



# **Centre Analytical Laboratories, Inc.**

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State College, PA 16801

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## **Analytical Report**

**Fluorochemical Characterization of Sediment and Sludge Samples**

**Cleveland, TN (W1973)**

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

**Revision Date 3/27/01**

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### ***Testing Laboratory***

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

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### ***3M Environmental Laboratory Contact***

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

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### ***Requester***

Kris Hansen Ph.D.  
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St. Paul, MN 55133-3331

## **1 Introduction**

Results are reported for the analysis of a series of sediment and sludge samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. Landfill leachate samples were not collected from this city. The samples were collected from Cleveland, Tennessee and are part of 3M Project W1973. 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 7 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 Sulfonamide | 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 (field blanks) were initially treated with 200  $\mu$ 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 C<sub>18</sub> 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 8/21/00 and analyzed by MS/MS between 8/23/00 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.

## **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 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.

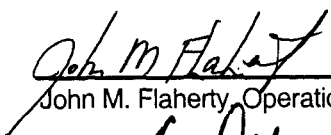
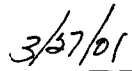
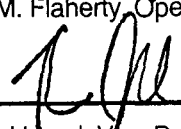
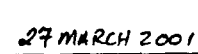
# **7 Data/Sample Retention**

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 W1973 Cleveland, Tennessee (GEN 013)

| 3M Sample Identification    | PFOS (ug/Kg)<br>(as received) | PFOSA (ug/Kg)<br>(as received) | POAA (ug/Kg)<br>(as received) | % Solids |
|-----------------------------|-------------------------------|--------------------------------|-------------------------------|----------|
| MC-110K Sediment Site 1     | NQ                            | ND                             | ND                            | 79.4     |
| MC-110K Sediment Site 1 dup | ND                            | ND                             | ND                            | 79.4     |
| MC-111K Sediment Site 2     | NQ                            | NQ                             | NQ                            | 88.07    |
| MC-111K Sediment Site 2 dup | NQ                            | NQ                             | NQ                            | 88.07    |
| MC-112K Sediment Site 3     | NQ                            | ND                             | ND                            | 81.71    |
| MC-112K Sediment Site 3 dup | NQ                            | ND                             | ND                            | 81.71    |
| MC-144K POTW Sludge         | 30.5                          | 0.441                          | 0.817                         | 26.26    |
| MC-144K POTW Sludge dup     | 34.1                          | 0.446                          | 0.741                         | 26.26    |

| 3M Sample Identification    | PFOS (ug/Kg)<br>(dry weight) | PFOSA (ug/Kg)<br>(dry weight) | POAA (ug/Kg)<br>(dry weight) |
|-----------------------------|------------------------------|-------------------------------|------------------------------|
| MC-110K Sediment Site 1     | NQ                           | ND                            | ND                           |
| MC-110K Sediment Site 1 dup | ND                           | ND                            | ND                           |
| MC-111K Sediment Site 2     | NQ                           | NQ                            | NQ                           |
| MC-111K Sediment Site 2 dup | NQ                           | NQ                            | NQ                           |
| MC-112K Sediment Site 3     | NQ                           | ND                            | ND                           |
| MC-112K Sediment Site 3 dup | NQ                           | ND                            | ND                           |
| MC-144K POTW Sludge         | 116                          | 1.68                          | 3.11                         |
| MC-144K POTW Sludge dup     | 130                          | 1.7                           | 2.82                         |

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





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## Analytical Results W1973 Cleveland, Tennessee (GEN 013)

| 3M Sample Identification | PFOS (ng/L) | PFOSA (ng/L) |    | POAA (ng/L) |
|--------------------------|-------------|--------------|----|-------------|
| MC-113K Field Blank      | ND          | ND           | ND | ND          |
| MC-114K Field Blank      | ND          | ND           | ND | ND          |
| MC-145K Field Blank      | ND          | 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



## Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-110K

Spiked Amount (ng/L): 250

|       | Sample<br>Concentration<br>(ng/L) | Matrix Spike<br>Result<br>(ng/L) | Matrix Spike<br>Result<br>(% Recovery) | Criteria<br>(Pass / Fail) |
|-------|-----------------------------------|----------------------------------|----------------------------------------|---------------------------|
| PFOS  | 2.9                               | 225                              | 88.8                                   | PASS                      |
| PFOSA | 0                                 | 238                              | 95.2                                   | PASS                      |
| POAA  | 0                                 | 237                              | 94.8                                   | 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 of compound present in the sample extract

## Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-111K

Spiked Amount (ng/L): 250

|       | Sample<br>Concentration<br>(ng/L) | Matrix Spike<br>Result<br>(ng/L) | Matrix Spike<br>Result<br>(% Recovery) | Criteria<br>(Pass / Fail) |
|-------|-----------------------------------|----------------------------------|----------------------------------------|---------------------------|
| PFOS  | 11.7                              | 249                              | 94.9                                   | PASS                      |
| PFOSA | 3.3                               | 237                              | 93.5                                   | PASS                      |
| POAA  | 12.9                              | 285                              | 108.8                                  | 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 of compound present in the sample extract

## Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-112K

Spiked Amount (ng/L): 250

|       | Sample<br>Concentration<br>(ng/L) | Matrix Spike<br>Result<br>(ng/L) | Matrix Spike<br>Result<br>(% Recovery) | Criteria<br>(Pass / Fail) |
|-------|-----------------------------------|----------------------------------|----------------------------------------|---------------------------|
| PFOS  | 9.1                               | 235                              | 90.4                                   | PASS                      |
| PFOSA | 0                                 | 217                              | 86.8                                   | PASS                      |
| POAA  | 0                                 | 240                              | 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.

