3M ENVIRONMENTAL LABORATORY
REPORT NO. E06-0151

Final Report

Analysis of PFOA, PFOS, PFHS, and PFBS From Newly Constructed Wells at the Oakdale, Minnesota Disposal Site

Laboratory Request Number: E06-0151

Method Requirement: 3M Method ETS-8-154.1 (modified)

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ACCREDITED

Certificate #2052-01

The testing reported herein meet the requirements of ISO/IED 17025-1999 "General Requirements for the Competence of Testing and Calibration Laboratories", in accordance with the A2LA Certificate #2052-01. Testing that complies with this International Standard also operate in accordance with ISO 9001/ISO 9002 (1994).

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Analytical Report E06-0151

Ground Water Samples from Newly Constructed Wells near the Oakdale, Minnesota Disposal Site
March 13, 2006

1 Introduction/Summary

The 3M Environmental Laboratory extracted and analyzed ground water samples collected by Weston Solutions, Inc. personnel on March 2-3, 2006 from newly constructed wells on and/or near the Oakdale, Minnesota 3M disposal site. Samples were returned to the 3M Environmental Laboratory for analysis of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHS), and perfluorobutane sulfonate (PFBS) under laboratory project number E06-0151 using 3M Environmental Laboratory Method ETS 8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry".

The 3M Environmental Laboratory prepared sets of sample containers for nine sampling locations. Each sample set consisted of a field sample, field sample duplicate, low field spike (1.0 ng/mL) and high field spike (10 ng/mL). Each empty container was marked with a "fill to here" line which corresponded to a final volume of 450 mL. Containers reserved for field matrix spikes were fortified with an appropriate matrix spike solution containing the four target analytes prior to being sent to the field for sample collection.

All samples were extracted on March 3, 2006 and analyzed on March 3, 2006 and on March 6, 2006. Table 1 below summarizes the sample results. All results for quality control samples prepared and analyzed with the samples will be reported and discussed elsewhere in this report.

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Certificate #2052-01

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Table 1. Sample Results Summary.

3M LIMS ID	Sample Description	[1] PFOA Concentration (ng/mL)	[2] PFOS Concentration (ng/mL)	[3] PFHS Concentration (ng/mL)	[4] PFBS Concentration (ng/mL)
E06-0151-082	OKMN GWS RW40 0 060302	<0.0250	<0.0249	<0.0252	<0.0397
E06-0151-083	OKMN GWS RW40 DB 060302	<0.0250	<0.0249	<0.0252	<0.0397
	Average	**<0.0250**	**<0.0249**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**NA**	**NA**	**NA**	**NA**
E06-0151-086	OKMN GWS SP42 0 060302	<0.0250	<0.0249	<0.0252	<0.0397
E06-0151-087	OKMN GWS SP42 DB 060302	<0.0250	<0.0249	<0.0252	<0.0397
	Average	**<0.0250**	**<0.0249**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**NA**	**NA**	**NA**	**NA**
E06-0151-090	OKMN GWS PL43 0 060302	<0.0250	<0.0249	<0.0252	<0.0397
E06-0151-091	OKMN GWS PL43 DB 060302	<0.0250	<0.0249	<0.0252	<0.0397
	Average	**<0.0250**	**<0.0249**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**NA**	**NA**	**NA**	**NA**
E06-0151-094	OKMN GWS RW39 0 060302	<0.0250	<0.0249	<0.0252	<0.0397
E06-0151-095	OKMN GWS RW39 DB 060302	<0.0250	<0.0249	<0.0252	<0.0397
	Average	**<0.0250**	**<0.0249**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**NA**	**NA**	**NA**	**NA**
E06-0151-098	OKMN GWS PC45 0 060303	0.592	0.390	0.0649	<0.0397
E06-0151-098[5]	OKMN GWS PC45 0 060303	0.522	0.464	0.0635	<0.0397
E06-0151-099	OKMN GWS PC45 DB 060303	0.514	0.449	0.0547	<0.0397
	Average	**0.543**	**0.434**	**0.0610**	**<0.0397**
	%RSD Sample/Sample Dup/Lab Dup	**7.9**	**9.0**	**9.1**	**NA**
E06-0151-102	OKMN GWS SP44 0 060303	<0.0250	<0.0249	<0.0252	<0.0397
E06-0151-103	OKMN GWS SP44 DB 060303	<0.0250	<0.0249	<0.0252	<0.0397
	Average	**<0.0250**	**<0.0249**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**NA**	**NA**	**NA**	**NA**
E06-0151-106	OKMN GWS RW38 0 060303	0.0525	0.187	<0.0252	<0.0397
E06-0151-107	OKMN GWS RW38 DB 060303	0.0556	0.195	<0.0252	<0.0397
	Average	**0.0540**	**0.191**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**5.7**	**4.2**	**NA**	**NA**
E06-0151-110	OKMN GWS RW37 0 060303	0.312	2.47	<0.0252	<0.0397
E06-0151-110[5]	OKMN GWS RW37 0 060303	0.282	2.51	<0.0252	<0.0397
E06-0151-111	OKMN GWS RW37 DB 060303	0.298	2.56	<0.0252	<0.0397
	Average	**0.297**	**2.51**	**<0.0252**	**<0.0397**
	%RSD Sample/Sample Dup/Lab Dup	**5.0**	**1.8**	**NA**	**NA**
E06-0151-114	OKMN GWS PL41 0 060303	0.0766	0.0268	<0.0252	<0.0397
E06-0151-115	OKMN GWS PL41 DB 060303	0.0796	<0.0249	<0.0252	<0.0397
	Average	**0.0781**	**[6]0.0268**	**<0.0252**	**<0.0397**
	%RPD Sample/Sample Dup	**3.8**	**NA**	**NA**	**NA**

