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Analytical Report

Fluorochemical Characterization of Water and Sediment Samples

Port St. Lucie Resampling (E00-2003)

Centre Analytical Laboratory Report No. 023-014P

Testing Laboratory

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1 Introduction

Results are reported for the analysis of a series of water and sediment 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 E00-2003. The Centre study number assigned to the project is 023-014.

Specific fluorochemical characterization by liquid chromatography / tandem mass spectrometry (LC/MS/MS) and ion chromatography was requested for all samples. A total of 45 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 water samples were validated by Centre. The validation protocol and results are on file with Centre. The methods were modified for the sediment samples, however the procedures have not been fully validated for this matrix. 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. Forty-five individual sample containers were received. Samples were received on 7/25/00. The samples were collected between 7/18/00 and 7/19/00. 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. Stability after this time period has not been validated, however it should be noted that field fortifications have shown acceptable recoveries at the 100 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 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.

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). Water samples were extracted between 8/15/00 and 8/17/00 and analyzed by MS/MS between 8/18/00 and 8/23/00. Sediment and sludge samples were extracted on 8/18/00 and were analyzed by MS/MS on 8/21/00. The HPLC and MS/MS methods used for analysis and instrument parameters can be found in Attachments D and E.

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 C.

Field spikes were submitted with the water samples. Field spike recoveries are also included in Attachment C. The results from the 200 ppt field spike for sample QSW Palm City-C-FMS-200ppt A indicate that this sample was spiked at 1000 ppt rather than 200 ppt. The results for QSW Palm City-C-FMS-200ppt B indicate a 200 ppt spiking concentration.

5.5 Duplicates

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

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 and E.

5.7 Sample Related Comments

There are no other sample related comments for this data set.

6 Data Summary

Please see Attachment B for a detailed listing of the analytical results. Surface water results are reported in parts per trillion (ppt) (ng/L). Sediment and sludge sample results are reported in parts per billion (ppb) (ng/g) 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: Chain-of-Custody

8.2 Attachment B: Results.

8.3 Attachment C: Matrix Spike Recoveries

8.4 Attachment D: LC/MS/MS Raw Analytical Data (Surface Water Samples)

8.5 Attachment E: LC/MS/MS Raw Analytical Data (Sediment and Sludge Samples)

9 *Signatures*

John M Flaherty — 8/24/00

John M. Flaherty, Manager- Operations Manager — Date

24 August 2000

Kevin J Lloyd, Vice President — Date

Other Lab Members Contributing to Data

Karen Smith

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Analytical Results E00-2003 Port St. Lucie, FL Resampling (water samples)

3M Sample Identification	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MDWPIN-R-O-C	< 25	< 25	< 25
MDWPIN-R-O-C dup	< 25	< 25	< 25
MDWPIN-Lime-C	< 25	< 25	< 25
MDWPIN-Lime-C dup	< 25	< 25	< 25
MDWPOut -C	< 25	< 25	< 25
MDWPOut-C dup	< 25	< 25	< 25
NPWWTPEff -C	14.7 J	< 25	15.1 J
NPWWTPEff-C dup	16.6 J	< 25	14.1 J
NPWWTPCC-C	85.5	4.4 J	42.9
NPWWTPCC-C dup	78.8	3.5 J	40.2
PSLF Leach-C	429	7.0 J	1030
PSLF Leach-C dup	425	8.0 J	1020
TW#2 Fire Dept-C	< 25	< 25	< 25
TW#2 Fire Dept-C dup	< 25	< 25	< 25
SW#3 SH-C	7.8 J	< 25	< 25
SW#3 SH-C dup	5.4 J	< 25	< 25
TW#3 Penpark-C	< 25	< 25	< 25
TW#3 Penpark-C dup	< 25	< 25	< 25
SW#1 Penpark-C	5.2 J	< 25	< 25
SW#1 Penpark-C dup	4.1 J	< 25	< 25
TW#1 Holiday Inn-C	< 25	< 25	< 25
TW#1 Holiday Inn-C dup	< 25	< 25	< 25
SW#2 MCM-C	7.7 J	< 25	< 25
SW#2 MCM-C dup	9.3 J	< 25	< 25
QSW Palm City-C	2930	30.0	96.9
QSW Palm City-C dup	2850	27.5	97.1
Blind Dup C1	< 25	< 25	< 25
Blind Dup C1 dup	< 25	< 25	< 25
Blind Dup C2	8.0 J	< 25	< 25
Blind Dup C2 dup	9.8 J	< 25	< 25

J - Compound is present, but below the reporting limit of 25 ng/L. The result is an estimated value.

Method Detection Limits are approximately 2.5 ng/L for PFOS and PFOSA and 7.5 ng/L for POAA.

