

**Environmental Monitoring – Multi-City Study
Water, Sludge, Sediment, POTW Effluent and Landfill Leachate Samples**

**Executive Summary
3M Environmental Laboratory**

June 25, 2001

Introduction

The Multi-City study was conducted to obtain data about the presence of fluorochemicals in the environment, foods, and drinking water, in order to understand the potential sources of human and environmental exposures. The study analyzed perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA) and perfluorooctane sulfonamide (FOSA) in a variety of media.

Results from the study appear in a number of documents. This Executive Summary presents results from the analysis of environmental samples taken at the Multi-City sites, including:

- Drinking water,
- Surface water column,
- Sediment,
- Publicly-Owned Treatment Works (POTW) sludge,
- POTW effluent, and
- Landfill leachate samples.

As originally designed by Battelle Memorial Institute, Columbus, Ohio, the Multi-City Study paired a city having manufacturing or industrial use of fluorochemical products with a city that does not. The cities were chosen in such a way that the pairs had similar populations and drinking water supplies. Supply chain cities included in the study are Mobile, Alabama; Columbus, Georgia; Decatur, Alabama; and Pensacola, Florida. The “control cities” are Cleveland, Tennessee and Port St. Lucie, Florida.

The sections below describe the cities in the study, the sample collection, and the results for PFOS, PFOA and FOSA.

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A. Locations Sampled

The paired cities and pertinent details are as follows:

Table 1
Locations Sampled in Multi-City Study

City	Population	Drinking Water Supply	City Type	Manufacturing Type in City
Decatur, Alabama	49,000	Surface water	Supply Chain	Fluorochemical manufacture known
Cleveland, Tennessee	30,000	Surface water	Control (to Decatur)	No known significant industrial use of fluorochemicals
Mobile, Alabama	196,000	Surface water	Supply Chain	Paper
Columbus, Georgia	179,000	Surface water	Supply Chain*	Nonwovens, household additives, apparel, carpet, home textiles
Pensacola, Florida	58,000	Ground water	Supply Chain	Carpet
Port St. Lucie, Florida	56,000	Ground water	Control (to Pensacola)	No known significant industrial use of fluorochemicals

*After the samples were collected and analyzed, it was discovered that Columbus should not be considered a “control” city, as several users of 3M fluorochemical products (“Supply Chain” facilities) were identified within the immediate vicinity. Also note that a report entitled Environmental Monitoring: Surface Water Multi-City Study provided to the U.S. EPA in the August 2000 submission incorrectly stated that five of the six cities fell into the category of supply locations. There are actually four of the six cities in the study that are supply chain cities.

B. Sampling Information

This Executive Summary should be read in conjunction with the detailed reports, which include sampling location maps of the six cities, field sampling reports, a field audit report, the quality assurance project plan, study-specific Standard Operating Procedures (SOPs), a document outlining the original design and structure of the study, a draft drinking water health advisory for PFOS, and multiple final analytical reports. Many of these documents have been submitted previously, but are also included here so the materials can be found together.

This Executive Summary describes results for samples taken from the following sources and media in each of the six cities:

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1. Final effluent from a Publicly Owned Treatment Works (POTW) domestic wastewater treatment plant serving the city.
2. Biological solids (sludge) from the same POTW as the effluent.
3. Raw water input to the city drinking water treatment plant (sampling point within the plant itself).
4. Treated drinking water, collected within the city drinking water plant itself before release to the distribution system.
5. Tap drinking water from three separate retail locations within the city.
6. Leachate from a municipal landfill that serves the city.
7. Surface water. For cities in which drinking water is derived from surface water, samples were taken from the water body that serves as the source of raw water input into the city drinking water treatment plant. Where groundwater is the drinking water source, a surface water body was substituted for the groundwater samples. Surface water was sampled in three locations per city, at sites at least 500 feet apart.
8. Sediment samples taken at the same sites as the surface water.
9. A quiet water, such as a pond, where there is no obvious flow.

As is always the case with field work, deviations from the original sampling plan occurred as the study progressed, and the design of the study evolved. Some samples were not analyzed or collected as originally planned:

- a. Alcohols and various intermediate metabolites were not found in preliminary biosphere samples, and the target analytes for the study were therefore narrowed to PFOS, PFOA, and FOSA.
- b. The 3M Environmental Laboratory Field Sampling Team identified errors in the air sampling procedure utilized. Air samples therefore were not analyzed.
- c. Electro-fishing for finfish was conducted; however, the catch was too limited for analysis.
- d. Surface microlayer samples were collected. However, an accepted method for sample handling and the evaluation and interpretation of data was not available. Samples therefore were not analyzed.