(1) The analytical uncertainty for PFOA was 100±5.8% based on method accuracy and precision. See Section 3.7 for additional explanation. The limit of quantitation (LOQ) was 0.0250 ng/mL. Results and average values are rounded to three significant figures according to EPA rounding rules. %RPD values are rounded to two significant figures.

Because of rounding, values may vary slightly from those listed in the raw data. Samples with reported results less than the LOQ of 0.0250 ng/mL may or may not have PFOA present. Results less than the LOQ are not quantified.

(2) The analytical uncertainty for PFOS was 100±3.7 % based on method accuracy and precision. See Section 3.7 for additional explanation. The limit of quantitation (LOQ) was 0.0249 ng/mL. Results and average values are rounded to three significant figures according to EPA rounding rules. %RPD values are rounded to two significant figures. Because of rounding, values may vary slightly from those listed in the raw data. Samples with reported results less than the LOQ of 0.0249 ng/mL may or may not have PFOS present. Results less than the LOQ are not quantified.

(3) The analytical uncertainty for PFHS was 100±8.6% based on method accuracy and precision. See Section 3.7 for additional explanation. The limit of quantitation (LOQ) was 0.0252 ng/mL. Results and average values are rounded to three significant figures according to EPA rounding rules. %RPD values are rounded to two significant figures. Because of rounding, values may vary slightly from those listed in the raw data. Samples with reported results less than the LOQ of 0.0252 ng/mL may or may not have PFHS present. Results less than the LOQ are not quantified.

(4) The analytical uncertainty for PFBS was 100±6.6 % based on method accuracy and precision. See Section 3.7 for additional explanation. The limit of quantitation (LOQ) was 0.0397 ng/mL. Results and average values are rounded to three significant figures according to EPA rounding rules. %RPD values are rounded to two significant figures. Because of rounding, values may vary slightly from those listed in the raw data. Samples with reported results less than the LOQ of 0.0397 ng/mL may or may not have PFBS present. Results less than the LOQ are not quantified.

(5) Sample results are for a laboratory extraction duplicate. The relative standard deviation (%RSD) is reported using all three results (sample, laboratory duplicate, and sample duplicate).

(6) The average value listed is the concentration for the sample or sample duplicate that produced a value above the LOQ. A true average and %RPD between the sample and sample duplicate was not determined.

2 Methods - Analytical and Preparatory

2.1 Sample Collection

Samples were collected in Nalgene™ (low-density polyethylene) bottles prepared at the 3M Environmental Laboratory. Prior to sample collection, bottles designated for field matrix spikes were spiked in the laboratory with a known volume of an appropriate matrix spiking solution containing the analytes of interest (PFOA, PFOS, PFHS, and PFBS). Collected sample bottles were returned to the laboratory at ambient conditions on March 3, 2006. Table 2 below details the bottles prepared and the corresponding spike levels for each sampling location. Samples were collected from nine individual sites. Table 3 provides the key code for the sample descriptions.

