Subsurface Investigation Work Plan
Neutralized HF Tar (D1) Disposal Area
3M Cottage Grove Facility

Prepared for:

3M Environmental Technology and Services
Building 42-2E
900 Bush Avenue
St. Paul, MN

Prepared by:

Environmental Resource Group, LLC
1000 IDS Center
80 South Eighth Street
Minneapolis, MN 55402

October 17, 2002

SITE SETTING AND INVESTIGATION PURPOSE

As part of the routine evaluation of groundwater quality at production wells that serve the 3M Cottage Grove facility (facility), 3M determined that low levels of fluorocarbons (FC's) were present in facility groundwater. Studies confirmed that the FC's present in the groundwater were prevented from leaving the facility by the facility's production wells. Water derived from the production wells, after use at the facility, is then discharged to the facility's wastewater ponds and subsequently discharged through the NPDES permitted outfall[1].

As an outcome of the reporting of the FC's in the production wells by 3M to the MPCA, MPCA staff requested that 3M reevaluate the D1 area (site) to determine if the HF tars were contributing FCs to the groundwater at the facility. The following Data Quality Objectives (DQOs) and work plan was developed to meet this request.

The site is described in detail in the February 1986, *Final Remedial Investigation Report for the 3M Chemolite Center, Cottage Grove, Minnesota* (Weston). To paraphrase Weston, the site was used to neutralize hydrofluoric acid (HF) tars with lime by mixing tars with lime in a concrete lined pit. The neutralization operation was believed to have taken place in the mid 1960's to early 1970's, after which it was closed and covered with local fill materials.

The site is located in the southeastern corner of the facility. The site is generally flat, with steep drop-offs to the north towards an unnamed creek and to the south towards the Mississippi River (River). The unnamed creek to the north is an ephemeral stream that conveys treated effluent from the facility's wastewater treatment ponds to the River. Groundwater levels measured at nearby monitoring well MW-13 indicate that the groundwater table is at least 20 feet lower than the bed elevation of this ephemeral stream at a point upgradient of the site. Groundwater discharge to this stream is therefore unlikely. Periodic surface water flow in this stream likely results in little change to regional groundwater flow from north to south. Recharge from precipitation in the site area should move vertically to the water table and then to the River approximately 400 feet to the south. A radial flow pattern is unlikely.

Primary growth trees bound the site immediately adjacent to the north and east, and a dirt access road bounds the site immediately adjacent to the south.

Weston completed an evaluation of the site by depicting the limits of the subsurface pit by geophysical survey and collecting samples of the interred neutralized tars for leach test analysis. Based on these analyses Weston reported the wastes were nonhazardous. The MPCA approved closure of this site in 1987.

Site reconnaissance, response actions at the facility, and document research have determined that regional groundwater flows from north to south at the site toward base discharge into the River. Only where production wells alter groundwater flow patterns is this system altered. Groundwater studies at the site have indicated that the groundwater elevation measured at MW-13 has been on occasion lower then the pool elevation of the River. This implies that the production well system at the facility may influence groundwater flow near the D1 area. Studies have documented that groundwater is constrained from downward vertical flow by the

[1] 3M operates under an existing permit and submitted an NPDES Upgrade Permit Application (20100) to the MPCA on February 5, 2002.

underlying St. Lawrence Formation (StL). Groundwater, below the StL, has been documented as being confined below the facility, and wells finished below the StL have produced flowing artesian conditions at pool elevation of the River. The log of the monitoring well installed west of the site (MW-13) indicates that the area piezometeric surface is in the alluvium. Borings completed during the investigation of the adjacent D2 area have documented alluvial conditions to depth, rather then bedrock, indicating alluvial conditions are likely present beneath the D1 site. There is no potable water use in the area of the site and no wells are present between the site and the River. No springs are present along the base of the bluff adjacent to the River; therefore, groundwater discharge from the area around the site enters the pool of the River by diffuse seepage.

PROJECT DATA QUALITY OBJECTIVES AND REQUIREMENTS

The following work plan is developed utilizing the seven step DQO process cited in the MPCA documents entitled *Draft Guidelines Risk Based Site Characterization and Sampling Guidance (1996) and Data Quality Objectives Memorandum (1998).*

1. Statement of Problem:

   a. Planning Team

3M Project Manager	Mark Gaetz
3M Engineer	Todd Fasking
ERG Hydrogeologist	Paul Book
ERG Samplers	Paul Book and Dan Comeau
3M Lab Manager	Mark Ellefson

   b. Decision Maker

      3M Corporate Programs Project Team

   c. Statement of Problem

      To determine if FC's are present in groundwater at the D1 site.

   d. Resource restrictions

      - Laboratory cost of a single FC analysis is approximately $1,000.
      - Terrain, grade and depth to groundwater limits groundwater sampling to installation of groundwater monitoring wells.

2. Identification of the Decision

   a. Study Question

      Are FC's present in groundwater above acceptable risk levels at the D1 site.

b. Action

Collect groundwater samples in the area of the D1 site.

c. Decision Statement

Determine if FC's are present in the D1 site groundwater above acceptable risk levels.

d. Decision Sequence

- Monitor site water quality for FC's
- If detected, meet with MPCA to evaluate if concentrations are above acceptable risk levels
- If not detected, close site

3. Inputs to the Decision

a. Variables

- Groundwater FC chemistry
- Site lithology

b. Information Source(s)

- Prior site work by Weston
- FC surface water effluent standards, if any, approved by the MPCA
- Site data collection

c. Action Level

Confirmation of the presence of FCs in groundwater at monitoring wells installed at D1 will require 3M to contact MPCA staff to discuss the results.

