AR 226 - 3691

Final Report

Analysis of PFBA, NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS in Aqueous Samples From Oakdale, Minnesota Municipal Wells

Laboratory Request Number: E06-0294

Method Requirement: 3M Methods ETS-8-11.0 and ETS-8-154.1 (modified)

Report - Revision 1, 07/18/06
(supersedes report 06/09/06)

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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

Reason for Report Revision

This report was revised in order to achieve analytical data of the highest quality for all target compounds. The PFBA data reported here were generated using method ETS-8-11.0 and was not changed from the original report. All other target analytes were requantitated using method ETS-8-154.1. PFOS and PFOA data generated by ETS-8-11.0 did not consistently meet method acceptance criteria requirements. Improved PFOS and PFOA data accuracy was obtained using ETS-8-154.1, a method validated for PFOS and PFOA. Data for the remaining target compounds were consistent between the methods. Only data from ETS-8-154.1 was reported for those analytes.

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Analytical Report E06-0294, Revision 1

Oakdale Municipal Well Samples: Minnesota Department of Health Co-Sampling May 11, 2006

Report Date: July 18, 2006
Supersedes report dated June 9, 2006

1. Project Summary

The 3M Environmental Laboratory prepared and analyzed municipal water samples collected by Pace Analytical Field Services personnel on May 11, 2006, from Oakdale municipal wells 1, 2, 3, 5, 7, 8, and 9 in conjunction with the monthly Minnesota Department of Health sampling. Samples were returned to the 3M Environmental Laboratory for analysis of perfluorobutanoic acid (PFBA), nonafluoropentanoic acid (NFPA), perfluorohexanoic acid (PFHA), perfluorooctanoic acid (PFOA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHS) and perfluorooctane sulfonate (PFOS) under laboratory project number E06-0294. Analysis was completed following 3M Environmental Laboratory method ETS 8-11.0 "Determination of C_4 – C_8 Highly Fluorinated Acids, Alcohols, Amides, and Sulfonates in Water by High Performance Liquid Chromatography/Mass Spectrometry" and 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".

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

Table 1 summarizes the sample results using both analytical methods identified above. All results for quality control samples prepared and analyzed with the samples will be reported and discussed elsewhere in this report.

ACCREDITED

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 9001/ISO 9002 (1994).

Table 1. Sample Results Summary [1]

