FLUORINATED ORGANIC COMPOUNDS IN AN EASTERN ARCTIC MARINE FOOD WEB

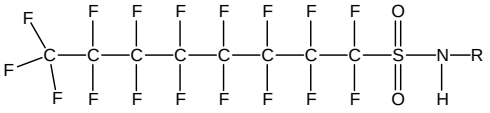
Gregg Tomy[1], Wes Budakowski[1], Thor Halldorson[1], Paul Helm[1],Gary Stern[1] and Sheryl Tittlemier[2]

[1] Department of Fisheries & Oceans, Freshwater Institute, Winnipeg, MB Canada
[2] Food Research Division, Health Canada, Ottawa, Ontario, Canada, K1A 0L2

Introduction

Fluorinated organic compounds (FOCs) constitute a diverse group of chemicals that have emerged as an environmental concern. They are used in a variety of specialized consumer and industrial products. The perfluorinated acids are the group of FOCs that has attracted much interest. Of these, perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA, $C_7F_{15}COO^-$) have recently received the most attention. Much of the concern surrounds the ubiquitous presence of both compounds in the environment. PFOS and PFOA have been detected in human sera[1], freshwater and marine biota[2,3,4], and surface water[5,6]. Their unique chemical and biological stability appears to preclude any degradation or metabolism, and contributes to the bioaccumulation and persistence of PFOS and PFOA.

The perfluorosulfonamide group of FOCs are used in some pesticide formulations, as surfactants, and as intermediates in the synthesis of other FOCs[7,8,9]. For example, *n*-ethyl perfluorooctanesulfonamide [N-EtPFOSA, $C_8F_{17}SO_2NH(C_2H_5)$, **I**] commonly known as Sulfluramid, is an insecticide used to control cockroaches, termites and ants[8,10]. Although not registered for use in Canada, it has recently been detected in air samples from Toronto, Ontario[11]. A recent study has shown that N-EtPFOSA can be biotransformed to PFOS in fish[12]. Two possible reaction pathways were found: (a) direct deamination of N-EtPFOSA followed by oxidation of sulfone group to form PFOS and, (b) deethylation to form perfluorooctanesulfonamide [PFOSA, $C_8F_{17}SO_2NH_2$, **I**], followed by deamination and oxidation to PFOS.



I (N-EtPFOSA: R = C_2H_5; PFOSA: R = H)

This study examines the extent of bioaccumulation and transfer of PFOA, PFOS and PFOS-precursors (N-EtPFOSA and PFOSA) in a marine food web from the Eastern Canadian Arctic.

Methods and Materials

Samples. Archived livers of beluga (*n=5*), arctic cod (*n=5*) and deepwater redfish (*n=5*) collected from Frobisher Bay (FB), narwhal (Grise Ford, *n=3*) and walrus (Cape Dorset, *n=5*) were analyzed for FOCs. Composites of zooplankton and shrimp from FB were also analyzed.

Extraction. The extraction of FOCs from samples was done in a similar manner to that described by Hansen et al.[13]. Perfluorobutanesulfonate (PFBS) was added to all samples and used as a recovery standard.

Liquid Chromatography. Samples were chromatographed on a Supelcosil C_8 analytical column (5.0 cm × 2.1 mm i.d., 5 μm particle size; Supelco, Oakville, ON, Canada). The analytical and C_8 guard columns (Phenomenex, USA) were installed on an Agilent 1100 Series HPLC system (Agilent Technologies, Palo Alto, CA, USA) equipped with a vacuum degasser, binary pump and autosampler. The mobile phase used consisted of water (A) and methanol (B), both of which contained 2 mM ammonium acetate. Flow rate was 300 µL/min, and the injection volume was 3 µL. Gradient elution was used, and it started at 20% B, increased to 95% B in 9.5 minutes, and was held for 2 minutes. The mobile phase was returned to starting conditions in 5 minutes. The column was allowed to equilibrate for 5 minutes between runs. A blank methanol solution was run twice after each sample or standard using the same gradient elution. Due to the known tendency of FOCs to contaminate systems through carryover, after every 10–15 samples, the LC/MS/MS system was rinsed with methanol containing 75 mM ammonium acetate for several hours.

Mass Spectrometry. Analyses were performed with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) using multiple reaction monitoring (MRM) in the negative ion ESI mode. The optimized parameters were: ionspray voltage, –1200 V, curtain gas, 15.00 arbitrary units (a.u.), sheath gas, 30.00 a.u., turbo gas, 35.00 a.u., temperature, 525 ˚C, focusing potential, –360 V, collision assisted dissociation gas 8 a.u.. The transitions monitored, and the corresponding collision energy (CE) of the transitions, were as follows: PFBS, 299>80 (CE= –51.00 V), 299>99 (CE= –37 V); PFOA, 413>369 (CE= –9 V), 413.169 (CE= –26); PFOS, 499>80 (CE= –80 V), 499>99 (CE= –63 V); PFOSA, 498>78 (CE= –45 V); N-EtPFOSA, 526>169 (CE= –34 V).

QA/QC. The average recovery of PFBS that was spiked into the samples and was used to correct for PFOS and PFOA, was 72 ± 13 %. The average recovery of N-EtPFOSA (*n = 7*) and PFOSA (*n = 7*) which were spiked into Optima grade water and taken through all phases of the analytical procedure were 40 and 20 %, respectively. The low recoveries of both the sulfonamides were somewhat expected as the analytical method adopted was designed especially for PFOS and PFOA, two anionic compounds in solution. Although the recoveries of the sulfonamides were low, especially for PFOSA, the reproducibility of the extraction was very good: the coefficient of variation was 13% in both cases. Even with its limitations, we chose to use the method because it allowed us to perform the analyses of all the targeted compounds using a single analytical detection technique.

Results and Discussion

PFOS and PFOA.

PFOS and PFOA were detected in all animals. Figure 1 shows the levels of PFOS and PFOA in the food web from the eastern Canadian arctic. It is clear that both PFOS and PFOA bioaccumulate in biota. The highest concentrations of PFOS were found in beluga (8.7–14.3 ng/g, w/w) and narwhal (3.9–16.2 ng/g, w/w). PFOA levels were highest for the deepwater redfish (2.9–57 ng/g, w/w). PFOS (1.1–2.1 ng/g, w/w) and PFOA (1.7–3.4 ng/g, w/w) present in zooplankton are possibly due to uptake directly from the water.

The biomagnification factors (BMF = mean wet wt. concentration in predator/mean wet wt. concentration in prey) of PFOS and PFOA between beluga and cod were 9.4 and 5.4, respectively. Between narwhal and cod, respective PFOS and PFOA BMFs were 8.5 and 3.1.

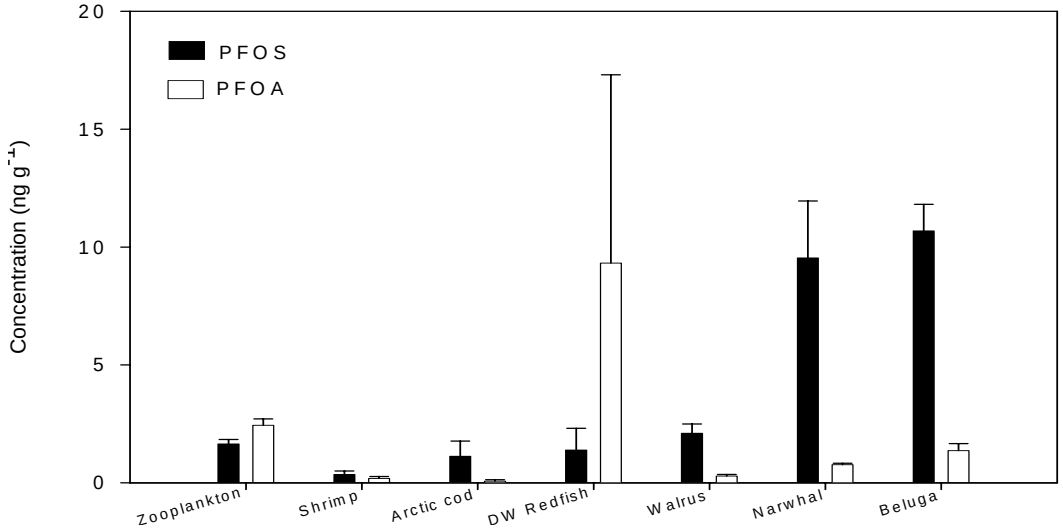


Figure 1. Concentrations (arithmetic mean ± 1 standard error) of PFOS and PFOA (ng/g, wet wt.) in an Eastern Arctic food web. Zooplankton and shrimp data are whole body concentrations, while fish and marine mammal data are liver concentrations.

N-EtPFOSA and PFOSA.

Levels of N-EtPFOSA and PFOSA in the food web were also examined since the biotransformation of N-EtPFOSA to PFOS in fish has been demonstrated[12]. One possible reaction pathway for the transformation of N-EtPFOSA to PFOS is via PFOSA.

Deepwater redfish had the highest levels of N-EtPFOSA (1.3–2.9 ng/g) of all the animals. Concentrations in zooplankton, shrimp, cod, and walrus were below method detection limits. Relative to redfish, the higher trophic level animals (beluga and narwhal) had much lower levels of N-EtPFOSA and higher levels of PFOSA.