No further action will be taken if the total FC concentration in site groundwater is lower then analytical detection limits or lower then effluent standards developed by the MPCA for FCs.

d. Analytical Methods

Laboratory FC analysis will be by 3M's analytical laboratory or by a 3M contract laboratory. Laboratory analytical protocols are outlined in Appendix A; the same laboratory protocols will be followed by 3M's analytical laboratory and by 3M's contract laboratory.

Field sampling protocols are outlined in Appendix B.

4. Definition of Study Boundaries and Work Plan Elements

a. Boundaries

- Data collection is limited to the immediate area of D1 and by sampling of groundwater at the water table.
- The downgradient and southern boundary of the site is the surface water pool of the River.
- The upgradient boundary is the unnamed ephemeral stream north of the site
- There are no temporal boundaries

b. Sampling Population

- Sample collection will be limited to groundwater at the water table.

c. Sampling Collection Period

- ERG will collect a single round of groundwater samples no sooner than 7 days after well development and again approximately 4-6 weeks later. There are no anticipated temporal constraints.

d. Sampling Location

- Sample collection will be limited to groundwater collected from a monitoring well located between the site and the River and a monitoring well located between the site and the unnamed ephemeral stream. The monitoring wells will be screened to monitor water table conditions.

e. Sampling Constraints

- None anticipated

5. Development of a Decision Rule

a. Statistical parameter

- The maximum concentration of total FC's in groundwater collected during each sampling round will be determined. The concentration of individual FC compounds will be quantified and reported.

b. Action Level

- Actions will be discussed with the MPCA if FC compounds are detected in groundwater.

c. Decision Rule

- The presence of FCs in groundwater at the site monitoring wells will require contacting the MPCA to discuss the results.
- If the FC concentration exceeds any effluent standards approved by the MPCA or the analytical detection limit, whichever is higher, 3M may install an additional well at the site and sample it for FCs based on the outcome of discussions with the MPCA.

- 3M will then discuss the results of the additional sampling with the MPCA upon receipt of the data.
- If the groundwater FC concentrations are lower then their respective analytical detection limits or the MPCA approved effluent standard, whichever is higher, 3M will take no further action.
-

6. Error Limits

Error tolerance on the proposed action level is +/- 10% and is based upon 2 rounds of sampling from the monitoring well.

7. Work Plan Design

- There are no anticipated specific gravity/solubility concerns with the FC's. The study is limited to water table monitoring.

- Monitoring well installation and future well abandonment will be in accordance with Minnesota Rule 4725.1830. A contractor licensed by the State of Minnesota will install the wells. Any water used for drilling purposes will utilize potable water brought to the site.

- All borings will be advanced through the unconsolidated glacial deposits at the site using conventional 7.25-inch outer diameter hollow-stem auger (HSA) drilling methods. Continuous split spoon samples of the upper 10 feet of unconsolidated materials in the well borings will be screened with a PID for worker health and safety. Split-spoon samples will be collected at approximate 10-foot intervals over the remainder of the borings. ERG will field screen using a portable photo-ionization detector (PID) calibrated at 100 parts per million (ppm) with isobutylene and equipped with a 10.6 electron volt lamp to determine soil volatile organic vapor concentrations. ERG will observe the soil samples for obvious indications of potential impact such as staining or chemical odors. Soil descriptions, field observations and screening results will be recorded on ERG field logs.

- The HSA borings will be advanced to the water table, where a 2-inch-diameter low carbon steel casing and 10-foot stainless steel screen will be set. The well screen will be set to intersect the apparent water table surface. The casing annulus will be sealed using bentonite slurry set with a tremmie line.

- After the monitoring wells are completed, the contractor will develop the wells. Development water will be containerized and transported to the site wastewater treatment plant for disposal.

- All down hole equipment will be properly cleaned prior to its arrival on-site. Equipment will be decontaminated between borings using a jet spray or brush and water containing Alconox soap and rinsing with deionized water.

- After the water level in the new wells are recovered completely, static water levels will be measured and the wells will be purged of at least three well volumes. Stabilization tests will be performed to document stable readings for pH, specific conductivity and temperature.

- Groundwater samples will be obtained from the wells using a new, disposable, double check-valve polyethylene bailer positioned to obtain samples from the aquifer formation. The samples will be submitted for laboratory analyses of FC's.
- Groundwater samples will be transported to the laboratory under appropriate chain-of-custody procedures.
- Each well's location will be verified by ERG using GPS and/or surveying to locally established benchmarks.
- The results of the environmental assessment will be presented in a written report to the MPCA. The report will include field methodologies and analytical results, will compare the analytical results to the proposed action limit and will discuss the implications of any confirmed environmental impacts and may include recommendations for additional site work, if appropriate.

APPENDIX A
Laboratory Testing Protocols

3M ENVIRONMENTAL LABORATORY

METHOD

DETERMINATION OF PERFLUOROOCTANE SULFONATE (PFOS), PERFLUOROOCTANE SULFONYLAMIDE (PFOSA), AND PERFLUOROOCTANOATE (POAA) IN WATER BY LIQUID-SOLID EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (HPLC/MS/MS)

Method Number: ETS-8-154.0 **Adoption Date:** 04/28/2000

Revision Date:

Author: Kristen J. Hansen/Harold O. Johnson

Approved By: William K. Reagen, Kent R. Lindstrom

William K. Reagen, Laboratory Management — Date 4/28/00

Kristen J. Hansen, Ph.D., Group Leader — Date 04/28/00

Kent R. Lindstrom, Technical Reviewer — Date 04/28/00

1.0 SCOPE AND APPLICATION

1.1 This method provides collection, extraction, and analytical procedures for the determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane Sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in groundwater, surface water, and drinking water samples.

1.2 This method was prepared according to the EPA document, "Guidelines and Format for Methods to be Proposed at 40 CFR Part 136 or Part 141" (see Reference 18.1), and is based in part on the report "Method of Analysis for the Determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in Water" (see Reference 18.2).

2.0 SUMMARY OF METHOD

2.1 Water samples are collected from a site of interest and shipped cold to an analytical facility. PFOS, PFOSA, and POAA are extracted from 40mL water samples using C_{18} solid phase extraction (SPE) cartridges. The compounds are eluted from the C_{18} cartridge, using methanol. Separation, identification, and measurement are accomplished by high-performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS) analysis using multiple response monitoring (MRM).

The concentration of each identified component is measured by comparing the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by the same compound in an extracted calibration standard (external standard).

3.0 DEFINITIONS

3.1 **Analytical Sample**—A portion of an extracted Laboratory sample prepared for analysis.

3.2 **Calibration Standard**—A solution prepared from the Working Standard (WS) and extracted according to this method. The calibration standard solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Duplicate Sample (DS)**—A separate aliquot of a sample, taken in the analytical laboratory and analyzed separately with identical procedures. Analysis of DSs compared to that of the first aliquot give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 **Field Blank Control Sample (FB)**—Type I water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FB is to determine if test substances or other interferences are present in the field environment.

3.5 **Field Duplicate (FD)**—A sample collected in duplicate at the same time as the sample and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of FD compared to that of the first sample gives a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.6 **Field Matrix Spike (FMS)**—A sample collected in duplicate to which known quantities of the target analytes are added in the field at the time of sample collection. The FMS should be spiked at approximately 50–150% of the expected analyte concentration in the sample. The FMS is analyzed to ascertain if any matrix effects, interferences, or stability issues may complicate the interpretation of the sample analysis.

3.7 **Field Spike Control Sample (FSCS)**—An aliquot of type I water to which known quantities of the target analytes are added in the field at the time of sample collection (at an appropriate concentration to be determined by the project lead). The FSCS is extracted and analyzed exactly like a sample to determine whether a loss of analyte could be attributed to sample storage and/or shipment.

3.8 **Laboratory Control Sample (LCS)**—An aliquot of type I water to which known quantities of the target analytes are added in the laboratory. Two levels are included, one at the LOQ (approx. 25Pg/mL), the other at a concentration of approx. 100–250Pg/mL or another concentration to be determined by the project lead. The LCS is extracted and analyzed exactly like a laboratory sample to determine whether the methodology is in control, and whether the laboratory is capable of making accurate measurements at the required method detection limit and higher.

3.9 **Laboratory Sample**—A portion of a sample received from the field for testing.

3.10 **Limit of Detection (LOD)**—The lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The LOD can be determined in several ways, including signal-to-ñoise ratio and statistical calculations.

3.11 **Limit of Quantitation (LOQ)**—The lowest concentration (LLOQ) or highest concentration (ULOQ) that can be reliably achieved within the specified limits of precision and accuracy during routine operating conditions.

Note: The LLOQ is generally 5–10 times the LOD. For many analytes, the LLOQ analyte concentration is selected as the lowest non-zero standard in the calibration curve. However, it may be nominally chosen within these stated guidelines to simplify data reporting. Sample LLOQs are matrix-dependent.

3.12 **Matrix Spike (MS)**—An aliquot of a sample, to which known quantities of target analytes are added in the laboratory. The MS is extracted and analyzed exactly like a laboratory sample to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations.

3.13 **Method Blank**—An aliquot of type I water that is treated exactly like a laboratory sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other laboratory samples. The method blank is used to determine if test substances or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.14 **Method Detection Limit (MDL) Determination**—One of several processes that may be used to establish a LOD value. The statistically calculated minimum amount of an analyte that can be measured with 99% confidence that the reported value is greater than zero. This term is usually associated with the EPA definition in 40 CFR Part 136 Appendix B.

3.15 **Sample**—A sample is a small portion collected from a larger quantity of material intended to represent the original source material.

3.16 **Spiking Stock Standard (SSS)**—A solution prepared from stock standards used to prepare the working standard.

3.17 **Stock Standard (SS)**—A concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound.

3.18 **Working Standard (WS)**—A solution of several analytes prepared in the laboratory from SSs and diluted as needed to prepare calibration standards and other required analyte solutions.

4.0 WARNINGS AND CAUTIONS

4.1 Health and Safety Warnings

4.1.1 The acute and chronic toxicity of the standards for this method have not been precisely determined; however, each should be treated as a potential health hazard.

4.1.2 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

4.1.3 The laboratory is responsible for maintaining a safe work environment and a current awareness of local regulations regarding the handling of the chemicals used in this method. A reference file of material safety data sheets (MSDS) should be available to all personnel involved in these analyses.

5.0 INTERFERENCES

5.1 During extraction and analysis, major potential contaminant sources are reagents and liquid-solid extraction devices.

5.2 All materials used in the analyses shall be demonstrated to be free from interferences under conditions of analysis by running method blanks.

5.3 Teflon® containing materials (e.g. caps, wash bottles) contain fluorocompounds which may cause interferences and should not be used during collection, storage, extraction, or analysis of the samples.

6.0 EQUIPMENT, SUPPLIES, AND MATERIALS

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Sampling Equipment

6.1.1 Sample collection bottles—LDPE (e.g., Nalgene™) narrow-mouth bottles with screw cap.

Note: Do not use Teflon bottles or Teflon lined caps.

6.1.2 Coolers for sample shipment.

6.1.3 Ice for sample shipment.

6.1.4 Bottles must be lot-certified to be free of artifacts by running Method blanks according to this method.

6.2 Laboratory Equipment (Extraction and Analytical)

6.2.1 Balance, analytical (display at least 0.0001g), Mettler.

6.2.2 Vacuum pump, Büchi.

6.2.3 Visiprep vacuum manifold, Supelco.

6.2.4 Sep Pak Vac 6cc (1g) tC_{18} cartridges (part # WAT 036795),Waters.

6.2.5 50mL disposable polypropylene centrifuge tubes, VWR.

