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Analytical Report

Fluorochemical Characterization of Sediment, POTW Sludge, and

Landfill Leachate Samples

Pensacola, FL (W2176)

Centre Analytical Laboratory Report No. 023-014T (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 Pensacola, Florida and are part of 3M Project W2176. 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 A.

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 8/22/00 and 8/23/00 and analyzed by MS/MS between 8/25/00 and 8/28/00. 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 +/-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 field 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.

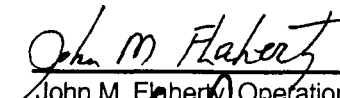
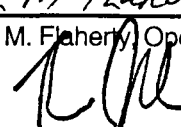
7 Data/Sample Retention

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

	<u>3/28/01</u>
John M. Flaherty, Operations Manager	Date
	<u>28 MARCH 2001</u>
Kevin J Lloyd, Vice President	Date

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 W2176 Pensacola, Florida (GEN 017)

3M Sample Identification	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-313K Field Blank	ND	ND	ND
MC-314K Field Blank	ND	ND	ND
MC-335K Landfill Leachate	ND	ND	ND
MC-335K Landfill Leachate dup	ND	ND	ND
MC-336K Field Blank	ND	ND	ND
MC-345K 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 W2176 Pensacola, Florida (GEN 017)

3M Sample Identification	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)	% Solids
MC-310K Sediment Site 1	ND	ND	ND	78.87
MC-310K Sediment Site 1 dup	ND	ND	ND	78.87
MC-311K Sediment Site 2	0.205	ND	NQ	84.78
MC-311K Sediment Site 2 dup	ND	ND	ND	84.78
MC-312K Sediment Site 3	0.329	ND	ND	80.66
MC-312K Sediment Site 3 dup	NQ	ND	ND	80.66
MC-344K POTW Sludge	27.8	0.285	0.564	22.48
MC-344K POTW Sludge dup	28.2	0.289	0.540	22.48

3M Sample Identification	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)
MC-310K Sediment Site 1	ND	ND	ND
MC-310K Sediment Site 1 dup	ND	ND	ND
MC-311K Sediment Site 2	0.242	ND	NQ
MC-311K Sediment Site 2 dup	ND	ND	ND
MC-312K Sediment Site 3	0.408	ND	ND
MC-312K Sediment Site 3 dup	NQ	ND	ND
MC-344K POTW Sludge	124	1.27	2.51
MC-344K POTW Sludge dup	125	1.29	2.40

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-310K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	0	198	79.2	PASS
PFOSA	0	186	74.4	PASS
POAA	0	196	78.4	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Concentrations represent the amount present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-311K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	25.6	205	71.8	PASS
PFOSA	0	191	76.4	PASS
POAA	10.6	210	79.8	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 the amount present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-312K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	41.1	624	233.2	FAIL
PFOSA	0	149	59.6	FAIL
POAA	0	263	105.2	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Concentrations represent the amount present in the sample extract

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-344K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	3477	4062	234.0	FAIL
PFOSA	35.7	54.2	7.4	FAIL
POAA	70.5	249	71.4	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Concentrations represent the amount present in the sample extract

PFOS sample concentration is greater than 10X the spiking level

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	84.8	84.8	PASS
PFOSA	0	69.2	69.2	FAIL
POAA	0	92.7	92.7	PASS

Lower Recovery Limit:

Upper Recovery Limit:

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

15089

3M Env. Lab Project #
For Internal Use Only

Project ID/Project Name *Water, Sediment & Leachate Samples take at Persicula sent from Battelle*
Template # *NA* Final Report Due Date
Project Lead *Kris J. Hansen* Internal Due Date
Dept. # (main) *4891* Class/Job/Project # *0010535009*

W2176

Report Results to:	Contact Name <i>Lisa Clemen</i>	Date Available	<i>072700</i>
	Company <i>3M</i>	Date Due	
	Mailing Address <i>Bldg 2-3E-09 935 Bush Ave.</i>	Contract Lab	<i>Centre</i>
	City, State, Zip <i>St. Paul, Minnesota</i>		
	Telephone # <i>651 778 5568</i>	FAX #	

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

Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/Media	Preservatives:					Total Number of Containers	Analysis Requested:			
						HNO ₃	H ₂ SO ₄	VOCs	None	Other		PFOS	PFOA	PDAA (PF ₆ A)	
1.	MC-310K-Site 1-PIN/Total PFOS/AL Ion Pair HPLC-ESMS Sediment - Persicula, FI				Sediment						1	X	X	X	
2.	MC-311K-Site 2-PIN/Total PFOS/AL Ion Pair HPLC-ESMS Sediment - Persicula, FI										1	X	X	X	
3.	MC-312K-Site 3-PIN/Total PFOS/AL Ion Pair HPLC-ESMS Sediment - Persicula, FI										1	X	X	X	
4.	MC-313K-Field Blank-PIN Ion Pair HPLC-ESMS Sediment - Persicula, FI										1	X	X	X	
5.	MC-314K-Field Blank-Total PFOS Ion Pair HPLC-ESMS Sediment - Persicula, FI										1	X	X	X	
6.	MC-335K-PIN Total PFOS/AL Ion Pair HPLC-ESMS Landfill Leachate - Persicula, FI				Leachate						1	X	X	X	
7.	MC-336K-Field Blank-PIN Ion Pair HPLC-ESMS Landfill Leachate - Persicula, FI										1	X	X	X	
8.	MC-344K-PIN Total PFOS/AL Ion Pair HPLC-ESMS POTW Sludge - Persicula, FI				Sludge						1	X	X	X	
9.	MC-345K-Field Blank-PIN Ion Pair HPLC-ESMS POTW Sludge - Persicula, FI										1	X	X	X	
10.															

Chain of Custody	Collected by (print): <i>Sally Linda</i>	Collector's signature: <i>S. Linda</i>						
	Item #	Relinquished by/Affiliation	Time	Date	Shipped Via:	Received by/Affiliation	Time	Date
	<i>1-9</i>	<i>Lisa A Clemen / 3M</i>	<i>—</i>	<i>07/27/00</i>		<i>K. Keller</i>	<i>1100</i>	<i>7-28-00</i>

Sample Condition Upon Receipt: ☒ Acceptable ☐ Other:	Comments:
Temperature: <i>°C</i> ☒ Received on Ice	
Other Associated CoCs: <i>N/A</i>	
Copies to: <i>KJH, LAC</i>	