Subreport

Analysis of PFOA, PFOS, PFHS, and PFBS in Aqueous Samples: 3M Decatur Offsite Sampling Event (BPP Sample Sites)

Laboratory Request Number: E06-0199

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

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ACCREDITED

The testing reported herein meet the requirements of ISO/IEC 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).

Certificate #2052-01

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Analytical Subreport E06-0199

Surface Water Samples BPP01, BPP02, and BPP03;
Ground Water Sample BPWell

Decatur Offsite Sampling Event
Report Date: May 1, 2006

1 Introduction/Summary

The 3M Environmental Laboratory extracted and analyzed ground water and surface water samples collected by Weston Solutions personnel on April 12 and 13, 2006 near the 3M Decatur facility. 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 E06-0199 using modified 3M Environmental Laboratory Method ETS 8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry".

Per the client's request, an initial subreport is being issued for the following four sample locations only:

- DAL SWS BPP01
- DAL SWS BPP02
- DAL SWS BPP03
- DAL GWS BPWELL

This report will contain information relevant to these four sample collection points only. These results will be reissued in a comprehensive final project report that includes results for all samples collected under E06-0199.

The 3M Environmental Laboratory prepared sets of sample containers for thirty-two separate sampling locations. At a minimum, each sample set consisted of a field sample, field sample duplicate, low field spike and high field spike. For some locations, a third mid-level field spike was prepared. 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. The spike amounts prepared for each of the four locations presented here will be provided later in this report.

Certificate #2052-01

The testing reported herein meet the requirements of ISO/IEC 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

Samples were initially extracted and analyzed on April 19, 2006. Samples were diluted, reextracted, and analyzed on April 21, 2006. Laboratory matrix spikes were prepared, diluted, extracted, and analyzed on April 25, 2006 in the analytical batch initiated on April 24, 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. All samples were diluted 1:50 in ASTM Type I water prior to extraction.

Table 1. Sample Results Summary.

3M LIMS ID	*Sample Description*	*[1] PFOA Concentration (ng/mL)*	*[2] PFOS Concentration (ng/mL)*	*[1] PFHS Concentration (ng/mL)*	*[1] PFBS Concentration (ng/mL)*
E06-0199-055	DAL SWS BPP01 0 060413	293	[2] >423	53.3	6.98
E06-0199-056	DAL SWS BPP01 DB 060413	307	[2] >380	54.3	7.17
	Average	*300*	[2] >402	*53.8*	*7.08*
	%RPD Sample/Sample Dup	*4.7*	*NA*	*1.8*	*2.7*
E06-0199-060	DAL SWS BPP02 0 060413	206	[2] >295	38.2	4.30
E06-0199-061	DAL SWS BPP02 DB 060413	219	[2] >314	39.8	4.72
	Average	*212*	[2] >304	*39.0*	*4.66*
	%RPD Sample/Sample Dup	*6.1*	*NA*	*4.1*	*2.6*
E06-0199-065	DAL SWS BPP03 0 060413	219	[2] >272	39.1	4.69
E06-0199-066	DAL SWS BPP03 DB 060413	214	[2] >256	40.1	5.05
	Average	*216*	[2] >264	*39.6*	*4.87*
	%RPD Sample/Sample Dup	*2.3*	*NA*	*2.5*	*7.4*
E06-0199-070	DAL GWS BPWELL 0 060413	[2] >774	[2] >1460	[2] >145	17.2
E06-0199-071	DAL GWS BPWELL DB 060413	[2] >779	[2] >1170	[2] >145	17.6
	Average	[2] >776	[2] >1320	[2] >145	*17.4*
	%RPD Sample/Sample Dup	*NA*	*NA*	*NA*	*2.3*

(1) The analytical method uncertainty for PFOA, PFHS, and PFBS was 100±11%, 100±5.8%, and 100±8.8%, respectively based on method accuracy and precision. See Section 3.7 for additional explanation. The limit of quantitation (LOQ) *for these samples only* was 2.50 ng/mL (PFOA) and 1.25 ng/mL (PFHS and PFBS). Results and average values are rounded to three significant figures according to EPA rounding rules. Percent relative difference (%RPD) values are rounded to two significant figures. Because of rounding, values may vary slightly from those listed in the raw data.

(2) ***All PFOS sample results presented here should be considered estimated minimum values as quality control samples (field matrix spikes and lab matrix spikes) associated with these four samples did not demonstrate adequate method performance. The accuracy of the PFOS results could be within an order of magnitude. %RPD values not calculated. BPWell results for PFOA and PFHS should also be considered estimated minimums as field matrix spike recoveries did not meet method acceptance criteria of 100±30%. The analytical accuracy of the PFOA and PFHS estimated values for this sample only could be within an order of magnitude. %RPD values not calculated.***

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

four analytes of interest (PFOA, PFOS, PFHS and PFBS). Collected sample bottles were received at the laboratory at ambient conditions on April 19, 2006. Table 2 below details the samples collected and spikes added to each bottle

Table 2. Sample Collection and Spike Information.