6.2.6 15mL disposable polypropylene centrifuge tubes, VWR.

6.2.7 Disposable micropipettes (50–100µL, 100–200µL), Drummond.

6.2.8 Class A pipettes and volumetric flasks, various.

6.2.9 Hypercarb drop-in guard column (4mm) (part # 844017–400), Keystone.

6.2.10 Stand-alone drop-in guard cartridge holder, Keystone.

6.2.11 125mL LDPE narrow-mouth bottles, Nalgene.

6.2.12 HPLC pump (LC10AD), Shimadzu.

6.2.13 2mL clear HPLC vial kit (cat # 5181–3400), Hewlett Packard.

6.2.14 Standard lab equipment (graduated cylinders, disposable tubes, etc.), various.

6.2.15 LC/MS/MS and HPLC systems, as described in section 10.1.

6.3 Equipment Notes

6.3.1 In order to avoid contamination, the use of disposable labware is highly recommended (tubes, pipettes, etc.).

6.3.2 Teflon or Teflon-lined containers or equipment, including Teflon-lined HPLC vials or caps for the HPLC auto sampler must **not** be used.

6.3.3 Type I water used during the sample and standard extraction should be filtered through a Hypercarb guard column using a HPLC pump. This water is referred to as "filtered type I water", hereafter in this report.

6.3.4 It is necessary to check the solvents (methanol) for the presence of contaminants (especially POAA) by LC/MS/MS prior to use. Certain lot numbers have been found to be unsuitable for use.

6.3.5 Use disposable micropipettes or pipettes to aliquot standard solutions to make calibration standards and matrix spikes.

7.0 REAGENTS AND STANDARDS

Note: Suppliers and catalog numbers are for illustrative purposes only. Equivalent performance may be achieved using chemicals obtained from other suppliers. Do not use a lesser grade of chemical than those listed.

7.1 Chemicals

7.1.1 Methanol (MeOH), HPLC grade, JT Baker, Catalog No. JT9093–2.

7.1.2 Ammonium Acetate, Reagent grade, Sigma-Aldrich, Catalog No. A–7330.

7.1.3 Water, type I, prepared in-house.

7.1.4 Sodium Thiosulfate, Reagent grade, JT Baker.

7.2 Standards

7.2.1 Potassium perfluorooctane sulfonate (see Attachment A, Figure 1).

7.2.2 Perfluorooctane sulfonylamide (see Attachment A, Figure 2).

7.2.3 Ammonium perfluorooctanoate (see Attachment A, Figure 3).

7.3 Reagent Preparation

7.3.1 **250mg/mL sodium thiosulfate solution (Extraction)**—Dissolve 25g of sodium thiosulfate in 100mL reagent water.

7.3.2 **40% methanol (Extraction)**—Measure 400mL methanol and adjust the volume to 1.0L with reagent water.

7.3.3 **100mM ammonium acetate solution (Analysis)**—Weigh 7.71g of ammonium acetate and dissolve in 1.0L of reagent water. Dilute the 100mM solution by a factor of 50 to make the 2mM ammonium acetate solution used for mobile phase A.

Note: Alternative volumes may be prepared as long as the ratios of the solvent to solute ratios are maintained.

7.4 Spiking Stock Standard (SSS) Preparation

7.4.1 **100µg/mL each PFOS, PFOSA, and POAA SSSs**—Weigh out 10mg of analytical standard (corrected for percent salt and purity—i.e., 10 mg $C_8F_{17}SO_3K$ purity 90% = 8.35mg $C_8F_{17}SO_3$–) and dilute to 100mL with methanol in a 100mL volumetric flask. Transfer to a 125mL LDPE bottle. Prepare a **separate** solution for each analyte. Store solutions in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.4.2 **1µg/mL mixed SSS**—Add 1.0mL each of the 100µg/mL SSSs (from 7.4.1) to a 100mL volumetric flask and bring up to volume with methanol.

7.4.3 **0.1µg/mL mixed SSS**—Add 10.0mL of the 1.0µg/mL-mixed solution (from 7.4.2) to a 100mL volumetric flask and bring up to volume with methanol.

7.4.4 **0.01µg/mL mixed SSS**—Add 10.0mL of the 0.1µg/mL-mixed solution (from 7.4.3) to a 100mL volumetric flask and bring up to volume with methanol.

7.4.5 **Storage Conditions**—Store all SSSs in a refrigerator in 125mL LDPE bottles at 4°±2°C for a maximum period of 3 months from the date of preparation.

7.5 Calibration Standards

7.5.1 **100µg/mL each PFOS, PFOSA, and POAA stock standard solutions**—Weigh out 10mg of analytical standard (corrected for percent salt and purity) and dilute to 100mL with methanol in a 100mL volumetric flask. Transfer to a 125mL LDPE bottle. Prepare a **separate** solution for each analyte. Store solutions in a refrigerator at 4°±2°C for a maximum period of 6 months from the date of preparation.

7.5.2 **1µg/mL Working Standard**—Add 1.0mL each of the 100µg/mL SS solutions (from 7.5.1) to a 100mL volumetric flask and bring up to volume with methanol.

7.5.3 **0.1µg/mL Working Standard** —Add 10.0mL of the 1.0µg/mL mixed solution (from 7.5.2) to a 100mL volumetric flask and bring up to volume with methanol.

7.5.4 **0.01µg/mL Working Standard** —Add 10.0mL of the 0.1µg/mL mixed solution (from 7.5.3) to a 100mL volumetric flask and bring up to volume with methanol.

7.5.5 **Storage Conditions**—Store all WSs in a refrigerator (in 125mL LDPE bottles) at 4°±2°C for a maximum period of 3 months from the date of preparation.