3M LIMS ID	Sample Description	PFBA[2] Concentration (ng/mL)	NFPA[3] Concentration (ng/mL)	PFHA[3] Concentration (ng/mL)	PFOA[3] Concentration (ng/mL)	PFBS[3] Concentration (ng/mL)	PFHS[3] Concentration (ng/mL)	PFOS[3] Concentration (ng/mL)
E06-0294-001	Bottle 1, Well 5, Sample	1.74	0.0765	0.208	0.732	0.0426	0.0858	1.02
E06-0294-002	Bottle 2, Well 5, Sample Duplicate	1.75	0.0781	0.198	0.722	0.0385	0.0817	0.905
	Average Well 5	**1.75**	**0.0773**	**0.203**	**0.727**	**0.0406**	**0.0838**	**0.962**
	%RPD Sample/Sample Dup Well 5	**1.0**	**2.1**	**4.9**	**1.4**	**10**	**4.9**	**12**
E06-0294-005	Bottle 5, Well 7, Sample	0.824	0.0306	0.0793	0.255	<0.0250	0.0343	0.204
E06-0294-006	Bottle 6, Well 7, Sample Duplicate	0.828	0.0269	0.0727	0.236	<0.0250	0.0315	0.198
	Average Well 7	**0.826**	**0.0288**	**0.0760**	**0.246**	**<0.0250**	**0.0329**	**0.201**
	%RPD Sample/Sample Dup Well 7	**0.56**	**13**	**8.7**	**7.7**	**NA**	**8.5**	**3.0**
E06-0294-009	Bottle 9, Well 8, Sample	1.28	0.0468	0.112	0.431	0.0251	0.0518	0.596
E06-0294-010	Bottle 10, Well 8, Sample Duplicate	1.28	0.0491	0.131	0.437	<0.0250	0.0508	0.647
	Average Well 8	**1.28**	**0.0480**	**0.122**	**0.434**	**[5]0.0251**	**0.0513**	**0.622**
	%RPD Sample/Sample Dup Well 8	**0.078**	**4.8**	**16[4]**	**1.4**	**NA**	**1.9**	**8.2**
E06-0294-013	Bottle 13, Well 9, Sample	2.04	0.0895	0.225	0.726	0.0521	0.106	0.567
E06-0294-014	Bottle 14, Well 9, Sample Duplicate	2.02	0.0914	0.235	0.652	0.0492	0.103	0.544
	Average Well 9	**2.03**	**0.0904**	**0.230**	**0.689**	**0.0506**	**0.104**	**0.556**
	%RPD Sample/Sample Dup Well 9	**0.79**	**2.1**	**4.3**	**11**	**5.7**	**2.9**	**4.1**
E06-0294-020	Bottle 20, Well 1, Sample	0.295	<0.0248	<0.0252	0.0781	<0.0250	<0.0252	0.0415
E06-0294-021	Bottle 21, Well 1, Sample Duplicate	0.287	<0.0248	<0.0252	0.0801	<0.0250	<0.0252	0.0381
	Average Well 1	**0.291**	**<0.0248**	**<0.0252**	**0.0791**	**<0.0250**	**<0.0252**	**0.0398**
	%RPD Sample/Sample Dup Well 1	**3.0**	**NA**	**NA**	**2.5**	**NA**	**NA**	**8.5**
E06-0294-024	Bottle 24, Well 2, Sample	0.381	<0.0248	0.0376	0.0931	<0.0250	<0.0252	0.0387
E06-0294-025	Bottle 25, Well 2, Sample Duplicate	0.373	<0.0248	0.0364	0.0915	<0.0250	<0.0252	0.0324
	Average Well 2	**0.377**	**<0.0248**	**0.0370**	**0.0923**	**<0.0250**	**<0.0252**	**0.0356**
	%RPD Sample/Sample Dup Well 2	**2.0**	**NA**	**3.2**	**1.7**	**NA**	**NA**	**[4]18**
E06-0294-028	Bottle 28, Well 3, Sample	0.0949	<0.0248	<0.0252	<0.0254	<0.0250	<0.0252	<0.0252
E06-0294-029	Bottle 29, Well 3, Sample Duplicate	0.0855	<0.0248	<0.0252	<0.0254	<0.0250	<0.0252	<0.0252
	Average Well 3	**0.0902**	**<0.0248**	**<0.0252**	**<0.0254**	**<0.0250**	**<0.0252**	**<0.0252**
	%RPD Sample/Sample Dup Well 3	**10**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**

N/A = Not Applicable

(1) The analytical method uncertainties are as follows: PFBA is 100% ± 8.0%, NFPA is 100% ± 8.4%, PFHA is 100% ± 20%, PFOA is 100% ± 8.9%, PFBS is 100% ± 4.6%, PFHS is 100% ± 3.3%, PFOS is 100% ± 5.5%. Refer to Sections 3 and 4 for data acceptance criteria and discussion.

(2) Sample results for PFBA were determined following method ETS-8-11.0.

(3) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

(4) The Relative Percent Difference between the Sample/Sample Duplicate exceeds 15%.

(5) Average and %RPD were not calculated due to one sample being <LOQ. Reported the higher of the two values.

2. Methods – Analytical and Sample Preparation

2.1 Methods

Analysis was completed following 3M Environmental Laboratory method ETS 8-11.0 "Determination of $C_4 - C_8$ Highly Fluorinated Acids, Alcohols, Amides, and Sulfonates in Water by High Performance Liquid Chromatography/Mass Spectrometry" and 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". ETS-8-154.1 is currently on the laboratory's scope of accreditation to ISO/IEC 17025:1999. ETS-8-11.0 is not currently on the laboratory's scope of accreditation.

2.2 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. Collected sample bottles were returned to the laboratory at ambient conditions on May 12, 2006.

2.3 Sample Preparation

PFBA Analysis:

All samples, calibration standards, and associated quality control samples were prepared using method ETS 8-11.0 "Determination of $C_4 - C_8$ Highly Fluorinated Acids, Alcohols, Amides, and Sulfonates in Water by High Performance Liquid Chromatography/Mass Spectrometry". Briefly, aqueous samples and calibrations standards were prepared for analysis by diluting the samples 1:1 using a 10-mM ammonium hydroxide in methanol solution. This method is currently not on the laboratory's scope of accreditation to ISO/IEC 17025:1999.

NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS Analysis:

All samples, calibration standards, and associated quality control samples were extracted using a modified procedure of ETS-8-154.1. 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.

