

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

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Title: Biomonitoring Assessment of the 3M Cottage Grove D9 Excavation Project

Study
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Summary

A total of 22 contingent workers (non-3M employees) were identified as having worked in the exclusion zone of the 3M Cottage Grove D9 excavation project. The duration of this project was approximately 5 months. Twenty (91%) contingent workers had baseline and end of project measurements for perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS). There was no statistically significant increase in the mean PFOA or PFOS serum concentrations. Mean serum concentrations actually significantly decreased. These 20 workers' mean baseline serum PFOA concentration was 4.3 ng/mL (95% CI 3.6 – 5.1). Their mean PFOS concentration was 15.3 ng/mL (95% CI 11.9 – 18.7). The mean serum concentration differences (end-of-project minus baseline) were -0.7 ng/mL (95% CI (-1.4) – (-0.1), $p = 0.03$) for PFOA and -2.2 ng/mL (95% CI (-3.1) – (-1.2), $p = 0.0002$) for PFOS. Conclusion: Based on the paired biomonitoring data of 20 contingent workers, there was no increase in serum PFOA or PFOS concentrations while working at the 3M Cottage Grove D9 excavation project.

Introduction

Several remediation projects have been completed regarding legacy perfluorochemicals. These include the 3M Woodbury primary and northeast landfill remediation projects, the 3M Cottage Grove Building 15/73 demolition and disposal project, the 3M Cottage Grove Building 25 re-roof project, the 3M Cottage Grove D1/D2 excavation project, and the 3M Decatur Building 2/49 demolition and disposal project. For each of these projects baseline and end-of-project assessments were required of 3M employees and contractor workers who entered specified exclusion 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 responses 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 D9 excavation project. The duration of this project was approximately 5 months.

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 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 22 contingent workers participated in biomonitoring for the Cottage Grove D9 excavation project (**Table 1**). Twenty (91%) individuals had baseline and end of project assessments.

Table 1. Distribution of workers by company and participation

Company	Baseline	End-of-Project	Reasons for “no show”
3M	0	1	Did not show for baseline
Bolander	11	12	Did not show for baseline
Metro Gravel	6	6	
Weston	3	3	
Total	20	22	

Tables 2 and 3 provide the measures of central tendency for the baseline and end-of-project PFOA and PFOS concentrations for the 20 subjects with paired measurements (baseline and end-of-project). Values are provided in ng/mL (parts-per-billion).

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

	Min	Q1	Median	Q3	Max	Arithmetic		Geometric	
						Mean	95% CI	Mean	95% CI
Baseline	2.2	3.0	3.7	5.9	7.5	4.3	3.6 – 5.1	4.0	3.4 – 4.8
End-of-Project	1.6	2.3	3.6	4.6	6.2	3.5	2.9 – 4.3	3.3	2.7 – 4.0

Table 3. 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	9.0	13.2	22.0	28.6	15.3	11.9 – 18.7	13.6	10.7 – 17.3
End-of-Project	2.8	8.3	10.7	20.9	24.4	13.2	10.0 – 16.4	11.4	11.4 – 15.0

There were no statistically significant differences of PFOA or PFOS concentrations between employers of these contingent workers. Mean baseline and end of project PFOA concentrations (ng/mL, in parentheses) were: Bolander (4.3, 3.3), Metro Gravel (4.6, 4.4), and Weston (3.7, 3.1). Mean baseline and end of project PFOS concentrations (ng/mL, in parentheses) were: Bolander (14.9, 13.0); Metro Gravel (17.5, 14.6), and Weston (12.4, 10.9).

As the data were paired samples, a matched-paired statistical analysis was performed (see Equation). The mean difference represents the average of the sum of the individual differences for the 20 subjects. Results are provided in **Table 4**. There were no statistically significant mean matched-pair differences for PFOA or PFOS.

Equation.

$$\text{Mean Difference} = \frac{\sum_{i=1}^{20} (\text{end-of-project} - \text{baseline})}{20}$$

Table 4. 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
	-0.7	-2.3	0.03	-2.2	-4.7	0.0002

Table 5 provides these matched-pair data by employer. All statistically significant differences occurred with a decline in PFOA or PFOS concentrations.

