EM-14

Quality Assurance Project Plan

for

Empirical Human Exposure Assessment
Multi-City Study Sampling Task

To
(Confidential)

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Prepared by

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1. PROJECT NAME

Empirical Human Exposure Assessment
Multi-City Sampling Task

2. REQUESTED BY

Confidential

3. DATE OF REQUEST

January 1999

4. DATE OF INITIATION

February 15, 1999

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7. PROJECT DESCRIPTION

7.1 Background

In the 1950's, surfactants and bath additives based upon perfluorooctyl sulfonyl fluoride (POSF) began limited introduction. Diversification of the POSF-based chemistry in the 1960's and 1970's led to the discovery and introduction of numerous N-methyl or N-ethyl perfluorooctyl sulfonamido ethyl alcohol-based (FOSE) chemicals. The FOSE-based fluorochemicals (FC) were incorporated into textiles, food packaging, and carpets to impart specific properties related to stain, moisture, and fat resistance. Although the number, chemical diversity, and range of applications of FC are quite extensive, all formulations share some similarities. All formulations have trace levels of several impurities in common: perfluorooctane sulfonate (PFOS), N-ethyl (or N-methyl) perfluorooctane sulfonamide (N-EtFOSA), and N-ethyl (or N-methyl) perfluorooctane sulfonamidoethyl alcohol (N-EtFOSE alcohol). In addition, the results of current metabolism studies suggest that all formulation FCs undergo some limited degradation to PFOS, N-EtFOSAmide (or N-MeFOSAmide) and N-EtFOSE alcohol (or N-MeFOSE alcohol) in humans and in the environment, via microbial and/or enzymatic mechanisms.

Recent chemical analyses of pooled human blood samples and selected analyses of biota samples from diverse regions of the United States have shown a general consistency in the detection rate and detected levels of PFOS therein. Because PFOS is unique to FCs, PFOS may be distributed in the greater environment as a result of the use and disposition of products containing FCs. Though limited, the data suggest that increasing levels of PFOS in human blood parallel the introduction and volume/use of FCs. It is unknown whether the PFOS in human blood is due to FC exposures in the residence from the use of products, or to the slow bioaccumulation of FC in the food web due to widespread dispersion of FCs through multiple sources.

Several hypotheses are considered to understand the life cycle of FCs in the environment.

- Dispersion of FC from sources results in long range transport via air and water.
- Effluent discharges, industrial spills, urban surface runoff and fire-fighting foam contribute FCs to surface water bodies. FCs in surface water can affect all aspects of the human diet: local drinking water and fish, and all agricultural products that rely indirectly on that water (meat and dairy, fruits/vegetables, and grains).
- Leachates from solid wastes percolate into groundwater and ultimately contribute FCs to some drinking water sources, surface water and eventually fish.
- Direct air deposition of FCs to food chain constituents and air deposition of FCs to surface waters contributes FCs to human food commodities.
- The FC levels in and around cities associated with FC production and use will be higher than the levels in and around cities where there is only general population use of such products.

7.2 Objectives

This project provides the foundation for all subsequent exposure assessment studies that the client will need to conduct. The initial focus will be the assessment, development and/or validation of analytical methods for representative FC in environmental media. This task will also assemble baseline information about the distribution of FC in selected media that represent environmental dispersion from a source and bioaccumulation in the human food chain.

The objective of the sampling task is to collect representative samples for trace-level analysis of FC residuals (Table 1) to assess sources, dispersion in the environment and human exposure via the food chain. Samples will be collected from 12 cities: major FC production facilities or FC-users are present in

the six "study" cities (Table 2), and the six "control" cities are matched to the "study" cities by general geographic location, population, and type of water supply for drinking water.