Modifications from ETS-8-154.1 that were used for this analysis:

- Samples were not extracted in duplicate as samples were collected in duplicate in the field.
- Extraction columns were not rinsed with 40% methanol after sample loading.
- After loading the sample onto the column, and just prior to eluting the column with methanol, vacuum was applied for approximately 5 minutes to remove as much sample as possible.

2.4 Analysis

All samples and quality control samples were analyzed for seven 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 2. Instrument Parameters.

Instrument Name	ETSGinger	ETSOllie
Analytical Method followed	ETS-8-11.0	ETS-8-154.1
Liquid Chromatograph	Agilent 1100	Agilent 1100
Guard column	Prism RP (2 mm.X 50 mm), 5 µm	Betasil C18 (2.1 mm.X100 mm), 5 µm
Analytical column	Betasil C18 (2.1 mm X 100 mm), 5 µm	Betasil C18 (2.1 mm X 100 mm), 5 µm
Injection Volume	10 µL	5 µL
Mass Spectrometer	Applied Biosystems API 5000	Applied Biosystems API 4000 Q trap
Ion Source	Turbo Spray	Turbo Spray
Electrode	Z-spray	Z-spray
Polarity	Negative	Negative
Software	Analyst 1.4.1	Analyst 1.4.1

Table 3. Liquid Chromatography Gradient Program.

ETS Ginger

Step Number	*Total Time (min)*	*Flow Rate (µL/min)*	*Percent A (2 mM ammonium acetate)*	*Percent B (Methanol)*
0	0	300	90.0	10.0
1	2.0	300	90.0	10.0
2	10.0	300	10.0	90.0
3	12.0	300	10.0	90.0
4	12.5	300	90.0	10.0
5	16.0	300	90.0	10.0

ETS Ollie

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 4. Mass Transitions

Analyte	Mass Transition Q1/Q3	Dwell Time (msec) ETSGinger	Dwell Time (msec) ETSOllie
PFBA	213/169	80	-
PFOA	413/369	80	100
	413/219	80	100
	413/169	80	100
PFOS	499/99	80	100
	499/80	80	100
	499/130	80	100
PFHS	399/99	80	100
	399/80	80	100
PFBS	299/80	80	100
	299/99	80	100
PFHA	313/119	80	100
NFPA	263/219	80	100

3.1 Calibration

PFBA Analysis:
Calibration standards were prepared by spiking known amounts of stock solutions containing the target analytes into 2 mL of ASTM type I water. A 750uL aliquot of each water standard was then transferred to an autosampler vial. Subsequently, a 750uL aliquot of a 10mM ammonium hydroxide in methanol solution was added to the vial. Ten spiked standards ranging from 0.025 ng/mL to 10 ng/mL (nominal) were prepared. After dilution, the nominal concentration of each analyte in the vial was 0.0125 ng/mL to 5.0 ng/mL. Quadratic, 1/x weighted, calibration curves were used to fit the data for each analyte.

NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS Analysis:
Calibration standards were prepared by spiking known amounts of stock solutions containing the analytes of interest 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 eleven spiked standards ranging from 0.025 ng/mL to 10 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 curve point was quantitated using the overall calibration curve and reviewed for accuracy. Method calibration accuracy requirements of 100±25% (100±30% for the lowest curve point) were met. The correlation coefficients (r) were greater than 0.999 for each analyte.

The analytes PFBA, NFPA, and PFHA were initially dissolved in acetonitrile before being further diluted into an intermediate standard solution. This is a deviation for ETS-8-154.1 which specifies that analytes should be dissolved in Methanol. This deviation has no adverse affect on the sample results.

3.2 Limit of Quantitation (LOQ)

The LOQ for this analysis, as defined in methods ETS-8-11.0 and ETS-8-154.1, is the lowest non-zero calibration standard in the curve that meets linearity and accuracy requirements and which the area counts are at least twice those of the appropriate blanks. The nominal LOQ for PFBA was 0.050ng/mL. The nominal LOQ for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS was 0.025ng/mL.

3.3 System Suitability

PFBA Analysis:
The 5ng/mL calibration standard was analyzed in triplicate at the beginning and end of the analytical sequence to demonstrate overall system suitability. 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 were met.

NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS Analysis:
The 1.0 ng/mL extracted-calibration standard was analyzed five times at the beginning and end of the analytical sequence to demonstrate overall system suitability. All compounds met the acceptance criteria of less than 5% relative standard deviation (RSD) for peak area and less than 2% RSD for retention time for the opening and closing system suitability injections with exception of NFPA and PFOA. The RSD for the area counts for the closing system suitability for NFPA was 6.2% and 6.9% for PFOA. As laboratory control samples and field matrix spikes are used to qualify the samples results, any instrument variability that may have occurred would be accounted for with these samples.

