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Analytical Report

Fluorochemical Characterization of Sediment, POTW Sludge, and

Landfill Leachate Samples

Columbus, GA (W2336)

Centre Analytical Laboratory Report No. 023-014U (Revision 1)

Revision Date 3/28/01

Testing Laboratory

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3M Environmental Laboratory Contact

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Requester

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1 Introduction

Results are reported for the analysis of a series of sediment, leachate, and sludge samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. The samples were collected from Columbus, Georgia and are part of 3M Project W2336. The Centre study number assigned to the project is 023-014.

Specific fluorochemical characterization by liquid chromatography / tandem mass spectrometry (LC/MS/MS) was requested for all samples. A total of 9 samples were received for analysis.

The samples were prepared and analyzed by LC/MS/MS for the following list of fluorochemicals:

- Table 1: Target Analysis

Compound Name	Acronym
Perfluorooctane Sulfonate	PFOS
Perfluorooctane Sulfonylamide	PFOSA
Perfluorooctanoate	POAA

The analytical methods used for originally developed for water samples and were validated by Centre. The water sample validation protocol and results are on file with Centre. The methods were modified for the sediment and sludge samples. The procedures have not been fully validated for these matrices. Data presented here is the highest quality data available at this time.

2 Sample Receipt

The samples were submitted in individual plastic containers and were not preserved. Seven individual sample containers were received. Samples were received on 7/28/00. Sample collection dates were not supplied. Chain-of-custody information is presented in Attachment C.

3 Holding Times

The analytical method used was validated against a maximum holding time of 14 days in water samples. Stability after this time period has not been validated. However, it should be noted that field fortifications in water and other matrices have shown acceptable recoveries at 100 and 1000 ng/L for periods longer than 14 days.

4 Methods - Analytical and Preparatory

4.1 LC/MS/MS

4.1.1 Sample Preparation for LC/MS/MS Analysis

Water samples (leachate and field blanks) were initially treated with 200 μ L of 250 mg/L sodium thiosulfate solution to remove residual chlorine. Solid phase extraction (SPE) was used to prepare the samples for LC/MS/MS analysis. A forty-milliliter portion of sample was transferred to a C₁₈ SPE cartridge. The cartridge was first eluted with 5 mL of 40% methanol in water solution. The eluate was discarded and the SPE column was then eluted with 100% methanol. A 5 mL portion of methanol was collected for analysis by LC/MS/MS. This treatment resulted in an eight-fold concentration of the samples prior to analysis.

For the sediment and sludge samples, a representative portion of sample (5 grams) was first extracted into 5 mL of methanol. The extracts were filtered and diluted to a final volume of 40 mL with Type I water. The diluted extracts were then treated in the same manner as the water samples, beginning with the solid phase extraction.

4.1.2 Sample Analysis by LC/MS/MS

In HPLC, an aliquot of extract is injected and passed through a liquid-phase chromatographic column. Based on the affinity of the analyte for the stationary phase in the column relative to the liquid mobile phase, the analyte is retained for a characteristic amount of time. Following HPLC separation, ES/MS provides a rapid and accurate means for analyzing a wide range of organic compounds, including fluorochemicals. Electrospray is generally operated at relatively mild temperatures; molecules are ionized, fragmented, and detected. Ions characteristic of known fluorochemicals are observed and quantitated against standards.

A Hewlett-Packard HP1100 HPLC system coupled to a Micromass Ultima MS/MS was used to analyze the sample extracts. Analysis was performed using selected reaction monitoring (SRM). Samples were extracted between 8/25/00 and 8/28/00 and analyzed by MS/MS between 8/28/00 and 8/29/00. The HPLC and MS/MS methods used for analysis and instrument parameters can be found in Attachments D.

5 Analysis

5.1 Calibration

A 7-point calibration curve was analyzed at the beginning and end of the analytical sequence for the compounds of interest. The calibration points were prepared at 0, 25, 50, 100, 250, 500, and 1000 ng/L (ppt) for LC/MS/MS analysis. The instrument response versus the concentration was plotted for each point. Using linear regression with 1/x weighting, the slope, y-intercept and correlation coefficient (r) and coefficient of determination (r^2) were determined. A calibration curve is acceptable if $r \geq 0.985$ ($r^2 \geq 0.970$).

Calibration standards are prepared using the same SPE procedure used for samples.

Calibration check standards were analyzed periodically (every three to five sample injections) throughout the analysis sequence. Compliance is obtained if the standard analyte concentrations are within $\pm 20\%$ of the actual value.

For the results reported here, calibration criteria were met.

5.2 Blanks

Extraction blanks were prepared and analyzed with every extraction batch of samples. The extraction blanks should not have any target analytes present at or above the concentration of the low-level calibration standard. For these samples, the extraction blanks were compliant.