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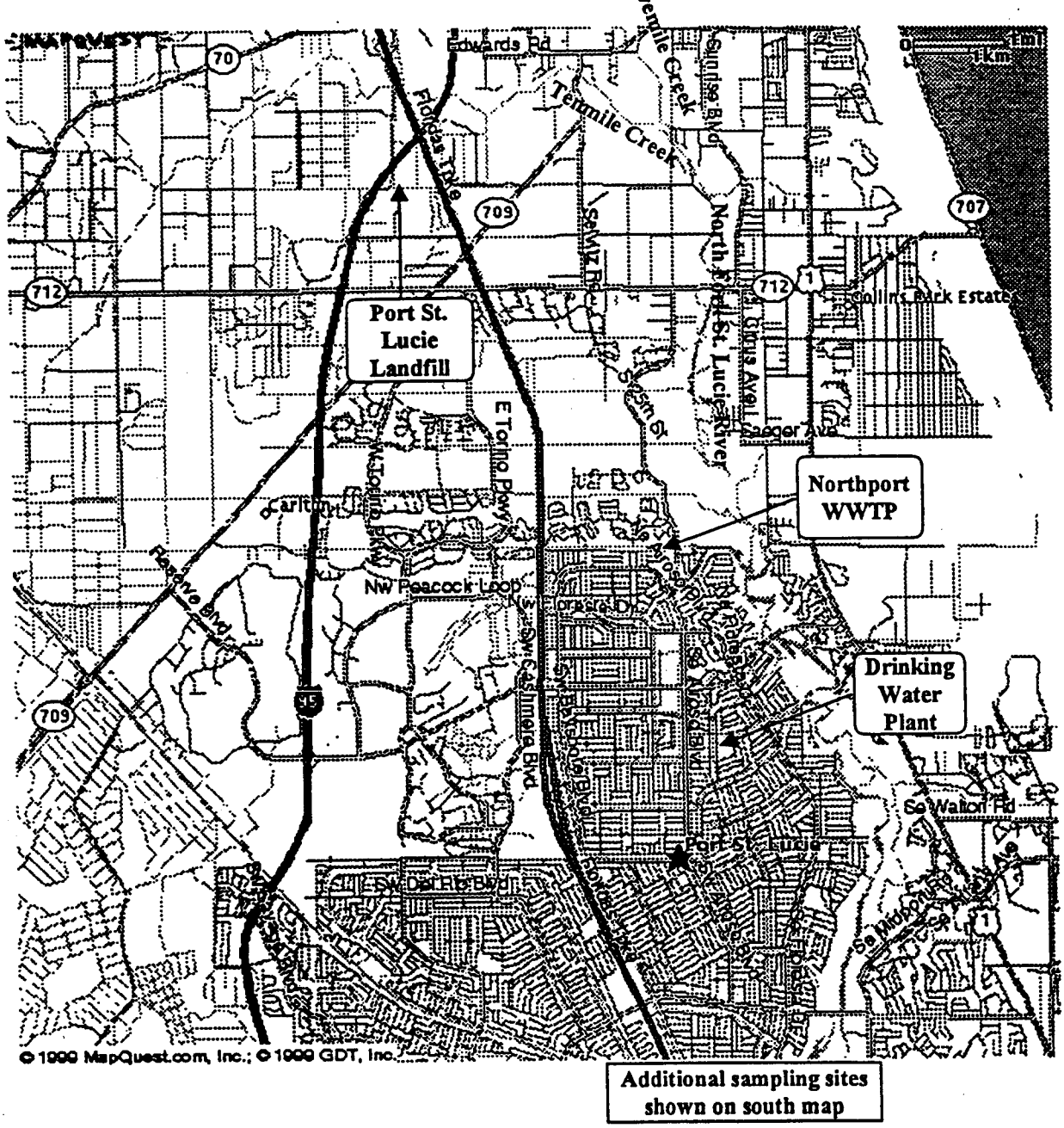
Analytical Results E00-2003 Port St. Lucie, FL Resampling (solids)