3M LIMS ID#	*Weston Sample Description*	*3M Bottle Number*	*Bottle Designation*	*Nominal Spike Level (ng/mL)*	*GPO Location Comment*
E06-0199-055	DAL SWS BPP01 0 060413	109	Sample	NA	FSIA Drainage
E06-0199-056	DAL SWS BPP01 DB 060413	110	Sample Dup	NA	FSIA Drainage
E06-0199-057	DAL SWS BPP01 LS 060413	111	FMS Low	1.0	FSIA Drainage
E06-0199-058	DAL SWS BPP01 MS 060413	112	FMS Mid	10	FSIA Drainage
E06-0199-059	DAL SWS BPP01 HS 060413	113	FMS High	100	FSIA Drainage
E06-0199-060	DAL SWS BPP02 0 060413	119	Sample	NA	FSIA Drainage
E06-0199-061	DAL SWS BPP02 DB 060413	120	Sample Dup	NA	FSIA Drainage
E06-0199-062	DAL SWS BPP02 LS 060413	121	FMS Low	1.0	FSIA Drainage
E06-0199-063	DAL SWS BPP02 MS 060413	122	FMS Mid	10	FSIA Drainage
E06-0199-064	DAL SWS BPP02 HS 060413	123	FMS High	100	FSIA Drainage
E06-0199-065	DAL SWS BPP03 0 060413	114	Sample	NA	FSIA Drainage
E06-0199-066	DAL SWS BPP03 DB 060413	115	Sample Dup	NA	FSIA Drainage
E06-0199-067	DAL SWS BPP03 LS 060413	116	FMS Low	1.0	FSIA Drainage
E06-0199-068	DAL SWS BPP03 MS 060413	117	FMS Mid	10	FSIA Drainage
E06-0199-069	DAL SWS BPP03 HS 060413	118	FMS High	100	FSIA Drainage
E06-0199-070	DAL GWS BPWELL 0 060413	72	Sample	NA	BP Property
E06-0199-071	DAL GWS BPWELL DB 060413	73	Sample Dup	NA	BP Property
E06-0199-072	DAL GWS BPWELL LS 060413	74	FMS Low	10	BP Property
E06-0199-073	DAL GWS BPWELL MS 060413	75	FMS Mid	100	BP Property
E06-0199-074	DAL GWS BPWELL HS 060413	76	FMS High	1000	BP Property

DAL = Decatur, AL
SWS = Surface Water Sample
GWS = Ground Water Sample
0 = Sample
DB = Duplicate
LS = Low Spike
MS = Mid Spike
HS = High Spike

2.2 Extraction

All samples, calibration standards, and associated quality control samples were extracted using a modified procedure of ETS-8-154.1 "Determination of Perfluorinated Acids, Alcohols, Amides, and Sulfonates in Water by Solid Phase Extraction 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). Lab control spikes extracted in the same manner cross-validate all the method modifications/deviations from ETS-8-154.1. See Section 3.6 for additional information.

The samples and sample duplicates for BPP01, BPP02, and BPP03 were initially extracted undiluted on April 19, 2006. Initial analysis of the undiluted samples exceeded the upper limit of quantiation (25 ng/mL nominal) for PFOA and PFOS. Likewise, the sample and sample duplicate for BPWELL were initially extracted on April 19, 2006. The final extracts were diluted 1:10 prior to analysis. Analysis of these diluted extracts also exceeded the upper limit of quantitation. All the samples, sample duplicates, and field matrix spikes were reextracted on April 21, 2006. For BPP01, BPP02, and BPP03, the samples and associated QC were diluted 1:50 using ASTM Type I water prior to extraction. For BPWELL, the sample, sample duplicate, low spike and mid spike were diluted 1:50, while the high spike was diluted 1:500.

2.3 Analysis

All sample and quality control extracts were analyzed for PFOA, PFOS, PFHS, and PFBS 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 3. 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 4. 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 5. 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

(1) The 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 stock solutions containing the target analytes 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 were 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 100±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 at least twice those of the method and solvent blank(s). The LOQs for PFOA, PFOS, PFHS, and PFBS were 0.0500 ng/mL, 0.0999 ng/mL, 0.0250 ng/mL, and 0.0250 ng/mL, respectively. Note: these LOQ values have not been corrected for sample specific dilution factors. Area count comparison for the method blanks and the lowest calibration standard will be provided in Section 3.5.1.