Table 5. 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
Bolander	-1.0	-2.6	0.03	-1.9	-3.0	0.01
Metro Gravel	-0.3	-0.3	0.75	-2.9	-3.0	0.03
Weston	-0.6	-6.0	0.03	-1.5	-2.5	0.13

Figures 1 and 2 provide another method to compare the baseline to end-of-project concentrations for PFOA and PFOS, respectively, for these 20 contingent workers. Data points near the diagonal identity line, where $x = y$, indicates no difference in concentrations between baseline (x) and end of project (y). As seen in both **Figures 1 and 2**, the majority of data are below the identity line. This indicates concentrations measured at end of project were less than those at baseline, as reported in **Tables 2 and 3**. There was one individual whose serum PFOA concentration did increase during the project by a few ng/mL (Figure 1) but not his PFOS level. There was not a strong linear trend centered along the identity line for PFOA (see Figure 1, $R^2 = 0.34$). This trend was stronger for PFOS (see Figure 2, $R^2 = 0.92$).

It was not possible to determine whether the 2 individuals without baseline measurements, as shown in **Table 1**, had increased serum PFOA or PFOS concentrations attributable to working on the Cottage Grove D9 excavation project. However, their individual end of project PFOA and PFOS serum concentrations (data not shown) were similar to the other 20 contingent workers and would therefore suggest exposure did not occur while working on the D9 project.

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 D9 excavation project. Given the fact that exposure potential during the course of this project was unknown, the use of biomonitoring data allowed for an assessment of the actual (unknown) exposure to PFOA or PFOS, or to materials that may degrade to them. The clinical chemistry data were not analyzed by paired statistics because the biomonitoring data indicated there were no substantive differences in exposure to PFOA or PFOS between the baseline and end-of-project measurements. Potential exposure to other materials was not known because only PFOA and PFOS were analyzed in the workers' serum.

Conclusion

Based on paired biomonitoring data of 20 contingent workers, there was no increase in serum PFOA or PFOS concentration while working at the Cottage Grove D9 excavation 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. Baseline and End of Project PFOA Concentrations, Cottage Grove D9 Excavation Project,
N = 20

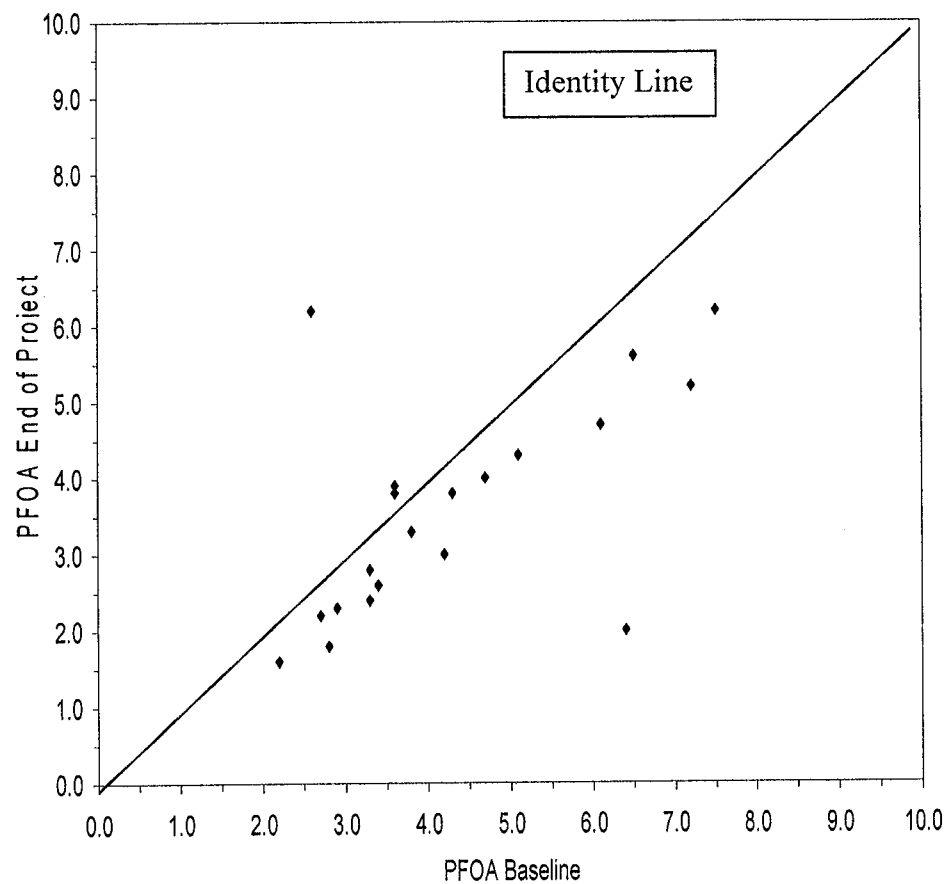


Figure 2. Baeline and End of Project PFOS Concentrations, Cottage Grove D9 Excavation Project, N = 20.

