FINAL REPORT

Epidemiology, 220-6W-08
Medical Department
3M Company
St. Paul, MN 55144

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Title: Perfluoroalkyl Biomonitoring Assessment of SKB Environmental Employees

Study
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Summary

A total of 16 SKB Environmental employees who worked on 3M remediation projects had baseline and end-of-project perfluoroalkyl (PFOA and PFOS) measurements as well as clinical chemistries analyzed. There were no statistically significant mean *increases* in PFOA and PFOS concentrations when the end-of-project values were compared to paired baseline assessments. The mean *decreases* in PFOA and PFOS concentrations observed were consistent with the known pharmacokinetics of PFOA and PFOS. Conclusion: Based on the biomonitoring data, there was no substantive occupational exposure to PFOA or PFOS for SKB Environmental employees while working on the various 3M remediation projects.

Introduction

Several 3M remediation projects have been completed in Minnesota regarding legacy perfluoroalkyls. These projects have included the 3M Cottage Grove Building 15/73 demolition and disposal project, the 3M Woodbury landfill remediation project, the 3M Oakdale landfill remediation project, the 3M Cottage Grove Building 25 re-roof project, and the 3M Cottage Grove D1/D2, D9, and East Cove remediation projects. For each of these projects, baseline and end-of-project assessments were required of 3M employees and contractor workers who entered specified work zones where potential exposure to legacy perfluorochemicals [PFOS (perfluorooctanesulfonate) and PFOA (perfluorooctanoate)] was possible but due to the uniqueness of the work the magnitude of exposure was unknown. Both baseline and end-of-project assessments required response to a medical questionnaire and blood (serum) measurements of PFOS, PFOA, and several clinical chemistries.

Waste material from these 3M remediation projects was hauled by SKB Environmental and subsequently deposited in the SKB Environmental industrial landfill operations located in Rosemount, Minnesota. The SKB Environmental Rosemount facility is a state-of-the-art disposal facility for industrial, mixed-municipal solid waste incinerator ash, and construction and demolition debris. Specifics about the SKB Environmental Rosemount facility can be found at http://www.skbinc.com/our-locations/rosemount-disposal.html.

As occurred with other 3M perfluoroalkyl remediation projects, SKB Environmental employees with potential exposure to 3M material obtained baseline and end-of-project measurements of PFOS, PFOA, and several clinical chemistries. SKB Environmental employees conducted their baseline assessments in the summer 2009. End-of-project assessments were completed in February 2013 after SKB Environmental completed its industrial landfill operations related to 3M's remediation projects.

The purpose of this report is to provide a descriptive analysis of the PFOA and PFOS serum concentrations (ng/mL) at baseline and end-of-project time periods for SKB Environmental employees who participated in its industrial disposal activities regarding 3M remediation materials.

Methods

1. Informed consent

The purpose of the project was explained in an Informed Consent. Subjects read and signed this informed consent at both baseline and end-of-project assessments. Subjects were informed they could not work on this specific project without such compliance.

2. Clinical chemistries

Clinical chemistries included a lipid panel profile, blood glucose, BUN, creatinine, serum electrolytes, and liver enzyme tests (including alkaline phosphatase, AST, ALT, and total bilirubin). Fasting was not a requirement because of the logistics of collecting blood samples during various times of the day. Clinical chemistries were analyzed by Quest Diagnostics. Individual clinical chemistry analyses at baseline and at end-of-project were medically reviewed by Dr. Buehrer. Subjects were informed in writing that this examination program was not a full medical 'check-up.' Values out of reference range were indicated with a notation for the subjects to follow up with their primary care physician if they had abnormal test results. However, questions could be directed to Dr. Buehrer regarding their clinical chemistry test results should the subject so desire.

3. Analytical measurements of PFOA and PFOS

Serum samples were analyzed for PFOA and PFOS by state-of-the-art high performance liquid chromatography mass spectrometry methods by the 3M Medical Department's Toxicology Laboratory under the direction of Dave Ehresman. Medical Department personnel collected blood samples that were processed to provide serum samples for analysis. These samples were assigned unique identification numbers prior to the samples being delivered for analysis. The 3M Medical Department's Toxicology Laboratory was "blinded" to the identity of all samples received for analysis.