Table 2. Sample Collection and Spike Information.

		Final Concentration (ng/mL)			
Description	*Nominal Final Volume (mL)*	*PFOA*	*PFOS*	*PFHS*	*PFBS*
Sample	450	NA	NA	NA	NA
Sample Duplicate	450	NA	NA	NA	NA
Low Field Matrix Spike	450	0.999	0.997	1.01	0.992
High Field Matrix Spike	450	9.99	9.97	10.1	9.92
Trip Blank	450	NA	NA	NA	NA
Trip Blank Low Matrix Spike	450	0.999	0.997	1.01	0.992
Trip Blank High Matrix Spike	450	9.99	9.97	10.1	9.92

Table 3. Sample Description Key Code.

Sample ID Code	Definition
RW	Residuum well
PL	Platteville Limestone well
SP	St. Peter Sandstone well
PC	Prairie du Chein well
OKMN	Oakdale Minnesota site
GW	Groundwater Sample
0	Sample
DB	Duplicate
LS	Low Spike
HS	High Spike

The ground water samples, sample duplicates, and field matrix spikes returned for analysis all had visible sediment present which "colored" the water sample when shaken to disperse the solids. All collected samples were centrifuged to remove particulate before extraction. See Section 2.2 for more information. Additionally, the samples associated with RW37 generated a fairly strong petroleum odor. The table below describes additional observations noted for each of the sample locations.

Table 4. Sample Observations.

	Observations		
Well Identification	Sediment Color	Sediment Amount	Other
RW37	Grey-brown	(1)Moderate	Strong petroleum odor present
RW38	Rust-brown	(2)Light	NA
RW39	Rust-brown	(2)Light	NA
RW40	Rust-brown	(1)Moderate	NA
PL41	Rust-brown	(1)Moderate	NA
SP42	Rust-brown	(1)Moderate	NA
PL43	Rust-brown	(1)Moderate	NA
SP44	Grey-brown	(1)Moderate	NA
PC45	Rust-brown	(2)Light	NA

(1) Moderate: after centrifugation of a 40 mL aliquot, solids roughly the size of a pea remained after removal of the supernatant.
(2) Light: after centrifugation of a 40 mL aliquot, solids present, but minimal.

2.2 Extraction

All samples, calibration standards, and associated quality control samples were extracted using the procedure outlined in ETS-8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extractions and High Performance Liquid Chromatography/Mass Spectrometry". Briefly, 40 mL of sample were loaded onto a pre-conditioned Waters C18 solid phase extraction (SPE) cartridge (Sep-Pak, 1.0 g, 6 cc) using a vacuum manifold. The loaded SPE cartridges were then eluted with 5 mL of methanol. This extraction procedure concentrates the samples by a factor of eight. (Initial volume = 40 mL, final volume = 5 mL). The calibration standards, lab control spikes, method blanks, and trip blank sample and spikes were extracted as described above. Because the collected ground water samples contained visibly significant amounts of sediment/particulate, the 40 mL aliquot was centrifuged at 3500 rpm for ten minutes for all samples, sample duplicates, low field matrix spikes and high field matrix spikes prior to extraction. After centrifugation, the supernatant was loaded onto the SPE cartridge for extraction similar to the calibration standards and laboratory quality control samples. The remaining solids were retained if further extraction was deemed necessary. ETS-8-154.1 does not describe sample centrifugation prior to extraction. This method modification was

necessary as the sediment completely clogged the SPE cartridges almost immediately preventing complete loading of the water sample. The final methanol sample extracts had a slight yellowish color. Recoveries of laboratory matrix spikes and field sample matrix spikes demonstrated that the centrifugation step did not significantly impact the method performance.

Samples were extracted and initially analyzed on March 3, 2006. The trip blank spikes for all four analytes produced recoveries of approximately 60%. Additionally, most field sample matrix spike recoveries were between 60-80%. Upon further review of the data, it was determined that an older standard was used to prepare the upper range of the calibration curve on March 3, 2006 and that this standard was not the same one used to prepare the collection bottle spikes. On March 6, 2006, a new extracted calibration curve was prepared using the same (newer) standard used to prepare the collection bottle spikes. Method blanks and lab control spikes at 1 ng/mL and 10 ng/mL were also prepared with the new curve. Additionally, the trip blank and trip blank field matrix spikes along with two samples (E06-0151-098 and E06-0151-0110) were also re-extracted. Furthermore, low and high lab matrix spikes at 1 and 10 ng/mL were prepared for the two samples selected for re-extraction. For the lab matrix spiked samples, an appropriate amount of spiking standard was added to the 40 mL sample aliquot before it was centrifuged to remove the solids. Analysis of selected calibration points from the first curve (March 3, 2006) against the the new curve (March 6, 2006) demonstrated that a systematic bias of 20-30% was present in the first analysis. All sample extracts from March 3, 2006 were then reanalyzed against the new curve. All results presented here are from the March 6, 2006 analysis against the new calibration curve.