7.5.6 **Calibration Standard**—Prepare a minimum of five calibration solutions in filtered type I water according to the following table:

Concentration of WS, µg/mL	Volume of WS, µL	Final Calibration Standard Volume, mL	Final Concentration of Calibration Standard, Pg/mL
0.0	0	40	0
0.010	100	40	25
0.010	200	40	50
0.010	400	40	100
0.10	100	40	250
0.10	200	40	500
0.10	300	40	750[1]
0.10	400	40	1000[2]

1 May be prepared to extend the range beyond 500Pg/mL.
2 May be prepared to extend the range beyond 750Pg/mL.

Note: The absolute volumes of the standards may be varied by the analyst as long as the correct proportions of solute to solvent are maintained.

7.5.7 The standards are processed through the extraction procedure (Section 9.0), identical to the laboratory samples. The extracted concentration of the calibration standard is equal to 8X the initial concentration, due to the concentration of the standard during the extraction process.

7.5.8 **Storage Conditions**—Store all extracted calibration standards in 15mL polypropylene tubes at 4°±2°C, for a maximum period of two weeks from the date of preparation.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

Note: Sampling equipment, including automatic samplers, must be free of Teflon tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated polypropylene sample containers if possible. Sample bottles should not be rinsed before sample collection.

8.1 **Tap Water**—Open the tap and allow the system to flush until the water temperature (15°±10°C) has stabilized (usually about two minutes). Adjust the flow to about 500mL/min and collect samples from the flowing stream.

8.2 **Ground Water**—Purge the well of standing water using a pump or a bailer. Collect the sample directly from the pump or from the bailer.

8.3 **Surface Water**—When sampling from an open body of water, fill the sample container with water from a representative area.

8.4 **Sample Dechlorination**—All samples should be iced or refrigerated at 4°±2°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced by adding 200µL of a 250mg/mL sodium thiosulfate solution to each water sample, FB, and FSCS (which may be placed in each bottle before leaving for the sampling site.).

8.5 **Holding Time (HT)**— Results of the time/storage study of all target analytes showed that the three compounds are stable for 14 days in water samples when the samples are dechlorinated and stored as described in section 8.4 (see also reference 18.3). Therefore, laboratory samples must be extracted within 14 days and the extracts analyzed within 30 days of sample collection. If the HT exceeds 14 days, great care is used when evaluating field spikes to avoid misrepresentation of the sample concentration.

8.6 **Field Blanks**

8.6.1 Process a Field Blank Control Sample (FB) along with each sample set (samples collected from the same general sample site at approximately the same time). At the laboratory, prior to sample collection, fill a sample container with filtered type I water, seal, and ship the FB to the sampling site along with the empty sample containers. Return the FB to the laboratory with the filled sample bottles.

8.6.2 When sodium thiosulfate is added to samples, use the same procedure to preserve the FB.

8.7 **Field Duplicates**

8.7.1 Collect a Field Duplicate (FD) for every ten (10) samples collected or per each sampling set, if less than 10 samples are collected.

8.7.2 Separate FDs must be collected for each type of water sample (ground, tap, etc.) collected.

8.7.3 Collect the FD immediately after the sample.

8.7.4 Preserve, store and ship FD using the same procedures as used for the samples.

8.8 Field Spike Control Sample (FSCS)

8.8.1 A Field Spike Control Sample (FSCS) must be prepared for each sample shipment. If multiple coolers are used to ship a set of samples, each cooler must contain a FSCS.

8.8.2 At the laboratory, fill a sample container with 100mL of type I water. Seal and ship to the sampling site along with the empty sample containers and FBs.

8.8.3 When sodium thiosulfate is added to samples, use the same procedure to add the same amounts to the FSCS.

8.8.4 Seal and gently invert the FSCS to mix. Store and ship the FSCS using the same procedures as used for the samples.

9.0 EXTRACTION PROCEDURE

9.1 Extraction Scheme

9.1.1 Allow samples to equilibrate to room temperature. Thoroughly mix samples by gently inverting the sample bottle.

9.1.2 Measure 40mL of sample into 50mL polypropylene centrifuge tubes (Spike the QC and Matrix spikes as required*, replace lid and mix well).

Note: * Samples may need to be prescreened to determine an appropriate matrix spike level (typically 50–150% of sample concentration).

9.1.3 Condition the C_{18} SPE cartridges (1g, 6mL) by passing 10mL methanol followed by 5mL filtered type I water (~2drop/sec). Do not let column run dry.

Note: For the following steps, maintain a ~1drop/sec flow rate. Do not allow the column to run dry at any time.

9.1.4 Load the analytical sample onto the C_{18} SPE cartridge. Discard eluate.

9.1.5 Wash with ~5mL 40% methanol in water. Discard eluate.

9.1.6 Elute with ~5mL 100% methanol. Collect 5mL of eluate into graduated 15mL polypropylene centrifuge tubes. This is the target elution fraction (final volume = 5mL).

9.1.7 Analyze a portion of the target elution fraction eluent using negative electrospray HPLC/MS/MS (Section 10.2).

Note: Samples are concentrated by a factor of eight during the extraction; Initial Vol = 40mL → Final Vol. = 5mL.

9.1.8 Samples are stable at room temperature for at least 24 hours. Analytical samples may be stored in a refrigerator at 4°±2°C until analysis.

9.1.9 **Standardization of C_{18} SPE columns**—If poor recoveries are observed, it may be necessary to standardize the C_{18} SPE columns in the following manner before analyzing samples.

9.1.9.1 Use a standard with an analyte concentration between 1000 and 4000 Pg/mL. Follow the extraction scheme as outlined from steps 9.1.1 to 9.1.6, except, collect the eluate fraction separately (approx. 5mL), as well as the target elution fraction.

9.1.9.2 After step 9.1.6, collect a post-elution fraction by, eluting with an additional 5mL of 100% methanol.

9.1.9.3 Analyze all three fractions by HPLC/MS/MS. If the target fraction contains a minimum of 85% of the respective analytes, it may be considered acceptable.