3.4 Continuing Calibration

PFBA Analysis:
During the course of the analytical sequence, several continuing calibration verification samples (CCVs) were analyzed to confirm that the instrument response and the initial curve were still in control. These CCVs were re-injections of two different concentrations of calibration standards from the first calibration curve (curve not used for quantitation) that were quantitated against the second curve (used for quantitation). All CCVs for PFBA met method criteria.

NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS Analysis:
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 CCV level for PFHA analyzed twice during the course of the run had recoveries of 129% and 131%, which did not meet method criteria of 100±25%. All other CCVs 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 result was reviewed and used to evaluate method performance to determine the LOQ for each analyte.

3.6 Lab Control Spikes (LCSs)

PFBA Analysis:
Low and high lab control spikes were prepared and analyzed in triplicate. LCSs were prepared by spiking known amounts of the analytes into 2 mL of ASTM Type I water and prepared exactly like the samples and standards. LCS results were be used to determine overall method uncertainty in Section 3.7.

NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS Analysis:
Low and high 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 were used to determine overall method uncertainty in Section 3.7. The RSD for the six LCS prepared for PFHA was 19%, which did not meet method acceptance criteria of <15%.

The following calculations were used to generate data in Table 5.

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

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

Table 5. [1,2]Lab Control Spike Results.

	PFBA[3]			NFPA			PFHA			PFOA		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-060615-1	0.494	0.457	92.5	0.990	0.870	87.9	1.01	1.10	109	1.02	0.920	90.2
LCS-060615-2	0.494	0.449	91.0	0.990	0.939	94.8	1.01	1.21	120	1.02	1.03	101
LCS-060615-3	0.494	0.464	94.0	0.990	0.969	97.9	1.01	1.15	114	1.02	1.07	105
LCS-060615-4	4.94	4.92	99.7	9.90	9.64	97.4	10.1	7.89	78.1	10.2	(5)	NA
LCS-060615-5	4.94	4.91	99.4	9.90	9.64	97.4	10.1	8.16	80.8	10.2	(5)	NA
LCS-060615-6	4.94	4.95	100	9.90	9.98	101	10.1	(5)	NA	10.2	(5)	NA
Average ± %RSD		96.1% ± 4.3%			96.0% ± 4.6%			100% ± 19%[4]			98.7% ± 7.7%	

	PFBS			PFHS			PFOS		
Lab ID	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery	Spiked Concentration (ng/mL)	Calculated Concentration (ng/mL)	%Recovery
LCS-060615-1	0.999	0.952	95.3	1.01	0.986	97.6	1.01	0.993	98.3
LCS-060615-2	0.999	0.985	98.6	1.01	1.05	104	1.01	1.03	102
LCS-060615-3	0.999	0.971	97.2	1.01	1.01	100	1.01	1.06	105
LCS-060615-4	9.99	(5)	NA	10.1	(5)	NA	10.1	9.14	90.5
LCS-060615-5	9.99	9.61	96.2	10.1	9.83	97.3	10.1	9.97	98.7
LCS-060615-6	9.9900	(5)	NA	10.1	(5)	NA	10.1	10.6	105
Average ± %RSD		96.8% ± 1.5%			99.7% ± 3.1%			99.9% ± 5.4%	

NA = Not applicable

(1) PFBA was determined by method ETS-8-11.0, all other analytes were determined by ETS-8-154.1

(2) 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.

(3) The LCS descriptions listed above are for the ETS-8-154.1 analysis. The LCS descriptions for PFBA were LCS-060605-1 through LCS-060605-6.

(4) The RSD did not meet method criteria of 100% ± 15%.

(5) Sample area counts exceeded the calibration range, recovery could not be determined. While many of the 10 ng/mL LCS could not be quantitated, the 1 ng/mL LCS was more in line with the concentrations detected in the samples.

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, if the overall accuracy and precision for PFOS based on LCS results was 99.9%±5.4%. The measured precision (%RSD) is then used to determine the range of the accuracy.

Example:

99.9*(0.054) = 5.4
99.9+ 5.4 =105.3; 99.9 – 5.4 = 94.5

Thus, LCS accuracy results range from 94.5% to 105.3%. The absolute difference of the low and high ends of this range, when compared to 100%, are then calculated.