2.3 Analysis

All sample and quality control extracts were analyzed for the target analytes using high performance liquid chromatography/ tandem mass spectrometry (HPLC/MS/MS). Pertinent instrument parameters, the liquid chromatography gradient program, and the specific mass transitions analyzed are described in the tables below.

Table 5. Instrument Parameters

Instrument Name	ETSStan
Liquid Chromatograph	Agilent 1100
Guard column	Betasil C18 (2.1 mm.X100 mm), 5 µm
Analytical column	Betasil C18 (2.1 mm X 100 mm), 5 µm
Injection Volume	5 µL
Mass Spectrometer	Applied Biosystems API 4000
Ion Source	Turbo Spray
Electrode	Z-spray
Polarity	Negative
Software	Analyst 1.4.1

Table 6. Liquid Chromatography Gradient Program

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	300	80.0	20.0
1	1.0	300	80.0	20.0
2	14.5	300	10.0	90.0
3	15.5	300	10.0	90.0
4	16.5	300	80.0	20.0
5	20.0	300	80.0	20.0

Table 7. Mass Transitions

Analyte	Mass Transition Q1/Q3	Dwell Time (msec)
[(1)]PFBS	299/80	125
	299/99	125
[(1)]PFHS	399/80	125
	399/99	125
[(1)]PFOS	499/130	125
	499/99	125
	499/80	125
[(1)]PFOA	413/369	125
	413/219	125
	413/169	125

*Individual transitions were summed to produce a "total ion chromatogram" (TIC). The TICs were used for quantitation.

3 Data Analysis

3.1 Calibration

Calibration standards were prepared by spiking known amounts of methanolic stock solutions containing PFOA, PFOS, PFHS, and PFBS into 40 mL of ASTM type I water. Each spiked water standard was then extracted in the same manner as the collected samples. A total of twelve spiked standards ranging from 0.025 ng/mL to 25 ng/mL (nominal) were prepared. A quadratic, 1/x weighted, calibration curve was used to fit the data for each analyte. The data was not forced through zero during the fitting process. Calculating the standard concentration using the peak area counts and the resultant calibration curve confirmed accuracy of each curve point. Each extracted calibration standard used to generate the final calibration curve met the method calibration accuracy requirement of ±25%. The correlation coefficients (r) were greater than 0.999 for all analytes.

3.2 Limit of Quantitation (LOQ)

The LOQ for this analysis, as defined in ETS-8-154.1, is the lowest non-zero calibration standard in the curve in which the area counts are twice those of the method blank(s). The limit of quantitation for PFOA, PFOS, PFHS, and PFBS is 0.0250 ng/mL, 0.0249 ng/mL, 0.0252 ng/mL, and 0.0397 ng/mL respectively Area count comparision for the method blanks and the lowest calibration standard will be provided in Section 3.5.1.

3.3 System Suitability

Fiver replicate injections of the 5 ng/mL extracted-calibration standard was analyzed at the beginning of the analytical sequence to demonstrate overall system suitability. The same standard was analyzed in triplicate at the end of the analytical sequence. All analytes met method acceptance criteria of less than 5% relative standard deviation (RSD) for peak area and less than 2% RSD for retention time for both opening and closing system suitability injections.

3.4 Continuing Calibration

During the course of the analytical sequence, several continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial calibration curve was still in control. All CCVs produced recoveries within 100%±25%, which met method criteria.

3.5 Blanks

Three types of blanks were prepared and analyzed with the samples: method blanks, solvent blanks, and field/trip blanks. Each blank type is described below.

3.5.1 Method Blanks

Several method blanks were prepared by loading 40 mL of ASTM Type I water onto a C18 SPE cartridge and eluting with 5 mL of methanol using the same extraction procedure as the samples. Method blanks were prepared to evaluate the levels of background contamination in the overall extraction process (reagent water, glassware, SPE cartridges, etc.) Table 8 lists the area counts for the method blanks and the LOQ standard associated with the given data set.