3.3 System Suitability

Replicate injections of the 1 ng/mL extracted calibration standard were analyzed at the beginning and end of the analytical sequence to demonstrate overall system suitability. 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 were still in control. One PFOS CCV (139%) and one PFHS CCV (153%) exceeded method acceptance criteria of 100±25% for accuracy. Both of these non-compliant CCVs followed a contaminated solvent blank and the high recovery is most likely carryover from the previous injection. A method deviation has been

issued. The overall impact to the data quality objectives for the sample results is considered minimal as all sample injections and sample related QC injections were bracketed by compliant CCVs.

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.) The calibration curve was prepared on a separate day as the samples. (Calibration standards: April 10, 2006; diluted samples: April 21, 2006). The method blanks prepared with the calibration standards as well as with the samples were both analyzed during the April 21, 2006 analysis. Additional lab matrix spikes were prepared and analyzed in a separate analytical run initiated on April 24, 2006. Again, the method blanks prepared with the calibration curve and the method blanks prepared with the spikes were analyzed. Method blank area count comparisons to the LOQ standard are provided in the Attachments section at the end of this report.

3.5.2 Solvent Blanks

Several methanol solvent blanks were analyzed to assess system contamination and/or instrument carryover. For the April 21, 2006 analysis, three separate vials of methanol solvent blanks were contaminated and produced area counts of the target analytes greater than one-half those of the LOQ standard. A method deviation has been issued. The solvent blank area count comparison for the April 21, 2006 is provided in the Attachments section at the end of this report. For the lab matrix spikes analyzed on April 24, 2006, only the initial solvent blanks injected before the opening system suitabilities and the solvent blanks analyzed after the highest calibration standard exhibited area counts greater than one-half the LOQ standard.

3.5.3 Field/Trip Blanks

Prior to sample collection, seven sets of trip/field blanks were prepared. A trip blank consists of a sample container filled with 450 mL of ASTM Type I water, sealed, and shipped to the sample collection site along with the empty containers. 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. Results of the trip blank analyses will be provided in the final comprehensive report.

3.6 Lab Control Spikes (LCSs)

Lab control spikes at nominal concentrations of 0.050 ng/mL, 5.0 ng/mL, 100 ng/mL, and 1000 ng/mL spikes were prepared and analyzed each day samples were extracted and analyzed. The 0.050 ng/mL and 5.0 ng/mL 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. For the 100 ng/mL and 1000 ng/mL LCSs, target analytes were added to 450 mL of ASTM Type I water to produce the final desired concentration. An aliquot of the LCS was then diluted 1:50 or 1:500 with ASTM Type I water prior to extraction, in the same manner as the diluted samples. This technique was done to demonstrate that the dilution procedure used for the samples was able to produce accurate results. Analysis of replicate LCSs at the various 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 6 summarizes the LCS recovery results.

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

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

Table 6. [1]Lab Control Spike Results.

