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Analytical Report

Fluorochemical Characterization of Surface Water Samples

Port St. Lucie, Fl (W2363)

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

Revision Date 3/22/01

Testing Laboratory

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Requester

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1 Introduction

Results are reported for the analysis of a series of surface water samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. The samples were collected from Port St. Lucie, Fl. 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 8 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 method used was validated by Centre. The validation protocol and results are on file with Centre. 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. Eight individual sample containers were received. Samples were received on 05/03/00. The 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. The stability of the analytes of interest for longer periods has not been determined. However, it should be noted that field fortifications prepared 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

Samples were initially treated with 200 uL 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_{18} 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.

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 5/19/00 and analyzed by MS/MS between 5/22/00 and 5/23/00. An initial analysis was performed on 5/21/00, however, the data was rejected because of unacceptable standard curves. The data is included in Attachment D for informational purposes only. The HPLC and MS/MS methods used for analysis and instrument parameters can be found in attachment 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) The response of the quantitation ion 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 method.

5.4 Matrix Spikes

Matrix spikes were prepared for every field sample (excluding blanks) at a concentration of 100 ng/L using all compounds of interest. Matrix spike recoveries are given in Attachment B. Sample MC-684H had PFOS at levels significantly greater than 10 times the spiking level; therefore accurate matrix spike recoveries could not be determined. All other compounds in all samples showed matrix spike recoveries between 70-130%.

Field spikes were also prepared on sample MC-601H for all compounds at a concentration of 100 ng/L using all compounds of interest. The field spike is identified as sample MC604H. Field spike recoveries are also given in Attachment B. All compounds showed recoveries between 70-130% in the field spikes.

5.5 Duplicates

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

5.6 Laboratory Control Samples

Milliq water was spiked with all compound of interest at 25 and 250 ng/L. PFOS showed a recovery of 133% in the 25 ng/L spike. All recoveries for all other compounds were between 70-130% in each LCS. Results are given along with the raw data in Attachment D.

5.7 Sample Related Comments

Field blank samples consisted of empty containers. Forty milliliters of type I water filtered through a hypercarb cartridge was added to the empty container and analyzed in the same manner as the other samples. The field blank for this sample did show PFOS above the reporting limit.

6 Data Summary

Please see Attachment A for a detailed listing of the analytical results.

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 (Field and Laboratory Spikes)

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: 3/27/01

Kevin J Lloyd, Vice President — Date: 07 MARCH 2001

Other Lab Members Contributing to Data

Enaksha Wickremesinhe
Karen Smith
David Bell
Tiffany Proctor

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Analytical Results W2363 Port St. Lucie, Fl

3M Sample Identification	Sample Description	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-601H	Site 1 Surface Water	ND	ND	ND
MC-603H	Site 1 Surface Water Duplicate	ND	ND	ND
MC-606H	Site 2 Surface Water	138	ND	NQ
NA	Site 2 Surface Water Duplicate	137	ND	NQ
MC-607H	Site 3 Surface Water	NQ	ND	ND
NA	Site 3 Surface Water Duplicate	NQ	ND	ND
MC-608H	Field Blank-P/N Empty	43.1	ND	ND
MC-684H	Quiet Surface Water	45300	83.6	737
NA	Quiet Surface Water Duplicate	51100	95.2	760

Limit of Detection (LOD) for the procedure is appoximately 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-605H

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	0	93.3	93.3	PASS
PFOSA	0	84.4	84.4	PASS
POAA	0	94.9	94.9	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Note that sample MC-605H is a laboratory spike of sample MC-601H

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-606H

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	138	222	84.0	PASS
PFOSA	0	92.7	92.7	PASS
POAA	18.4	118	99.6	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.

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-607H

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	18.8	97.6	78.8	PASS
PFOSA	0	102	102.0	PASS
POAA	0	95.6	95.6	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.

Attachment B: LC/MS/MS Laboratory Spike Recovery

Sample ID: MC-684H

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	45300	39000	-6300.0	FAIL
PFOSA	83.6	174	90.4	PASS
POAA	737	820	83.0	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

The PFOS sample concentration is greater than 10X the spiking level.
Matrix spike recoveries are not applicable for the interpretation of the PFOS result.

Attachment B: LC/MS/MS Field Spike Recovery

Sample ID: MC-604H

Spiked Amount (ng/L): 100

	Sample Concentration (ng/L)	Matrix Spike Result (ng/L)	Matrix Spike Result (% Recovery)	Criteria (Pass / Fail)
PFOS	0	99.4	99.4	PASS
PFOSA	0	74.4	74.4	PASS
POAA	0	103	103.0	PASS

Lower Recovery Limit: 70

Upper Recovery Limit: 130

Note that sample MC-604H is a field spike of sample MC-601H

BACK TO MAIN

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 14270

Project ID/Project Name	GEN019/Water Samples Taken at Port St. Lucie, FL		
Template #		Final Report Due Date	Sent from Battelle
Project Lead	KJH	Internal Due Date	
Dept. # (main)	4291	Class/Job/Project #	0010535009

3M Env. Lab Project # For Internal Use Only: W2363

Report Results to:

Contact Name	Kris Hansen
Company	3M
Mailing Address	Building 2-3E-09 PO Box 33331
City, State, Zip	St. Paul, MN 55133
Telephone #	(651) 778-6018 FAX # (651) 778-6176

Date Available	05/30/00
Date Due	
Contract Lab	CENTRE

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

Preservatives: HNO_3 | H_2SO_4 | VOCs | None | Other

Total Number of Containers

Analysis Requested:
Complete below. Attach any associated information.

KJH 5/2/00

Item #	Client Sample Identification	3M LIMS#	Date Sampled	Time Sampled	Matrix/ Media	Enter the number of containers of each	Total	(Enter an 'X' in the box below to indicate request)
1.	ML-601H-Site 1 PIN Ion Pair HPLC-ESMS Surface Water - Port St. Lucie, FL	W2363	N/A	N/A	Water		1	
2.	ML-602H-Site 1 - Field Lab Dup-PIN Ion Pair HPLC-ESMS-Surface Water - Port St. Lucie, FL						1	
3.	ML-604H-Site 1 - Field Spike-PIN Ion Pair HPLC-ESMS-Surface Water - Port St. Lucie, FL.						1	
4.	ML-605H-Site 1 - Lab Spike-PIN Ion Pair HPLC-ESMS-Surface Water-Port St. Lucie, FL						1	
5.	ML-606H-Site 2 - PIN Ion Pair HPLC-ESMS Surface Water - Port St. Lucie, FL						1	
6.	ML-607H-Site 3-PIN Ion Pair HPLC-ESMS Surface Water - Port St. Lucie, FL						1	
7.	ML-608H-Field Blank-PIN-Empty Ion Pair HPLC-ESMS-Surface Water - Port St. Lucie, FL						1	
8.	ML-634H-Quiet Ion Pair HPLC-ESMS Surface Water - Port St. Lucie, FL						1	
9.								
10.	KJH 5/2/00						8	

KJH 5/2/00

KJH 5/2/00

Chain of Custody

Collected by (print): Battelle

Collector's signature: N/A

Item #	Relinquished by/Affiliation	Time	Date	Shipped Via:	Received by/Affiliation	Time	Date
1-8	Kelly Dowuiler/3M	14:00	5/2/00	FedEx	R. Kelly	10:30	5-3-00

Sample Condition Upon Receipt: ☑ Acceptable ○ Other:

Temperature: 'C ☑ Received on Ice

Other Associated CoCs: 14265, 14266, 14267, 14268, 14269

Copies to: ~~KJH~~, LAL, DMA

Comments: