FINAL REPORT

Epidemiology, 220-3W-05
Medical Department
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Title: Biomonitoring Assessment of the 3M Woodbury Northeast Landfill Remediation Project

Study
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Summary

There were 15 contingent workers (non-3M employees) who worked within the exclusion zone at the 3M Woodbury northeast landfill remediation project that had baseline and end-of-project perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) measurements. The duration of this project was approximately 4 months. An additional 7 contingent workers participated in either a baseline (n = 4) or end of project (n = 3) assessment; thus, a trend assessment of these 7 individuals was not possible. The 15 contingent workers with paired assessments showed no statistically significant increases in either their mean PFOA or PFOS serum concentrations. These 15 workers' mean baseline PFOA concentration was 3.8 ng/mL (95% CI 2.7 – 5.0). Their mean PFOS concentration was 13.1 ng/mL (95% CI 9.6 – 16.5). The mean concentration differences (end-of-project minus baseline) were 0.0 ng/mL (95% CI (-0.3) – 0.4, p = 0.97) for PFOA and -0.3 ng/mL (95% CI (1.1) – 0.4, p = 0.38) for PFOS. Conclusion: Based on the paired biomonitoring data of 15 contingent workers, there was no increase in serum PFOA or PFOS concentrations while working at the 3M Woodbury northeast landfill remediation project.

Introduction

Several remediation projects have been completed regarding legacy perfluorochemicals. These include the 3M Woodbury (primary) landfill remediation project, 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 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 Woodbury northeast landfill remediation project. The duration of this project was approximately 4 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 this remediation project (**Table 1**). Fifteen individuals had both baseline and end of project assessments.

Table 1. Distribution of workers by company and participation

Company	Baseline	End-of-Project	Reasons for "no show"
Veit	13	9	4 did not show for end of project
AECOM	1	1	
Briscoe Trucking	0	1	(Did not show for baseline)
Kortech Consulting	0	1	(Did not show for baseline)
Weston	5	6	(One did not show for baseline)
Total			

It was not possible to determine whether the 7 individuals, without paired measurements as shown in **Table 1**, had increased serum PFOA or PFOS concentrations attributable to working on the Woodbury northeast landfill remediation project. The 4 Veit workers that had only a baseline assessment had PFOA concentrations comparable to their 9 Veit colleagues with paired measurements (3.0 ng/mL vs. 3.0 ng/mL, t = 0.08; p value = 0.94); however, these 4 workers had a significantly higher baseline PFOS concentration (21.3 ng/mL vs. 9.9 ng/mL, 5 = 4.3, p = 0.01). Reason for this difference is unknown. The three workers assessed only at end of project worked for different employers. Two of these workers had prior work exposures with other 3M remediation sites. Their serum PFOA and PFOS concentrations were higher than the average of the 15 contingent workers with paired measurements.

Tables 2 and 3 provide the measures of central tendency for the baseline and end-of-project PFOA and PFOS concentrations for the 15 subjects with paired measurements. Values are provided in ng/mL (parts-per-billion). There were no statistically significant differences between baseline and end of project measurements for these 15 contingent workers.

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

						Arithmetic		Geometric	
	Min	Q1	Median	Q3	Max	Mean	95% CI	Mean	95% CI
Baseline	1.3	2.4	3.5	4.8	10.1	3.8	2.7 - 5.0	3.4	2.6 - 4.5
End-of-Project	1.0	2.5	3.5	4.6	10.	3.8	2.7 - 5.0	3.4	2.6 - 4.5

Table 3. PFOS Baseline and End-of-Project Concentrations (ng/mL)

						Arithmetic		Geometric	
	Min	Q1	Median	Q3	Max	Mean	95% CI	Mean	95% CI
Baseline	4.9	8.7	12.0	18.1	29.1	13.1	9.6 - 16.5	11.9	9.2 - 15.2
End-of-Project	3.5	9.3	12.2	15.6	28.2	12.8	9.5 - 16.0	11.5	8.9 - 15.0

A matched-pair statistical analysis was performed (see Equation). The mean difference represents the average of the sum of the individual differences for the 15 subjects. There were no statistically significant mean matched-pair differences for PFOA or PFOS (**Table 4**).

Equation.

$$\text{Mean Difference} = \sum_{i=1}^{15}(\text{end-of-project} - \text{baseline})/15$$

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
Equation	0.0	0.04	0.97	-0.3	-0.90	0.38

Table 5 provides the statistically nonsignificant matched-pair differences by the 2 employers (Veit and Weston) for 14 of these 15 contingent workers with paired assessments.

Table 5. Matched-pair Analysis Comparing Baseline to End-of-Project PFOA and PFOS Concentration (ng/mL) by Employer

Mean Paired Difference	PFOA (ng/mL)	t-ratio	p value	PFOS (ng/mL)	t-ratio	p value
Veit	0.0	0.12	0.91	0.0	-0.04	0.97
Weston	-0.1	-0.40	0.71	-1.2	-1.37	0.24

Figures 1 and **2** provide another method to compare the baseline to end-of-project concentrations for PFOA and PFOS, respectively, for these 15 contingent workers. Data points near the diagonal identity line, where $x = y$, indicate no difference in concentrations between baseline (x) and end of project (y). The strong linear trend centered along the identity line is indicative of no change between the paired measurements. The R^2 was 0.93 for PFOA (Figure 1) and 0.95 for PFOS (Figure 2).

The paired baseline and end of project PFOA and PFOS concentrations were compared between the 9 Veit employees and the 5 Weston employees. The baseline mean PFOA and PFOS concentrations were higher among the Weston workers (PFOA baseline Weston = 5.3 ng/mL vs Veit

= 3.0 ng/mL, t = 1.7, p = 0.15; PFOS baseline Weston = 17.7 ng/mL compared to Veit 9.9 ng/mL, t = 2.1, p = 0.09). The 5 Weston employees had worked at other 3M remediation projects.

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 Woodbury northeast landfill remediation project. Given the fact that exposure potential during the course of the landfill remediation 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 any other materials was not known since only PFOA and PFOS were analyzed in the workers' serum.

Conclusion

Based on the paired biomonitoring data of 15 contingent workers, there was no increase in serum PFOA or PFOS concentrations while working at the 3M Woodbury northeast 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 (x axis) and End of Project (y axis) PFOA Concentrations (ng/mL) for 15 Contingent Workers, Woodbury NE Project.

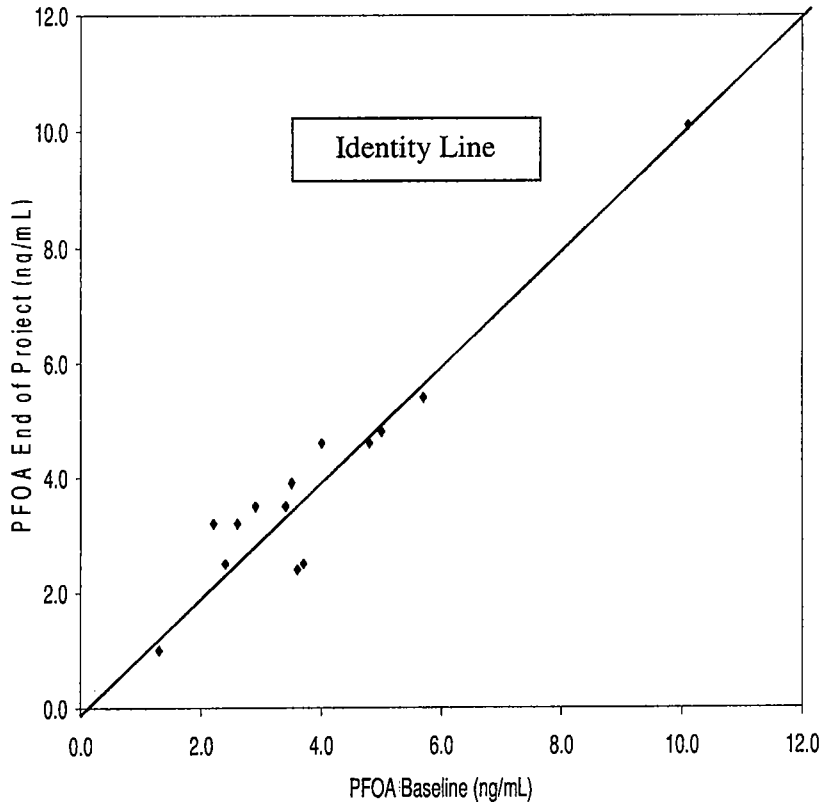

Figure 2. Baseline (x axis) and End of Project (y axis) PFOS Concentrations (ng/mL) for 15 Contingent Workers, Woodbury NE Project.