates (PFCAs) were determined in liver of harbor seals (n=68) collected from the northwest Atlantic between 2000 and 2007. Of ten PFCs measured, perfluorooctane sulfonate (PFOS) concentrations were the highest in liver (8 to 1388 ng/g, ww), followed by perfluoroundecanoic acid (PFUnDA) (<1 to 30.7 ng/g, ww). An unusual accumulation profile of long-chain (C7-C12) PFCAs, and the predominance of PFUnDA, followed by PFNA in seal liver suggested that fluorotelomer alcohols (FTOHs) may be a major source of PFCAs in the northwest Atlantic. No gender-related differences in the concentrations of individual PFCs or total PFCs were found. Concentrations of PFOS and PFDS were higher in tissues of the pups than the adults, whereas concentrations of the PFCAs were similar between pups and adults.

PFOS concentrations in the pups were 2.6-fold higher than those in the adult females, suggesting the importance of maternal transfer of PFCs. Hepatic PFOS concentrations were strongly, positively correlated with PFOSA, PFDS and individual PFCAs, indicating that harbor seals are exposed simultaneously to these compounds. Temporal comparisons of hepatic PFC concentrations showed a marginal increase of PFOS and PFCAs in the adult seals from 2000 to 2007. Unlike the spatial trend observed for polychlorinated biphenyls (PCBs), no south to north (urban-rural-remote) decreasing trend was observed for PFCs, suggesting the presence of diffuse sources of PFC contamination throughout the northwest Atlantic. Shaw et al. (2009) *Chemosphere* 74: 1037–1043.

Background
Perfluorochemicals (PFCs) are persistent halogenated contaminants that are widely distributed in the environment, in wildlife, and in humans worldwide. For over 40 years, PFCs have been used in a variety of industrial and consumer products, including protective coatings for carpets and apparel, nonstick cookware, paper coatings, insecticide formulations, and surfactants in fire-fighting foams. PFCs have been shown to bioaccumulate and biomagnify in marine food webs and elevated concentrations are detected in marine mammals.

Two major classes of PFCs are perfluoroalkyl sulfonic acids (PFSAs), and perfluoroalkyl carboxylic acids (PFCAs). The PFSAs (e.g., perfluorooctanesulfonate [PFOS] and perfluorooctane sulfonamide [PFOSA]), are degradation products of perfluoroalkyl sulfamido alcohols via biotransformation processes and abiotic oxidation. Concerns about widespread global contamination by PFOS led to a phase-out of production of PFOS-based compounds by a major producer in 2001 (3M, 2000); however, PFCAs continue to be manufactured worldwide for use as emulsifiers and additives in the polymerization process

PFCs are known to adversely affect both pre- and post-natal development and the neuroendocrine and immune systems in animals via at least five different pathways. Recent field studies suggest that PFC-mediated effects occur in marine mammals, including infectious disease in California sea otters and modulation of the peroxisome proliferator-activated receptor α-cytochrome P450 4A-signaling pathway associated with carcinogenesis in Baikal seals. There is no evidence for biodegradation of PFCs in the environment, thus the toxic potential of PFSAs and long-chain PFCAs in wildlife and humans is of concern.

Findings

This is the first report of PFC contamination in marine mammals from the northwest Atlantic marine coastal region.

PFOS was the dominant PFC found in seal liver at concentrations ranging from 8 to 1388 ng/g ww (mean 216 ng/g ww). Other perfluoroalkyl sulfonates (PFDS and PFOSA) were detected at much lower concentrations than PFOS, ranging from <1 to 25.8 ng/g ww. Perfluoroalkyl carboxylates (PFCAs, C7-C12) were detected at concentrations ranging from <1 to 87.4 ng/g, ww (mean 25.9 ng/g, ww).

PFOS concentrations in northwest Atlantic harbor seals were within the range of concentrations detected in liver of marine mammals from various mid-latitude locations. Levels in our samples were an order of magnitude higher than those reported in harbor seals from the US Pacific coast but lower than levels in bottlenose dolphins from the Florida coast and the South Carolina coast.

We found a new and unusual accumulation profile of long-chain PFCAs in liver of harbor seals which suggests a shift in recent sources of emission of PFCs. This profile is unusual because for most marine mammals from North American and European coastal waters, perfluorononanoic acid (PFNA) is the second most prevalent PFC, after PFOS, whereas in this study, perfluoroundecanoic acid (PFUnDA) is the second most abundant PFC in seals.

Another interesting finding of this study was the unusual pattern of long-chain PFCAs in seal liver: PFUnDA (C11)> PFNA (C9)>PFDA (C10)>PFDoDA (C12), which differs from the general odd/even pattern observed in biota.

This study represents the first comprehensive dataset to provide evidence for higher accumulation of PFCs in seal pups than in adults. Although not mother-pup pairs, mean PFOS concentrations in the pups were 2.6-fold higher than those in adult females, indicating that maternal transfer is a significant exposure route for PFCs to pups.

There were no differences in PFC concentrations between adult males and females. This pattern differs from other POPs in which concentrations are lower in adult females due to placental and lactational transfer to pups. This implies that the elimination capacity for PFCs is significant in adult animals. Moreover, the half-lives of the compounds may be relatively short.

Although several studies have reported an increasing trend in PFOS and PFCA concentrations in marine mammals over the past 20 to 30 years No temporal trend was observed for PFC concentrations in harbor seals between 2000 and 2007, suggesting continuous inputs and/or recycling of these persistent compounds in the northwest Atlantic.

There was a lack of an urban-rural-remote decreasing spatial trend (from New York to Maine) in hepatic PFC concentrations in these seals which, along with their unusual PFC profile, implies that diffuse common sources are significant throughout the northwest Atlantic marine ecosystem. These may include landfill leachate and wastewater effluent from households and industries as well as precursor molecules (sulfonamido alcohols and FTOHs)

These novel findings underline the growing problem of PFC contamination of marine ecosystems and the need for policy decisions regarding the production and use of PFCs.

Publications resulting from this research:

Shaw, S. D., Berger, M. L., Brenner, D., Tao, L., Wu, Q., Kannan, K. (2009). Specific accumulation of perfluorochemicals in harbor seals (*Phoca vitulina concolor*) from the northwest Atlantic. *Chemosphere* 74: 1037–1043.

Shaw, S.D., Berger, M.L., Brenner, D., Kannan, K. (2006). Perfluorooctane sulfonate and related perfluorinated hydrocarbons in harbor seals (*Phoca vitulina concolor*) from the northwest Atlantic. *Organohalogen Compounds* 68: 2042-2046.

Shaw, S.D. (2006). Seals as Sentinels: Assessing Toxic Contaminants in Northwestern Atlantic Coast Seals. Final Project Report to the National Oceanographic and Atmospheric Administration. Marine Environmental Research Institute, Blue Hill, ME, 123 pp. Contract No. EA133F05CN1358.