		PFOA			PFOS			PFHS			PFBS		
Sample Description	*Lab ID*	*Spiked Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*% Recovery*	*Spiked Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*% Recovery*	*Spiked Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*% Recovery*	*Spiked Conc. (ng/mL)*	*Calc. Conc. (ng/mL)*	*% Recovery*
0.05 ppb LCS	LCS-060410-1	0.0500	<0.0500	[2]NA	0.0500	<0.0999	[2]NA	0.0500	0.0504	101	0.0499	0.0505	101
0.05 ppb LCS	LCS-060410-2	0.0500	<0.0500	[2]NA	0.0500	<0.0999	[2]NA	0.0500	0.0480	96.0	0.0499	0.0456	91.3
0.05 ppb LCS	LCS-060410-3	0.0500	0.0517	104	0.0500	<0.0999	[2]NA	0.0500	0.0483	96.6	0.0499	0.0480	96.1
5.0 ppb LCS	LCS-060410-4	5.00	4.93	98.6	5.00	4.93	98.7	5.00	4.98	99.6	4.99	4.94	98.9
5.0 ppb LCS	LCS-060410-5	5.00	4.86	97.2	5.00	5.01	100	5.00	4.94	98.8	4.99	4.88	97.7
5.0 ppb LCS	LCS-060410-6	5.00	5.30	106	5.00	5.05	101	5.00	4.98	99.6	4.99	4.94	98.9
0.05 ppb LCS	LCS-060421-1	0.0500	<0.05	[2]NA	0.0500	<0.0999	[2]NA	0.0500	0.0501	100	0.0499	0.0426	85.3
0.05 ppb LCS	LCS-060421-2	0.0500	<0.05	[2]NA	0.0500	<0.0999	[2]NA	0.0500	0.0485	97.0	0.0499	0.0427	85.5
0.05 ppb LCS	LCS-060421-3	0.0500	0.0514	103	0.0500	<0.0999	[2]NA	0.0500	0.145	[3]289	0.0499	0.0441	88.3
5.0 ppb LCS	LCS-060421-4	5.00	5.02	100	5.00	4.53	90.7	5.00	4.88	97.6	4.99	4.80	96.1
5.0 ppb LCS	LCS-060421-5	5.00	4.81	96.2	5.00	4.34	86.9	5.00	4.79	95.8	4.99	4.71	94.3
5.0 ppb LCS	LCS-060421-6	5.00	4.82	96.4	5.00	4.49	89.9	5.00	4.90	98.0	4.99	4.76	95.3
100 ppb LCS	LCS-060421-7	100.0	95.0	95.0	99.9	87.3	87.4	100	98.1	98.1	99.9	98.5	98.6
100 ppb LCS	LCS-060421-8	100.0	99.7	99.7	99.9	89.2	89.3	100	100.0	100.0	99.9	100.0	100
100 ppb LCS	LCS-060421-9	100.0	96.9	96.9	99.9	88.5	88.6	100	99.4	99.4	99.9	98.0	98.1
1000 ppb LCS	LCS-060421-10	1000	928	92.8	999	855	85.6	1000	940	94.0	999	909	91.0
1000 ppb LCS	LCS-060421-11	1000	977	97.7	999	899	90.0	1000	988	98.8	999	973	97.4
1000 ppb LCS	LCS-060421-12	1000	1030	103	999	929	93.0	1000	1020	102	999	1040	104
0.05 ppb LCS	LCS-060425-1	0.0500	0.0689	[4]138	0.0500	0.0631	[4]126	0.0500	0.0578	116	0.0499	0.0563	113
0.05 ppb LCS	LCS-060425-2	0.0500	0.0600	120	0.0500	0.152	[5]304	0.0500	0.0592	118	0.0499	0.0507	102
5.0 ppb LCS	LCS-060425-3	5.00	4.91	98.2	5.00	4.79	95.9	5.00	4.98	99.6	4.99	4.89	97.9
5.0 ppb LCS	LCS-060425-4	5.00	4.87	97.3	5.00	4.94	98.9	5.00	5.08	102	4.99	4.86	97.3
100 ppb LCS	LCS-060425-5	100.0	95.3	95.3	99.9	84.5	84.6	100	95.9	95.9	99.9	95.2	95.3
100 ppb LCS	LCS-060425-6	100.0	98.6	98.6	99.9	89.8	89.9	100	96.8	96.8	99.9	96.6	96.7
1000 ppb LCS	LCS-060425-7	1000	977	97.7	999	878	87.9	1000	978	97.8	999	988	98.9
1000 ppb LCS	LCS-060425-8	1000	972	97.2	999	849	85.0	1000	966	96.6	999	975	97.6
Average %Recovery ±%RSD		***101%±9.7%***			***93.1%±10%***			***99.8%±5.6%***			***96.8%±5.8%***		

(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.

(2) Low end of the calibration curve disabled for PFOS and PFOA due to solvent blank contamination. Recovered LCS concentrations were below the established LOQ and are not reported.

(3) High recovery due to instrument carryover from the previous injection of a contaminated methanol blank. Recovery excluded from average and %RSD calculations.

(4) Recovery was outside the method acceptance criteria of 100±25%; however, the recovery was included in the calculation of the overall average and %RSD.

(5) Recovery was outside the method acceptance criteria of 100±25%; the recovery value was not included in the calculation of the overall average and %RSD as it was clearly a statistical outlier. The 5 ppb, 100 ppb, and 1000 ppb LCSs are more representative of the sample concentrations for the results reported in this subreport. Impact to data quality objectives is minimal.

3.7 Analytical Method 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 101%±9.7%. The measured precision (%RSD) is then used to determine the range of the accuracy.

Example:

101*(0.097) = 9.84
101+ 9.84 =111.1; 101 – 9.84 = 91.45

Thus, LCS accuracy results range from 91.45% to 111.1%. The absolute difference of the low and high ends of this range, when compared to 100%, are then calculated.

111.1%-100 = 11.1%
100%-91.45 = 8.54%.

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±11% (two significant figures) for these results. For PFOS, PFHS, and PFBS, the analytical method uncertainty is 100±16%, 100±5.8%, and 100±8.8%, respectively. It should be emphasized that the analytical method uncertainty described above **only** applies to the method and the procedures performed within. Additional quality control samples specific to the sample matrix, in the form of field matrix spikes and lab matrix spikes, demonstrate that the individual **sample** results are accurate to within 100±30%, the targeted data quality objectives.

3.8 Field Matrix Spikes (FMS)

At a minimum, low and high field matrix spikes were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. For some locations, a mid-level spike was also collected. 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 spikes will be presented in the next section with the sample data. The field matrix spike should be at least 50% of the endogenous sample concentration to be considered an appropriate spike level for the given sample matrix.