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- e. Landfill leachate and quiet surface water samples could not be collected in Cleveland, TN, as the sampling team was not given permission to sample by local authorities or property owners.
- f. In Mobile, AL and Pensacola, FL, the landfill leachate could not be collected at the landfill facility. Samples were instead collected from creeks, which appeared to be flowing from the direction of the landfill site. However, this likely is not representative of leachate.
- g. The samplers could not get access to post-chlorination POTW influent samples at any site. Samples of POTW influent were not collected at any city due to health concerns for the sampling personnel.
- h. The quiet water site in Port St. Lucie was sampled two additional times in an attempt to verify PFOS concentrations that were higher than in any other surface water site.

Appendix I contains selected observations made by field sampling personnel during sample collection. Actual field notes are contained in the separate documentation.

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Results - PFOS

Table 2
PFOS Concentration, Parts per Billion

Results of Duplicate Samples

Sample	Decatur	Cleveland	Mobile	Columbus	Pensacola	Port St. Lucie*	Port St. Lucie**
POTW effluent	4.67 5.29	0.417 0.454	0.041 0.054	0.416 0.437	0.833 0.959	0.048 0.063	0.086 0.079
POTW sludge (dry wt)	2,840 3,120	116 130	60.0 57.7	157 159	124 125	NQ	62.9 60.2
Drinking water influent	ND	ND	ND	0.053 0.061	ND	ND	ND
Drinking water treated	ND	ND	ND	0.062 0.063	ND	ND	ND
Drinking water tap 1	ND	ND	ND	0.056 0.058	ND	ND	ND
Drinking water tap 2	not analyzed	ND	ND	0.055 0.057	ND	ND	ND
Drinking water tap 3	not analyzed	ND	ND	0.058 0.062	0.042 0.047	ND	ND
Landfill leachate	53.1 52.3	not collected	ND	ND	ND	0.344 0.329	0.429 0.425
Surface water 1	NQ	NQ ND	NQ	0.064 0.060	NQ	ND	NQ
Surface water 2	NQ	ND	0.040 0.043	0.077 0.083	NQ 0.029	0.137 0.138	NQ
Surface water 3	ND	ND	0.035 0.036	0.055 0.055	NQ	NQ	NQ
Sediment 1 (dry wt)	NQ	NQ ND	0.303 0.282	0.472 0.419	ND	NQ	ND
Sediment 2 (dry wt)	0.295 0.785	NQ	0.699 0.570	NQ	0.242 ND	1.13 1.09	ND
Sediment 3 (dry wt)	0.360 0.368	NQ	0.670 0.616	0.467 0.388	0.408 NQ	0.763 0.804	ND
Quiet water	0.108 0.114	not collected	0.032 0.033	ND	NQ	45.3 51.1***	2.93 2.85

*Data from 1999 sample event

**Data from 2000 sample event

*** Additional data presented below

LOD (Limit of Detection) approximately 0.0025 µg/L for water, 0.080 µg/kg for sludge and sediment as received (wet weight)

LOQ (Limit of Quantitation) is 0.025 µg/L for water and 0.2 µg/kg for sludge and sediment as received (wet weight)

ND = not detected

NQ = compound detected at a level between the LOD and LOQ

The highest concentrations of PFOS in POTW effluent, POTW sludge and landfill leachate were found in the city of Decatur samples. The 3M Decatur plant used the Morgan county landfill for disposal of industrial biological wastewater treatment sludge and other non-hazardous materials prior to 1998. This landfill, in turn, sends its leachate to the City of

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Decatur POTW for treatment. All surface water sample points and the drinking water plant intake are located upstream of the 3M Decatur fluorochemical manufacturing facility.

PFOS was detected at measurable concentrations in all of the POTW sludge samples collected, except for the first Port St. Lucie sampling. Concentrations (based on dry weight of sludge) in Cleveland, Columbus, and Pensacola sludge ranged from 116 to 159 µg/kg (ppb). In Port St. Lucie (second sampling) and Mobile, it was detected at 58 – 63 µg/kg (dry weight). A recent study (3M Environmental Laboratory, 2001, submitted to EPA June 29, 2001) of PFOS sorption/desorption utilizing soil, sediment and sludge samples concluded that:

Perfluorooctane sulfonate (PFOS) strongly adsorbs to all of the soil/sediment/sludge matrices tested. The test substance, once adsorbed, does not desorb readily, even when extracted with an organic solvent.