100%-105.3= 5.3%
100%-94.5 = 5.5%.

The most conservative (largest) absolute difference is then used as the analytical uncertainty for the given analyte.

Table 6. Analytical Method Uncertainty

Analyte	Method Uncertainty
PFBA	100% +/- 8.0%
NFPA	100% +/- 8.4%
PFHA	100% +/- 20%
PFOA	100% +/- 8.9%
PFBS	100% +/- 4.6%
PFHS	100% +/- 3.3%
PFOS	100% +/- 5.5%

3.8 Field Matrix Spikes (FMS)

Low and high field matrix spikes were collected at each sampling point to verify that the analytical method is applicable to the collected matrix. Field matrix spikes are generated by adding a measured volume of field sample to a container spiked by the laboratory with the target analytes prior to shipping sample containers for sample collection. Field matrix spike recoveries within method acceptance criteria of 100±30% confirm that "unknown" components in the sample matrix do not significantly interfere with the extraction and analysis of the analytes of interest. Field matrix spikes are presented in section 4 of this report.

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

Table 7. Field Matrix Spike Concentrations

		Final Concentration (ng/mL)						
Location	Description	PFBA	NFPA	PFHA	PFOA	PFBS	PFHS	PFOS
Well 5	Low Field Matrix Spike	0.0987	0.0990	0.101	0.508	0.0999	0.101	0.503
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Well 7	Low Field Matrix Spike	0.0987	0.0990	0.101	0.102	0.0999	0.101	0.101
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Well 8	Low Field Matrix Spike	0.0987	0.0990	0.101	0.305	0.0999	0.101	0.302
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Well 9	Low Field Matrix Spike	0.0987	0.0990	0.101	0.305	0.0999	0.101	0.302
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Trip Blank	Low Field Matrix Spike	0.0987	0.0990	0.101	0.0508	0.0999	0.101	0.503
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Well 1	Low Field Matrix Spike	0.0987	0.0990	0.101	0.102	0.0999	0.101	0.101
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Well 2	Low Field Matrix Spike	0.0987	0.0990	0.101	0.102	0.0999	0.101	0.101
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01
Well 3	Low Field Matrix Spike	0.0987	0.0990	0.101	0.102	0.0999	0.101	0.101
	High Field Matrix Spike	0.987	0.990	1.01	1.02	0.999	1.01	1.01

Data Summary

The tables below summarize the sample results and field matrix spike recoveries for the seven locations as well as the Trip Blank. Each table provides the average concentration and the relative percent difference (RPD) of the sample and sample duplicate.

Table 8. Well 5 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-001	Bottle 1, Well 5, Sample	1.74	NA	0.0765	NA	0.208	NA	0.732	NA
E06-0294-002	Bottle 2, Well 5, Sample Duplicate	1.75	NA	0.0781	NA	0.198	NA	0.722	NA
E06-0294-003	Bottle 3, Well 5, Field Matrix Spike Low	1.92	NR	0.181	105	0.294	NR	1.23	99.0
E06-0294-004	Bottle 4, Well 5, Field Matrix Spike High	2.82	109	1.03	96.2	1.29	108	1.36	[3]62.1
Average Concentration (ng/mL) ± %RPD		1.74 ng/mL ± 1.0%		0.0773 ng/mL ± 2.1%		0.203 ng/ml ± 4.9%		0.727 ng/mL ± 1.4%	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-001	Bottle 1, Well 5, Sample	0.0426	NA	0.0858	NA	1.02	NA
E06-0294-002	Bottle 2, Well 5, Sample Duplicate	0.0365	NA	0.0817	NA	0.905	NA
E06-0294-003	Bottle 3, Well 5, Field Matrix Spike Low	0.151	111	0.238	[3]153	1.55	117
E06-0294-004	Bottle 4, Well 5, Field Matrix Spike High	1.00	96.0	1.13	104	1.93	95.8
Average Concentration (ng/mL) ± %RPD		0.0406 ng/mL ± 10%		0.0838 ng/mL ± 4.9%		0.962 ng/mL ± 12%	

N/A = Not Applicable
NR = Not Reported = Endogenous concentration of analyte exceeded 2x the spiked level and therefore an accurate recovery cannot be calculated.
(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratories A2LA scope of accreditation.
(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1
(3) One of two field matrix spikes prepared and analyzed did not meet method criteria of 100% ± 30%. As one of the two matrix spikes did meet method criteria, the data quality is not affected.

