Centre Analytical Laboratories, Inc.
3048 Research Drive, State College PA 16801 · 814-231-8032 FAX 814-231-1253

**Analytical Results W2336 Columbus, GA**

| 3M Sample Identification | Sample Description | PFOS (ng/L) | PFOSA (ng/L) | POAA (ng/L) |
|---|---|---|---|---|
| MC-501H | Site 1 P/N Surface Water | 63.8 | 11.7 J | 26.1 |
| MC-503H | Site 1 P/N Surface Water Duplicate | 59.9 | 13.2 J | 25.6 |
| MC-506H | Site 2 P/N Surface Water | 76.6 | 16.5 J | 26.1 |
| NA | Site 2 P/N Surface Water Duplicate | 83.3 | 17.6 J | 26.7 |
| MC-507H | Site 3 P/N Surface Water | 55.4 | 12.0 J | 23.6 J |
| NA | Site 3 P/N Surface Water Duplicate | 55.4 | 14.9 J | 24.3 J |
| MC-508H | Field Blank-P/N Empty | < 25 | < 25 | < 25 |
| MC-584H | Quiet Surface Water | < 25 | < 25 | < 25 |
| NA | Quiet Surface Water Duplicate | < 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.

Centre Analytical Laboratories, Inc.
3048 Research Drive State College, PA 16801
Phone: (814) 231-8032 Fax: (814) 231-1253 or (814) 231-1580

# Analytical Report

## Fluorochemical Characterization of Surface Water Samples

## Columbus, GA (W2336)

## Centre Analytical Laboratory Report No. 023-014E

***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 J. 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 surface water samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. The samples were collected from Columbus, GA. 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 A.

## 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 5/18/00 and analyzed by MS/MS between 5/20/00 and 5/21/00. 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 compounds showed matrix spike recoveries between 70-130% in all samples.

Field spikes were prepared on sample MC-501H at a concentration of 100 ng/L using all compounds of interest. Field spike recoveries are also given in Attachment C. The field spike results showed low recovery for PFOSA. All other compounds showed matrix spike recoveries between 70-130%.

### 5.5 Duplicates

All 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. 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.

## *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, Manager-Operations Manager — Date

24 MAY 2000

Kevin J Lloyd, Vice President — Date

Other Lab Members Contributing to Data

**Enaksha Wickremesinhe**
**Karen Smith**
**David Bell**

# ENVIRONMENTAL MONITORING: SURFACE WATER MULTI-CITY STUDY

August 2000

As fully described in the May 4, 2000 submittal to EPA, the multi-city study was designed to obtain preliminary data about dispersion of fluorochemicals in the environment, uptake into foods, and presence in drinking water to understand the potential sources of human and environmental exposures that might result from this type of dispersion. The multi-city study paired a city having manufacturing or commercial use of fluorochemical products based on customer sales with a city that does not. Initially six cities, (three pairs) are being examined. The study may be expanded depending on further results.

Based on further review and analysis of information pertaining to manufacturing or commercial use of fluorochemicals, it has been learned that five of the six city locations fall into that category of supply locations. Thus, the six-city study program should be considered as a broad based environmental monitoring program only, without the ability to differentiate supply chain from non-supply chain cities.

The multi-city study will yield environmental distribution data as well as data on potential sources of human exposure. The cities were selected to represent urban locations with various levels of fluorochemical releases and various types of municipal water supplies. The samples to be obtained, where possible, include: urban air, surface water column and surface microlayer, sediment, river fish, drinking water intake, treated drinking water, tap water, the influent to and effluent from publicly-owned waste treatment works, sludge, and municipal landfill leachate. Additionally, a "market basket" of several food products will be sampled. These include: beef, pork, chicken, hot dogs, catfish, eggs, milk, bread, green beans, apples from grocery stores and, if possible, produce from local farmers' markets.

The May 4, 2000 data provided detail on the design and structure of the study and represents the first results from the multi-city study. Included in that submittal were reports on the quality assurance plan and field sampling procedures used and the results of the drinking water samples taken from the six cities. The results indicate that drinking water in four cities (Decatur, Alabama; Cleveland, Tennessee; Mobile, Alabama; and Port St. Lucie, Florida) did not contain detectable levels of fluorochemicals. Only two cities (Columbus, Georgia, and Pensacola, Florida) contained detectable levels of sulfonated fluorochemicals in the drinking water. See the May 4, 2000 submittal for more detail regarding these drinking water results. Included again in this submittal are the field reports for use in reviewing the surface water data.

