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

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Title: Biomonitoring Assessment of the 3M Oakdale Landfill Remediation Project

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Summary

A total of 11 contingent workers (non-3M employees) entered the exclusion zone of the 3M Oakdale landfill remediation project and therefore participated in biomonitoring. The duration of this project was approximately 5 months. All 11 contingent workers had baseline and end of project measurements for serum concentrations of perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS). These 11 workers' mean baseline serum PFOA concentration was 4.9 ng/mL (95% CI 3.4 – 6.5; range 1.8 – 10.1). Their mean baseline PFOS concentration was 12.2 ng/mL (95% CI 8.1 – 16.3). The mean serum concentration differences (end-of-project minus baseline) were -0.6 ng/mL (95% CI (-1.0) – (-0.2), p = 0.006) for PFOA and -0.4 ng/mL (95% CI (-1.5) – (0.8), p = 0.49) for PFOS. Conclusion: Based on the paired biomonitoring data of 11 contingent workers, there was no increase in serum PFOA or PFOS concentrations while working at the 3M Oakdale landfill remediation 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 and D9 excavation projects, 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. These zones were defined as 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 of exposure 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 Oakdale landfill remediation 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 11 contingent workers participated in a biomonitoring assessment for the Oakdale landfill remediation project because of their entry into the exclusion zone. An undetermined number of other individuals worked on this project but did not enter the exclusion zone; therefore they were not tested. These individuals were primarily truck drivers who hauled landfill material away to be disposed of in an industrial landfill in Rosemount, MN.

Tables 1 and 2 provide the measures of central tendency for the baseline and end-of-project PFOA and PFOS serum concentrations for the 11 subjects with paired measurements (baseline and end-of-project). Values are provided in ng/mL (parts-per-billion).

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

						Arithmetic	
	Min	Q1	Median	Q3	Max	Mean	95% CI
Baseline	1.8	3.3	3.9	6.3	10.1	4.9	3.4 – 6.5
End-of-Project	2.0	2.9	4.0	5.3	8.5	4.3	3.0 – 5.7

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

	Min	Q1	Median	Q3	Max	Arithmetic Mean	95% CI
Baseline	2.8	8.5	11.5	18.4	22.0	12.2	8.1 – 16.3
End-of-Project	3.9	7.6	10.0	16.8	22.1	11.8	8.2 – 11.8

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 11 subjects.

Equation.

$$\text{Mean Difference} = \sum_{i=1}^{11}(\text{end-of-project} - \text{baseline})/11$$

There was a statistically significant change (decrease) of -0.6 ng/mL PFOA between baseline and end of project (95% CI (-1.0) – (-0.2); $p < 0.006$). There was no statistically significant change in PFOS concentrations between baseline and end of project (mean difference -0.4 ng/mL; 95% CI (-1.5) – (0.8); $p = 0.49$).

Figures 1 and **2** provide another method to compare the baseline to end of project concentrations for PFOA and PFOS, respectively, for these 11 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 near the identity line. This indicates concentrations measured at end of project approximated those at baseline given the analytical variability of the measurements.

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 Oakdale landfill remediation 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 exposure to PFOA or PFOS, or to materials that may degrade to them. Matched pair analyses did not indicate any substantive exposure during the course of this project to PFOA or PFOS. The clinical chemistry data were therefore 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 11 contingent workers who entered the exclusion zone, there was no increase in serum PFOA or PFOS concentrations while working at the Oakdale landfill remediation 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 Serum Concentrations (ng/mL), Oakdale Landfill Remediation Project

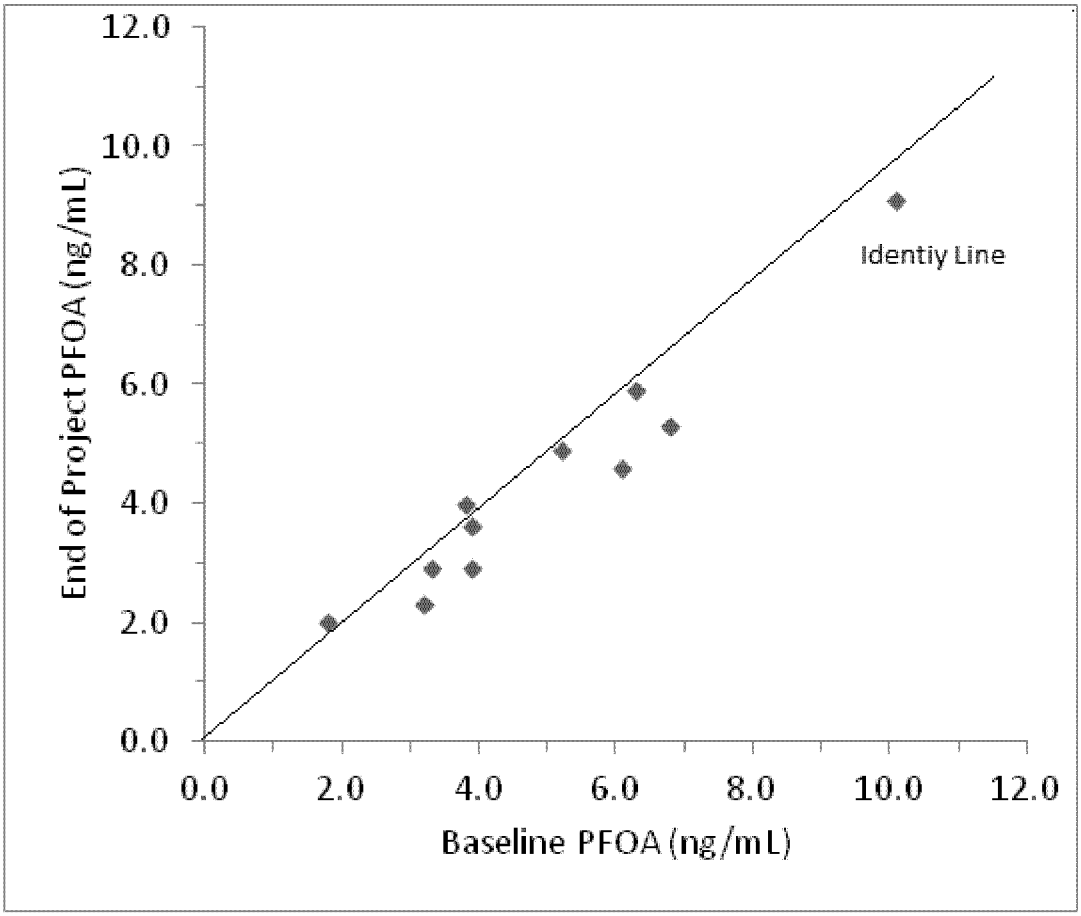

Figure 2. Baseline and End of Project PFOS Serum Concentrations (ng/mL), Oakdale Landfill Remediation Project