9.1.9.4 If the wash contains significant standard (>15%), either the wash volume or percentage of MeOH should be decreased.

9.1.9.5 If the post-elution fraction contains significant standard (>15%), the target elution volume should be increased.

10.0 CALIBRATION AND STANDARDIZATION (ANALYTICAL SETUP)

Note: Other instruments may be used and the equipment and conditions may be very different as long as the method criteria are met. The operator must optimize and document the equipment and settings used.

10.1 Establish the LC/MS/MS system and operating conditions equivalent to the following:

Mass Spec: Micromass Quattro Ultima (Micromass)
Interface: Electrospray (Micromass)
Mode: Electrospray Negative, Multiple Response Monitoring (MRM)
Harvard infusion pump (Harvard Instruments), for tuning
Computer: COMPAQ Professional Workstation AP200
Software: Windows NT, MassLynx 3.3
HPLC: Hewlett Packard (HP) Series 1100
HP Quat Pump
HP Vacuum Degasser
HP Autosampler
HP Column Oven

Note: A 4 × 10mm Hypercarb drop-in guard cartridge (Keystone, part # 844017–400) is attached on-line after the purge valve and before the sample injector port to trap any residue contaminants that may be in the mobile phase and/or HPLC system.

HPLC Column: Genesis C_8 (Jones Chromatography), 2.1mm x 50mm, 4µm
Column Temperature: 35°C
Injection Volume: 15µL
Mobile Phase (A): 2mM Ammonium Acetate in filtered type I water (See 7.3.1)
Mobile Phase (B): Methanol

HPLC Gradient Program:

Time, min	Percent Mobile Phase A	Percent Mobile Phase B	Flow Rate, mL/min
0.0	60	40	0.3
0.4	60	40	0.3
1.0	10	90	0.3
7.0	10	90	0.3
7.5	0	100	0.3
9.0	0	100	0.4
9.5	60	40	0.4
13.5	60	40	0.4
14.0	60	40	0.3

Note: Other HPLC gradients may be used as long as the method criteria are met.

It may be necessary to adjust the HPLC gradient in order to optimize instrument performance. Columns with different dimensions (e.g. 2.1mm x 30mm) and columns from different manufacturers (Keystone Betasil C_{18} etc.) may be used.

Ions Monitored:

Analyte	Primary Ion	Product Ion	Approximate Retention Time
POAA	413.0	169.0	5.0
PFOS	499.0	99.0	5.2
PFOSA	498.0	78.0	5.8

Other product ions may be chosen at the discretion of the analyst, although m/z 99 is suggested for PFOS. Use of the suggested primary ion is recommended. Retention times may vary slightly, on a day-to-day basis, depending on the batch of mobile phase etc. Drift in retention times is acceptable within an analytical run, as long as the drift continues through the entire analysis and the standards are interspersed throughout the analytical run.

10.2 Tune File Parameters

10.2.1 The following values are provided as an example. Actual values may vary from instrument to instrument. Also, these values may be changed from time to time in order to optimize for greatest sensitivity.

Analyte	Dwell, sec	Collision Energy, eV	Cone, V
POAA	0.2–0.4	10–25	20–30
PFOS	0.2–0.4	30–60	50–80
PFOSA	0.2–0.4	20–50	30–60

Source	Set
Capillary	2.56–3.5kV
Hexapole 1	0.5V
Aperture 1	0.2V
Hexapole 2	0.8V
Source Block Temp.	100–150°C
Desolvation Temp.	250–400°C

Analyzer	Set
LM Res 1	12.0–15.0V
HM Res 1	12.0–15.0V
IEnergy 1	0.7V
Entrance	–2V
Exit	1V
LM Res 2	11.0V
HM Res 2	11.0V
IEnergy 2	1.0V
Multiplier	650V

Gas Flows	Set
Cone Gas	150L/hr
Desolvation	700L/hr

Pressures	Set
Gas Cell	3.0e–3mbar

11.0 ANALYTICAL QUALITY CONTROL

11.1 Analytical results of the FB, FMS, FD, and FSCS should be evaluated at the conclusion of the study to help interpret the data quality of samples data. Analytical results for these control/duplicate samples must be reported with the sample data.

12.0 ANALYTICAL PROCEDURE

12.1 Sample Analysis

12.1.1 Set up analysis sample queue.

12.1.2 Inject the same aliquot (between 5–25µL) of each standard, analytical sample, recovery, control etc. into the LC/MS/MS system.

12.1.3 All samples showing a response for one or more analytes above the response of the highest, active calibration curve level must be diluted and reanalyzed.

12.2 Calibration Curve

12.2.1 Starting with the standard of lowest concentration, inject the same size aliquot (between 10–25µL) of each extracted calibration standard according to Section 12.1 and tabulate the response (peak height or area) versus the concentration in the standard. Use linear standard curves for quantitation generated for each analyte by linear regression with 1/x weighting of peak area versus calibration standard concentration. The correlation coefficient (r) for the calibration curves must be ≥0.990 (r^2≥0.980). If calibration results fall outside these limits, then appropriate steps must be taken to adjust instrument operation and the standards reanalyzed.

12.2.2 **Curve**—The measured value for each curve point must be within ± 30% of theoretical values when curve is evaluated over a range appropriate to the data. High or low points may be deactivated to achieve these criteria, but an acceptable curve must contain at least five active curve points.

12.2.3 **Continuing Curve Verification (CCV)**—Mid- and low-level calibration checks should be analyzed every 5–10 injections. The analyte level measured in the CCVs should be within ± 30% of theoretical values. If CCVs fall outside of this range, data collected subsequent to the last passing CCV should not be used. Only data collected between acceptable CCVs or the initial curve can be used.