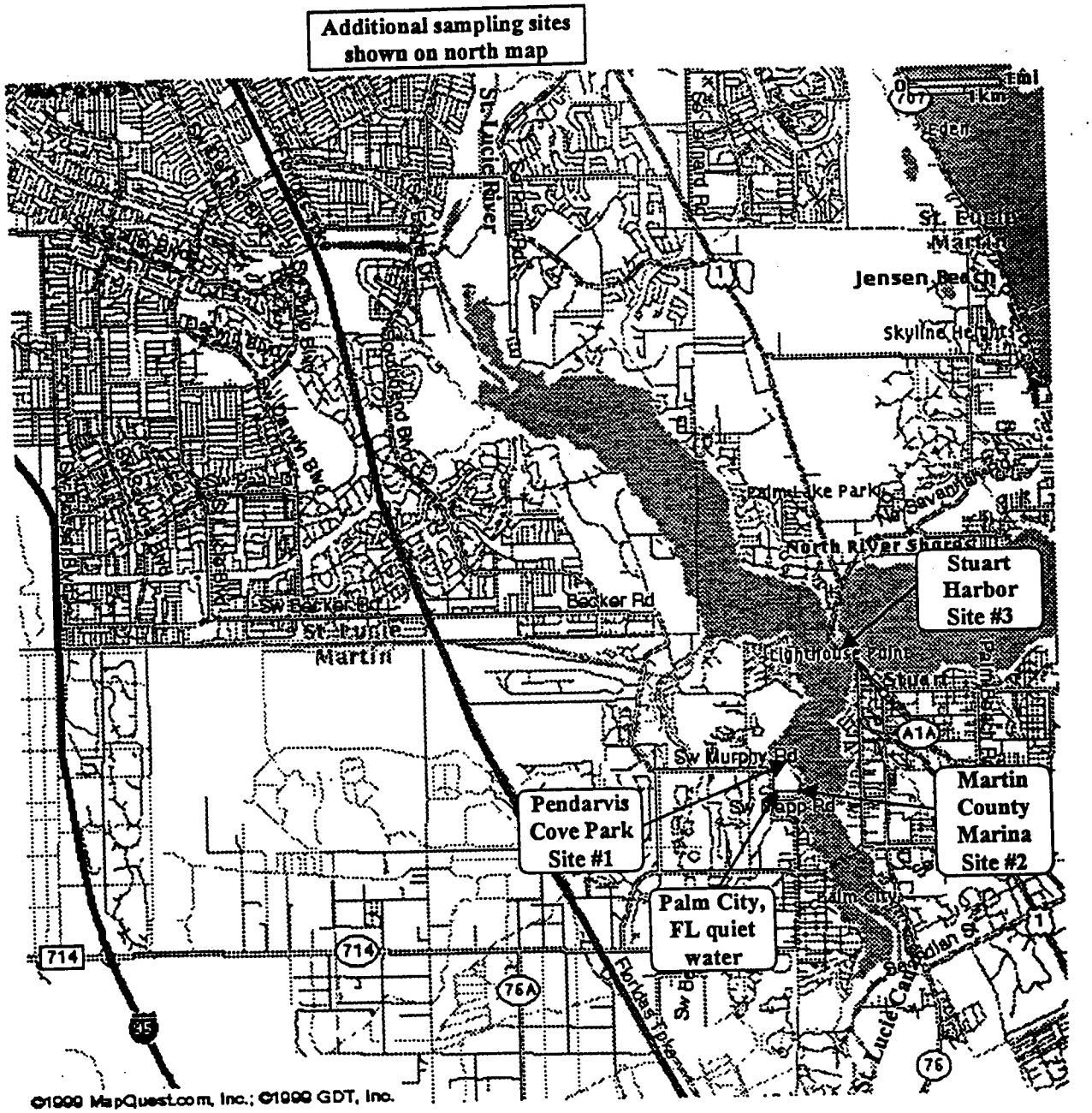
3M Sample Identification	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)
NPWWTP Sludge-C	1.36	< 0.200	< 0.200
NPWWTP Sludge-C dup	1.30	< 0.200	< 0.200
SED #3 SH-C	< 0.200	< 0.200	< 0.200
SED #3 SH-C dup	< 0.200	< 0.200	< 0.200
SED#1 Penpark-C	< 0.200	< 0.200	< 0.200
SED#1 Penpark-C dup	< 0.200	< 0.200	< 0.200
SED#2 MCM-C	< 0.200	< 0.200	< 0.200
SED#2 MCM-C dup	< 0.200	< 0.200	< 0.200

3M Sample Identification	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)
NPWWTP Sludge-C	62.9	< 9.3	< 9.3
NPWWTP Sludge-C dup	60.2	< 9.3	< 9.3
SED #3 SH-C	< 0.261	< 0.261	< 0.261
SED #3 SH-C dup	< 0.261	< 0.261	< 0.261
SED#1 Penpark-C	< 0.263	< 0.263	< 0.263
SED#1 Penpark-C dup	< 0.263	< 0.263	< 0.263
SED#2 MCM-C	< 0.304	< 0.304	< 0.304
SED#2 MCM-C dup	< 0.304	< 0.304	< 0.304

J - Compound is present, but below the reporting limit. The result is an estimated value.



Environmental Sampling Sites North of Port St. Lucie, FL



Environmental Sampling Sites South of Port St. Lucie, FL