Table 9. Well 7 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-005	Bottle 5, Well 7, Sample	0.824	NA	0.0306	NA	0.0793	NA	0.255	NA
E06-0294-006	Bottle 6, Well 7, Sample Duplicate	0.828	NA	0.0269	NA	0.0727	NA	0.236	NA
E06-0294-007	Bottle 7, Well 7, Field Matrix Spike Low	0.910	NR	0.132	104	0.192	115	0.324	NR
E06-0294-008	Bottle 8, Well 7, Field Matrix Spike High	1.81	99.8	0.998	97.9	1.18	109	0.998	73.8
Average Concentration (ng/mL) ± %RPD		*0.826 ng/mL ± 0.56%*		*0.0288 ng/mL ± 13%*		*0.0760 ng/mL ± 8.7%*		*0.246 ng/mL ± 7.7%*	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-005	Bottle 5, Well 7, Sample	<0.0250	NA	0.0343	NA	0.204	NA
E06-0294-006	Bottle 6, Well 7, Sample Duplicate	<0.0250	NA	0.0315	NA	0.198	NA
E06-0294-007	Bottle 7, Well 7, Field Matrix Spike Low	0.114	114	0.121	87.2	0.282	80.2
E06-0294-008	Bottle 8, Well 7, Field Matrix Spike High	1.05	105	1.09	105	1.11	90.0
Average Concentration (ng/mL) ± %RPD		*<0.0250 ng/mL*		*0.0329 ng/mL ± 8.5%*		*0.201 ng/mL ± 3.0%*	

N/A = Not Applicable
NR = Not Reported = Endogenous concentration of analyte exceeded 2x the spiked level and therefore an accurate recovery cannot be calculated.
(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratories A2LA scope of accreditation.
(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

Table 10. Well 8 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-009	Bottle 9, Well 8, Sample	1.28	NA	0.0468	NA	0.112	NA	0.431	NA
E06-0294-010	Bottle 10, Well 8, Sample Duplicate	1.28	NA	0.0491	NA	0.131	NA	0.437	NA
E06-0294-011	Bottle 11, Well 8, Field Matrix Spike Low	1.36	NR	0.162	115.2	0.263	[3]140	0.689	83.6
E06-0294-012	Bottle 12, Well 8, Field Matrix Spike High	2.46	120	0.961	92.2	1.21	108	1.23	78.0
Average Concentration (ng/mL) ± %RPD		1.28 ng/mL ± 0.078%		0.0480 ng/mL ± 4.8%		0.122 ng/mL ± 16%[4]		0.434 ng/mL ± 1.4%	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-009	Bottle 9, Well 8, Sample	0.0251	NA	0.0518	NA	0.596	NA
E06-0294-010	Bottle 10, Well 8, Sample Duplicate	<0.0250	NA	0.0508	NA	0.647	NA
E06-0294-011	Bottle 11, Well 8, Field Matrix Spike Low	0.137	114	0.176	123	0.981	NR
E06-0294-012	Bottle 12, Well 8, Field Matrix Spike High	1.05	103	1.09	103	1.59	95.9
Average Concentration (ng/mL) ± %RPD		0.0251		0.0513 ng/mL ± 1.9%		0.622 ng/mL ± 8.2%	

N/A = Not Applicable

NR = Not Reported = Endogenous concentration of analyte exceeded 2x the spiked level and therefore an accurate recovery cannot be calculated.

(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratory's scope of accreditation to ISO/IEC 17025:1999.

(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

(3) One of two field matrix spikes prepared and analyzed did not meet method criteria of 100% ± 30%. As one of the two matrix spikes did meet method criteria, the data quality is not affected.

(4) RPD exceeded 15% acceptance criteria.