Table 1. FC Residuals for Analysis

Polar anions	Moderately polar neutrals
PFOS	
PFOSAA	N-EtFOSE Amide/ N-MeFOSE Amide
M-556	N-EtFOSE Alcohol/ N-MeFOSE Alcohol
PFOSA	N-EtFOSE Chloride/ N-MeFOSE Chloride
POAA	N-EtFOSEA/ N-MeFOSEA

Table 2. Study and Control Cities for Baseline Study

Group[1]	Water Source	Study or Control	City	State	1990 Census Population
High	Ground	Study	Pensacola	FL	58,165
		Control	Port St. Lucie	FL	55,866
Middle	Ground	Study	Kaukauna	WI	11,982
		Control	Englewood	OH	11,432
High 1	Surface	Study	Dalton	GA	21,761
		Control	Greeneville	TN	13,532
High 2	Surface	Study	Decatur	AL	48,761
		Control	Cleveland	TN	30,354
Middle 1	Surface	Study	Mobile	AL	196,278
		Control	Columbus	GA	178,681
Middle 2	Surface	Study	Spartansburg	SC	43,467
		Control	Bowling Green	KY	40,641

[1]Defined by the ratio of FC production or useage:population

7.3 Technical Approach

This quality assurance project plan (QAPP) (Revision 0) is intended to comply with the requirements for Good Laboratory Practice (GLP) protocols defined in 40 CFR Part 792 *Toxic Substances Control Act (TSCA); Good Laboratory Practice Standards; Final Rule* (July 1, 1998) to the extent possible at this point in the program.

The types of samples, sample volumes (or weights) and sampling devices are summarized in Table 3. The total numbers of samples of each type, collected at each site, are listed in Table 4. This listing provides an indication of the type of sample analysis intended for that sample with analysis being either analysis for the polar anions (P), the moderately polar neutrals (N), or Total PFOS. This table also indicates the number of samples that will be collected of each type and/or at each location to provide necessary field and lab QC samples. The QC samples are outlined specifically in Table 5, and the level of

Table 3. Sample Types, Sampling Devices, and Sample Volumes

Sample type	Sampling Device	Volume or Amount collected per sample
Drinking Water		
Surface Water source (3 locations ~ 500 ft apart)	Sample bottle[a]	1 L from each location; bulk water, not surface
Sediment from surface water source (3 locations, match w/ water sample)	Grab sampler or scoop	200 g from top 2 cm
Plant intake	Sample bottle	1 L
Treated water from plant	Sample bottle	1 L
Tap water from retail establishment (from 3 locations in city)	Sample bottle	1 L
Microlayer from surface water[b]	Sample plate	1 L
Water from groundwater source[b]	Sample bottle	1 L
Publicly-Owned Treatment Works (POTW)		
Post-chlorination influent (if available)	Sample bottle	1 L
Sludge	Scoop	200 g
Effluent	Sample bottle	1 L
Landfill		
Leachate	Sample bottle	1 L
Urban Air		
Particulates (glass fiber filter)	General Metal Works Model PS-1 air sampler	12 h at 250 L/min
Vapor (polyurethane foam cartridge)		12 h at 250 L/min
Local Food Supply		
Ground beef (3 stores)	Store packaging	1 lb
Pork chops with bone (3 stores)	Store packaging	1 lb (~ 2 chops)
Boneless, skinless chicken breast (3 stores)	Store packaging	1 lb (1 whole breast)
Pork-and-beef hot dogs (3 stores)	Store packaging	1 lb (1 package)
Regional fish (3 stores)	Store packaging	1 lb (filleted)
Eggs (3 stores)	Store packaging	6 large
Whole milk in plastic or cardboard container (3 stores)	Store packaging	1 qt
White bread (3 stores)	Store packaging	1 loaf
Frozen green beans in plastic bag (3 stores)	Store packaging	1 pkg
Fresh apples (3 stores)	Store packaging	1 lb (at least 2 apples)
Organic bread or flour (1 store)	Store packaging	1 lb or 1 loaf
Fish		
Finfish (electroshock) from surface water source (above)	Smith-Root Type VII backpack shocker	3 fish

(a) Sample bottles will be ESE precleaned, certified polyethylene bottles
(b) Not planned for Multi-City Study

