AR 226-0671

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Analytical Report

Fluorochemical Characterization of Surface Water Samples

Cleveland, Tennessee (W1973)

Centre Analytical Laboratory Report No. 023-014A

Testing Laboratory

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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 Cleveland, Tennessee. 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	PFOA

The analytical method used here 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 A.

Sample MC-102H was not analyzed as per client request. (E-mail communication from Kris Hansen on 5/16/00).

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.

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 5/16/00 and analyzed by MS/MS on 5/18/00. Sample MC-108H was extracted on 5/22/00 and analyzed on 5/23/00. 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 C. All laboratory matrix spikes showed recoveries of all compounds between 70-130%.

Field spikes were prepared on sample MC-101H at a concentration of 100 ng/L using all compounds of interest. Field spike recoveries are also given in Attachment C. PFOSA showed low recovery in the field spike. All other compounds showed recoveries between 70-130%.

5.5 Duplicates

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

5.6 Laboratory Control Samples

Milliq water was spiked with all compound of interest at 25 and 250 ng/L. All recoveries for all compounds were between 70-130% in each LCS. Recoveries are given 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.

6 Data Summary

Please see Attachment B 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: Chain-of-Custody

8.2 Attachment B: Results.

8.3 Attachment C: Matrix Spike Recoveries (Field and Laboratory Spikes)

8.4 Attachment D: LC/MS/MS Raw Analytical Data

9 *Signatures*

John M Flaherty — 5/24/00

John M. Flaherty, Operations Manager — Date

24 May 2000

Kevin J Lloyd, Vice President — Date

Other Lab Members Contributing to Data

Enaksha Wickremesinhe
Karen Smith
David Bell

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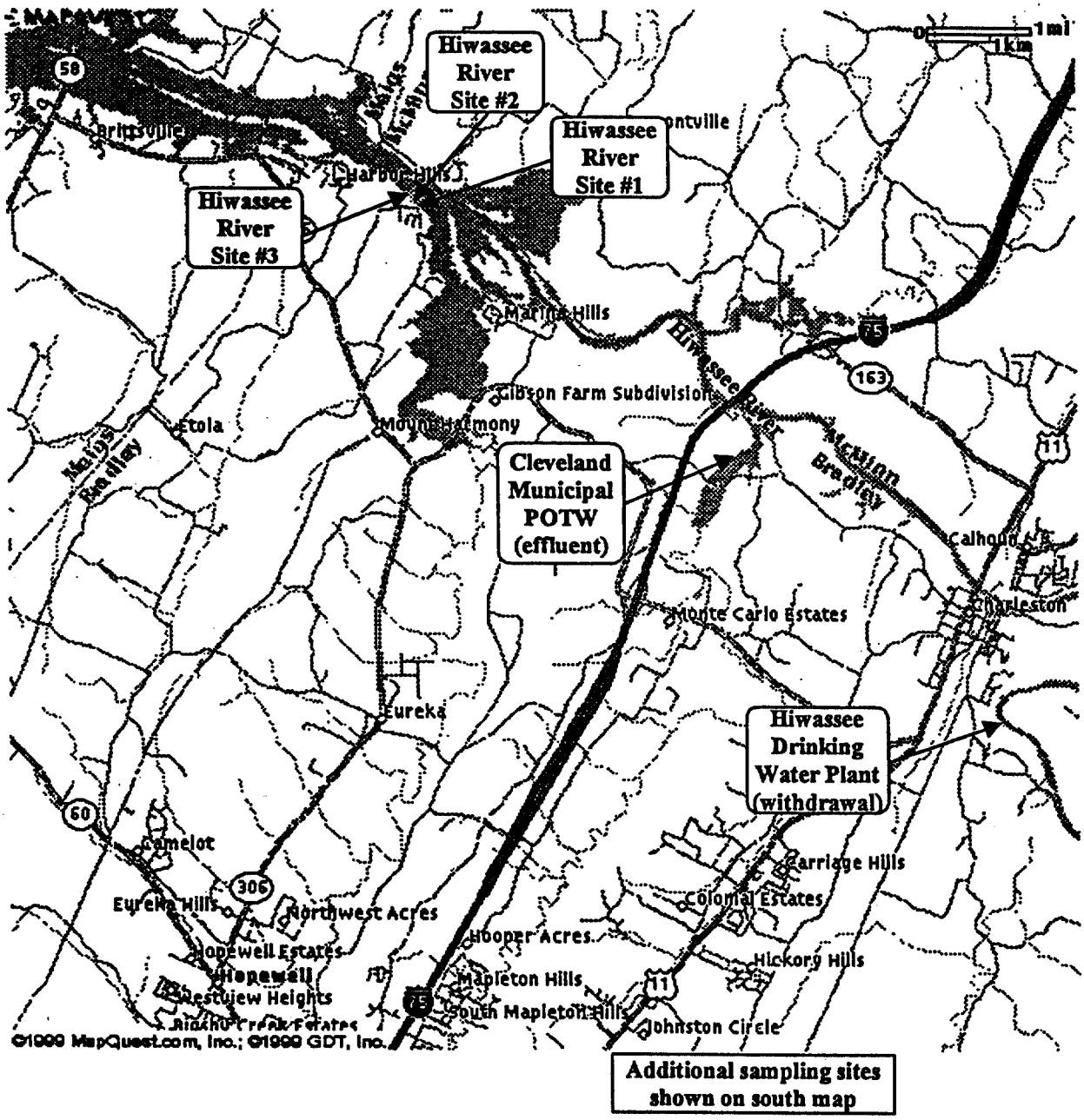
Analytical Results W1973 Cleveland, Tennesse

