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Preliminary evidence of a decline in perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) concentrations in American Red Cross blood donors

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Abstract

The purpose of this pilot study was to determine whether perfluorooctanesulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA, $C_7F_{15}CO_2^-$) concentrations in American Red Cross blood donors from Minneapolis-St. Paul, Minnesota have declined after the 2000–2002 phase-out of perfluorooctanesulfonyl-fluoride (POSF, $C_8F_{17}SO_2F$)-based materials by the primary global manufacturer, 3M Company. Forty donor plasma samples, categorized by age and sex, were collected in 2005, and PFOS and PFOA concentrations were compared to 100 (non-paired) donor serum samples collected in 2000 from the same general population that were analyzed at the time using ion-pair extraction methods with tetrahydroperfluorooctanesulfonate as an internal standard. Eleven of the 100 samples originally collected were reanalyzed with present study methods that involved ^{13}C- labeled PFOA spiked into the donor samples, original samples, control human plasma, and the calibration curve prior to extraction, and was used as a surrogate to monitor extraction efficiency. Quantification was performed by high performance liquid chromatography tandem mass spectrometry methods. Among the 100 serum samples analyzed for PFOS, the geometric mean was 33.1 ng ml^{-1} (95% CI 29.8–36.7) in 2000 compared to 15.1 ng ml^{-1} (95% CI 13.3–17.1) in 2005 ($p < 0.0001$) for the 40 donor plasma samples. The geometric mean concentration for PFOA was 4.5 ng ml^{-1} (95% CI 4.1–5.0) in 2000 compared to 2.2 ng ml^{-1} (95% CI 1.9–2.6) in 2005 ($p < 0.0001$). The decrease was consistent across donors' age and sex. To confirm these preliminary findings, additional sub-sets of year 2000 samples will be analyzed, and a much larger biomonitoring study of other locations is planned.

Keywords: Biomonitoring; Fluorochemicals; Perfluoroalkyl acids; Perfluorooctanoate; PFOA; Perfluorooctanesulfonate; PFOS

1. Introduction

For more than 40 years, the 3M Company (3M) produced perfluorooctanesulfonyl-fluoride (POSF, $C_8F_{17}SO_2F$)-based materials that had a variety of applications including surfactants, paper and packaging treatments, and surface protectants (e.g., for carpet, upholstery and textile applications). Depending on the specific functional derivatization or the degree of polymerization, such POSF-based products may have degraded or metabolized, to an undetermined degree, to perfluorooctanesulfonate (PFOS, $C_8F_{17}SO_3^-$), a stable and persistent end-product that has the potential to bioaccumulate. In addition, PFOS has been used as a surfactant in a number of applications, including fire-fighting foam. In May 2000, 3M, the primary POSF-based global manufacturer, announced that it would voluntarily cease manufacturing POSF-based materials after PFOS was found to be widespread in human

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populations and wildlife (Giesy and Kannan, 2001; Butenhoff et al., 2006). 3M discontinued the manufacture of POSF-based chemicals by 2002. The majority of 3M POSF-based materials were from the Decatur, Alabama and Antwerp, Belgium manufacturing facilities.

As part of the phase-out of manufacturing POSF-based materials, 3M also discontinued manufacture of the ammonium salt of perfluorooctanoic acid (APFO), an important processing aid in the production of certain fluoropolymers. APFO was a major product of 3M's Cottage Grove, Minnesota manufacturing facility. Perfluorooctanoate (PFOA, $C_7F_{15}CO_2^-$) has also been found widely distributed in human blood and is found in samples from wildlife (Giesy and Kannan, 2001; Butenhoff et al., 2006). Whereas the majority of global production of POSF-based materials and related environmental emissions has ceased, direct and indirect sources of PFOA exposure remain through a variety of other companies' production activities although industry efforts have resulted in reductions in emissions.

The mechanisms and pathways leading to the presence of PFOS in human blood likely involved environmental exposure to PFOS or to precursor molecules and residual levels of PFOS or PFOS precursors in industrial and commercial products. Potential sources of human exposure to PFOS likely included manufacturing operations (e.g., air emissions) and waste streams (e.g., wastewater) of POSF-based fluorochemical products, and the use or degradation of some final commercial and consumer products, including indirect food-contact applications (3M Company, 2003).