Table 4. Sample Types and Numbers at Sampling Locations at Each City

Matrix	Analysis for Site 1 Sample	Sample Volume			Analysis for Sites 2&3 Samples
		Site 1	Site 2	Site 3	
Surface Water (one water body)	Sample: P&N residuals (P & N)	1 L	1 L	1 L	P & N
	Sample: Total PFOS (in duplicate)	1 L			
	Field duplicate & laboratory duplicate: P	1 L			
	Field spike: P&N	1 L			
	Laboratory spike: P&N	1 L			
	Field Blank: P & N				
	Field Blank: Total PFOS				
Sediment	Samples and laboratory QC (no field spike): P & N; Total PFOS	200 g	200 g	200 g	P&N; Total PFOS
	Field Blank: P & N				
	Field Blank: Total PFOS				
Drinking water (plant influent)	Sample: P&N	1 L			
	Sample: Total PFOS (in duplicate)	1 L			
	Field duplicate & laboratory duplicate: P	1 L			
	Field spike: P&N	1 L			
	Laboratory spike: P&N	1 L			
	Field Blank: P & N				
Drinking water (plant outflow)	Sample: P&N	1 L			
	Sample: Total PFOS (in duplicate)	1 L			
	Field duplicate &laboratory duplicate: P	1 L			
	Field spike: P&N	1 L			
	Laboratory spike: P&N	1 L			
Tap water (retail outlet)	Sample: P&N	1 L	1 L	1 L	P & N
	Sample: Total PFOS (in duplicate)	1 L			
	Field duplicate & laboratory duplicate: P	1 L			
	Field spike: P&N	1 L			
	Laboratory spike: P&N	1 L			
	Field Blank: P & N				
Landfill leachate	Samples and laboratory QC (no field spikes): P & N; Total PFOS	1 L			
	Field Blank: P & N				
POTW influent	Sample and laboratory duplicate: P & N	1 L			
	Sample: Total PFOS (in duplicate)	1 L			
POTW sludge	Samples and laboratory QC (no field spikes): P & N; Total PFOS	200 g			
	Field Blank: P & N				
POTW effluent	Sample and laboratory duplicate: P&N	1 L			
	Sample: Total PFOS (in duplicate) Field duplicate: P & N	1 L			
	Field spike: P & N	1 L			
	Laboratory spike: P & N	1 L			
	Field Blank: P & N				
Urban air	Sample: P&N	Filter/PUF			
	Field spike- no air	Filter/PUF			
	Field Blank: P & N	Filter/PUF			
Food	Samples and laboratory QC (no field blanks/field spikes): P & N; Total PFOS	All	All	All	P&N; Total PFOS
Finfish	Sample and laboratory QC				
Organic flour	Samples and laboratory QC (no field blank/field spike): P & N; Total PFOS	1 lb			
Trip Blank	MilliQ water: P & N	1 L			
Trip Blank	MilliQ water: Total PFOS	1 L			

P= polars: PFOS, POAA, PFOSA, PFOSAA, M556; N= neutrals: Et/Me of FOSE-OH, FOSE-Cl, FOSE-Amide

Table 5. QC Samples by Matrix

Matrix and Analysis Type	Field Sites	Field Rep	Lab Reps	Spikes		Field Blank	Field Spike Conc.
				Field	Lab		
Surface Water							
P & N	3	1	(1)[a]	1	1	1	100 ng/L
Total PFOS	1	0	(1)	0	0	1	
Sediment							
P & N	3	0	(3)[b]	0	(1)	1	
Total PFOS	(3)	0	(3)	0	(1)	1	
Drinking Water (influent)							
P & N	1	1	(1)	1	1	1	100 ng/L
Total PFOS	1	0	(1)	0	0	0	
Drinking Water (outflow)							
P & N	1	1	(1)	1	1	0	100 ng/L
Total PFOS	1	0	(1)	0	0	0	
Tap Water							
P & N	3	1	(1)	1	1	1	100 ng/L
Total PFOS	1	0	(1)	0	0	0	
Landfill Leachate							
P & N	1	0	(3)	0	(1)	1	
Total PFOS	(1)	0	(3)	0	(1)	0	
POTW (influent)							
P & N	1	0	(1)	0	0	0	
Total PFOS	1	0	(1)	0	0	0	
POTW sludge							
P & N	1	0	(3)	0	(1)	1	
Total PFOS	(1)	0	(3)	0	(1)	0	
POTW (effluent)							
P & N	1	(1)	(1)	1	1	1	1000 ng/L
Total PFOS	1	0	(1)	0	0	0	
Urban Air							
P & N	1	0	0	1	0	1	Filter: 100 ng PFOS & POAA PUF: 100 ng Et- & -Me-FOSE-OH
Total PFOS	0	0	0	0	0	0	
Food (including finfish)							
P & N	3[c]	0	(1)[d]	0	(1)	0	
Total PFOS	(3)[c]	0	(1)[d]	0	(1)	0	