13.0 DATA ANALYSIS AND CALCULATIONS

13.1 Calculate the analytical sample (extract) concentration from the standard curve using the following equation:

$$\text{Extract Concentration, pg/mL} = \frac{(\text{Peak area} - \text{intercept})}{(\text{slope})}$$

13.2 Calculate the percent recovery of the FSCS using the following equation:

$$\text{FSCS \% rec.} = \frac{(\text{FSCS conc., Pg/mL})}{(\text{Conc. added, Pg/mL})} \times 100$$

13.3 Calculate the percent recovery of the MSs using the following equation:

$$\text{MS\% rec.} = \frac{(\text{MS conc., Pg/mL} - \text{Sample Conc., Pg/mL})}{(\text{Conc. added, Pg/mL})} \times 100$$

14.0 METHOD PERFORMANCE PARAMETERS

Note: Any method performance parameters that are not achieved must be considered in the evaluation of the data. Nonconformance to any specified parameters must be described and discussed in any reporting of the data.

14.1 Linearity—Linear standard curves for quantitation generated for each analyte by linear regression with 1/x weighting of peak area versus calibration standard concentration. The correlation coefficient (r) for the calibration curves must be ≥0.990 (r^2≥0.980).

14.2 Calibration Curve Standards—The measured value for each curve point must be within ± 30% of theoretical values when curve is evaluated over a range appropriate to the data. High or low points may be deactivated to achieve these criteria, but an acceptable curve must contain at least five active curve points.

14.3 CCV Performance—Mid and low level calibration checks to be analyzed every 5–10 injections. The analyte level measured in the CCVs should be within ± 30% of theoretical values. If CCVs fall outside of this range, data collected subsequent to the last passing CCV should not be used. Only data collected between acceptable CCVs can be used.

14.4 Limit of Detection (LOD)—The lowest calibration standard with a peak area at least 2X the peak area of the extraction blank that can be measured at a concentration greater than zero.

14.5 Limits of Quantitation (LOQ)—The lower LOQ (LLOQ) is the lowest non-zero active standard in the calibration curve; the peak area of the LLOQ must be at least 2X that of the extraction blank. By definition, the measured value of the LLOQ must be within 30% of the theoretical value.

14.6 Matrix Spikes—Matrix spike percent recoveries must be within ± 30% of the spiked concentration.

14.7 Solvent Blanks, Method Blanks, and Matrix Blanks—Values must be below the lowest non-zero active standard in the calibration curve. Matrix blanks are considered compliant if no test substance is detected above the LOD for that analyte.

14.8 Reproducibility—Reproducibility of the method is defined by the results of the matrix spikes and matrix spike duplicates. The MS/MSD should be reproducible to within 20%.

14.9 Use of Confirmatory Methods—None

14.10 Demonstration of Specificity—Specificity is demonstrated by chromatographic retention time (within 3% of standard) and the mass spectral response of unique product ions generated from a characteristic primary ion.

14.11 Documentation

14.11.1 If criteria listed in this method performance section are not met, maintenance may be performed on the system and samples reanalyzed, or other actions taken as determined by the analyst. Document all actions in the appropriate logbook.

14.11.2 If data are to be reported when performance criteria have not been met, the data must be footnoted on tables and discussed in the text of the report.

15.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 Sample extract waste and flammable solvent is discarded in high BTU containers, and glass pipette waste is discarded in broken glass containers located in the laboratory.

16.0 RECORDS

16.1 Each page generated for a study must have the following information included, either in the header or hand-written on the page: study or project number, acquisition method, integration method, sample name, extraction date, dilution factor (if applicable), and analyst.

16.2 Print the tune page, sample list, and acquisition method from MassLynx to include in the appropriate study folder. Copy these pages and tape into the instrument run log.

16.3 Plot the calibration curves as described in this method, then print these graphs and store in the study folder.

16.4 Print data integration summary, integration method, and chromatograms, from MassLynx, and store in the study folder.

16.5 Summarize data using suitable software (MS Excel 97) and store in the study folder.

16.6 Back up electronic data to appropriate medium. Record in study notebook the file name and location of backup electronic data.

17.0 ATTACHMENTS

17.1 **Attachment A:** Figures—Fluorochemical Compounds

18.0 REFERENCES

18.1 "Guidelines and Format for Methods to be Proposed at 40 CFR Part 136 or Part 141", U.S. Environmental Protection Agency, Office of Science and Technology Office of Water, Washington, D.C. Draft 1996.

18.2 "Method of Analysis for the Determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in Water", E. Wickremesinhe and J. Flaherty, Study Number 023–002, Centre Analytical Laboratories, Inc., State College, Pennsylvania, January 2000.

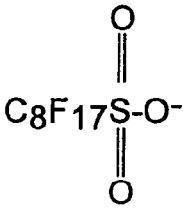
18.3 Validation report for the "Method of Analysis for the Determination of Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonylamide (PFOSA), and Perfluorooctanoate (POAA) in Water", E. Wickremesinhe and J. Flaherty, Study Number 023–002, Centre Analytical Laboratories, Inc., State College, Pennsylvania, (Approval pending)

19.0 REVISIONS

Revision Number.	Reason For Revision	Revision Date

Figure 1: PFOS

Chemical Name = Perfluorooctane sulfonate
Molecular ion = 499 ($C_8F_{17}SO_3^-$)

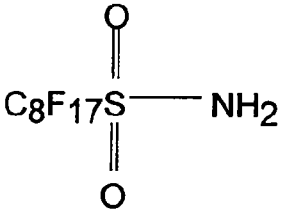


PFOS

Note: Standards are made from the salt, potassium perfluorooctane sulfonate [$C_8F_{17}SO_3K$], m/w 538.