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

3.9 Lab Matrix Spikes (LMS)

If the sample and sample duplicate produced concentrations where none of the associated field matrix spikes were at least 50% of the endogenous concentration, then laboratory matrix spikes (LMS) were prepared. LMSs were prepared by spiking a known amount of target analytes into a measured aliquot of the sample matrix. The spiked matrix was then diluted, if necessary, and extracted in the same manner as the samples. LMS recoveries within 100±30% demonstrated that the analytical method was appropriate for the given sample matrix **only** in the absence of an appropriate field matrix spike.

4 Data Summary

The data tables below summarize the sample results, field matrix spike recoveries, and laboratory matrix spike recoveries for the four locations (BPP01, BPP02, BPP03, and BPWell). Each table provides the average concentration and the relative percent difference (RPD) of the sample and sample duplicate.

BPP01
The endogenous concentration for BPP01 was at least twice the spike concentration for the low spike (1 ng/mL), mid spike (10 ng/mL) and high spike (100 ng/mL) for both PFOA and PFOS. A laboratory matrix spike at 500 ng/mL was prepared and analyzed. The LMS recovery met method acceptance criteria of 100±30% for PFOA (79.6%), but not for PFOS (60.6%). **Therefore, the sample results for PFOS should be considered estimated minimums with a sample analytical accuracy within an order of magnitude as the analytical method has not been demonstrated to be suitable for the given sample matrix.** FMS and/or LMS recoveries within 100±30% for PFOA, PFHS, and PFBS demonstrate that the analytical method is appropriate for the given sample matrix for these analytes.

BPP02
The endogenous concentration for BPP02 was at least twice the spike concentration for the low spike (1 ng/mL) and mid spike (10 ng/mL) for both PFOA and PFOS as well as the high spike (100 ng/mL) for PFOS only. A laboratory matrix spike at 250 ng/mL was prepared and analyzed. The LMS recovery met method acceptance criteria of 100±30% for PFOA (75.0%), but not PFOS (59.8%). **Therefore, the sample results for PFOS should be considered estimated minimums with a sample analytical accuracy within an order of magnitude as the analytical method has not been demonstrated to be suitable for the given sample matrix.** FMS and/or LMS recoveries within 100±30% for PFOA, PFHS, and PFBS demonstrate that the analytical method is appropriate for the given sample matrix for these analytes.

BPP03
The endogenous concentration for BPP03 was at least twice the spike concentration for the low spike (1 ng/mL) and mid spike (10 ng/mL) for both PFOA and PFOS as well as the high spike (100 ng/mL) for PFOS only. A laboratory matrix spike at 250 ng/mL was prepared and analyzed. The LMS recovery met method acceptance criteria of 100±30% for PFOA (73.8%), but not PFOS (60.8%). **Therefore, the sample results for PFOS should be considered estimated minimums with a sample analytical accuracy within an order of magnitude as the analytical method has not been demonstrated to be suitable for the given sample matrix.** The high level PFBS FMS exceeded method acceptance criteria of 100±30% (134%). However, the PFBS results for this sample are still considered accurate within 100±30% because the criteria exceedence was minimal (within 4%) and mid level FMS and LMS recoveries were excellent, 101% and 90.2%, respectively. High level FMS and LMS recoveries within 100±30% for PFOA and PFHS also demonstrate that the analytical method is appropriate for the given sample matrix for these two analytes as well.

BPWell
The endogenous concentration for BPWell was at least twice the spike concentration for the low spike (10 ng/mL) for PFOA, PFOS, PHFS, and PFBS as well as the mid spike for PFOA, PFOS, and PFHS. Although the high level spike (1000 ng/mL) was an appropriate level for all four analytes, the recoveries were consistently less than 30% for all analytes, with PFOS showing no measuring recovery. The high FMS was reextracted to rule out a potential preparatory error during the extraction process. The second extraction produced similar recoveries as the first. A laboratory matrix spike at 1000 ng/mL was also prepared. The LMS recovery met method acceptance criteria of 100±30% for PFOA (85.4%), PFHS(93.5%), and PFBS(97.2%) but not for PFOS (13.5%). **Therefore, the sample results for PFOS should be considered estimated minimums with a sample analytical accuracy within an order of magnitude as the analytical method has not been demonstrated to be suitable for the given sample matrix. Although the LMS produces acceptable recoveries for PFOA and PFHS, the sample results should be considered estimated minimums as no appropriate supplementary FMS recovery was available.** Low and mid level FMS and LMS recoveries within 100±30% for PFBS demonstrate that the analytical method is appropriate for the given sample matrix for this analyte only. Further method development for the BP Well sample matrix will be performed to see if improved PFOA, PFOS, and PFHS recoveries can be achieved.