Instrument blanks in the form of clean methanol solvent were also analyzed after every high-level calibration standard, and after known high-level samples. Again, the blanks should not have any target analytes present at or above the low-level calibration standard. For the samples presented here the instrument blanks are compliant.

5.3 Surrogates

Surrogate spikes are not a component of the LC/MS/MS analytical methods.

5.4 Matrix Spikes

Matrix spikes were prepared for every field sample using all compounds of interest. Matrix spike recoveries are given in Attachment B. No field spikes were collected from this site.

5.5 Duplicates

All field samples were analyzed in duplicate. Results are given along with the sample results in Attachment A.

5.6 Laboratory Control Samples

For LC/MS/MS analyses, MilliQ water was spiked with all compounds of interest at 25 and 250 ng/L during each extraction set. All recoveries for all compounds were between 70-130% in each LCS. Results are given along with the raw data in Attachments D.

5.7 Sample Related Comments

Empty containers were submitted as filed blanks. The containers were treated with 40 mL of MilliQ water and analyzed as per the method. There are no other sample related comments for this data set.

6 Data Summary

Please see Attachment A for a detailed listing of the analytical results. Field blank water and leachate results are reported in parts per trillion (ppt) (ng/L). Sediment and sludge sample results are reported in parts per billion (ppb) (ug/Kg) on both an as-received and dry-weight basis.

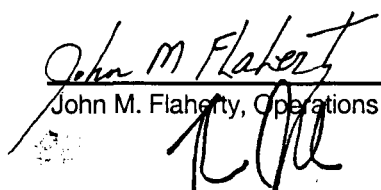
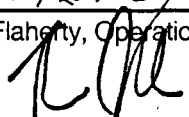
7 Data/Sample Retention

Samples are disposed of one month after the report is issued unless otherwise specified. All electronic data is archived on retrievable media and hard copy reports are stored in data folders maintained by Centre.

8 Attachments

- 8.1 Attachment A: Results
- 8.2 Attachment B: Matrix Spike Recoveries
- 8.3 Attachment C: Chain of Custody
- 8.4 Attachment D: LC/MS/MS Raw Analytical Data

9 Signatures

 _____ John M. Flaherty, Operations Manager	 _____ Kevin J Lloyd, Vice President	3/28/01 _____ Date 28 MARCH 2001 _____ Date
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Other Lab Members Contributing to Data

Karen Smith



Centre Analytical Laboratories, Inc.

3048 Research Drive, State College PA 16801 814-231-8032 FAX 814-231-1253

Analytical Results W2336 Columbus, Georgia (GEN 018)

3M Sample Identification	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-513K Field Blank	NQ	ND	ND
MC-514K Field Blank	ND	ND	ND
MC-535K Landfill Leachate	ND	ND	NQ
MC-535K Landfill Leachate dup	ND	ND	27.9
MC-536K Field Blank	ND	ND	ND
MC-545K Field Blank	ND	ND	ND

Limit of Detection (LOD) for the procedure is approximately 2.5 ng/L for PFOS and PFOSA and 7.5 ng/L for POAA

Limit of Quantitation (LOQ) for the procedure is 25 ng/L for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ





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Analytical Results W2336 Columbus, Georgia (GEN 018)

3M Sample Identification	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)	% Solids
MC-510K Sediment Site 1	0.342	NQ	ND	72.50
MC-510K Sediment Site 1 dup	0.304	NQ	ND	72.50
MC-511K Sediment Site 2	NQ	NQ	ND	71.20
MC-511K Sediment Site 2 dup	NQ	NQ	ND	71.20
MC-512K Sediment Site 3	0.318	NQ	ND	68.00
MC-512K Sediment Site 3 dup	0.264	NQ	ND	68.00
MC-544K POTW Sludge	5.12	1.35	0.537	3.26
MC-544K POTW Sludge dup	5.19	1.42	0.532	3.26

3M Sample Identification	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)
MC-510K Sediment Site 1	0.472	NQ	ND
MC-510K Sediment Site 1 dup	0.419	NQ	ND
MC-511K Sediment Site 2	NQ	NQ	ND
MC-511K Sediment Site 2 dup	NQ	NQ	ND
MC-512K Sediment Site 3	0.467	NQ	ND
MC-512K Sediment Site 3 dup	0.388	NQ	ND
MC-544K POTW Sludge	157	41.3	16.5
MC-544K POTW Sludge dup	159	43.4	16.3

Limit of Detection (LOD) for the procedure is approximately 0.08 ug/Kg for all compounds (as received)

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds (as received)

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ



Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-510K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	42.8	285	96.9	PASS
PFOSA	6.3	231	89.9	PASS
POAA	0	244	97.6	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Note: Sample results less than 25 ng/L are reported as NQ in the results section as they are below the limit of quantitation. Results are given in this table for recovery calculations only.