[a]Numbers in parentheses indicate samples that will be created from splits or aliquots in the laboratory.
[b]Triplicate analysis of one sediment sample.
[c]Organic flour at one site, only.
[d]Duplicate analysis of the fish samples.
P= polars: PFOS, POAA, PFOSA, PFOSAA, M556; N= neutrals: Et/Me of FOSE-OH, FOSE-Cl, FOSE-Amide

each field QC spike addition is listed also. SOPs are listed in Table 6, and the methods are summarized in this QAPP. The analytical QAPP will be provided under separate cover.

Table 6. Standard Operating Procedures

SOP Title	SOP No.
Collection and Handling of Air Samples for the Multi-Cities Project	M3-F-1
Collection and Handling of Water Samples for the Multi-Cities Project	M3-F-2
Spiking Field Samples for the Multi-Cities Project	M3-F-4
Assigning Sample IDs for the Multi-Cities Project	M3-F-6
Collection and Handling of Sediment Samples for the Multi-Cities Project	M3-F-7
GPS Operation and Calibration (draft)	Battelle 3-164
Sample Shipping for the Multi-Cities Project	Battelle 5-210
Sample Custody	Battelle 6-010

An outline of the survey plan that will describe all sampling logistics is provided in Appendix A.

7.3.1 Permissions

Following an initial Internet search, a list of municipal officials for each target city was compiled. Phone calls were made to initiate contact with the officials and assess who is responsible for granting permissions for the collection of environmental samples. Once determined, this person was informed of the nature of the project and the nature of the samples that we would like to collect (*i.e.*, treated water, sludge, or leachate). Following the phone conversation, a written letter of request to collect a sample was faxed to the municipal official. The letter was then taken under consideration and a decision was issued from the municipal official as to whether or not we can conduct the sampling.

The collection of an atmospheric sample using EPA method TO-13 (EPA 1990) (SOP M3-F-1) requires that the sampler run continuously for twelve hours. To collect this sample we have decided to enlist the assistance of local fire departments for the placement of the sampler. The rational for the use of fire stations is that they are constantly manned and therefore provide secure areas where the sampler will not be subject to interference. The same method for attaining approval from other municipal facilities was employed for the fire stations. This also included an offer to donate $50 to a local charity of the departments' choice. If a donation is needed, then the appropriate approvals must be secured in advance so the donation can be presented when sampling is initiated.

Based on the confidential nature of the study being conducted the following information **may** or **may not** be discussed with the municipal officials.

Information that **MAY** be revealed to the officials includes:

- We are seeking to collect various matrices including POTW influent, effluent, and sludge; raw drinking water, treated drinking water and sediment from the surface water body (if applicable); landfill leachate; and atmospheric samples
- These samples are being collected and analyzed to support a life cycle analysis that is being conducting for a confidential client.

- The chemicals of interest are NOT listed as regulated pollutants or carcinogens by EPA.
- The results of these tests will be reported to our client and only under extenuating circumstances would a disclosure of the results be contemplated

Information that **MAY NOT** be revealed to the officials includes:

- Who the client is
- What chemical we are looking
- What the chemical is used for
- What the nature of the chemical is (chemical class or structure)

These formal requests were made to the various facilities within a given municipality in February and March 1999. Generally the wastewater treatment plant, the drinking water plant, and the landfill required separate requests. These facilities will again be contacted to confirm the permissions granted during the Winter and to establish a sampling schedule based on the matrices to be collected. If an approval is denied, then an alternative site may be sought to collect a sample that is representative of the required matrix. Examples of Requests for Permissions are provided in Appendix B.