Table 7. [1]BPP01 Results.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery
E06-0199-055	DAL SWS BPP01 0 060413	293	NA	423	NA	53.3	NA	6.98	NA
E06-0199-056	DAL SWS BPP01 DB 060413	307	NA	380	NA	54.3	NA	7.17	NA
E06-0199-057	DAL SWS BPP01 LS 060413	292	[2]NR	330	[2]NR	53.4	[2]NR	7.44	[2]NR
E06-0199-058	DAL SWS BPP01 MS 060413	328	[2]NR	484	[2]NR	66.6	[2]NR	18.8	117
E06-0199-059	DAL SWS BPP01 HS 060413	361	[2]NR	365	[2]NR	136	82.2	93.8	86.8
LMS-060425-1	DAL SWS BPP01 0 060413 500ppb LMS	698	79.6	704	[3]60.6	485	86.2	444	87.5
Average Concentration (ng/mL) ±%RPD		*300±4.7%*		*[4]>402*		*53.8±1.9%*		*7.08±2.7%*	

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. All samples and associated FMSs were diluted 1:50 in ASTM Type I water prior to extraction. LMS was diluted 1:100 prior to extraction.

(2) NR=Not reportable. FMS level not appropriate for the given matrix. The endogenous sample concentration was at least twice spike level.

(3) LMS recovery outside of method acceptance criteria of 100±30%.

(4) PFOS sample results should be considered estimated minimums only. Sample matrix specific QC did not meet method criteria. The analytical sample accuracy is arbitrarily estimated to within an order of magnitude. %RPD values not reported.

Table 8. [1]BPP02 Results.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery
E06-0199-060	DAL SWS BPP02 0 060413	206	NA	295	NA	38.2	NA	4.6	NA
E06-0199-061	DAL SWS BPP02 DB 060413	219	NA	314	NA	39.8	NA	4.72	NA
E06-0199-062	DAL SWS BPP02 LS 060413	234	[2]NR	388	[2]NR	42.3	[2]NR	5.9	[2]NR
E06-0199-063	DAL SWS BPP02 MS 060413	220	[2]NR	346	[2]NR	48.0	[2]NR	14.4	97.5
E06-0199-064	DAL SWS BPP02 HS 060413	314	102	437	[2]NR	134	95.0	102	97.5
LMS-060425-2	DAL SWS BPP02 0 060413 250ppb	400	75.0	454	[3]59.8	256	86.8	223	87.4
Average Concentration (ng/mL) ±%RPD		*212±6.1%*		*[4]>304*		*39.0±4.1%*		*4.66±2.6%*	

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. All samples and associated QC were diluted 1:50 in ASTM Type I water prior to extraction.

(2) NR=Not reportable. FMS level not appropriate for the given matrix. Endogenous concentration was at least twice spike level.

(3) LMS recovery outside of method acceptance criteria of 100±30%

(4) PFOS sample results should be considered estimated minimums only. Sample matrix specific QC did not meet method criteria. The analytical sample accuracy is arbitrarily estimated to within an order of magnitude. %RPD values not reported.

Table 9. BPP03 Results.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery
E06-0199-065	DAL SWS BPP03 0 060413	219	NA	272	NA	39.1	NA	4.69	NA
E06-0199-066	DAL SWS BPP03 DB 060413	214	NA	256	NA	40.1	NA	5.05	NA
E06-0199-067	DAL SWS BPP03 LS 060413	211	[2]NR	258	[2]NR	40.2	[2]NR	5.76	[2]NR
E06-0199-068	DAL SWS BPP03 MS 060413	228	[2]NR	255	[2]NR	50.0	[2]NR	15.0	101
E06-0199-069	DAL SWS BPP03 HS 060413	324	108	315	[2]NR	143	103	139	[3]134
LMS-060425-3	DAL SWS BPP03 0 060413 250ppb LMS	401	73.8	416	[4]60.8	262	89.0	230	90.2
Average Concentration (ng/mL) ±%RPD		216±2.3%		[5]>264		39.6±2.5%		4.87±7.4%	

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. All samples and associated QC were diluted 1:50 in ASTM Type I water prior to extraction.

(2) NR=Not reportable. FMS level not appropriate for the given matrix. Endogenous concentration was at least twice spike level.

(3) FMS recoveries outside method acceptance criteria of 100±30%.

(4) LMS recovery outside of method acceptance criteria of 100±30%.

(5) PFOS sample results should be considered estimated minimums only. Sample matrix specific QC did not meet method criteria. The analytical sample accuracy is arbitrarily estimated to within an order of magnitude. %RPD values not reported.

Table 10. [1]BPWell results.

