Serum concentrations of polyfluoroalkyl compounds in Faroe Islands residents

Kato K[1)], Calafat AM[1)], Reidy JA[1)], Bryant XA[1)], Nielsen F[2)], Weihe P[2),3)], Grandjean, P[2),4)], Needham LL[1)]
1. Division of Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, GA 30341 2.Institute of Public Health, University of Southern Denmark, Odense, Denmark
3.Faroese Health Care System, Torshavn, Faroe Islands
4.Harvard School of Public Health, Boston, MA, USA

Abstract

We measured the serum concentrations of 9 polyfluoroalkyl compounds (PFCs), including perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA), perfluorohexane sulfonate (PFHxS), and perfluorononanoate (PFNA), by on-line solid-phase extraction coupled to isotope dilution-high performance liquid chromatography-tandem mass spectrometry in two groups of Faroe Islands residents. The first group included 103 adolescents 7 years of age, and the second was of 12 mothers and their 5 year old children. We detected PFOS in all samples analyzed. PFOA and PFNA were detected in at least 99% of the samples. In the 7 year old children, median concentrations were highest for PFOS (26.3 ng/mL) followed by PFOA (5.0 ng/mL). These concentrations were comparable to those reported in the United States and other countries. PFOS concentrations were higher for the mothers than their 5 year old children ($p=0.002$); both were comparable to values reported for other human populations. The concentrations of PFOA ($p<0.001$) and PFNA ($p=0.007$) were higher for the children than their mothers. These concentration data are the first ever reported for Faroese residents. The high frequency of detection of most of these PFCs suggests widespread exposure to these compounds among both the young and adult population in the Faroe Islands.

Introduction

Polyfluoroalkyl compounds (PFCs) have been used in numerous commercial applications, such as water, oil, soil and grease repellents for fabric, leather, rugs, carpets, stone, and tile; fire-fighting foams; alkaline cleaners; floor polish; in sizing agents (to resist the spreading and penetration of liquids) for packaging, and paper products; and agents for coatings. Several PFCs, including perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), are persistent chemicals which have been found in wildlife, humans, and the environment worldwide. Some PFCs have demonstrated developmental, reproductive, genotoxic, and carcinogenic toxicity in animal studies[1-3)]. However, the relevance between human exposure to PFCs and adverse health effects has not been established. In addition, environmental sources of PFCs may have not been clearly identified.

To determine the prevalence and magnitude of exposure to PFCs in the Faroe Islands, we measured the serum concentrations of 9 PFCs by on-line solid-phase extraction coupled to isotope dilution-high performance liquid chromatography-tandem mass spectrometry in two groups of Faroe Islands residents.

Materials and Methods

Study populations

The first group included 24 people: 12 of mothers and their 5 year old children. Samples were collected in 2000 for the pregnant mothers and in 2005 for the children. The second group consisted of 103 children 7 years of age and samples were collected in 1993 - 1994. After collection, the blood was allowed to clot for approximately 30 min and then spun at 10000 rpm for 30 min to separate the serum portion of the blood. The serum was transferred to clean cryovials, frozen, and shipped to the Centers for Disease Control and Prevention. Samples were stored at -70 °C until analysis.

Laboratory measurements

The serum concentrations of PFOS, PFOA, perfluorooctane sulfonamide (PFOSA), 2-(N-methyl-perfluorooctane sulfonamido) acetate (Me-PFOSA-AcOH), 2-(N-ethyl-perfluorooctane sulfonamido) acetate (Et-PFOSA-AcOH), perfluorohexane sulfonate (PFHxS), perfluorononanoate (PFNA), perfluorodecanoate (PFDeA), and perfluorododecanoate (PFDoA) were measured using on-line solid phase extraction (on-line SPE) - high performance liquid chromatography- tandem mass spectrometry (HPLC-MS/MS)[4]. We used the following isotope-labeled internal standards: $^{13}C_2$-PFOA, $^{18}O_2$-PFOS, $^{18}O_2$-PFOSA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDeA, D_3-Me-PFOSA-AcOH, and D_5-Et-PFOSA-AcOH. Briefly, to 100 μL of serum, we added 250 μL of 0.1 M formic acid and 25 μL of internal standard solution, the spiked serum was voltex-mixed and sonicated. The samples were placed on a Symbiosis on-line SPE system (Spark Holland, Plainsboro, NJ) for the preconcentration of the analytes on a HySphere HD C18 cartridge (7 μm, 10 mm × 1 mm; Spark Holland). The analytes were transferred onto a Betasil C8 HPLC column (3 mm × 50 mm, 5 μm; ThermoHypersil Keystone, Bellefonte, PA), separated by HPLC (mobile phase A: 20 mM ammonium acetate in water, pH = 4; mobile phase B: Methanol), and detected by Negative-ion TurboIonspray-MS/MS on a API 4000 mass spectrometer (Applied Biosystems, Foster City, CA). The limits of the detection (LODs) were 0.1 ng/mL for PFHxS, PFOA, and PFNA, 0.2 ng/mL for PFOS, PFOSA, Me-PFOSA-AcOH, Et-PFOSA-AcOH, PFDeA, and PFDoA. Low-

concentration quality control materials (QCs) and high-concentration QCs, prepared from a calf serum pool, were analyzed with the unknown samples to insure accuracy and reliability of the data[4].

