

FINAL REPORT
Epidemiology, 220-3W-05
Medical Department
3M Company
St. Paul, MN 55144

Date: December 15, 2009

Title: Biomonitoring Assessment of the Cottage Grove Building 25 Re-Roof Project

Study
Start Date: September 1, 2009

Protocol Number N/A
IRB Approval N/A

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Summary

A total of 37 subjects, who worked on the 3M Cottage Grove Building 25 re-roof project, had baseline and end-of-project serum clinical chemistry and perfluorochemical (PFOA and PFOS) measurements. There were no statistically significant increases in paired PFOA and PFOS concentrations when the end-of-project values were compared to baseline assessments. Conclusion: Based on the biomonitoring data, there was no substantive occupational exposure to PFOA or PFOS while working on the 3M Cottage Grove Building 25 re-roof project.

Introduction

Several remediation projects were launched in 2009 regarding legacy perfluorochemicals. These included the 3M Cottage Grove Building 15/73 demolition and disposal project, the 3M Woodbury landfill remediation project, the Decatur Building 2/49 demolition and disposal project, and the 3M Cottage Grove Building 25 re-roof project. 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 (e.g., PFOS (perfluorooctanesulfonate) and PFOA (perfluorooctanoate) was possible but due to the uniqueness of the work the magnitude 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. 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 the 3M Cottage Grove Building 25 re-roof project.

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. Gibson. 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. Gibson 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 and randomized 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 "with-in" 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

A total of 37 3M employees and contract workers had paired baseline and end-of-project assessments. Six subjects had baseline assessments but did not participate in end-of-project assessments. One subject worked on both the Building 25 re-roof project and the Building 15/73 demolition and disposal project and remained on the 15/73 project after the completion of his assignment on the re-roof project. His results are not included herein because they could be confounded by other PFOA and PFOS workplace exposure at Cottage Grove.

Table 1 and Table 2 (below) provide the measures of central tendency for baseline and end-of-project PFOA and PFOS concentrations for the 37 subjects with paired measurements. Values are provided in ng/mL (parts-per-billion). To convert to parts-per-million, divide the values by 1,000.

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

	Min	Q1	Median	Q3	Max	<u>Arithmetic</u>		<u>Geometric</u>	
						Mean	95% CI	Mean	95% CI
Baseline	1.0	3.2	5.0	16.1	275.0	34.0	9.8 – 58.1	7.8	4.7 – 13.0
End-of-Project	<1.0	2.9	4.9	14.0	265.0	32.6	9.7 - 55.5	8.3	5.0 – 13.8

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

	Min	Q1	Median	Q3	Max	<u>Arithmetic</u>		<u>Geometric</u>	
						Mean	95% CI	Mean	95% CI
Baseline	4.7	14.8	19.6	30.0	317.0	49.1	22.2 – 76.1	24.2	17.1 – 34.3
End-of-Project	4.7	14.8	22.0	33.7	297.0	49.8	23.2 – 76.5	25.2	17.8 – 35.6

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 37 subjects. See Equation 1.

Equation 1.

$$\text{Mean Difference} = \sum_{i=1}^{37} (\text{end-of-project} - \text{baseline}) / 37$$

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.

$$\text{Mean} = \sum_{i=1}^{37} [(\ln(\text{end-of-project value})) - (\ln(\text{baseline value}))] / 37$$

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 concentration (ng/mL)

Mean Paired Difference	PFOA (ng/mL)	t-ratio	p value	PFOS (ng/mL)	t-ratio	p value
<i>Equation 1</i>	-1.4	-1.78	0.04	+0.7	0.94	0.83
<i>Equation 2</i>	+0.012	+0.57	0.71	+0.039	2.04	0.97

The only statistically significant difference was a *decrease* in the mean of the differences for PFOA (*Equation 1*). In other words, the end-of-project PFOA concentration was statistically significantly less than the baseline PFOA concentration (ng/mL) when analyzed as paired differences. This counterintuitive finding is likely well-within the variation of the analytical measurements performed.

Figures 1 and 2 provide another method to compare the baseline to end-of-project concentrations for PFOA and PFOS, respectively. [Note: These figures are graphed in log scale.] The strong linear correlation centered along the diagonal is indicative of no changes between the paired measurements. The R^2 values for both figures are 0.997, indicative of strong linearity between baseline and end-of-project concentrations (i.e., no differences between the individual's end-of-project and baseline concentrations).

Discussion

Comparison of baseline and end-of-project serum concentrations of PFOA and PFOS provided each worker an excellent method to assess his/her exposure experience for the 3M Cottage Grove Building 25 re-roof project. Historically, Building 25 has had the potential for both exposures, but primarily PFOS and its related chemistries. Given the fact that exposure potential during the course of the re-roof project was unknown, the use of biomonitoring data allowed for an assessment the actual exposure. Because the biomonitoring data indicated there were no substantive differences 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 materials would not be known since only PFOA and PFOS were analyzed in the workers' serum.

Conclusion Based on the biomonitoring data, there appeared to be no substantive occupational exposures to PFOA or PFOS for the 37 total 3M and contract workers involved with the 3M Cottage Grove Building 25 re-roof project.

References

Ehresman DJ, Froehlich JW, Olsen GW, Chang SC, Butenhoff JL. 2007. Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals. Environ Res 103:176-184.

Figure 1. Cottage Grove Re-Roof Project:
Baseline vs End-of-Project PFOA Serum Concentrations (ng/mL)

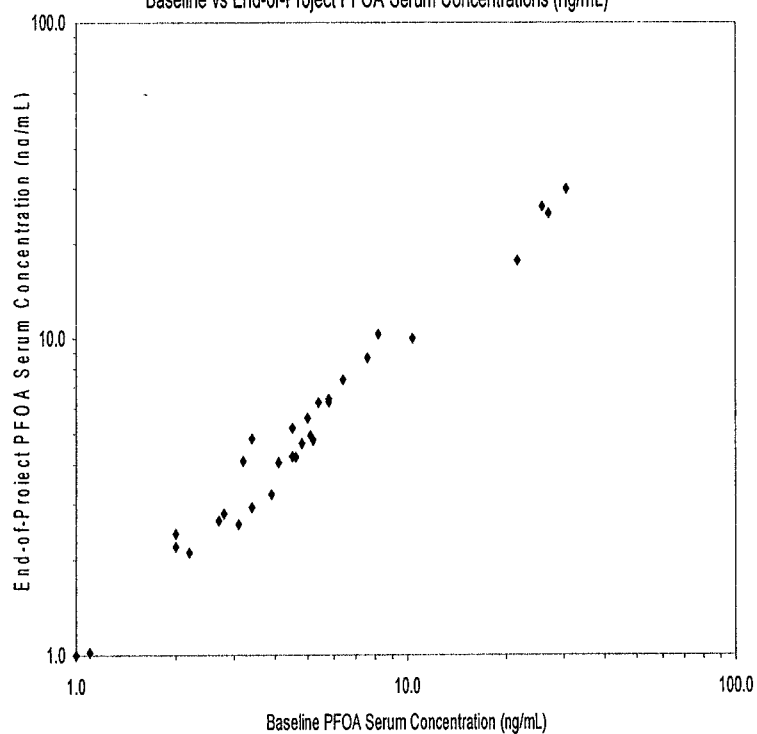


Figure 2. Cottage Grove Re-Roof Project:
Baseline vs End-of-Project PFOS Serum Concentrations (ng/mL)