Table 11. Well 9 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-013	Bottle 13, Well 9, Sample	2.04	NA	0.0895	NA	0.225	NA	0.726	NA
E06-0294-014	Bottle 14, Well 9, Sample Duplicate	2.02	NA	0.0914	NA	0.235	NA	0.652	NA
E06-0294-015	Bottle 15, Well 9, Field Matrix Spike Low	2.21	NR	0.169	79.3	0.384	NR	0.949	85.2
E06-0294-016	Bottle 16, Well 9, Field Matrix Spike High	3.15	114	1.1	102.0	1.27	103	1.51	80.5
Average Concentration (ng/mL) ± %RPD		*2.03 ng/mL ± 0.79%*		*0.0904 ng/mL ± 2.1%*		*0.230 ng/mL ± 4.3%*		*0.689 ng/mL ± 11%*	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-013	Bottle 13, Well 9, Sample	0.0521	NA	0.106	NA	0.567	NA
E06-0294-014	Bottle 14, Well 9, Sample Duplicate	0.0492	NA	0.103	NA	0.544	NA
E06-0294-015	Bottle 15, Well 9, Field Matrix Spike Low	0.166	115	0.211	105	0.833	91.9
E06-0294-016	Bottle 16, Well 9, Field Matrix Spike High	1.08	103	1.14	103	1.51	94.5
Average Concentration (ng/mL) ± %RPD		*0.0506 ng/mL ± 5.7%*		*0.104 ng/mL ± 2.9%*		*0.556 ng/mL ± 4.1%*	

N/A = Not Applicable
NR = Not Reported = Endogenous concentration of analyte exceeded 2x the spiked level and therefore an accurate recovery cannot be calculated.
(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratory's scope of accreditation to ISO/IEC 17025:1999.
(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

Table 12. Well 1 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-020	Bottle 20, Well 1, Sample	0.295	NA	<0.0248	NA	<0.0252	NA	0.0781	NA
E06-0294-021	Bottle 21, Well 1, Sample Duplicate	0.287	NA	<0.0248	NA	<0.0252	NA	0.0801	NA
E06-0294-022	Bottle 22, Well 1, Field Matrix Spike Low	0.416	126	0.100	101	0.142	[3]141	0.172	91.1
E06-0294-023	Bottle 23, Well 1, Field Matrix Spike High	1.35	107	1.01	102	1.18	117	0.924	82.8
Average Concentration (ng/mL) ± %RPD		0.291 ng/mL ± 3.0%		<0.0248 ng/mL		<0.0252 ng/mL		0.0791 ng/mL ± 2.5%	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-020	Bottle 20, Well 1, Sample	<0.0250	NA	<0.0252	NA	0.0415	NA
E06-0294-021	Bottle 21, Well 1, Sample Duplicate	<0.0250	NA	<0.0252	NA	0.0381	NA
E06-0294-022	Bottle 22, Well 1, Field Matrix Spike Low	0.0978	97.9	0.117	116	0.128	87.3
E06-0294-023	Bottle 23, Well 1, Field Matrix Spike High	1.12	112	1.19	109	1.06	101
Average Concentration (ng/mL) ± %RPD		<0.0250 ng/mL		<0.0252 ng/mL		0.0398 ng/mL ± 8.5%	

N/A = Not Applicable

(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratory's scope of accreditation to ISO/IEC 17025:1999.

(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

(3) One of two field matrix spikes prepared and analyzed did not meet method criteria of 100% ± 30%. As one of the two matrix spikes did meet method criteria, the data quality is not affected.

Table 13. Well 2 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-024	Bottle 24, Well 2, Sample	0.381	NA	<0.0248	NA	0.0376	NA	0.0931	NA
E06-0294-025	Bottle 25, Well 2, Sample Duplicate	0.373	NA	<0.0248	NA	0.0364	NA	0.0915	NA
E06-0294-026	Bottle 26, Well 2, Field Matrix Spike Low	0.489	NR	0.117	118	0.157	119	0.222	127
E06-0294-027	Bottle 27, Well 2, Field Matrix Spike High	1.47	111	1.05	106	1.19	114	0.838	73.1
Average Concentration (ng/mL) ± %RPD		0.377 ng/mL ± 2.0%		<0.0248ng/mL		0.0370 ng/mL ± 3.2%		0.0923 ng/mL ± 1.7%	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-024	Bottle 24, Well 2, Sample	<0.0250	NA	<0.0252	NA	0.0387	NA
E06-0294-025	Bottle 25, Well 2, Sample Duplicate	<0.0250	NA	<0.0252	NA	0.0324	NA
E06-0294-026	Bottle 26, Well 2, Field Matrix Spike Low	0.107	107	0.118	117	0.135	98.5
E06-0294-027	Bottle 27, Well 2, Field Matrix Spike High	1.11	111	1.02	101	0.961	91.6
Average Concentration (ng/mL) ± %RPD		<0.0250 ng/mL		<0.0252 ng/mL		0.0356 ng/mL ± 18%[3]	

N/A = Not Applicable
NR = Not Reported = Endogenous concentration of analyte exceeded 2x the spiked level and therefore an accurate recovery cannot be calculated.
(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratories laboratory's scope of accreditation to ISO/IEC 17025:1999.
(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1.
(3) RPD exceeded 15% acceptance criteria.

