



Centre Analytical Laboratories, Inc.

3048 Research Drive
Phone: (814) 231-8032

State College, PA 16801

www.centrelab.com

Fax: (814) 231-1253 or (814) 231-1580

Analytical Report

Fluorochemical Characterization of Sediment, POTW Sludge, and

Landfill Leachate Samples

Port St. Lucie, Florida (W2363)

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

Revision Date 3/28/01

Testing Laboratory

Centre Analytical Laboratory, Inc.
3048 Research Drive
State College, PA 16801

3M Environmental Laboratory Contact

Kent R. Lindstrom
Bldg. 2-3E-09
P.O. Box 33331
St. Paul, MN 55133-3331
Phone: (651) 778-5352

Requester

Kris Hansen Ph.D.
3M Environmental Technology & Safety Services
Bldg. 2-3E-09
P.O. Box 33331
St. Paul, MN 55133-3331

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 Port St. Lucie, Florida and are part of 3M Project W2363. 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 on 8/28/00 and analyzed by MS/MS between 8/29/00 and 8/30/00. 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.

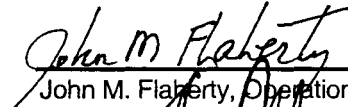
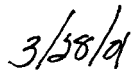
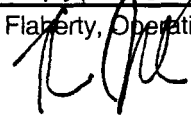
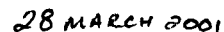
7 Data/Sample Retention

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	 _____ Date
 _____ 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 W2363 Port St. Lucie, Florida (GEN 019)

3M Sample Identification	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-613K Field Blank	ND	ND	ND
MC-614K Field Blank	NQ	NQ	ND
MC-635K Landfill Leachate	344	NQ	953
MC-635K Landfill Leachate dup	329	NQ	939
MC-636K Field Blank	ND	ND	ND
MC-645K Field Blank	ND	ND	NQ

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 W2363 Port St. Lucie, Florida (GEN 019)

3M Sample Identification	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)	% Solids
MC-610K Sediment Site 1	NQ	NQ	0.291	78.66
MC-610K Sediment Site 1 dup	NQ	NQ	0.257	78.66
MC-611K Sediment Site 2	0.934	NQ	0.262	83.01
MC-611K Sediment Site 2 dup	0.906	NQ	0.244	83.01
MC-612K Sediment Site 3	0.594	NQ	1.31	77.91
MC-612K Sediment Site 3 dup	0.626	NQ	1.36	77.91
MC-644K POTW Sludge	NQ	NQ	NQ	0.24
MC-644K POTW Sludge dup	NQ	NQ	NQ	0.24

3M Sample Identification	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)
MC-610K Sediment Site 1	NQ	NQ	0.37
MC-610K Sediment Site 1 dup	NQ	NQ	0.326
MC-611K Sediment Site 2	1.13	NQ	0.316
MC-611K Sediment Site 2 dup	1.09	NQ	0.294
MC-612K Sediment Site 3	0.763	NQ	1.68
MC-612K Sediment Site 3 dup	0.804	NQ	1.75
MC-644K POTW Sludge	NQ	NQ	NQ
MC-644K POTW Sludge dup	NQ	NQ	NQ

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-610K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	13.9	275	104.4	PASS
PFOSA	6.8	208	80.5	PASS
POAA	36.4	270	93.4	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 found in the sample extracts

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-611K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	117	316	79.6	PASS
PFOSA	6.6	206	79.8	PASS
POAA	32.8	263	92.1	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 found in the sample extracts

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-612K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	74.3	284	83.9	PASS
PFOSA	3.7	200	78.5	PASS
POAA	164	392	91.2	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 found in the sample extracts

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-644K

Spiked Amount (ng/L): 250

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	21.8	204	72.9	PASS
PFOSA	4.3	185	72.3	PASS
POAA	16.5	251	93.8	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 amounts found in the sample extracts

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-635K

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	344	422	78.0	PASS
PFOSA	7.2	88.8	81.6	PASS
POAA	953	1049	96.0	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.

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

15094

3M Env. Lab Project #
For Internal Use Only

Project ID/Project Name Gen-019 Pt St Lucie, FL
Template # NA Final Report Due Date
Project Lead Krist J. Hansen Internal Due Date
Dept. # (main) 4291 Class/Job/Project # 0010535009

W2363

Report Results to:	Contact Name <u>Lisa Clemens</u>	Date Available	<u>072800</u>
	Company <u>3M</u>	Date Due	
	Mailing Address <u>Bldg. 2-3E-09 935 Bush Ave.</u>	Contract Lab	<u>Centre</u>
	City, State, Zip <u>St Paul, Minnesota</u>		
	Telephone # <u>651 778 4568</u>	FAX #	

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

Preservatives:

HNO ₃	H ₂ SO ₄	VOCs	None	Other

Total Number of Containers

Analysis Requested:

Complete below. Attach any associated information.

Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/Media	Enter the number of containers of each					(Enter an 'X' in the box below to indicate request)									
1.	MC-610K-Site 1-PIN/Total PFOS/LC Ion Pair HPLC-ESMS Sediment-Port St. Lucie, FL				Sediment						1	X	X	X						
2.	MC-611K-Site 2-PIN/Total PFOS/LC Ion Pair HPLC-ESMS Sediment-Port St. Lucie, FL										1	X	X	X						
3.	MC-612K-Site 3-PIN/Total PFOS/LC Ion Pair HPLC-ESMS Sediment-Port St. Lucie, FL										1	X	X	X						
4.	MC-613K-Field Blank-PIN-Empty Ion Pair HPLC-ESMS Sediment-Port St. Lucie, FL										1	X	X	X						
5.	MC-614K-Field Blank-Total PFOS-Empty Ion Pair HPLC-ESMS Sediment-Port St. Lucie, FL										1	X	X	X						
6.	MC-635-PIN/Total PFOS/LC Ion Pair HPLC-ESMS Landfill Leachate-Port St. Lucie, FL				Leachate						1	X	X	X						
7.	MC-636K-Field Blank-PIN-Empty Ion Pair HPLC-ESMS Landfill Leachate-Port St. Lucie, FL										1	X	X	X						
8.	MC-644K-PIN/Total PFOS/LC Ion Pair HPLC-ESMS POTW Sludge-Port St. Lucie, FL				Sludge						1	X	X	X						
9.	MC-645K-Field BK-PIN-Empty Ion Pair HPLC-ESMS POTW Sludge-Port St. Lucie, FL										1	X	X	X						
10.																				

Chain of Custody	Collected by (print): <u>Sally Linda</u>	Collector's signature: <u>[Signature]</u>						
	Item #	Relinquished by/Affiliation	Time	Date	Shipped Via:	Received by/Affiliation	Time	Date
	1-9	<u>Lisa A. Clemens / 3M</u>		<u>7/27/00</u>		<u>R. Hall</u>	<u>1100</u>	<u>7-28-00</u>

Sample Condition Upon Receipt: ☒ Acceptable ☐ Other:	Comments:
Temperature: <u>1</u> °C ☒ Received on Ice	
Other Associated CoCs: <u>NA</u>	
Copies to: <u>KJH, LAL</u>	