Subsequent to the original submittal of information for the Multi-city study, additional analytical data has been obtained for various water column samples from the six cities. Samples were collected from surface water sources, both flowing

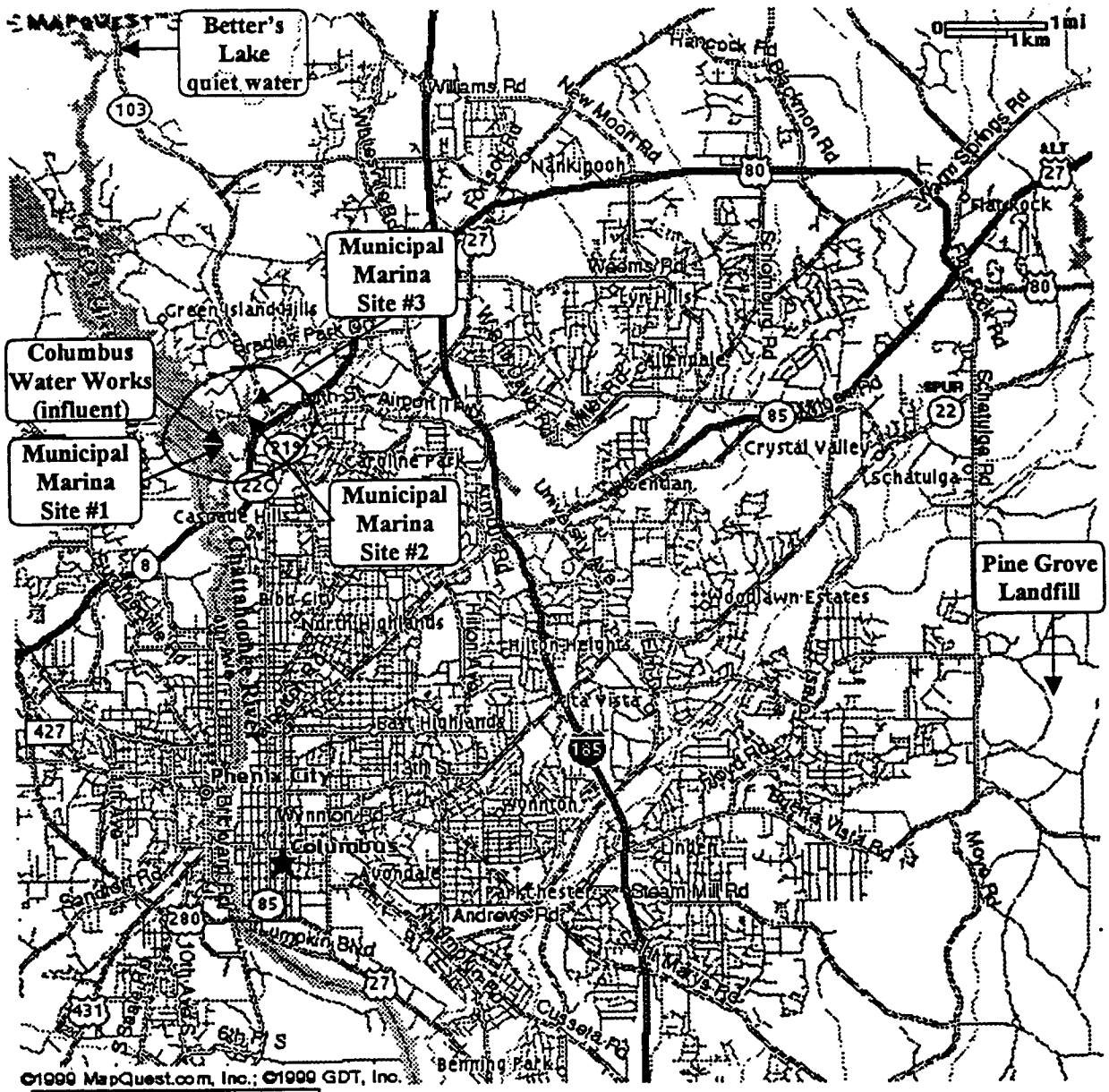
**streams and in areas of quiet water. Analyses were performed for PFOS, PFOA, and PFOSA. Maps of the sample locations and the data are presented in the attached data sheets.**

**In summary, the data indicates that in most samples of the water column in flowing streams, the level of PFOS was either below the detection limit of 25 ppt or at levels ranging from 25ppt to 83ppt. Analyses of samples collected from quiet waters in three cities, Mobile, Al, Decatur, Al, and Port St. Lucie Fl, showed the presence of PFOS in varying concentrations. There are two sets of data and reports for the quiet water samples in the Port St. Lucie location. The first set of data, May 2000, showed anomalous results. Thus, a second set of samples were collected and analyzed, and summarized in the report dated August 2000.**

**The analyses of samples of the quiet water for Mobile, Decatur, and Port St. Lucie showed levels of approximately 30ppt, 110ppt, and 2900ppt, respectively. In general, the levels found in all samples are well below the chronic No Observable Effect Level for PFOS in both fathead minnows, and daphnia magna, both of which have been determined to be 0.30 ppm. This would yield a safety factors of 100 to 10,000. It is unclear the reason for the finding in the Port St. Lucie quiet water samples, other than to note that the sample location indicated the presence of considerable manmade debris.**