		PFOA		PFOS		PFHS		PFBS	
3M LIMS ID	Description	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery	Conc. (ng/mL)	% Recovery
E06-0199-070	DAL GWS BPWELL 0 060413	774	NA	1460	NA	145	NA	17.2	NA
E06-0199-071	DAL GWS BPWELL DB 060413	779	NA	1170	NA	145	NA	17.6	NA
E06-0199-072	DAL GWS BPWELL LS 060413	723	[2]NR	960	[2]NR	152	[2]NR	26.9	95.1
E06-0199-073	DAL GWS BPWELL MS 060413	821	[2]NR	1020	[2]NR	244	[2]NR	122	105
[3]E06-0199-074	DAL GWS BPWELL HS 060413	1020	[5]24.4	1200	[6]NMR	375	[5]23.0	280	[5]26.9
[4]E06-0199-074	DAL GWS BPWELL HS 060413	987	[5]21.0	1320	[6]NMR	348	[5]20.3	254	[5]23.7
LMS-060425-4	DAL GWS BPWELL 0 060413 1000ppb LMS	1630	85.4	1450	[7]13.5	1080	93.5	980	97.2
Average Concentration (ng/mL) ± %RPD		[8]>776		[8]>1320		[8]>145		17.4±2.3%	

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. The sample, sample duplicate, low FMS, and mid FMS were diluted 1:50 in ASTM Type I water prior to extraction. The high FMS and 1000 ppb LMS were diluted 1:500 prior to extraction.

(2) NR=Not reportable. FMS level not appropriate for the given matrix. Endogenous concentration was at least twice spike level.

(3) FMS extracted on 4-21-2006 with the samples.

(4) FMS re-extracted on 4-25-0006.

(5) FMS recovery outside of method acceptance criteria of 100±30%.

(6) NMR = No measurable recovery.

(7) LMS recovery outside method acceptance criteria of 100±30%.

(8) PFOA, PFOS, and PFHS sample results should be considered estimated minimums only. Field matrix spikes did not meet method criteria. The analytical sample accuracy is arbitrarily estimated to within an order of magnitude. %RPD values not reported.

5 Conclusion

Sample matrix QC samples for the four samples reported herein did not meet method acceptance criteria of 100±30% for PFOS. ***Therefore, the values listed in Table 1 and Tables 7-10 for PFOS should be considered estimated minimums. The sample analytical accuracy is arbitrarily estimated to be within an order of magnitude.*** Further method development is needed for this matrix as the QC results demonstrated that unknown matrix components preclude accurate analysis with the method as performed here. Field matrix spikes yielding recoveries within 100±30% demonstrated that the analytical method was suitable for the given sample matrices for PFOA, PFHS, and PFBS for BPP01, BPP02, and BPP03. The analytical method uncertainty for these analytes was presented in Table1. ***PFOA and PFHS results for BPWell should also be considered estimated minimums with a sample analytical accuracy within an order of magnitude as no acceptable field matrix spikes recoveries were produced.***

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

Michelle D. Malinsky, Ph.D., 3M Technical Lead — Date: 5/1/06

Kent R. Lindstrom, 3M Technical Reviewer — Date: 05/01/06

William K. Reagen, Ph.D., Environmental Laboratory Management — Date: 05/01/06

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

Quality Assurance Representative — Date: 5-1-06

8 Attachments

8.1 Method Blank/LOQ Area Count Comparison.

Table 11. Method Blank/LOQ Area Count Comparison: April 21, 2006.

Analytical Run: April 21, 2006			Area Counts			
Datafile	Sample Description	Sample Name	PFOA	PFOS	PFHS	PFBS
Method Blanks Prepared with the Extracted Curve						
s060421a025	Method Blank-1	MB-060410-1	55982	3413	1591	2760
s060421a026	Method Blank-2	MB-060410-2	18376	1082	668	2001
s060421a027	Method Blank-3	MB-060410-3	16127	1718	1970	2336
s060421a028	Method Blank-4	MB-060410-4	22714	1116	639	1305
s060421a029	Method Blank-5	MB-060410-5	21587	792	1686	2109
s060421a030	Method Blank-6	MB-060410-6	25928	4338	2077	5711
s060421a031	Method Blank-7	MB-060410-7	21060	2143	2436	3561
s060421a032	Method Blank-8	MB-060410-8	16383	1776	1660	4235
Method Blanks Prepared with the Extracted Samples						
s060421a045	Method Blank-1	MB-060421-1	12933	1437	(1)**121128**	277
s060421a046	Method Blank-2	MB-060421-2	12809	1446	(1)**129379**	715
s060421a047	Method Blank-3	MB-060421-3	13875	2228	(1)**66834**	595
s060421a048	Method Blank-4	MB-060421-4	22242	2053	(1)**42902**	1052
s060421a049	Method Blank-5	MB-060421-5	19675	1762	(1)**33923**	826
s060421a050	Method Blank-6	MB-060421-6	17774	1568	(1)**13105**	2071
s060421a051	Method Blank-7	MB-060421-7	13843	1084	6059	(2)**19419**
s060421a052	Method Blank-8	MB-060421-8	14073	1492	5570	450
Area Counts of the LOQ standard			163373	14600	13176	25766
Area Counts of the LOQ standard*0.5			81686.5	7300	6588	12883
Concentration of LOQ standard (ng/mL)			0.0500	0.0999	0.025	0.025

(1) Method blanks injected immediately after a highly contaminated solvent blank. Carryover present. Values excluded when establishing the LOQ for PFHS.