Table 8. Method Blank Area Counts for Extractions performed on 3/6/2006.

Sample Name	*Sample Comment*	*Sample ID*	*Area Counts*			
			PFOA	*PFOS*	*PFHS*	*PFBS*
s060306a025	Method Blank-1	MB-060306-1	11741	[1]2880	5939	13417
s060306a026	Method Blank-2	MB-060306-2	11689	1412	2265	4009
s060306a027	Method Blank-3	MB-060306-3	11131	1814	5101	18787
s060306a028	Method Blank-4	MB-060306-4	6189	993	1824	4178
s060306a029	Method Blank-5	MB-060306-5	8872	1510	1613	4717
s060306a030	Method Blank-6	MB-060306-6	5558	655	1218	1874
s060306a031	Method Blank-7	MB-060306-7	20205	1982	5292	11821
s060306a032	Method Blank-8	MB-060306-8	15076	1802	4387	14398
Area Counts of highest method blank multiplied by two			***40410***	***3964***	***11878***	***37574***
Area Counts LOQ standard			***50284***	***5254***	***21147***	***54306***
LOQ concentration, ng/mL			***0.0250***	***0.0249***	***0.0252***	***0.0397***

(1) Determined to be a statistical outlier at the 80% confidence level using Dixon's Q-test. Area value not used to establish the LOQ for PFOS.

3.5.2 Solvent Blanks

Several methanol solvent blanks were analyzed to assess system contamination and/or instrument carryover. Analyte peak area counts in all blank samples were less than half the area counts of the calibration standard used to establish the LOQ.

3.5.3 Field/Trip Blanks

Prior to sample collection, one sample container was filled with 450 mL of ASTM Type I water, sealed, and shipped to the sample collection site along with the empty containers. This sample was analyzed as field/trip blank. The trip blank serves as an additional method blank that accounts for any storage conditions and/or holding time issues that the samples may experience. The target analytes were not detected above the stated LOQ in the trip blank.

3.6 Lab Control Spikes (LCSs)

For the extractions performed on March 3, 2006, low (0.25 ng/mL nominal concentration) and high (7.5 ng/mL nominal concentration) lab control spikes were prepared and analyzed in triplicate. LCSs were prepared by spiking known amounts of the analytes into 40 mL of ASTM Type I water to produce the desired concentration. The spiked water samples were then extracted and analyzed in the same manner as the samples. Analysis of triplicate LCSs at the two specified levels cross-validates the

analytical method as used here for any modifications/deviations from ETS 8-154.1. Additionally, LCS results will be used to determine overall method uncertainty in Section 3.7. Table 9 summarizes the LCS recovery results from the March 6, 2006 extraction set.. LCS recoveries from the March 3, 2006 extraction are not given here as no sample results were reported from this run.

Table 9. [1]Lab Control Spike Results.

		PFOA			PFOS		
Sample Description	*Lab ID*	*Spiked Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*% Recovery*	*Spiked Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*% Recovery*
1 ppb Lab Control Spike	LCS-060306-1	0.999	1.00	100	0.997	1.04	104
1 ppb Lab Control Spike	LCS-060306-2	0.999	1.01	101	0.997	1.03	103
1 ppb Lab Control Spike	LCS-060306-3	0.999	0.961	96.2	0.997	1.00	100
10 ppb Lab Control Spike	LCS-060306-4	9.99	9.19	92.1	9.97	9.91	99.4
10 ppb Lab Control Spike	LCS-060306-5	9.99	9.65	96.6	9.97	10.2	102
10 ppb Lab Control Spike	LCS-060306-6	9.99	9.85	98.6	9.97	10.1	101
Average %Recovery ± %RSD		*97.4%±3.3%*			*102%±1.8%*		

		PFHS			PFBS		
Sample Description	*Lab ID*	*Spiked Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*% Recovery*	*Spiked Conc. (ng/mL)*	*Calculated Conc. (ng/mL)*	*% Recovery*
1 ppb Lab Control Spike	LCS-060306-1	1.01	1.08	107	0.992	1.04	105
1 ppb Lab Control Spike	LCS-060306-2	1.01	1.11	110	0.992	1.05	106
1 ppb Lab Control Spike	LCS-060306-3	1.01	1.08	107	0.992	1.03	104
10 ppb Lab Control Spike	LCS-060306-4	10.1	9.85	97.7	9.92	9.17	92.4
10 ppb Lab Control Spike	LCS-060306-5	10.1	9.93	98.5	9.92	9.32	94.0
10 ppb Lab Control Spike	LCS-060306-6	10.1	9.84	97.6	9.92	9.49	95.7
Average %Recovery ± %RSD		*103%±5.5%*			*99.4%±6.1%*		