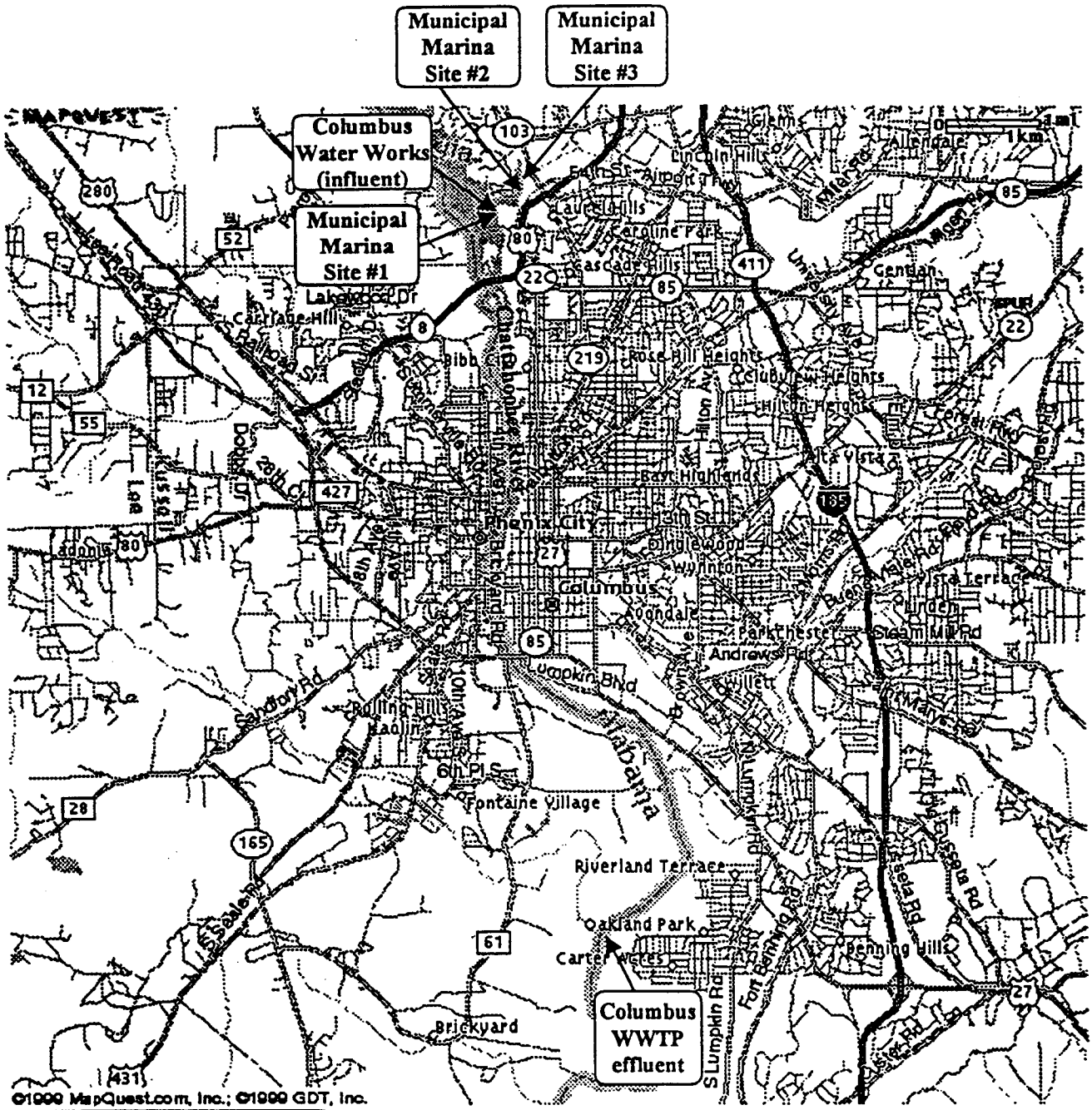
**The concentrations of the other analytes, PFOA and PFOSA, are very low, with most results at or below the levels of quantification of 25ppt. At three city locations, PFOA was found in levels less than 100ppt. There are no environmental effects expected at these levels.**

**The overall multi-city study is continuing. Samples of the leachate and publicly owned treatment works (POTW) plant influent and effluent are being analyzed. Validated analytical procedures have been developed recently for various food stuffs, and the market basket sampling program will commence shortly.**




Additional sampling sites shown on south map

# Environmental Sampling Sites N & E of Columbus, GA




# Environmental Sampling Sites for Columbus, GA