LEVLES OF PERFLUOROOCTANESULFONATE AND RELATED FLUOROCHEMICALS IN HUMAN BLOOD FROM THE GERNERAL POPULATION OF KOREA

Jae-Ho Yang[1], Kurunthachalam Kannan[2], Sun-Young Kim[1], Im-Hee Shin[1]

[1]Catholic University of Daegu, School of Medicine, Dept of Pharmacololgy/Toxicology, Daegu, Korea
[2]Wardsworth Center, New York State Dept of Health and Dept of Env. Health and Tox, SUNY, Albany, NY, USA

Introduction

Perfluorooctanesulfonate (PFOS) was found to be widespread in human populations and wildlife[1-2] Major applications of these POSF-based products have included surfactants in: specialty paper and packaging products, carpet, upholstery, and textile products and in certain insecticide formulation[3]. Depending on the specific functional derivatization or the degree of polymerization, such POSF-based products may degrade or metabolize to PFOS, a stable and persistent end product that has the potential to bioaccumulate in the food chain[4]. The mechanisms and pathways leading to the presence of PFOS in human blood are not well characterized but likely involve environmental and dietary exposure to PFOS or to precursor molecules of PFOS. PFOS and related perfluorinated compounds have recently been detected at low parts per billion (nanogram per milliliter) concentrations in the general population from 10 different countries including Korea[5]. In the present report, the levels of perfluoroalkylated compounds in the general population from Korea were analyzed with respect to occupation, smoking status, sex, age and socio-economic status. The degree of association between the four target fluorochemicals measured in this study (PFOS, PFHxS, PFOA, and PFOSA) were also analyzed by linear regression to determine the potential association between their sources of exposure..

Materials and Methods

Blood samples were collected form the volunteer donors who visited a local hospital in Daegu as an outpatient during the month of July, 2003. All the samples were kept at –20 ^{o}C until analysis. Daegu is the fourth largest city in Korea with a population of 3.5 million. Most of the blood donors are the residents of the industrial section of the city. Due to the presence of anticoagulant, EDTA, in the blood samples, whole blood samples were analyzed and the data were converted on a serum basis by multiplying by a factor of 2 for the comparison purpose. PFOS, PFHxS PFOA and PFOSA were extracted using an ion-pairing extraction procedure and were determined by use of a high-performance liquid chromatograph (HPLC) interfaced with an electrospray tandem mass spectrometer (ES-MS/MS) [6]

Results and discussion

Concentrations of PFOS, PFHxS PFOA and PFOSA in sera samples collected form the general population of Korea are shown in Table 1. For the calculation of mean and median values, serum concentrations below the LOQ were not included. Therefore, the mean and median values in this report may overestimate the actual values, in particular, for PFOA that showed a low frequency of occurrence in blood samples. For correlation analysis, values below the LOQ were considered as zero.

No correlation was found between donors' occupations and concentrations of perfluorochemicals studied. Socio-economic status, as self-classified by the donors, was not associated with the levels of perfluorochemicals in blood. However, it is interesting to note that the family income of this region is lower than the average for the city of Daegu. Thus, further studies are required in the future to elaborate the relationship between the socio-economic status and the levels of perfluorochemical contamination. While no correlation with age was found for PFOA, PFHxS and PFOSA concentrations, there was a trend of marginally statistical decrease ($p<0.1$; $R^2 = 0.118$) in PFOA concentrations with age among the male samples (Fig. 1). Among the perfluorochemicals studied, only PFOS showed a significant gender difference, where males showed significantly higher levels than females. Smoking status may play a role on the level of perfluorochemicals in blood. While PFOA concentrations did not show any difference between smokers and non-smokers, there were a marginal statistical increase ($p<0.1$) in PFOSA and PFOS concentrations and a statistically significant increase in PFHxS concentrations ($p<0.05$) among the smokers. Effects of age, gender or smoking may be due to other confounding variables including the number of samples analyzed and the frequency of analyte detection. Further studies with a larger number of samples are needed. When the correlation between perfluorochemicals was analyzed, relationships between PFOSA and PFOS and between PFHxS and PFOA were significant in sera from the donors. Gender difference seemed to influence the pattern of relationship between perfluorochemicals examined. While PFOS had a significant correlation ($p<0.05$) with both PFOSA and PFOA in male, PFOA showed a significant relationship ($p<0.05$) with PFHxS and a marginally significant ($p<0.1$) relationship with PFOSA in female. Such a gender difference may reflect the differential exposure and/or metabolism of these substances in the body. It has been reported that female rat had a higher metabolic capacity to eliminate perfluorinated chemicals from the body[7]. Whether the statistical association observed in this study is due to the differential metabolism or other related biochemical or degradation processes remains to be determined. In particular, the association between PFOA and PFOS in male is of significant interest because PFOA can not convert to PFOS or vice versa (Fig. 2)[8]. Thus, it is suggested that co-exposure to these compounds present in a variety of products exist.

Prolonged use of perfluorochemicals for a variety of application including cleaners, residential carpet spraying and packing products may be a source of human exposure to these compounds. Occurrence of PFOS and its precursors from indoor environment has been reported in Japan and Canada[9-10]. Issues over indoor pollution have recently drawn a great deal of public attention in Korea, since diseases related to new residential buildings, so called, new house syndrome, were reported. However, there has been no investigation on the occurrences of perfluorinated compounds in houses as possible sources.

While PFOS, PFOSA and PFHxS were frequently detected in all of the donors, PFOA was detected in 19% of female and 25% of male donors, respectively. However, the frequency of detection of PFOA in Korea is much higher than in other countries such as Japan, India, and Italy[1]. Due to the

lower detection rate of PFOA, direct comparison between average concentrations of PFOA and other perfluorochemicals was not possible. Mean, median and range of PFOA concentrations in sera from Korea were higher than those reported for the U.S.A., Italy, Japan, and India[1]. In particular, two sera samples from female donors exceeded 100ng PFOA/mL. This is greater than the concentrations reported for any general population so far. Even if the concentrations of PFOA found in the two female donors are outliers, frequency of occurrence of PFOA among Korean population is still higher than in countries like Italy, Japan and India[1]. The results suggest that there may be specific sources of exposure to PFOA in Korea. PFOA and related perfluorocarboxylates are used in several industrial segments including semi-conductor manufacturing, automotive, building/construction, electrical and electronics, and textile industries. Rapid increase of the manufacturing capacity in these industries in Korea can be related to the high occurrence of PFOA in the blood of Korean general population. In addition, several household items known to contain PFOA or its precursors (e.g. hair conditioner containing fluorotelomer alcohols) are widely and routinely used in daily life. Further, the residential area of all of the donors is in close proximity to the industrial sector of the city, where manufacturers of automotive parts, electronic devices and textiles are concentrated. Thus, particular sources of exposure in their surroundings may contribute to such a high level of occurrence and concentrations of PFOA. Since sources and exposure pathways leading to the presence of perfluorinated chemicals in human blood are not clearly understood, the present results suggest further extensive studies in Korea to better understand exposure pathways and sources and to minimize future exposure to PFOA and other fluorinated chemicals.

References

1. Kannan K, Kumar K.S., Corsolini S., and Aldous K.M. (2003) Organohalogen Comp. 64, 29-32
2. Giesy J.P., Kannan K (2001) Environ Sci Technol 35, 1339-1342
3. 3M company, St. Paul, MN, U.S. EPA docket No. AR-226, 2000
4. Olsen G.W., Burris J.M., Mandel J.H., and Zobel L.R. (1999) J. Occup Environ Med 41, 799-
5. Kannan K, Corsolini S, Falandysz J, Fillmann G, Kumar K., S., Loganathan B.G., Mohd M.A., Olivero J., Wouwe N.V., Yang J.H. and Aldous K.M. (2004) Environ Sci Technol (submitted)
6. Hansen K.J., Clemen L.A., Ellefson M.E. and Johnson H.O.(2001) Environ Sci Technol. 35, 766-770
7. Johnson J.D., Gibson S.J., and Ober R.F.(1984) Fundam. Appl. Toxicol. 4, 972-976
8. Tomy G.T., Tittlemier S.A., Palace V.P., Braekevett E, Brinkworth L., and Friesenk K. (2004) Environ Sci Technol. 38, 758-762
9. Moriwaki H, Takata Y, and Arakawa R (2003) J. Environ Monitor 5, 753-757
10. Shoeib M, Harner T, Ikonomou M, and Kannan K. (2004) Environ Sci Technol 38, 1313-1320.

Table 1. Perfluorochemical Concentrations in Sera of Korean donors (ng/mL)

Sex		PFOS	PFHxS	PFOA	PFOSA
Female(n=25)	Mean	15.1	3.8	88.1	1.1
	Median	11.3	2.9	30.9	1.1
	Range	3.0 - 61.3	0.9 - 20	<15 - 256	<0.1 - 2.1
	% positive	100	100	19	96
Male(n=25)	Mean	27.1	4.1	35.5	1.5
	Median	21.7	3.4	26.8	1.3
	Range	6.6 - 92	1.3 - 9.6	<15 - 71.4	0.4 - 7.2
	% positive	100	100	25	100

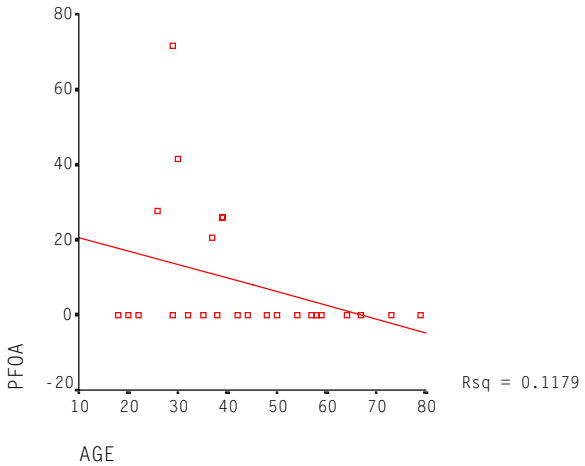

Figure1. Relationship between age and PFOA in sera of male donors

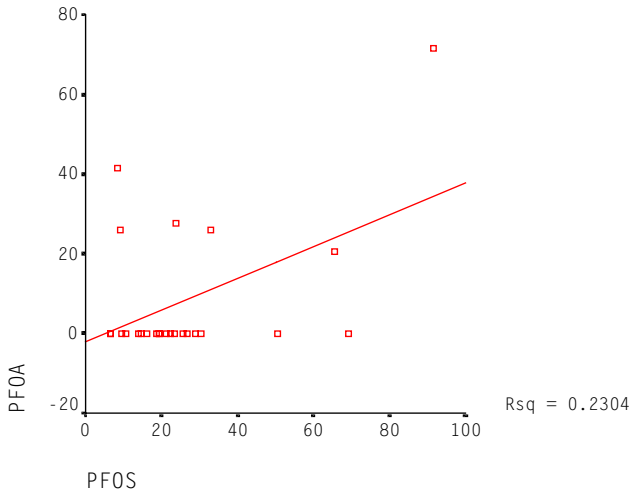

Figure2. Relationship between PFOS and PFOA in sera of male donors