Communication logs are maintained and include who was contacted and topics discussed. Any discussion related to data reporting will be clearly documented and summarized in a letter to the client's legal representative.

7.3.2 Precautions

Safety considerations will be incorporated in the Survey Plan. In addition to normal measures taken to avoid sample contamination, such as the of cleaning sampling gear between uses and the use of precleaned sample bottles, the following precautions will be taken to avoid contamination during sample collection.

- Post-Its® will not be used at any time during sample handling, or mobilization/demobilization.
- Field scientists will wear only old, well laundered (at least 6 washings since purchase) clothing. The use of water-resistant clothing will be avoided as much as possible.
- Tyvek® suits will not be worn during sample handling.
- Nitrile gloves will be worn at all times while collecting and handling samples, except in grocery stores and other retail establishments.
- Many food and snack products – microwave popcorn, fast-food (sandwiches chicken, French fries) pizza, bakery items, beverages, candy, cookies – are packaged in wrappers treated with the chemicals of interest. Therefore, hands will be thoroughly washed after handling fast food, carryout food, or snacks. Prewrapped foods or snacks (like candy bars) will not be in the possession of the sampling team during sampling.
- Field personnel may not consume microwave popcorn during the surveys
- No blue ice will be used during this project

7.3.3 Sampling Locations within Each City

The location, including street address, of samples collected from municipal facilities will be recorded on the sampling log. A Garmin 12XL hand-held GPS (global positioning system) or equivalent will be used to determine the exact location (coordinates) at each sample collection location. The position will be read

from the display and recorded by hand on the Site Log. The unit will be operated according to SOP No. 3-164. Also, each sampling location will be marked on a local map.

7.3.4 Air Sampling

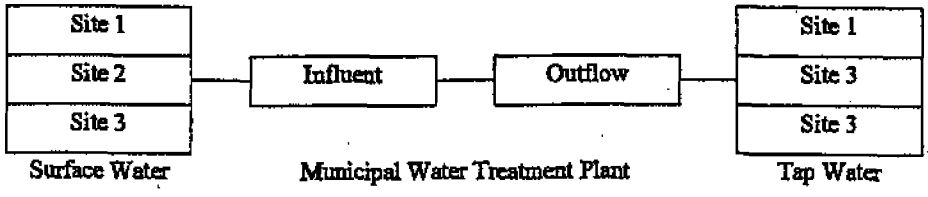
Air sampling will be accomplished by using a General Metal Works Modal PS-1 Air Sampler. The PS-1 sampling head (shown in Attachment 1), which is contained within the sampler, consists of a 4" diameter inlet filter (made of Teflon coated glass fiber filter medium) and a 2.3" diameter x 5" glass cartridge containing a PUF, which is 3" in length and fits snugly into the cartridge.

The high volume (~250 lpm) polyurethane foam (PUF) sampling method based on U. S. EPA's Method TO-13 is applicable to measuring ambient air concentrations of organic components at concentrations from 0.001-50 $\mu g/m^3$ over a 4-24 hour sampling period. The procedure allows for the collection of the semi-volatile organic chemicals present in the air on a glass-fiber filter (particulate) and PUF (vapor phase). The limits of detection are specific to the nature of the analyte and the length of the sampling period.

One 12-hour air sample, consisting of a particulate fraction collected on a glass fiber filter and a vapor fraction collected on polyurethane foam (PUF), will be collected at each city. Air samples will be collected at ground level at any site for which permission to sample can be obtained is acceptable. Ideally, a fire station should be chosen because it is somewhat secure and usually has personnel on-site 24 h per day. Other locations may include a local college or university, retail establishment, the POTW plant, or drinking water plant if the facility staff are willing to accommodate the sampler. The sampler requires 120 V power, and should not be run if it is raining. Sampling also is not performed if there are consistent high winds (>25 mph). If possible, a copy of the weather section from the local daily newspaper will be obtained and added to the field log book for the sampling date to document weather conditions. Once the field sample is collected, routine air sampler cleaning is performed and the quality control samples are collected as described in Section 11.2.3.