We performed the statistical analyses using SAS (SAS Institute, Cary, NC, version 9.1). For concentrations below the LOD, a value equal to the LOD divided by the square root of 2 was used. The analyses were considered to be statistically significant when $p < 0.05$.

Results and Discussion

The frequencies of detection of most analytes in the 7 year old children samples (except Me-PFOSA-AcOH, PFDeA, and PFDoA) were over 96%. The relative high frequency of detection of several of the 9 PFCs measured suggests a high prevalence of exposure to these PFCs in the Faroe Islands. Statistically significant correlations existed between the concentrations of PFOS and PFOA (correlation coefficient R = 0.632); and between the concentrations of PFOA and PFNA (R = 0.401). The correlations of PFOS with fluorooctanyl sulfonamide derivatives were R = 0.546. These data suggest similar or common source(s) or pathway(s) of exposure for these PFCs.

The median concentrations in the 7 year old children in 1993 - 1994 were 29.0 ng/mL (PFOS), 5.5 ng/mL (PFOA), 1.5 ng/mL (PFOSA), 0.6 ng/mL (Me-PFOSA-AcOH), 1.8 ng/mL (Et-PFOSA-AcOH), 0.8 ng/mL (PFHxS), 0.9 ng/mL (PFNA), 0.5 ng/mL (PFDeA), and <LOD (PFDoA). These concentrations were similar to the concentrations in adolescents 12 -19 year old from the general US population during 1999 – 2000[5] (Figure 1).

The median concentrations in mothers and their 5 year children, respectively, were: 23.7 and 16.3 ng/mL (PFOS), 2.4 and 4.5 ng/mL (PFOA), 0.6 ng/mL and <LOD (PFOSA), <LOD and 0.3 ng/mL (Me-PFOSA-AcOH), 0.9 ng/mL and <LOD (Et-PFOSA-AcOH), <LOD and 0.6 ng/mL (PFHxS), 0.6 and 1.3 ng/mL (PFNA), 0.3 and 0.3 ng/mL (PFDeA), <LOD and <LOD (PFDoA). The frequencies of detection for most analytes were very similar regardless of age. In these mother-children samples, mothers appeared to have higher concentrations of PFOS than their 5 year old children ($p=0.002$). However, the children had higher concentrations of PFOA ($p<0.001$) and PFNA ($p=0.007$) than their mothers. These concentration data are the first ever reported for Faroese residents. Future research to evaluate associations between serum concentrations of PFCs and lifestyle factors among Faroese residents may provide insight into the main source(s) and pathway(s) of exposure to PFCs in the Faroe Islands.

Acknowledgements

This research was supported in part by an appointment (X.B.) to the Research Participation Program at the Centers for Disease Control and Prevention, National Center for Environmental Health, Division of Laboratory Sciences, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and CDC.

Disclaimer: The use of trade names is for identification only and does not constitute endorsement by the U.S. Department of Health and Human Services or the CDC. The findings and conclusions in this report are those of the authors and do not necessarily represent the views of CDC.

References

1. Kennedy GL, Butenhoff JL, Olsen GW. *Crit Rev Toxicol*. 2004: 34; 351
2. Lau C, Butenhoff JL, Rogers JM. Toxicol Appl Pharmacol. 2004; 198: 231
3. Lau C, Thibodeaux JR, Hanson RG, Narotsky MG, Rogers JM. *Toxicol Sci*. 2006; 90: 510
4. Kuklenyik Z, Needham LL, Calafat AM. *Anal Chem.* 2005; 77: 6085
5. Calafat AM, Kuklenyik Z, Reidy JA, Caudill SP, Tully JS, Needham LL. *Environ Sc. & Technol*. 2007; 41: 2237..

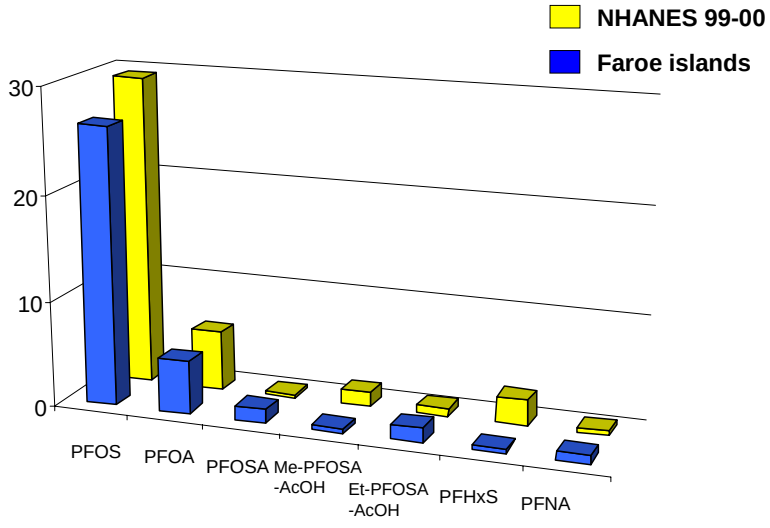

Figure 1. Comparison of serum median concentrations between Faroe island residents 7 years of age (N = 103; blue) and the U.S. general population 12-19 years old (NHANES 1999-2000, N=543; yellow).