In the above study, PFOS sorbed to sludge very strongly (> 96% sorbed) within the first few hours of exposure. The K_d values obtained for sediment and sludge were 7.42 mL/g and 120 mL/g, respectively. Because PFOS is a strong acid, it forms strong bonds with sludge and sediment via the mechanism of chemisorption. Thus, the POTW sludge results most likely are attributable to the fact that PFOS strongly sorbs to sludge.

Sediment concentrations were much lower than those seen in POTW sludge. The measured sediment values in Columbus, Mobile, Pensacola and Port St. Lucie were often just above the limit of quantitation (LOQ). (The LOQ varied with the percent solids in the sample, and was approximately 0.2– 0.4 µg/kg or ppb on a dry weight basis.) The sorptive characteristic of PFOS may also explain the concentrations seen in sediments at Columbus, Mobile, and Pensacola. The source of PFOS in the sediments in Port St. Lucie is probably not the POTW effluent, as that effluent is injected into the ground, not discharged into the river.

PFOS was detected at very low levels (<0.14 µg/L) in some surface waters. In Pensacola, Port St. Lucie and Mobile, it was detected in 1 or 2 of the three sites sampled. In Columbus, PFOS was detected consistently across all surface water, drinking water influent, treated drinking water, and tap water samples, at relatively similar concentrations (0.053 – 0.083 ppb). This is not surprising, as the surface water samples and drinking water intake samples were taken in the same vicinity. PFOS was detected in tap water at one site in Pensacola, where replicate samples had 0.042 and 0.047 µg/L. Samples from the other two tap water sites in Pensacola, as well as the drinking water intake and output, did not have detectable concentrations of PFOS. In order to provide perspective in interpreting the findings in drinking water, 3M's July 1999 calculation of a draft Drinking Water Advisory Level for PFOS is included in this submission. Using EPA methodology, 3M calculated a PFOS drinking water advisory level of 1 µg/L (ppb). All of the findings in drinking water were substantially below this level.

PFOS was initially detected at relatively higher concentrations than seen elsewhere in the quiet water site in Port St. Lucie. Further investigation of the quiet water site was undertaken

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to verify the results and to try to identify a source of PFOS. The quiet water site, a small water pond, was sampled two more times after the initial results were obtained. The samples collected in the third sampling event were split and analyzed at two different laboratories; the third round of sampling included the original quiet water site, two additional quiet water sites, and sediments associated with each of the three sampling sites. The data for PFOS is presented below:

Table 3
Port St. Lucie Quiet Water
PFOS Concentration, Parts per Billion

Sample Description	First Sample 7/29/99	Second Sample 7/18-19/00	Third Sample 1/24/01 3M Env. Lab Results	Third Sample 1/24/01 Centre Results*	Corresponding Third Sample Sediments (dry weight)
Site I	45.3	2.93			
East	51.1	2.85			
South	not sampled	not sampled	1.60	(1.97, 2.22, 2.31)	(9.64, 9.34)
West	not sampled	not sampled	1.54	(2.12, 2.09)	(12.0, 14.3)
North	not sampled	not sampled	1.59	(2.20, 2.34)	(10.8, 10.5)
	not sampled	not sampled	1.78	(2.08, 2.01, 2.37, 2.23)	(9.28, 9.80, 8.29, 8.37)
Site I Culvert Discharge				1.84	
	not sampled	not sampled	1.38	1.98	not sampled
Additional Quiet Water Site 2				NQ	
	not sampled	not sampled	NQ	NQ	
			0.015	0.025	NQ
Additional Quiet Water Site 3				0.026	
	not sampled	not sampled	NQ	NQ	NQ

*Several samples taken. Where 4 values in a row, includes sample, lab dup., blind dup. and lab blind dup.;

3 values in a row are sample, lab dup and field dup. Where only 2 values, are sample and lab dup.

LOD (Limit of Detection) approximately 0.0025 µg/L for water and 0.080 µg/kg for sludge and sediment as received (wet weight)

LOQ (Limit of Quantitation) is 0.025 µg/L for surface water at Centre, 0.010 µg/L at 3M Env. Lab and 0.2 µg/kg for sludge and sediment as received (wet weight)

NQ = compound detected at a level between the LOD and LOQ

Despite diligent investigation, 3M has been unable to confirm the initial sampling results, nor to identify any potential source of the initial readings. Samples of the same quiet water collected in 2000 and 2001 contained markedly lower levels of PFOS. In addition, the samples from the other two quiet water ponds in Port St. Lucie had either no detectable or quantifiable levels of PFOS, or very low levels similar to those seen in water column samples from other cities. Moreover, a culvert draining into the pond used for the initial quiet water sampling was sampled in the third round of sampling and found to contain concentrations similar to those in the more recent sampling of the pond itself. Finally, the sediment sampling results are more consistent with the subsequent sampling results. Thus, the initial quiet water results in Port St. Lucie appear to be an anomaly.