Sample extractions were performed using solid phase extraction (SPE) technique. The extraction and sample clean-up was based on a 100 uL sample size and utilized Waters (Milford, MA) Oasis® hydrophilic–lipophilic balance (HLB) 3.0mL cartridges (Ehresman et al. 2007).

The method used two stable labeled internal standards for quantitation. The internal standards used were a dual labeled PFOS where two ^{18}O molecules were included in the sulfonate group (internal standard, >99% purity, synthesized by Research Triangle Institute, Research Triangle Park, NC) and a dual labeled PFOA molecule, where the carboxyl and alpha carbons were labeled with ^{13}C stable isotope (greater than 97%, provided by DuPont, Wilmington, DE). All quantitations were based on matrix matched extracted standard curves.

A 5 uL injection of the sample eluate was introduced into the High Pressure Liquid Chromatograph (HPLC) which was directly interfaced into the triple quadrupole mass spectrometer (Applied Biosystems/MDS-Sciex Instrument Corporation, Forest City, CA). Standard curves covered the range from 1.0 - 150 ng/mL. Standard curves were evaluated using a quadratic regression model where the standards were weighted at 1/x, and each curve had an ''R'' value equal to or greater than 0.9998. Matrix spiked controls (QC samples) evaluated during this study all had acceptable results "within" their previously established ranges. Matrix-matched dilutions were used for samples requiring dilution to bring the samples into the linear range of the assay. Extracted serum and aqueous blanks remained below the lower limit of quantitation established at 1.0 ng/mL (lowest standard fitted on the standard curve used for this project).

4. Communication

After each blood collection, individual letters were sent to the participants describing their results. In the baseline assessments, two letters were sent. One referred to the clinical chemistries and the other letter provided baseline PFOA and PFOS concentrations. At the end-of-project, two letters were again sent to each participant. The first letter provided the

individual's clinical chemistry results. The second letter compared baseline to end-of-project serum PFOA and PFOS concentrations.

Results

Sixteen SKB Environmental employees had paired baseline and end-of-project assessments. Nine SKB Environmental employees had baseline assessments but did not participate in end-of-project assessments as they had left the company.

Table 1 and Table 2 (below) provide the measures of central tendency for baseline and end-of-project PFOA and PFOS concentrations for the 16 subjects with paired measurements. Values are provided in ng/mL (parts-per-billion).

Table 1. PFOA Baseline and End-of-Project Concentrations (ng/mL)

						Arithmetic		Geometric	
	Min	Q1	Median	Q3	Max	Mean	95% CI	Mean	95% CI
Baseline	1.9	3.0	4.4	5.7	9.0	4.5	3.4 – 5.6	4.1	3.2 – 5.2
End-of-Project	1.0	2.0	2.9	3.9	7.1	3.2	2.4 – 4.1	2.9	2.0 – 3.7

Table 2. PFOS Baseline and End-of-Project Concentrations (ng/mL)

						Arithmetic		Geometric	
	Min	Q1	Median	Q3	Max	Mean	95% CI	Mean	95% CI
Baseline	6.4	9.3	15.8	22.0	31.1	16.7	12.3 – 21.0	14.7	11.0 – 19.5
End-of-Project	11.6	3.6	10.1	16.4	26.2	11.6	8.3 – 15.0	9.9	7.2 – 13.7

As the data are paired samples, a matched-paired statistical analysis was performed where the mean value was determined for the average of the sum of the individual differences for the 16 subjects. See Equation 1.

Equation 1.

$$\text{Mean Difference} = \sum_{i=1}^{16}(\text{end-of-project} - \text{baseline})/16$$

Because of the skewed PFOA and PFOS distributions, as seen in Tables 1 and 2, the mean differences of the natural logs of the paired values were also determined. See Equation 2.