(1) All results and average values listed to three significant figures according to EPA rounding rules. %RSD values given to two significant figures. Due to rounding, values may vary slightly from those in the raw data.

$$\text{LCS Percent Recovery} = \frac{\text{Calculated Concentration}}{\text{Spike Concentration}} * 100\%$$

$$\text{LCS\% RSD} = \frac{\text{standard deviation LCS replicates}}{\text{average LCS recovery}} * 100\%$$

3.7 Analytical Uncertainty

Both the accuracy (percent recovery) and precision (%RSD) of the lab control spikes were used to estimate the overall method's analytical uncertainty for a given analyte. For example, the overall accuracy and precision for PFOA based on LCS results was 97.4% ± 3.3%. The measured precision (%RSD) is then used to determine the range of the accuracy.

Example:

97.4*(0.033) = 3.25

97.4 + 3.25 = 100.7; 97.4–3.25 = 94.20

Thus, LCS accuracy results range from 94.2% to 100.7%. The absolute difference of the low and high ends of this range when compared 100%, are then calculated.

100.7%-100% = 0.70%
100%-94.2% = 5.8%.

The most conservative (largest) absolute difference is then used as the analytical uncertainty for the given analyte. Therefore, the analytical uncertainty for PFOA is given as 100 ± 5.8% for these results. For PFOS, PFHS, and PFBS, the analytical uncertainty, as defined here, is 100 ± 3.7%, 100 ± 8.6%, and 100 ± 6.6%, respectively.

3.8 Field Matrix Spikes (FMS)

Low (nominal concentration of 1.0 ng/mL) and high (nominal concentration 10 ng/mL) field matrix spikes were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not interfere with the extraction and analysis of the analytes of interest. Field matrix spike results will be presented in the next section with the sample data.

$$\text{FMS Recovery} = \frac{(\text{Calculated Sample Concentration} - \text{Average Concentration : Field Sample \& Field Sample Dup.})}{\text{Spike Concentraton}} * 100\%$$

4 Data Summary

The tables (Tables 10-19) below summarize the sample results, field matrix spike recoveries, and lab matrix spike reovoeries (if applicable) for the nine locations as well as the Trip Blank. Each table provides the average concentration and the relative percent difference (RPD) or relative percent standard deviation (RSD) of the sample and sample duplicate (and laboratory duplicate – if applicable). All field matrix spike recoveries were within 100±30% for all analytes except for the high level PFOS field matrix spike associated with PC45 (LIMS ID# E06-0151-101) which produced a recovery of 148%. The analytical accuracy for the PFOS results associated with this well have not been adjusted as the low field matrix spike, as well as the low and high level lab matrix spikes, produced recoveries within 100±30%.

Table 10. [1]Sample Results for OKMN GWS RW40.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-082	OKMN GWS RW40 0 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-083	OKMN GWS RW40 DB 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-084	OKMN GWS RW40 LS 060302	1.15	115	1.22	122	1.15	114	0.976	98.4
E06-0151-085	OKMN GWS RW40 HS 060302	7.26	72.7	9.93	99.6	9.05	90.0	8.4	84.6
Average Concentration (ng/mL) ±%RPD		<0.0250		<0.0249		<0.0252		<0.0397	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

Table 11. [1]Sample Results for OKMN GWS SP42.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-086	OKMN GWS SP42 0 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-087	OKMN GWS SP42 DB 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-088	OKMN GWS SP42 LS 060302	0.93	93.1	1.18	118	1.03	102	0.963	97.0
E06-0151-089	OKMN GWS SP42 HS 060302	7.25	72.6	10.1	101	8.54	84.9	8.21	82.7
Average Concentration (ng/mL) ±%RPD		<0.0250		<0.0249		<0.0252		<0.0397	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