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Results: PFOA

Table 4
PFOA Concentration, Parts per Billion

Results of Duplicate Samples

Sample	Decatur	Cleveland	Mobile	Columbus	Pensacola	Port St. Lucie*	Port St. Lucie**
POTW effluent	2.14 2.42	0.655 0.674	0.067 0.088	0.139 0.147	0.084 0.090	0.041 0.044	0.043 0.040
POTW sludge (dry wt)	101 244	3.11 2.82	NQ	16.5 16.3	2.51 2.40	NQ	ND
Drinking water influent	ND	ND	ND	0.026 NQ	ND	ND	ND
Drinking water treated	ND	ND	ND	0.025 0.029	ND	ND	ND
Drinking water tap 1	ND	ND	ND	0.026 NQ	ND	ND	ND
Drinking water tap 2	not analyzed	ND	ND	0.026 NQ	ND	ND	ND
Drinking water tap 3	not analyzed	ND	ND	0.025 NQ	ND	ND	ND
Landfill leachate	48.1 46.8	not collected	ND	NQ 0.028	ND	0.953 0.939	1.03 1.02
Surface water 1	NQ ND	NQ ND	0.026 0.027	0.026 0.026	ND	ND	ND
Surface water 2	ND NQ	ND	0.054 0.060	0.026 0.027	ND	NQ	ND
Surface water 3	ND	ND	0.083 0.083	NQ	ND	ND	ND
Sediment 1 (dry wt)	ND NQ	ND	NQ	ND	ND	0.370 0.326	ND
Sediment 2 (dry wt)	NQ	NQ	ND	ND	NQ ND	0.316 0.294	ND
Sediment 3 (dry wt)	NQ	ND	NQ	ND	ND	1.68 1.75	ND
Quiet water	0.057 0.063	not collected	NQ 0.027	ND	ND	0.737 0.760	0.097 0.097

*Data from 1999 sample event

**Data from 2000 sample event. Additional samples in 2001 (not shown) showed similar results.

LOD (Limit of Detection) approximately 0.0075 µg/L for water and 0.80 µg/kg for sludge and sediment as received (wet weight)

LOQ (Limit of Quantitation) is 0.025 µg/L for water, 0.2 µg/kg for sludge and sediment as received (wet weight).

ND = not detected

NQ = compound detected at a level between the LOD and LOQ

PFOA was found in similar samples in the same cities as PFOS. The concentrations of PFOA were generally lower than those of PFOS, although in some cases the concentrations were similar.

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Results: FOSA

Table 5
FOSA Concentration, Parts per Billion

Results of Duplicate Samples

Sample	Decatur	Cleveland	Mobile	Columbus	Pensacola	Port St. Lucie*	Port St. Lucie**
POTW effluent	0.056 0.056	NQ	NQ	0.085 0.085	NQ	NQ	NQ
POTW sludge (dry wt)	107.0 97.8	1.68 1.70	NQ	41.3 43.4	1.27 1.29	NQ	ND
Drinking water influent	ND	ND	ND	NQ	ND	ND	ND
Drinking water treated	ND	ND	ND	NQ	ND	ND	ND
Drinking water tap 1	ND	ND	ND	NQ	ND	ND	ND
Drinking water tap 2	not analyzed	ND	ND	NQ	ND	ND	ND
Drinking water tap 3	not analyzed	ND	ND	NQ	ND	ND	ND
Landfill leachate	0.258 0.249	not collected	ND	ND	ND	NQ	NQ
Surface water 1	ND	NQ ND	NQ	NQ	ND	ND	ND
Surface water 2	ND	ND	NQ	NQ	ND	ND	ND
Surface water 3	ND	ND	NQ	NQ	ND	ND	ND
Sediment 1 (dry wt)	ND NQ	ND	NQ	NQ	ND	NQ	ND
Sediment 2 (dry wt)	NQ	NQ	0.383 0.343	NQ	ND	NQ	ND
Sediment 3 (dry wt)	NQ	ND	0.538 0.516	NQ	ND	NQ	ND
Quiet water	NQ	not collected	NQ	ND	ND	0.084 0.095	0.030 0.028

*Data from 1999 sample event

**Data from 2000 sample event. Additional samples in 2001 (not shown) showed similar results.

LOD (Limit of Detection) approximately 0.0025 µg/L for water and 0.080 µg/kg for sludge and sediment as received (wet weight)

LOQ (Limit of Quantitation) is 0.025 µg/L for water, 0.2 µg/kg for sludge and sediment as received (wet weight)

ND = not detected

NQ = compound detected at a level between the LOD and LOQ

FOSA was detected at low levels in a few locations. The highest concentrations were seen in Decatur POTW sludge and landfill leachate, with somewhat similar results in Columbus.