7.3.5 Water Sampling

Water samples will be collected from several points within the municipal drinking water system, as shown below. [Note: Microlayer samples will not be collected during the Multi-City Study but may be collected during subsequent samplings under the program].



Whole (bulk) water will be collected from three sites (at least 500 ft apart) within a surface-water source (e.g., lake, pond, reservoir) of drinking water, and at the water treatment plant influent and outflow. Tap water will be collected from three retail establishments within the city. One-liter water samples will be collected into I-L ESE pre-cleaned (certified) polyethylene sample bottles by either directly placing the container into the water stream, or, if a valve withdrawal system is available, by using the valve. Due to the difficulty in obtaining a true surface sample with a bottle, these samples will be from bulk water to minimize variability due to sampling technique. For the environmental samples (lake, river, reservoir), the bottle will be lowered below the surface of the water and will be filled with bulk water. Once the field sample is collected the quality control samples are collected as described in Section 11.3.2.

If the drinking water source is ground-water then the surface water samples will be collected from any selected lake, pond, or river, using methods described above.

7.3.6 Sediment Sampling from Municipal Water Source

Sediment samples will be collected synoptically with the bulk water from three sites within surface-water sources. The sites will be located at least 500 ft apart. After the water sampling is completed, the sediment will be collected at the same site by using a 0.04-m^2 Young grab sampler that is hand-deployed. The top 2 cm of sediment will be retained for analysis. Alternatively, a stainless steel spoon or scoop will be used.

7.3.7 POTW Sampling

Battelle will provide appropriate sample containers and detailed written instructions to the designated POTW official, who will collect each influent (post-chlorination), sludge, and effluent sample. Battelle will assume custody of the samples and will be responsible for packing and shipping the samples to BCL for analysis. Once the field samples are collected, the quality control samples are collected as described in Section 11.4.2.

7.3.8 Landfill Leachate Sampling

Battelle will provide appropriate sample containers to the designated municipal landfill official, who will collect each sample according to detailed written instructions provided by Battelle. Battelle will assume custody of the samples and will be responsible for packing and shipping the samples to BCL for analysis. No industrial landfills will be sampled.

7.3.9 Food Sampling

In each city, two or three major grocery-store chains will be identified and representative food samples will be collected from each chain. The intent of this sampling is to determine the dietary exposures of residents within each region based on typical foods consumed. The food products will be collected as listed, and as packaged. For the milk and eggs, the selection of these foodstuffs in the store will be checked to determine whether there are any from regional or local sources, and these will be selected. If there are no local or regional sources, any type is acceptable. The grocery store fish should be representative of a fish that is typically raised or caught in that general region of the U.S. For many of the inland southeastern US cities, this would include catfish. Fish may be fresh or frozen, and should be scaled, filleted, with the head removed. In addition, one organic grocery store in each city will be identified and either a loaf of organic bread or a pound of organically raised flour will be purchased.

Each foodstuff will be packaged individually in a zip-seal bag, with bubble wrap if necessary (e.g., for the eggs) for transport. The bag labels will indicate the grocery store from which the food items were purchased.

7.3.10 Finfish

Finfish species (i.e., perch and bluegill) will be collected from waterbodies (i.e., small streams or ponds) in the vicinity of the area in which water samples are collected. Finfish will be collected through electrofishing or seining. Electrofishing is a fisheries technique which involves generating a DC or an AC electric current (either with a gasoline-powered generator or batteries) through various styles of electrodes into the water to create an electric field. Fish that pass through the field are stunned, then collected by dipnet. Seining involves encircling a shoreline area with a fine-mesh net and entrapping fish present in this location. [Note: Finfish samples will not be collected during the Multi-City Study but may be collected during subsequent samplings under the program].