Figure 2: PFOSA

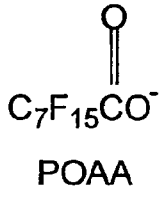
Chemical Name = Perfluorooctane sulfonylamide
Molecular ion = 498 ($C_8F_{17}SO_2NH_2$)



PFOSA

Figure 3: POAA

Chemical Name = Perfluorooctanoate
Molecular ion = 413 ($C_7F_{15}COO^-$)



POAA

Note: Standards are made from the salt, ammonium perfluorooctanoate [$C_7F_{15}COONH_4$], m/w 431

APPENDIX B
Field Sampling Protocols

WATER SAMPLING INSTRUCTIONS

SAMPLING PROCEDURES IN SECTION 6.2

1.0 SCOPE AND APPLICATION

1.1 This document describes the procedure to use when collecting water samples in the field for laboratory analysis. Prior to the shipment of field samples, refer to ETS-4-3.0, "Use of Chain of Custody," for sample documentation requirements.

2.0 DEFINITIONS

2.1 **Sample:** A sample that is maintained *as is* after it is collected and identified by sample number, location, collection date, identity, and amount (Also *sample duplicate*).

2.2 **Field Spike:** A field sample spiked with a known concentration of a specific analyte.

2.3 **Sample Log:** A log that accompanies each sample shipment and includes information on the sample identity, location, collection date, amount, and the volume and concentration of spike solution used to prepare *field spikes*.

2.4 **Low-level Field Spike:** A sample spiked with a known concentration of the specified analytes at the low end of the method calibration range prescribed in the analytical method being used to quantitate the target analytes.

2.5 **Mid-level Field Spike:** A sample spiked with a known concentration of the specified analytes at the mid point of the method calibration range prescribed in the analytical method being used to quantitate the target analytes.

2.6 **Field Spike Control Sample:** A clean water sample, prepared from a clean water source known not to contain the target analytes and spiked with a known concentration of the specified analytes.

2.7 **Field Blank Control Sample:** A clean water sample, prepared from a clean water source known not to contain the target analytes.

3.0 PRECAUTIONS

3.1 Field personnel are responsible for taking precautions that are proper for the site and sample.

4.0 RESPONSIBILITIES

4.1 Field personnel are responsible for insuring accurate sampling procedures are used when collecting, spiking and shipping the samples.

5.0 EQUIPMENT

5.1 Polypropylene labware and sample bottles.

6.0 PROCEDURES

6.1 Pre-rinsing of Sample Bottles

6.1.1 Pre-rinsed sample bottles will be supplied by 3M Environmental Laboratory before each sampling event. The sample bottles will be rinsed according to the following procedure.

6.1.1.1 Add approximately 10mL of HPLC grade methanol to empty bottle, cap and shake for ~20 seconds. Empty the bottle into waste container and repeat once with methanol and twice with Type 1 water.

6.1.1.2 Invert rinsed bottles and caps on clean Teri-wipes and allow to dry.

6.2 Field Collection of Water Samples

6.2.1 Sample Collection: Four (4) homogeneous samples from each sampling location will be collected.

6.2.1.1 As accurately as possible, make certain each sample is homogeneous and representative of the source being sampled.

6.2.1.2 Pre-rinsed 250 mL polypropylene sample bottles will be provided by the Environmental Laboratory. As accurately as possible, fill each bottle to the mark indicating the 200 mL level.

6.2.1.3 Field Blank Control Samples: Four (4) sample bottles containing 200 mL of HPLC grade water will be included with the empty sample bottles. Two (2) of these pre-filled sample bottles will be left *as is* and will be referred to as *field blank control samples*. The *field blank control samples* will be kept with the filled sample bottles and returned to the laboratory along with the filled sample bottles.

6.2.1.4 Immediately after filling, each sample bottle will be sealed and clearly labeled with the sample number, sample location, collection date, sample identity, sample amount, volume and where appropriate, the concentration of spike solution used to prepare the *field spike* samples.

6.2.1.5 Low-level Field Spike: Using one of the Environmental Laboratory-supplied disposable pipettes, one (1) of the four (4) samples from each sampling location will be spiked with one (1) mL of a methanol solution containing 0.2 micrograms/mL of each of the target analytes. This sample will be labeled as the *low-level field spike*. Do not reuse the pipette.

6.2.1.6 Mid-level Field Spike: Using one of the laboratory supplied disposable pipettes, one (1) of the four (4) samples from each sampling location will be spiked with one (1) mL of a methanol solution containing 20 micrograms/mL of each of the target analytes. This sample will be labeled as the *mid-level field spike*. Do not reuse the pipette.

6.2.1.7 **Sample/ Sample Duplicate:** Two (2) of the four (4) samples from each sampling location will be maintained *as is* and will be identified as the *sample* and *sample duplicate*.

6.2.1.8 **Field Spike Control Samples**: Two (2) of the pre-filled sample bottles will be used to prepare *field spike control samples*. After sampling the first well, and preparing *the low-level field spike*, One (1) of the pre-filled sample bottles will be spiked with one (1) mL of a methanol solution containing 0.2 micrograms/mL of each of the target analytes. This sample will be identified as *low-level field spike control sample.* Do not reuse the pipette.

After sampling the last well, and preparing *the low-level field spike*, One (1) of the pre-filled sample bottles will be spiked with one (1) mL of a methanol solution containing 20 micrograms/mL of each of the target analytes. This sample will be identified as *mid-level field spike control sample.* Do not reuse the pipette.

6.2.2 **Sample Identification:** All sample bottles will be sealed and properly labeled for shipping to the laboratory.

6.2.3 **Sample Log:** A *sample log* will accompany each shipment of samples. The *sample log* will include information on the sample identity, sample location, collection date, sample amount, and the volume and concentration of spike solution used to prepare the *field spikes* along with other relevant information.

ENVIRONMENTAL RESOURCE GROUP

1000 IDS Center 80 South Eighth Street Minneapolis, MN 55402
phone 612.339.4750 fax 612.339.4990