Concentrations represent amounts present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-511K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	21.8	235	85.3	PASS
PFOSA	8.4	206	79.0	PASS
POAA	0	248	99.2	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Note: Sample results less than 25 ng/L are reported as NQ in the results section as they are below the limit of quantitation. Results are given in this table for recovery calculations only.

Concentrations represent amounts present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-512K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	39.7	250	84.1	PASS
PFOSA	4.0	215	84.4	PASS
POAA	0	254	101.6	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Note: Sample results less than 25 ng/L are reported as NQ in the results section as they are below the limit of quantitation. Results are given in this table for recovery calculations only.

Concentrations represent amounts present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-544K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	640	1093	181.2	FAIL
PFOSA	168	239	28.4	FAIL
POAA	67.1	313	98.4	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Concentrations represent amounts present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID:

Spiked Amount (ng/L):

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	0	97.7	97.7	PASS
PFOSA	0	94.8	94.8	PASS
POAA	19.9	141	121.1	PASS

Lower Recovery Limit:

Upper Recovery Limit:

Note: Sample results less than 25 ng/L are reported as NQ in the results section as they are below the limit of quantitation. Results are given in this table for recovery calculations only.

3M Environmental Laboratory

Form 38778 - PWO

Shipping Address:
3M Bldg 2-3E-09
935 Bush Avenue
St. Paul, MN 55106

Telephone:
Sample Receiving: (651) 778-4948
Alternate: (651) 778-6753
FAX: (651) 778-6176

Chain of Custody /Request for Laboratory Analytical

15092

3M Env. Lab Project #
For Internal Use Only

Project ID/Project Name Gen018 Columbus, GA
Template # NA Final Report Due Date
Project Lead Kris J. Hansen Internal Due Date
Dept. # (main) 4291 Class/Job/Project # 0010535009

W2336

Report Results to:	Contact Name <u>Lisa Clemen</u>	Date Available	<u>0</u>	<u>7</u>	<u>2</u>	<u>8</u>	<u>0</u>	<u>0</u>						
	Company <u>3M</u>	Date Due												
	Mailing Address <u>Bldg 2-3E-09 935 Bush Ave</u>	Contract Lab	<u>C</u>	<u>e</u>	<u>n</u>	<u>t</u>	<u>r</u>							
	City, State, Zip <u>St. Paul, Minnesota</u>													
	Telephone # <u>651-778-5568</u> FAX # <u>651-778-6176</u>													

Special Instructions and/or Specific Regulatory Requirements:
(method, limit of detection, reporting units, etc.)

Preservatives:

Analysis Requested:

Complete below. Attach any associated information.

Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/Media	Preservatives:					Total Number of Containers	Analysis Requested:				
						HNO3	H2SO4	VOCs	None	Other		PFOS	PFOS A	PFOS (PEA)		
1.	MC-510K-Site 1 - PIA Total PFOs/QC For Pair HPLC-ESMS Sediment - Columbus, GA				Sediment						1	X	X	X		
2.	MC-511K-Site 2 - PIA Total PFOs/QC For Pair HPLC-ESMS Sediment - Columbus, GA										1	X	X	X		
3.	MC-512K-Site 3 - PIA Total PFOs/QC For Pair HPLC-ESMS Sediment - Columbus, GA										1	X	X	X		
4.	MC-513K-Field Blank - PIA For Pair HPLC-ESMS Sediment - Columbus, GA										1	X	X	X		
5.	MC-514K-Field Blank - Total PFOs For Pair HPLC-ESMS Sediment - Columbus, GA										1	X	X	X		
6.	MC-535K-Field Blank PIA Total PFOs/QC For Pair HPLC-ESMS Landfill Leachate - Columbus, GA				Leachate						1	X	X	X		
7.	MC-536K-Field Blank - PIA For Pair HPLC-ESMS Landfill Leachate - Columbus, GA										1	X	X	X		
8.	MC-544K-PIA Total PFOs/QC For Pair HPLC-ESMS POTW Sludge - Columbus, GA				Sludge						1	X	X	X		
9.	MC-545K-Field Blank - PIA For Pair HPLC-ESMS POTW Sludge - Columbus, GA										1	X	X	X		
10.																

Chain of Custody	Collected by (print): <u>Kelly Kuehlwein</u>	Collector's signature: <u>Kelly Kuehlwein</u>				
	Item # <u>1-9</u>	Relinquished by/Affiliation <u>Lisa A Clemen / 3M</u>	Time <u>—</u> Date <u>07/27/00</u>	Shipped Via: <u>R. Kuehl</u>	Received by/Affiliation <u>1106</u>	Time <u>7-28-00</u>

Sample Condition Upon Receipt: ☒ Acceptable ☐ Other:	Comments:
Temperature: <u>°C</u> ☒ Received on Ice	
Other Associated CoCs: <u>NA</u>	