Concentrations represent amounts of compound present in the sample extract

## Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-144K

Spiked Amount (ng/L): 250

|       | Sample<br>Concentration<br>(ng/L) | Matrix Spike<br>Result<br>(ng/L) | Matrix Spike<br>Result<br>(% Recovery) | Criteria<br>(Pass / Fail) |
|-------|-----------------------------------|----------------------------------|----------------------------------------|---------------------------|
| PFOS  | 3810                              | 4081                             | 108.4                                  | PASS                      |
| PFOSA | 55.2                              | 126                              | 28.3                                   | FAIL                      |
| POAA  | 102                               | 221                              | 47.6                                   | FAIL                      |

Lower Recovery Limit: 70

Upper Recovery Limit: 130

PFOS sample concentration is greater than 10X the spiking amount

Concentrations represent amounts of compound present in the sample extract

# 3M Environmental Laboratory

Form 38778 - PWO

Chain of Custody / Request for Laboratory Analytical

15090

3M Env. Lab Project #  
For Internal Use Only

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

Project ID/Project Name Gen 013 Cleveland TN  
Template # NA Final Report Due Date  
Project Lead Kris J. Hansen Internal Due Date  
Dept. # (main) 4291 Class/Job/Project # 0010535009

W1973

|                    |                  |                                   |       |                |               |  |
|--------------------|------------------|-----------------------------------|-------|----------------|---------------|--|
| Report Results to: | Contact Name     | <u>Lisa Clemen</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>651-778-5568</u>               | 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 <sub>3</sub> | H <sub>2</sub> SO <sub>4</sub> | VOCs | None | Other |                            | PFS                 | PFOA | PFAA (PFOA) |
| 1.     | MC-110K-Site 1-PIN/Total PFOS/OC Ion Pair HPLC-ESMS Sediment-Cleveland, TN     |          |              |              | Sediment     |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 2.     | MC-111K-Site 2-PIN/Total PFOS/OC Ion Pair HPLC-ESMS Sediment-Cleveland, TN     |          |              |              |              |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 3.     | MC-112K-Site 3-PIN/Total PFOS/OC Ion Pair HPLC-ESMS Sediment-Cleveland, TN     |          |              |              |              |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 4.     | MC-113K-Field Blank-PIN/Empty Ion Pair HPLC-ESMS Sediment-Cleveland, TN        |          |              |              |              |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 5.     | MC-114K-Field Blank-Total PFOS empty Ion Pair HPLC-ESMS Sediment-Cleveland, TN |          |              |              |              |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 6.     | MC-144K-PIN/Total PFOS/OC Ion Pair HPLC-ESMS PATW Sludge-Cleveland, TN         |          |              |              | Sludge       |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 7.     | MC-145K-Field Blank-PIN-Empty Ion Pair HPLC-ESMS PATW Sludge-Cleveland, TN     |          |              |              |              |                  |                                |      |      |       | 1                          | X                   | X    | X           |
| 8.     |                                                                                |          |              |              |              |                  |                                |      |      |       |                            |                     |      |             |
| 9.     |                                                                                |          |              |              |              |                  |                                |      |      |       |                            |                     |      |             |
| 10.    |                                                                                |          |              |              |              |                  |                                |      |      |       |                            |                     |      |             |

|                  |                       |                             |          |                |                 |                         |                        |      |  |  |
|------------------|-----------------------|-----------------------------|----------|----------------|-----------------|-------------------------|------------------------|------|--|--|
| Chain of Custody | Collected by (print): | <u>Kelly Kuehlwein</u>      |          |                |                 | Collector's signature:  | <u>Kelly Kuehlwein</u> |      |  |  |
|                  | Item #                | Relinquished by/Affiliation | Time     | Date           | Shipped Via:    | Received by/Affiliation | Time                   | Date |  |  |
|                  | 1-7                   | <u>Lisa A Clemen</u>        | <u>—</u> | <u>7/27/00</u> | <u>R. Kelle</u> | <u>1100</u>             | <u>7-28-00</u>         |      |  |  |
|                  |                       |                             |          |                |                 |                         |                        |      |  |  |

|                                |                                                                          |                 |
|--------------------------------|--------------------------------------------------------------------------|-----------------|
| Sample Condition Upon Receipt: | <input checked="" type="radio"/> Acceptable <input type="radio"/> Other: | Comments:       |
| Temperature:                   | <u>°C</u> <input checked="" type="radio"/> Received on Ice               |                 |
| Other Associated CoCs:         | <u>N/A</u>                                                               |                 |
| Copies to:                     |                                                                          | <u>KJH, LAC</u> |