(2) Method blank determined to be a statistical outlier at the 99% confidence level using Dixon's Q-test. Value excluded when establishing the LOQ for PFBS.

Table 12. Method Blank/LOQ Area Count Comparison: April 24, 2006.

Analytical Run: April 24, 2006			Area Counts			
Datafile	Sample Description	Sample Name	PFOA	PFOS	PFHS	PFBS
Method Blanks Prepared with the Extracted Curve						
s060424a025	Method Blank-1	MB-060410-1	(1)36625	3514	2029	3078
s060424a026	Method Blank-2	MB-060410-2	(1)42239	2274	2890	3938
s060424a027	Method Blank-3	MB-060410-3	25302	2950	1147	2248
s060424a028	Method Blank-4	MB-060410-4	22151	804	1197	1638
s060424a029	Method Blank-5	MB-060410-5	30401	2565	1955	2593
s060424a030	Method Blank-6	MB-060410-6	17458	827	1275	5242
s060424a031	Method Blank-7	MB-060410-7	23074	1195	1974	3516
s060424a032	Method Blank-8	MB-060410-8	22049	1192	1512	4294
Method Blanks Prepared with the Extracted Laboratory Matrix Spikes						
s060424a090	Method Blank-1	MB-060425-1	30448	2301	1778	1906
s060424a091	Method Blank-2	MB-060425-2	15006	1266	1311	2990
s060424a092	Method Blank-3	MB-060425-3	11262	991	1039	1703
s060424a093	Method Blank-4	MB-060425-4	11867	836	707	6142
s060424a094	Method Blank-5	MB-060425-5	16236	1024	717	2723
s060424a095	Method Blank-6	MB-060425-6	15924	1107	589	5446
s060424a096	Method Blank-7	MB-060425-7	22758	1530	1038	4359
s060424a097	Method Blank-8	MB-060425-8	19284	1071	1135	1677
Area Counts of the LOQ standard			36060	6724	12166	27032
Area Counts of the LOQ standard*0.5			18030	3362	6083	13516
Concentration of LOQ standard (ng/mL)			0.025	0.04	0.025	0.025

(1) Value excluded for the LOQ determination for the given set. Area counts are very close to one-half the LOQ value. Prior analysis of this extract demonstrated area counts below one-half the 25 ppt standard. LMSs analyzed on this day are well above the LOQ.

8.2 Solvent Blank/LOQ Comparison.

Table 13. Area Counts of Solvent Blank.

		Area Counts			
File	Vial Position	PFOA	PFOS	PFHS	PFBS
s060421a001	91	70233	3067	1853	192
s060421a002	91	16249	2196	1851	563
s060421a003	91	18222	1642	567	471
s060421a009	91	48287	4524	1505	447
s060421a010	92	(1)84762	5006	2424	889
s060421a023	92	48308	4192	4524	6609
s060421a024	92	(1)84666	5317	4738	7007
s060421a035	93	(1)162166	(1)283547	(1)52950	(1)41582
s060421a037	93	23806	(1)8904	2706	2357
s060421a042	93	15939	2135	1693	1823
s060421a044	94	49169	4298	(1)274354	1118
s060421a055	94	12685	1141	(1)328841	547
s060421a057	94	47071	3382	(1)257946	946
s060421a068	95	53698	2525	5237	1137
s060421a070	95	74125	5907	6588	975
s060421a081	95	62139	2124	3945	1225
s060421a083	95	68329	3139	3951	1149
s060421a094	96	76799	4192	3512	1054
s060421a096	96	77269	3358	3905	1173
s060421a107	97	14824	1166	852	335
s060421a109	97	19120	1763	1499	1289
s060421a120	97	9918	1028	1024	698
s060421a122	98	24599	1589	2321	3275
s060421a127	98	37573	1305	6127	2190
s060421a129	99	18673	1100	1909	937
s060421a135	99	31743	1944	1472	632
LOQ Standard		163373	14600	13176	25766
½*LOQ Standard		81687	7300	6588	12883

(1) Area counts of the solvent blank were greater than ½*the LOQ standard area counts.