Conclusions

Of the three fluorochemicals studied in environmental samples from the six cities, PFOS is found most often, followed by PFOA, then FOSA, all in very low concentrations. The two cities that were intended to be “control” cities (Cleveland and Port St. Lucie) did, in some cases, have much lower concentrations of these analytes than the supply chain cities. However, there was not a consistently higher concentration of the target analytes in all

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sample matrices from all supply chain cities. Mobile, a supply chain city, generally had lower concentrations of fluorochemicals than the other supply chain cities.

Most fluorochemicals measured were associated with wastewater treatment/sediment samples; very little to none were found in surface waters and drinking water. All detected concentrations of PFOS in drinking water were well below 3M's 1999 calculated draft Drinking Water Health Advisory (DWHA) of 1 ppb lifetime exposure for PFOS. In all surface water sites sampled, the concentrations of PFOS, PFOA and FOSA were below laboratory-derived no-observed-effect concentrations for aquatic organisms (see various aquatic studies submitted to EPA).

In light of these results, further sampling in additional cities is not likely to materially improve our understanding of the presence and extent of PFOS, PFOA and FOSA in the environment. Accordingly, initial plans for sampling in six further cities were not pursued.

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Appendix I

FIELD SAMPLING COMMENTS

Decatur:

1. Surface water samples were collected in an area of a highly active marina complex.
2. Landfill leachate samples were collected from a recently constructed collection pond, which contained a variety of wildlife living in and around it.
3. Sediments and surface water were obtained upstream from the POTW.

Cleveland:

1. The drinking water plant intake is approximately 2 miles east/northeast of the plant.
2. Sediments and surface water were obtained upstream from the POTW.

Mobile:

1. Landfill leachate was not collected; an alternative sample was taken from a creek located downslope from the landfill.
2. The POTW is adjacent to a coal depot in a highly industrialized area.
3. The spring-fed reservoir used as the drinking water source was not sampled. The sampling crew erroneously assumed that the Mobile River, which is brackish and tidally influenced, was the drinking water intake, and took samples there.
4. The water treatment plant sampled is the smaller of the two the city maintains.
5. Sediments and surface water were obtained from a region upstream of the POTW.

Columbus:

1. The POTW diffuses its discharge 100 feet from shore.
2. POTW sludge is dried and land-applied.
3. Sediments and surface water were obtained from a region in the vicinity of or just downstream of the POTW.

Pensacola:

1. Landfill leachate was not collected; an alternative sample was taken from a creek located close to the landfill.
2. Sediments and surface water were obtained from a bayou upstream of the POTW. Since Pensacola uses groundwater, the Texar Bayou was sampled as the surface water and sediment site. This bayou contains brackish water and is tidally influenced. A local newspaper described Texar Bayou as heavily contaminated with heavy metals from two industrial sites and high levels of fecal coliform. Some city wells are contaminated with volatile organics, and fitted with charcoal filters. The well sampled was not filtered.
3. POTW sludge is incinerated onsite.

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Port St. Lucie:

1999 Sampling

1. Surface water was taken from brackish, tidally-influenced waters. Sediments and surface water were obtained from a region approximately 10 miles north of the POTW.
2. Drinking water is ground water; surface water does not relate directly to drinking water.
3. Sludge sample was taken after the chlorine contact chamber (pre-treated).
4. The POTW effluent is injected into the ground, not discharged to a river.

First resampling (2000)

1. POTW samples were collected at two points – at the injection well, and at the chlorine contact chamber (chlorination was not occurring at the time of sampling). The samples from the chlorine contact chamber are representative of the samples collected in 1999.
2. The quiet surface water pond was approximately 200 feet by 200 feet. The water was noted to be fairly clear with some minnows present. Styrofoam, plastic, bags, a can and a bottle were some of the litter noted in the water. Sampling was conducted approximately 45 feet away from visible litter.

Second resampling (2001)

1. In quiet water site I, the water was noted to be fairly clear with some minnows present. A large fish, estimated to be 10 pounds, was noted in the pond. Styrofoam, plastic bags, cans and bottles were some of the litter noted in the water. A greenish film was also noted on the water surface. Sediment samples were sandy with some clams present.
2. In quiet water site I, a culvert was noted running into the pond. The influent created a tan to gray plume as it entered the pond. The samplers were informed that it had rained approximately ½ an inch two days prior to sampling.