Equation 2.

$$\text{Mean} = \sum_{i=1}^{16}[(\ln(\text{end-of-project value})) - (\ln(\text{baseline value}))/16$$

Results for *Equation 1 and Equation 2*, and associated statistics of the mean differences of the paired comparisons, are provided in Table 3 (below) for both PFOA and PFOS.

Table 3. Matched-pair Analysis Comparing Baseline to End-of-Project PFOA and PFOS Concentrations (ng/mL)

Mean Paired Difference	PFOA (ng/mL)	t-ratio	p value	PFOS (ng/mL)	t-ratio	p value
Equation 1	-1.3	-3.5	0.002	-5.0	-5.3	<0.0001
Equation 2	-0.36	-5.3	<0.0001	-0.39	-6.6	<0.0001

Statistically significant differences were observed for a *decrease* in the mean of the differences for PFOA and PFOS (Equations 1 and 2). In other words, the end-of-project PFOA and PFOS concentrations were statistically significantly less than their respective baseline concentrations (ng/mL) when analyzed as paired differences.

Assuming there was no occupational exposure in this study, the percent of end-of-project concentrations measured for arithmetic means (Table 1 and 2) that could be attributable to PFOA and PFOS as a consequence of pharmmacokinetics was 56% for PFOA and 86% for PFOS (Table 4). This calculation assumes serum elimination half-lives of 3.5 years for PFOA and 4.8 years for PFOS (Olsen et al. 2007). The amount of follow-up time from baseline to end-of project in this SKB Environmental biomonitoring project was 3.4 years except for 1 individual whose time was slightly longer (3.5 years).

Table 4. Percentage of End-of-Project PFOA and PFOS Serum Concentrations Expected to Occur Based on Serum Elimination Half-lives for PFOA (3.5 years) and PFOS (4.8 years). See Olsen et al. (2007)

	Mean (ng/mL) Baseline[a]	Mean (ng/mL) Change at End-of-Project[b]	Mean (ng/mL) Expected Change[c]	Mean (%) Change Observed Based on Expected[d]
PFOA	4.5	-1.3	-2.2	56
PFOS	16.7	-5.1	-5.9	86

a. See Tables 1 and 2

b. Mean baseline value minus mean end-of-project value from Tables 1 and 2

c. Absent any background or occupational exposure this is the Mean Baseline Value (ng/mL) x Proportion of Half-life in Study x 0.5 years. For PFOA the proportion was estimated as 3.4 years/3.5 years For PFOS the proportion was estimated as 3.4 years/4.8 years.

d. (Column 2 divided by Column 3) x 100

Discussion

Comparison of baseline and end-of-project serum concentrations of PFOA and PFOS provided each SKB Environmental employee an excellent method to assess his/her exposure experience to the various 3M remediation projects. Given the fact that exposure potential during the course of the remediation project was unknown, the use of biomonitoring data allowed for an assessment the actual exposure. The above data (Table 4) show that the decrease in PFOS concentration between baseline and end-of-project could be largely (86%) attributed to its known pharmacokinetics (Olsen et al. 2007). It is possible that the 56% decrease observed for PFOA may be the consequence of its known pharmacokinetics (Olsen et al. 2007) coupled with an underlying low background (nonoccupational) level of exposure to PFOA (Bartell et al, 2012). These calculations do not suggest there were any substantive occupational exposures for SKB Environmental employees during the course of their work on the 3M perfluoroalkyl remediation projects. Because the biomonitoring data indicated there were no substantive differences in any increase in exposure to PFOA or PFOS between baseline and end-of-project, the clinical chemistry data were therefore not analyzed in aggregate by paired statistics. Potential exposure to any other material would not be known since only PFOA and PFOS were analyzed in the workers' serum.

Conclusion Based on the biomonitoring data, there were no substantive occupational exposures to PFOA or PFOS for the 16 SKB Environmental employees involved in the hauling and industrial landfill disposal of materials from the 3M remediation projects.

References

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