One possible explanation for this difference among species is that N-EtPFOSA may be readily transformed by narwhal and beluga, but to a lesser extent by redfish. This may be due to a lower metabolic capacity of redfish compared to marine mammals. Such a difference in metabolic capabilities towards organohalogen contaminants amongst different marine biota species has been observed[14]. The low levels of PFOSA observed in redfish (an intermediate in the metabolism of N-EtPFOSA to PFOS) is also consistent with the explanation of a low metabolic capability.

The higher PFOSA levels in beluga and narwhal relative to redfish may be due to the higher capacity of these species to biotransform N-EtPFOSA. Ecological differences likely also contribute to the difference in concentrations of PFOSA. As with some other halogenated contaminants, narwhal and beluga are likely exposed to larger amounts of PFOS precursors (ie. N-EtPFOSA and PFOSA) than redfish because of their higher trophic level in the marine food web. Even though the marine mammals may have a greater ability to biotransform the PFOS precursors, a variation in exposure could also be reflected in the body burdens of PFOSA, especially if the biotransformation of this compound to PFOS occurs at a slower rate than the biodegradation of N-EtPFOSA.

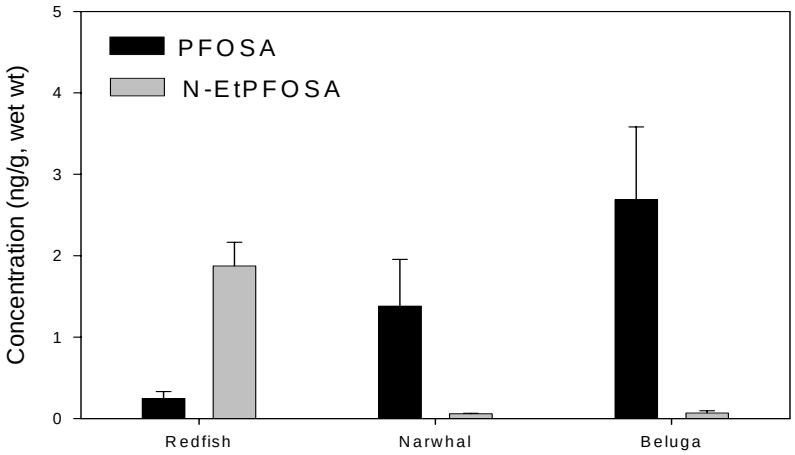


Figure 2. Concentrations (arithmetic mean ± 1 standard error) of N-EtPFOSA and PFOSA (ng/g, wet wt) in livers of redfish, narwhal and beluga from the eastern arctic

Acknowlegdements
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References

1. Olsen, GW, Burris, JM; Mandel, JH; Zobel, LR (1999) J. Occ. Envir. Med. *41*, 799
2. Giesy, JP, Kannan, K (2002). Environ. Sci. Technol. *36*, 147A
3. Giesy, JP, Kannan, K (2001) Environ. Sci. Technol. *35*, 1339
4. Kannan, K; Koistinen, J; Beckmen, K; Evans, T; Gorzelany, J; Hansen, KJ; Jones, PD; Helle, E; Nyman, M; Giesy, JP (2001) Environ. Sci. Technol. *35*, 1593
5. Moody, CA; Kwan, WC; Martin, JW; Muir, DCG; Mabury, SA (2001) Anal. Chem. *73*, 2200
6. Moody, CA; Martin, JW; Kwan, WC; Muir, DCG; Mabury, SA (2002) Anal. Chem. *36*, 545
7. *Fluorochemical Use, distribution and release overview:* (1999). U.S. Environmental Protection Agency. Washington, DC 1999; AR226-0550
8. Key, BD; Howell, RD; Criddle, CS (1997) Environ. Sci. Technol. *31*, 2445
9. Kissa, E. *Fluorinated surfactants and repellents*, (2001) 2nd; Marcel Dekker Inc.: New York
10. Grossman, MR; Mispagel, ME; Bowen, JM (1992) J. Agri. Food Chem. *40*, 2505
11. Martin JW, Muir DCG, Moody CA, Ellis DA, Kwan WC, Solomon K, Mabury SA. (2002) Anal. Chem. *74*, 584
12. Tomy GT, Tittlemier SA, Palace VP, Braekevelt E, Budakowski WR, Lau BPY, Eales G, Plohman JC. (2002) *Proceedings SETAC 23rd Annual Meeting*, November 16-20, Salt Lake City, Utah, USA.
13. Hansen, KJ; Clemen, LA; Ellefson, ME; Johnson, HO (2001) Environ. Sci. Technol. *35*, 766
14. Boon, JP; Eijgenraam, F; Everaarts, JM (1989) Mar Environ Res *27*, 159.