Table 14. Well 3 Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-028	Bottle 28, Well 3, Sample	0.0949	NA	<0.0248	NA	<0.0252	NA	<0.0254	NA
E06-0294-029	Bottle 29, Well 3, Sample Duplicate	0.0855	NA	<0.0248	NA	<0.0252	NA	<0.0254	NA
E06-0294-030	Bottle 30, Well 3, Field Matrix Spike Low	0.213	124	0.101	102	0.106	105	0.0745	73.0
E06-0294-031	Bottle 31, Well 3, Field Matrix Spike High	1.19	111	0.967	98	1.08	107	0.671	[3]65.8
Average Concentration (ng/mL) ± %RPD		0.0902 ng/mL ± 10%		<0.0248 ng/mL		<0.0252 ng/mL		<0.0254 ng/mL	

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-028	Bottle 28, Well 3, Sample	<0.0250	NA	<0.0252	NA	<0.0252	NA
E06-0294-029	Bottle 29, Well 3, Sample Duplicate	<0.0250	NA	<0.0252	NA	<0.0252	NA
E06-0294-030	Bottle 30, Well 3, Field Matrix Spike Low	0.115	115	0.101	100	0.0734	72.7
E06-0294-031	Bottle 31, Well 3, Field Matrix Spike High	1.05	105	1.04	103	0.881	87.2
Average Concentration (ng/mL) ± %RPD		<0.0250 ng/mL		<0.0252 ng/mL		<0.0252 ng/mL	

N/A = Not Applicable

(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratory's scope of accreditation to ISO/IEC 17025:1999.

(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

(3) Since the low FMS spike recovery met acceptance criteria and the measured values were below LOQ the data is acceptable.

Table 15. Trip Blank Results

		PFBA[1]		NFPA[2]		PFHA[2]		PFOA[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-017	Bottle 17, NA, Trip Blank	<0.0494	NA	0.0295[4]	NA	<0.0252	NA	<0.0254	NA
E06-0294-018	Bottle 18, NA, Trip Blank Matrix Spike Low	0.103	105	0.097	[3]68.2	0.104	103	0.053	104
E06-0294-019	Bottle 19, NA, Trip Blank Matrix Spike High	1.08	109	1.00	98	1.10	109	0.821	80.5

		PFBS[2]		PFHS[2]		PFOS[2]	
3M LIMS ID	Description	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery	Concentration (ng/mL)	%Recovery
E06-0294-017	Bottle 17, NA, Trip Blank	<0.0250	NA	<0.0252	NA	<0.0252	NA
E06-0294-018	Bottle 18, NA, Trip Blank Matrix Spike Low	0.114	114	0.0987	97.7	0.0364	72.4
E06-0294-019	Bottle 19, NA, Trip Blank Matrix Spike High	1.02	102	1.08	107	1.05	104

N/A = Not Applicable

(1) Sample results for PFBA were determined following method ETS-8-11.0. This method is currently not covered on the laboratories laboratory's scope of accreditation to ISO/IEC 17025:1999.

(2) Sample results for NFPA, PFHA, PFOA, PFBS, PFHS, and PFOS were determined following method ETS-8-154.1

(3) FMS or trip blank spike recovery did not meet method criteria of 100%±30%.

(4) The trip blank contained a trace amount of NFPA above the LOQ (0.0248 ng/mL). Samples have not been corrected for the trip blank concentration.

5 Conclusion

Laboratory control spikes were used to determine the analytical method accuracy and precision for all analytes. The accuracy and precision were then used to estimate the method uncertainty for the results. Field matrix spike recoveries demonstrated that the analytical method was appropriate for the given sample matrix. Analysis was successfully completed following 3M Environmental Laboratory method ETS 8-11.0 "Determination of $C_4 - C_8$ Highly Fluorinated Acids, Alcohols, Amides, and Sulfonates in Water by High Performance Liquid Chromatography/Mass Spectrometry" and 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". Analytical results are reported in Table 1 of this report.

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: 7/18/06

Mark E. Ellefson, 3M Senior Chemist — Date: 7/18/06

Kent R. Lindstrom, 3M Senior Chemist — Date: 07/18/06

William K. Reagen, Ph.D., Environmental Laboratory Technical Manager — Date: 07/18/06

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

Quality Assurance Representative — Date: 07/18/06