Table 12. [1]Sample Results for OKMN GWS PL43.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-090	OKMN GWS PL43 0 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-091	OKMN GWS PL43 DB 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-092	OKMN GWS PL43 LS 060302	1.02	102	1.2	120	1.09	108	0.982	99.0
E06-0151-093	OKMN GWS PL43 HS 060302	8.29	83.0	11.7	117	10.1	100	9.31	93.8
Average Concentration (ng/mL) ±%RPD		<0.0250		<0.0249		<0.0252		<0.0397	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

Table 13. [1]Sample Results for OKMN GWS RW39.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-094	OKMN GWS RW39 0 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-095	OKMN GWS RW39 DB 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-096	OKMN GWS RW39 LS 060302	0.954	95.5	1.07	107	0.968	96.2	0.951	95.8
E06-0151-097	OKMN GWS RW39 HS 060302	7.43	74.4	10.5	105	9.52	94.6	9.25	93.2
Average Concentration (ng/mL) ±%RPD		<0.0250		<0.0249		<0.0252		<0.0397	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

Table 14. [1]Sample Results for OKMN GWS PC45.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	*Description*	*Conc. (ng/mL)*	*%Recovery*	*Conc. (ng/mL)*	*%Recovery*	*Conc. (ng/mL)*	*%Recovery*	*Conc. (ng/mL)*	*%Recovery*
E06-0151-098	OKMN GWS PC45 0 060303	0.522	NA	0.464	NA	0.0649	NA	<0.0397	NA
E06-0151-099	OKMN GWS PC45 DB 060303	0.514	NA	0.449	NA	0.0547	NA	<0.0397	NA
E06-0151-098[2]	OKMN GWS PC45 0 060303	0.592	NA	0.390	NA	0.0635	NA	<0.0397	NA
E06-0151-100	OKMN GWS PC45 LS 060303	1.45	90.6	1.64	121	1.11	105	1.05	106
E06-0151-101	OKMN GWS PC45 HS 060303	9.93	94.0	15.2	[3]148	10.3	102	9.74	98.2
[4]E06-0151-098-LMS Low	Laboratory Matrix Spike at 1 ng/mL	1.59	105	1.41	97.5	1.07	100	0.944	95.1
[4]E06-0151-098-LMS High	Laboratory Matrix Spike at 10 ng/mL	11.3	108	11.0	106	10.5	104	9.05	91.2
Average Concentration (ng/mL) ± %RSD		*0.543 ± 7.9*		*0.434 ± 9.0*		*0.0610 ± 9.1*		*<0.0397*	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data.

(2) Sample results are from a duplicate laboratory extraction of the sample. All three replicate values used to determine average and %RSD.

(3) FMS recovery exceeded method acceptance criteria of 100±30%.

(4) Laboratory matrix spikes were prepared by spiking the 40 mL sample aliquot prior to centrifugation.

Table 15. [1]Sample Results for OKMN GWS SP44.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-102	OKMN GWS SP44 0 060303	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-103	OKMN GWS SP44 DB 060303	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-104	OKMN GWS SP44 LS 060303	0.943	94.4	1.08	108	0.991	98.5	0.942	94.9
E06-0151-105	OKMN GWS SP44 HS 060303	8.82	88.3	11.9	119	9.60	95.4	9.16	92.3
Average Concentration (ng/mL) ±%RPD		*<0.0250*		*<0.0249*		*<0.0252*		*<0.0397*	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

Table 16. [1]Sample Results for OKMN GWS RW38.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-106	OKMN GWS RW38 0 060303	0.0525	NA	0.187	NA	<0.0252	NA	<0.0397	NA
E06-0151-107	OKMN GWS RW38 DB 060303	0.0556	NA	0.195	NA	<0.0252	NA	<0.0397	NA
E06-0151-108	OKMN GWS RW38 LS 060303	1.02	96.7	1.42	123	1.06	105	0.969	97.6
E06-0151-109	OKMN GWS RW38 HS 060303	7.94	78.9	10.2	100	9.27	92.1	8.86	89.3
Average Concentration (ng/mL) ±%RPD		*0.0540 ± 5.7*		*0.191 ± 4.2*		*<0.0252*		*<0.0397*	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