Potential sources of human exposure to perfluorooctanoate (PFOA, $C_7F_{15}CO_2^-$) have included both direct exposure through the production of APFO and its use as a processing aid for fluoropolymer production (e.g., poly(tetrafluoroethylene and polyvinylidine fluoride)), and indirect sources through production from precursor organofluorines (e.g., degradation of fluorotelomer phosphate surfactants and volatization of fluorotelomer alcohols) (Joyce et al., 2004; De Silva and Mabury, 2006). Martin et al. (2006) have recently proposed perfluorooctanesulfonamides may serve as sources of perfluorocarboxylates, including PFOA, through its hydroxyl radical and chlorine atom initiated oxidation in the trophosphere.

There have been no studies reported that have examined human biomonitoring temporal trends post 3M phase-out. Environmentally, a decline in PFOS and PFOA concentrations in guillemot eggs from the Baltic Sea was reported between 1998–2002 but could not be positively linked to the phase-out of POSF-based materials (Holmström et al., 2005).

In order to characterize PFOS and PFOA serum concentrations in the general population in 2000, Olsen et al. (2003) analyzed 645 American Red Cross blood donor samples, including 100 samples from the Minneapolis-St. Paul area. The samples from that study serve as a baseline for adult serum concentrations at the time of the manufacturing phase-out decision.

Because the mean half-lives of human serum elimination of PFOS and PFOA have been estimated at 5 and 4 years, respectively (Olsen et al., 2005), the study reported herein was undertaken to determine if a reduction in adult American Red Cross blood donor serum concentrations of PFOS and PFOA may have resulted in the five years since the beginning of the phase-out of POSF-based materials. Five years would represent approximately one serum elimination half-life for both PFOS and PFOA and the hypothesis was that an approximately 50% reduction might be observed. The purpose of the present study was to offer a preliminary assessment as to whether PFOS and PFOA concentrations, measured in 2005 in non-paired blood donor samples from this same location, may have substantively declined. If observed, then confirmation of a declining trend with the other five locations from the original American Red Cross blood donor study (Olsen et al., 2003) would be highly warranted.

2. Materials and methods

A total of 40 plasma samples were collected in 2005 from the American Red Cross North Central Blood Services (Minneapolis-St. Paul). Samples were equally distributed into four groups by age ($<$40 years and $\geqslant$40 years) and sex (male, female). The study was approved by the American Red Cross Institutional Review Board (IRB). No personal identifiers were maintained by the American Red Cross North Central Blood Services or provided to 3M. Per the past policy of the American Red Cross North Central Blood Services (Olsen et al., 2003), a signed consent form specific for analysis of PFOS and PFOA was not required.

PFOS and PFOA were extracted from human plasma samples by protein precipitation in acetonitrile (Flaherty et al., 2006). Briefly, analytes were extracted from serum or plasma by protein precipitation in acetonitrile via a MultiPROBE II HT EX robotic liquid handling system (PerkinElmer, Wellesley, MA) utilizing 96 well plates. Fifty microliter aliquots of plasma sample were added to a 96 well plate containing Argonaut ISOLUTE array protein precipitation wells (2 ml volume) (Biotage, Uppsala, Sweden). To each well, 50 μl of a spiking solution in water was added and mixed with the sample. After allowing the sample to equilibrate for 20 min, 450 μl of acetonitrile was added to each well. After 5 min, a vacuum was applied to the entire plate to separate the proteins from the solvent extracts. The extracts were collected in an Argonaut ISOLUTE array collection plate (1 ml volume). Following collection, the solvent extracts were transferred to glass microvials for analysis. The solvent extracts were found to be stable in glass (Flaherty et al., 2006). Quantification was accomplished by high performance liquid chromatography tandem mass spectrometry. External calibration with control rabbit plasma was used for quantitation of human plasma samples. The internal standard ^{13}C-perfluorooctanoic acid (C_6F_{13} $^{13}CF_2$ $^{13}CO_2H$, ^{13}C-PFOA) was