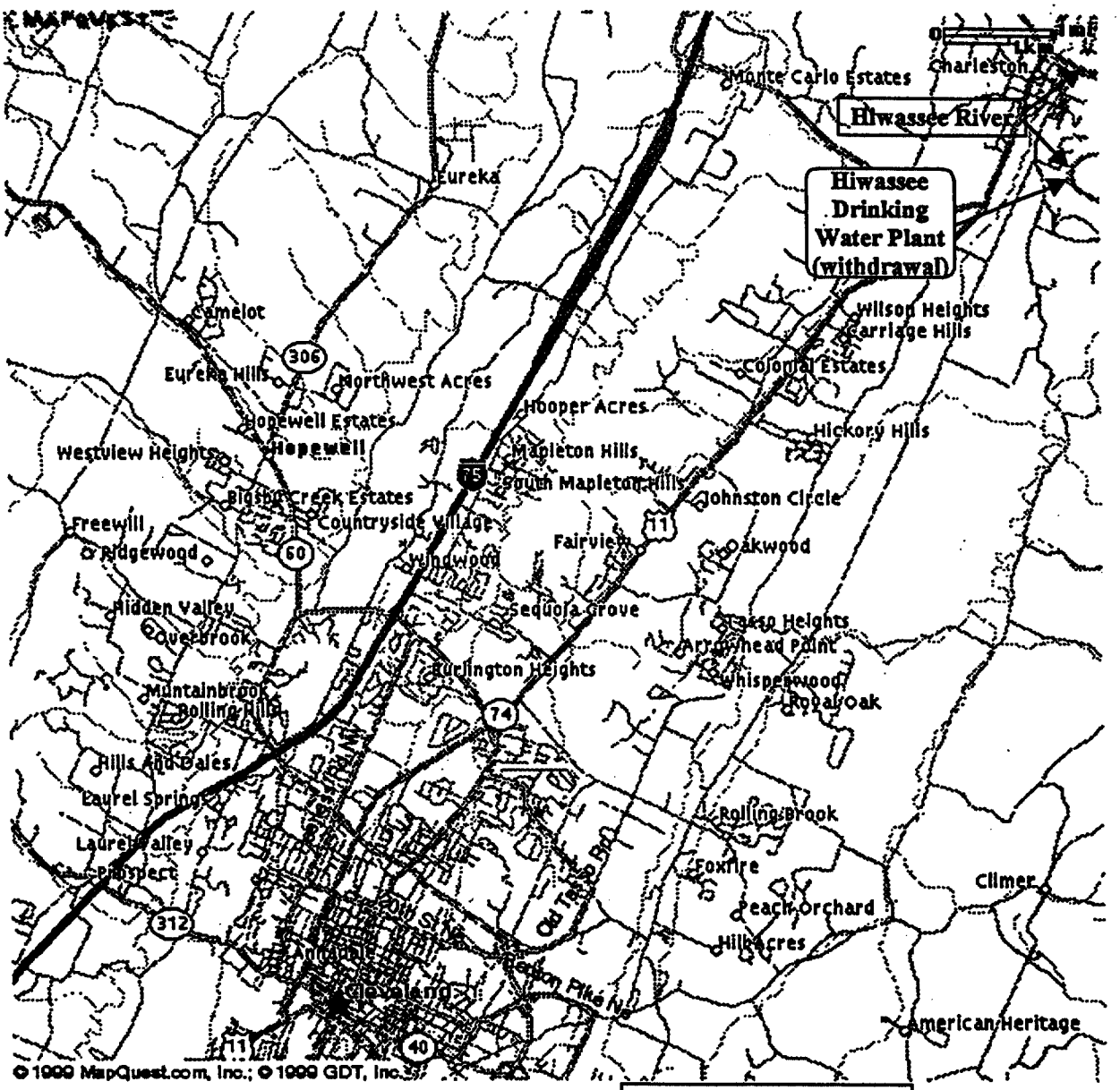
3M Sample Identification	Sample Description	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)
MC-101H	Site 1 P/N Surface Water	14.7 J	5.6 J	16.7 J
MC-103H	Site 1 P/N Surface Water Duplicate	< 25	< 25	< 25
MC-106H	Site 2 P/N Surface Water	< 25	< 25	< 25
NA	Site 2 P/N Surface Water Duplicate	< 25	< 25	< 25
MC-107H	Site 3 P/N Surface Water	< 25	< 25	< 25
NA	Site 3 P/N Surface Water Duplicate	< 25	< 25	< 25
MC-108H	Field Blank P/N Empty –	< 25	< 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.



Environmental Sampling Sites North of Cleveland, TN



Additional sampling sites shown on north map

Environmental Sampling Sites for Cleveland, TN