Table 17. [1]Sample Results for OKMN GWS RW37.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-110	OKMN GWS RW37 0 060303	0.282	NA	2.51	NA	<0.0252	NA	<0.0397	NA
E06-0151-111	OKMN GWS RW37 DB 060303	0.298	NA	2.56	NA	<0.0252	NA	<0.0397	NA
E06-0151-110[2]	OKMN GWS RW37 0 060303	0.312	NA	2.47	NA	<0.0252	NA	<0.0397	NA
E06-0151-112	OKMN GWS RW37 LS 060303	1.22	92.3	3.43	92.2	1.19	118	1.16	117
E06-0151-113	OKMN GWS RW37 HS 060303	7.73	74.4	11.7	92.1	10.2	101	9.83	99.1
[3]E06-0151-110-LMS Low	Laboratory Matrix Spike at 1 ng/mL	1.47	117	3.71	120	0.983	97.7	0.941	94.8
[3]E06-0151-110-LMS High	Laboratory Matrix Spike at 10 ng/mL	9.62	93.3	12.3	98.2	8.91	88.6	8.82	88.9
Average Concentration (ng/mL) ±%RSD		*0.297 ± 5.0*		*2.51 ± 1.8*		*<0.0252*		*<0.0397*	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data.

(2) Sample results are from a duplicate laboratory extraction of the sample. All three replicate values used to determine average and %RSD.

(3) Laboratory matrix spikes were prepared by spiking a 40 mL sample aliquot prior to centrifugation.

Table 18. [1]Sample Results for OKMN GWS RW39.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
E06-0151-114	OKMN GWS PL41 0 060303	0.0766	NA	0.0268	NA	<0.0252	NA	<0.0397	NA
E06-0151-115	OKMN GWS PL41 DB 060303	0.0796	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-116	OKMN GWS PL41 LS 060303	1.11	103	1.13	111	1.10	109	0.995	100
E06-0151-117	OKMN GWS PL41 HS 060303	9.93	98.6	12.1	121	11.7	116	10.3	104
Average Concentration (ng/mL) ± %RPD		0.0781 ± 3.8		[2]0.0268		<0.0252		<0.0397	

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

(2) The average value reported reflects the single result that was above the LOQ. A true sample average and %RSD were not determined.

Table 19. [1]Sample Results for the Trip Blank.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery	Conc. (ng/mL)	%Recovery
[2]Extracted 3-3-06									
E06-0151-079	OKMN PW TRIP2 0 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-080	OKMN PW TRIP2 LS 060302	0.808	80.9	0.788	79.0	0.808	80.3	0.783	78.9
E06-0151-081	OKMN PW TRIP2 HS 060302	7.47	74.8	8.25	82.7	8.04	79.9	7.67	77.3
Extracted 3-6-06									
E06-0151-079	OKMN PW TRIP2 0 060302	<0.0250	NA	<0.0249	NA	<0.0252	NA	<0.0397	NA
E06-0151-080	OKMN PW TRIP2 LS 060302	1.04	104	0.928	93.0	1.04	103	0.982	99.0
E06-0151-081	OKMN PW TRIP2 HS 060302	9.04	90.5	10.2	102	10.0	99.4	9.58	96.5

NA= Not Applicable.

(1) Table displays rounded values for all concentrations and percent recovery values (3 significant figures), %RPD values (2 significant figures). Recovery and RPD values may vary slightly from the values in the raw data. %RPD values not given with both the sample and sample duplicate concentrations are less than the reported LOQ.

(2) Samples extracted on 3-3-06 but analyzed against the calibration curve prepared on 3-6-06.

5 Conclusion

PFOA, PFOS, PFHS, and PFBS results for the collected samples were presented in Table 1. Laboratory control spikes were used to determine the method accuracy and precision for all analytes. The accuracy and precision were then used to estimate the analytical uncertainty for the results (100 ± 5.8% for PFOA; 100 ± 3.7% for PFOS, 100 ± 8.6% for PFHS, and 100± 6.6% for PFBS). Field matrix spike recoveries within 100± 30% demonstrated that the analytical method was appropriate for the given sample matrix.

6 Data / Sample Retention

All remaining sample and associated project data (hardcopy and electronic) will be archived according to 3M Environmental Laboratory standard operating procedures.

7 Signatures

Susan T. Wolf, 3M Senior Chemist — Date: 3/10/06

Michelle D. Malinsky, Ph.D., 3M Technical Lead — Date: 3/13/06

William K. Reagen, Ph.D., Environmental Laboratory Management — Date: 3/13/06

The 3M Environmental Laboratory's Quality Assurance Unit has audited the data and report for this project.

Quality Assurance Representative — Date: