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SELECTED FLUOROCHEMICALS IN THE DECATUR, ALABAMA AREA

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3M
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1 EXECUTIVE SUMMARY

A monitoring study was conducted to assess the current extent, status, and magnitude of fluorochemical concentrations from a 3M Facility near the Tennessee River in the Decatur Alabama area. The objectives of the study were to determine the concentrations of selected fluorochemicals in biotic and abiotic phases within the Tennessee River in the vicinity of the 3M Facility. Surface water, sediments, clams and fish were collected from locations upstream and downstream of the 3M facility and analyzed for four fluorochemicals: perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (FOSA), perfluorooctanoate (PFOA), and perfluorohexanesulfonate (PFHS).

Surface waters and sediments were collected from five primary locations. These areas consisted of a location near the 3M point of discharge (Outfall), a stream the receives the 3M Facility effluent (Bakers Creek), a downstream location (Fox Creek), a location upstream of 3M Facility but below the City of Decatur (DWTP), and a reference location upstream of Guntersville Dam. Clams were collected from the Guntersville location and the Fox Creek location. Fish were collected from the 3M Outfall and from the Guntersville location. All samples were collected according to standard procedures and analyzed for fluorochemicals according to 3M Environmental Laboratory methods.

Results from the monitoring study indicate that the while the effluent from the 3M Outfall did cause changes in some water quality parameters within Bakers Creek, it did not cause any statistically significant changes in water quality parameters at the farthest downstream location, Fox Creek. Average surface water PFOS concentrations ranged from 0.009 to 151 µg/L for Guntersville and Outfall, respectively. Average PFOS sediment concentrations ranged from 0.180 to 5930 µg/kg (wet weight) for Guntersville and the 3M Outfall, respectively. However, while fluorochemical concentrations in sediments and surface waters were greater in locations downstream of the 3M Outfall, the downstream sample locations within the main stem of the Tennessee River (Fox Creek) were not statistically greater than those upstream (DWTP and Guntersville) of the 3M Outfall. Only samples collected from the 3M Outfall and Bakers Creek, locations that are in the immediate vicinity the 3M Outfall, were significantly greater than those in the

reference location. From these results, it can be concluded that the effluent from the 3M Outfall does not significantly affect fluorochemical concentrations in sediments or surface waters in the main stem of the Tennessee River.

Fluorochemicals were detected in all fish collected from both the Guntersville reference area and 3M Outfall. The least fluorochemical concentrations were observed in fish collected from Guntersville while the greatest concentrations were observed in fish from the Outfall. For instance, at Guntersville, average whole body concentrations for PFOS, FOSA, PFOA, and PFHS were 59.1, 9.43, 11.7 and 7.50 µg/kg, (wet weight) respectively. For fish from the outfall, average whole body concentrations for PFOS, FOSA, PFOA and PFHS were 1332.0, 20.1, 106.4, and 86.9 µg/kg, (wet weight) respectively. While there were species specific differences in the accumulation of the selected fluorocarbons into fish collected from either Guntersville or 3M Outfall locations, these differences were not statistically significant due to the small sample size and among-individual variability. Concentrations of FOSA and PFOA in clams collected from the Outfall were greater than concentrations observed in clams collected from the Guntersville reference site. However, PFOS and PFHS tissue concentrations in Outfall clams were not greater than concentrations in clams collected from Guntersville. In conclusion, fish downstream of the 3M Outfall contained greater concentrations of fluorochemicals than did fish from the Guntersville area but the significance of these differences is difficult to assess due to the small sample size and variability.

2 INTRODUCTION

Entrix, Inc (ENTRIX) is providing a report on activities to assess the impact of effluents containing fluorochemicals from the 3M Facility in Decatur, Alabama to the Tennessee River. Water, sediment, clams and fish were collected from upstream and downstream locations of the 3M Facility and were used to evaluate the magnitude of releases of target compounds from the Facility to the Tennessee River. The objectives of the research are to determine concentrations of selected fluorochemicals in abiotic and biotic phases of the Tennessee River system in the vicinity of the 3M Facility at Decatur, Alabama. Fluorochemicals selected for evaluation in this study included: perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (FOSA), perfluorooctanoate (PFOA) and perfluorohexane sulfonate (PFHS) (Appendix A). In addition, trifluoroacetic acid was also evaluated in water and sediment samples taken from the Tennessee River.

3 FIELD SAMPLING

3.1 Site Description

Four primary locations were selected for the field investigation (Figure 1, Appendix B). These areas consisted of a location near the 3M point of discharge (Outfall), a downstream location, a location upstream of 3M but below the City of Decatur, and a reference location upstream of Guntersville Dam. Specifically, samples were collected adjacent to the 3M Facility Outfall (includes Outfall and Bakers Creek) that corresponds River miles 301-302. Samples were also collected downstream of the 3M Facility near the mouth of Fox Creek (River miles 296-297). Sediment and water were collected upstream of the 3M Facility adjacent to the Decatur Wastewater Treatment Plant (approximately river mile 303.5). Finally, fish, clams, sediment, and water were collected from a reference site above the Guntersville Dam (approximately river mile 370). To better evaluate the impact of the effluent from the 3M Outfall, the Bakers Creek location was divided into two sub-locations, Bakers Creek-1 included Stations 1, 2 and 3 that were collected near the outfall and within Bakers Creek. Stations 4, 5 and 6 and were collected near the interface of the mouth of Bakers Creek and the Tennessee River and are identified as Bakers Creek-2.

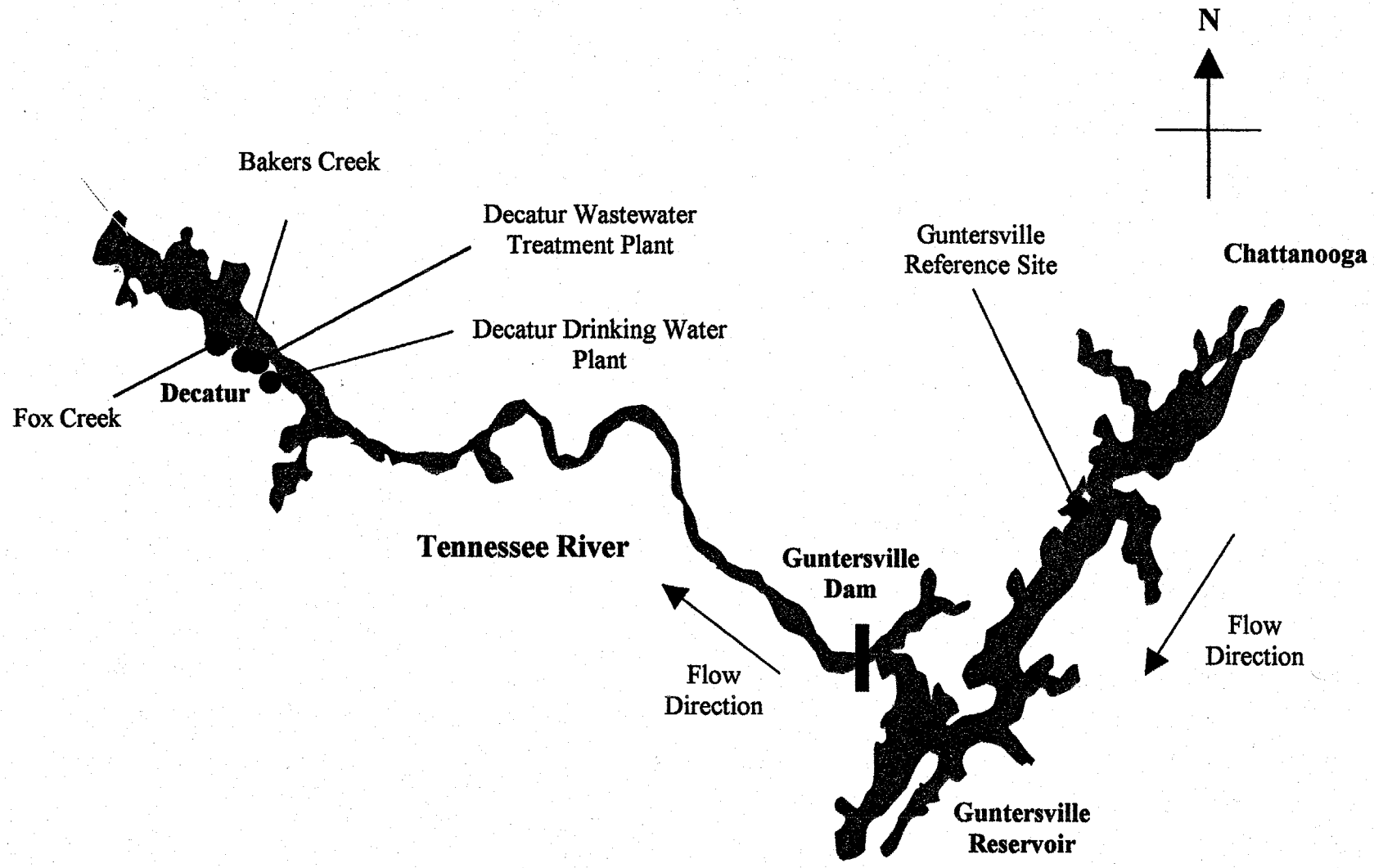

Figure 1. Tennessee River and sampling locations evaluated during study.

Fox Creek sampling locations were also divided into two sub-locations. Fox Creek-1 included Stations 7, 11, 12 and 26/27 that were collected from the mouth of Fox Creek. Fox Creek-2 included Stations 8, 9, and 10 that were collected on the northern side of the Tennessee River across from the mouth of Fox Creek. Locations and sample codes for samples collected from the Tennessee River are given (Table 1).

3.2 Field Sampling Logistics

Sampling at selected sites on the Tennessee River was initiated on June 19, 2000 by ENTRIX. Collection of water and sediment samples continued until June 21, 2000. During the collection of sediments, clams were also collected. Fish collection was initiated on June 21 and continued through June 22, 2000. Water, sediment, clams and fish were collected as outlined in Entrix sampling protocols (Appendix C).

3.3 SAMPLE COLLECTION

3.3.1 Water Collection

Water samples were collected using ENTRIX sampling protocols from a total of 26 locations (Table 1, Appendix B). At each location, water quality parameters were measured using YSI Model 63 and 95 meters. Six samples were collected from the areas surrounding the 3M Outfall, the City of Decatur wastewater treatment facility and the upstream reference location. Seven water samples were collected from the area downstream of the 3M Facility near Fox Creek. In addition to these 25 samples of surface water, water was collected from the 3M Facility effluent stream. All sampling locations were documented using TRIMLBE PRO-XRS Global Positioning Satellite technology and these locations were recorded on topographic maps. Samples were properly labeled, stored on ice at 4°C, and delivered to the 3M Environmental Laboratory, St. Paul, MN.

3.3.2 Sediment Collection

Sediment samples were collected from the same location, as were the water samples (Table 1, Appendix B). A total of 25 grab samples were collected from the Tennessee River. Six samples were collected from areas surrounding the 3M Outfall, the City of Decatur's wastewater treatment facility, and the upstream reference location using either a Petite PONAR and/or Eckman dredge. Seven samples were collected from the

downstream area in the vicinity of Fox Creek. All sampling locations were documented using TRIMLBE PRO-XRS Global Positioning Satellite technology and these locations were recorded on topographic maps. Sediments were collected by use of a PONAR dredge following standard protocols. Sediments were placed into labeled 250 ml wide-mouth LDPE containers, stored on ice at 4°C, and shipped to the 3M Environmental Laboratory, St. Paul, MN.

Table 1. Location and identification of sediment and water samples collected from the Tennessee River in Alabama

Water Sample	Sediment Sample	Location	Sublocation/Code
SW-01	SED-01	Bakers Creek	BCR1
SW-02	SED-02	Bakers Creek	BCR1
SW-03	SED-03	Bakers Creek	BCR1
SW-04	SED-04	Bakers Creek	BCR2
SW-05	SED-05	Bakers Creek	BCR2
SW-06	SED-06	Bakers Creek	BCR2
SW-07	SED-07	Fox Creek	FCR1
SW-08	SED-08	Fox Creek	FCR2
SW-09	SED-09	Fox Creek	FCR2
SW-10	SED-10	Fox Creek	FCR2
SW-11	SED-11	Fox Creek	FCR1
SW-12	SED-12	Fox Creek	FCR1
SW-13	SED-13	Decatur WWTP	WWTP
SW-14	SED-14	Decatur WWTP	WWTP
SW-15	SED-15	Decatur WWTP	WWTP
SW-16	SED-16	Decatur WWTP	WWTP
SW-17	SED-17	Decatur WWTP	WWTP
SW-18	SED-18	Decatur WWTP	WWTP
SW-19	SED-19	Guntersville	GTVL
SW-20	SED-20	Guntersville	GTVL
SW-21	SED-21	Guntersville	GTVL
SW-22	SED-22	Guntersville	GTVL
SW-23	SED-23	Guntersville	GTVL
SW-24	SED-24	Guntersville	GTVL
SW-25	SED-25	3M Outfall	OUTF
SW-26		Fox Creek	FCR1
SW-27	SED-27	Fox Creek	FCR1

3.3.3 Clam Collection

Samples of the Asian clam (*Corbicula fluminea*) were targeted for collection from a location downstream of the 3M Facility and from a location upstream of Guntersville

Dam. Historically, various state and federal agencies have used clams in monitoring programs for organic and inorganic pollutants in aquatic systems, as a result, they were also included in this study. Furthermore, due to their ubiquitous distribution in the Tennessee River and their sessile behavior, they provide site-specific information concerning the potential accumulation of fluorochemicals into aquatic biota. Due to the habitat requirements of *C. fluminea*, clam samples were not co-located with water or sediment samples. Clams were collected using a Petit PONAR dredge. However, due to difficulties in locating clam beds as well as interference of substratum with the PONAR dredge, the collection of clams was limited to two composite samples from locations in the vicinity of sediment samples. One sample (approximately 25 clams/sample) was taken from a location downstream of the 3M Facility (SED-08, -09, -10) and one upstream sample was collected from the Guntersville location (SED-20, - 21, - 22, -23, - 24). Clams from each location were placed into labeled plastic bags and shipped on ice to the MSU-ATL (Michigan State University-Aquatic Toxicology Laboratory), East Lansing, MI.

3.3.4 Fish Collection

Fish were collected from two locations (Table 2). One location was in the vicinity of the 3M Outfall and the other was located within the reference area upstream of Guntersville Dam. The fish samples were collected using both hook and line as well as gill net. Gill nets (passive gear) were placed in the lower energy environments where concentrations of fish were generally greater. Due to the techniques employed for collection of fish, all fish caught in each of the sampling locations were retained for analysis. Collected fish were removed from the nets, measured (total length), weighed, and immediately wrapped in aluminum foil and stored in plastic bags. Samples were labeled placed on ice, and shipped to the MSU-ATL (East Lansing, MI) for processing.

4 CHEMICAL ANALYSIS

Water and sediment samples were collected from the Tennessee River and analyzed by the Centre Analytical Laboratories, State College, PA (CLA, Report No. 023-0140; Appendix D). The analytical methods used for the water samples were validated by Centre.

The methods were modified for the analysis of sediment samples but were not fully validated for this matrix. Fish livers and clam samples were extracted and processed at MSU-ATL. LC/MS/MS characterization of fluorochemicals was conducted at 3M Environmental Laboratory. Summaries of each protocol are given:

Table 2. Sample identification and location of individual fish collected from the Tennessee River.

Sample ID	Location	Species	
LM1	Guntersville	Largemouth bass	Micropterus salmoides
LM2	3M Outfall	Largemouth bass	Micropterus salmoides
SHAD1	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD2	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD3	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD4	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD5	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD6	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD7	3M Outfall	Skipjack Herring	Alosa chrysochloris
SHAD8	3M Outfall	Skipjack Herring	Alosa chrysochloris
WP1	3M Outfall	White Perch	Morone americana
WP2	3M Outfall	White Perch	Morone americana
CAT1	Guntersville	Catfish	Ictalurus punctatus
CAT2	Guntersville	Catfish	Ictalurus punctatus
CAT3	3M Outfall	Catfish	Ictalurus punctatus
CAT4	3M Outfall	Catfish	Ictalurus punctatus
GAR1	Guntersville	Gar	Lepisosteus sp.
GAR2	Guntersville	Gar	Lepisosteus sp.
GAR3	Guntersville	Gar	Lepisosteus sp.
GAR4	Guntersville	Gar	Lepisosteus sp.
GAR5	3M Outfall	Gar	Lepisosteus sp.
GAR6	3M Outfall	Gar	Lepisosteus sp.
SB1	Guntersville	Striped Bass	Morone saxatilis
SB2	Guntersville	Striped Bass	Morone saxatilis
SB3	Guntersville	Striped Bass	Morone saxatilis
SB4	Guntersville	Striped Bass	Morone saxatilis
SB5	Guntersville	Striped Bass	Morone saxatilis
SB6	Guntersville	Striped Bass	Morone saxatilis
SB7	Guntersville	Striped Bass	Morone saxatilis
SB8	Guntersville	Striped Bass	Morone saxatilis
SB9	Guntersville	Striped Bass	Morone saxatilis
SB10	Guntersville	Striped Bass	Morone saxatilis
SB11	Guntersville	Striped Bass	Morone saxatilis
SB12	Guntersville	Striped Bass	Morone saxatilis
SB13	Guntersville	Striped Bass	Morone saxatilis
SB14	Guntersville	Striped Bass	Morone saxatilis

4.1 Water Analysis

Water samples were initially treated with 200 µl of 250 mg/L sodium thiosulfate to remove residual chlorine. Solid phase extraction was used to prepare the samples for LC/MS/MS analysis. A forty-milliliter portion of sample was transferred to a C_{18} SPE cartridge and the cartridge was eluted with 5 ml of 40% methanol in water. The eluate was discarded and the SPE column was eluted with 5 ml of 100% methanol. The eluate was collected for analysis by LC/MS/MS. This treatment resulted in an eight-fold concentration of the samples.

4.2 Sediment Analysis

For sediment samples, a 5 g portion was extracted into 5 ml methanol. The extracts were filtered and diluted to final volume of 40 ml with ASTM Type I water. The diluted extracts were then treated in the same manner as the water samples, beginning with the solid phase extraction.

Sediment and water extracts were analyzed by use of a Hewlett-Packard HP1100 HPLC system coupled to a MicroMass Ultima MS/MS. Analysis was performed using selected reaction monitoring (SRM). HPLC conditions and MS/MS methods used for analysis and instrument parameters are given in the procedure described below.

4.3 Fish Liver Analysis

Fluorochemical surfactants were extracted from fish livers using an ion pairing reagent and methyl-*tert*-butyl ether (MtBE). Details of the analytical procedure have been outlined in 3M Environmental Laboratory (St. Paul, MN) standard operating procedures of the analysis of fluorochemicals in tissues. The title of the SOP is: ETS-8-6.0, "Extraction of Potassium Perfluorooctanesulfonate or other Fluorochemical Compounds from Liver for Analysis using HPLC-Electrospray/Mass Spectrometry". Briefly, fish were thawed and livers were removed, weighed and then homogenized in HPLC grade water. An aliquot of liver homogenates were spiked with a surrogate standard and then 0.5 M tetrabutyl ammonium hydrogen sulfate (TBA) and 0.25 M sodium carbonate/sodium bicarbonate was added to each sample. Five ml methyl-*tert*-butyl ether was added to each tube and the sample was capped and shaken for 20 min. The samples were then centrifuged for 25 min at 3500 rpm and 4.0 ml of the organic layer was

transferred to a fresh tube. The extracts were evaporated under nitrogen gas to dryness then reconstituted in methanol. The methanol extracts were then passed through 0.2 µm nylon filters into glass autovials for chromatographic analyses.

4.4 Clam Tissue Analysis

Clam tissues were extracted with acetonitrile followed by a solid phase column cleanup of the extract. Briefly, frozen clam tissues were thawed and the tissues were composited and homogenized in an Omni homogenizer. A 5 gram sample was weighed a 50 ml polypropylene tube and 15 ml acetonitrile was added. Samples were shaken for 30 min and then centrifuged for 30 min at 3500xg. The supernatant was passed through a column of Florisil and activated charcoal and the eluate was collected in 50 ml polypropylene tube. The column was eluted with 15 ml methanol and both eluates were combined. Two drops of octanol were added to the eluate and then the sample was reduced to near dryness under a flow of nitrogen gas. The sample was resuspended in 1 ml methanol and passed through a 0.2 µm nylon filter into autovials for chromatographic analysis.

5 QA/QC

Standard operating procedures for sample collection and preparation were maintained during the entire project. Proper QA/QC samples, as required by 3M, were collected in the field (Appendix C). Two field matrix spikes and two field control samples were collected. Field matrix spikes solutions were prepared by collecting one liter of site water and spiking with 20 or 100 µl of a 10 ppm stock solution containing PFOS, FOSA, PFOA, and PFHS to yield 200 and 1000 ppt solutions, respectively. The same procedure was followed to spike one liter of distilled water to prepare the field spike control samples. All samples were shipped under ENTRIX chain of custody forms and a field book was used to document conditions and activities. A field camera was used to document all locations and to provide a visual record of the conditions of the site during the sampling events. In addition, ambient water quality parameters, such as temperature, conductivity, salinity, pH and dissolved oxygen were measured at each location during each sampling event. Since the method detection limit (MDL) and limit of quantification (LOQ) are analyte and matrix specific, method and matrix blanks along with matrix

spikes were used to determine accuracy and precision of the extractions and final chemical determination. Water and sediment concentrations were not corrected for either matrix spike recoveries or corrected for purity of the fluorochemical standards. Fish tissue fluorocarbon concentrations were reported as wet weight and were not converted to a dry weight basis.

6 STATISTICAL ANALYSES

Statistical analyses were preformed with SAS® (Version 8, SAS Institute, Cary NC, USA). General linear models (PROC GLM) were used to test for differences among locations for all endpoints measured in the study. If values of F tests indicated a significant difference, Tukey's HSD test for multiple comparisons was used to compare means of the different locations.

7 RESULTS

7.1 Water quality parameters

Water quality parameters of river water from each location are reported (Table 3, Appendix E and F: figures 1a, 1b, 1c, and 1d). Dissolved oxygen and pH were variable within the study there were no significant differences observed between values measured in waters collected from the 3M Outfall or Bakers Creeks and those from upstream or downstream locations. Conductivity and temperature measured at the 3M Outfall and within Bakers Creek (BCR1) were significantly different from the upstream and downstream sample locations. However, there was no significant difference between that from Bakers Creek 2 samples and those collected from either the upstream and downstream sampling locations. This result indicates that the effect of the effluent from the 3M Facility on water quality parameters was limited to a small area near the 3M Outfall.

Table 3. Water quality parameters for samples collected from the Tennessee River, in the Decatur Alabama area. Values are reported as means and standard deviations

Location	DO (mg/L)	Conductivity (µmhos/cm)	Temperature (°C)	pH (s.u)
Guntersville	7.6 (0.8)	192.8 (5.4)	29.0 (0.3)	8.2 (0.4)
DWTP	10.0 * (1.3)	184.7 (3.4)	29.3 (0.3)	8.8 (0.2)
Outfall	6.5	4650 *	33.2 *	7.2
Bakers Creek-1	7.75 (1.4)	1843.3 * (1749.0)	30.7 * (1.4)	7.7 (0.5)
Bakers Creek-2	9.0 (0.6)	463.0 (108.9)	29.6 (0.6)	8.0 (0.1)
Fox Creek-1	8.1 (0.4)	179.0 (2.9)	27.8 (0.2)	8.2 (0.3)
Fox Creek-2	8.8 (1.3)	162.7 (8.1)	27.8 (0.5)	8.2 (0.5)

* Significantly different from Guntersville Reservoir at $\alpha = 0.05$

7.2 Fluorochemicals in Surface waters

Fluorochemicals were detected in all surface waters collected from the sample locations in the Tennessee River (Table 4) (Appendix F: figures 2a, 2b, 2c, and 2d). The least concentrations of all measured fluorochemicals, were observed in samples taken at Guntersville while the greatest concentrations were observed at 3M Outfall. In increasing order, the concentrations of PFOS, FOSA, PFOA and PFHS in surface water was as follows: GTVL < DWTP < FCR1 < FCR2 < BCR2 < BCR1 < Outfall. Concentrations of surface water fluorochemicals at only the 3M Outfall and Bakers Creek 1 locations were significantly greater than those measured at Guntersville Reservoir. Trifluoroacetic acid (TFA) concentrations were elevated in 3M Outfall (mean =1420 µg/L), Bakers Creek 1(mean = 680 µg/L) and Bakers Creek 2 (143 µg/L) samples but were less than the reporting limit of 100 µg/L in water samples collected from the other

sampling locations. This result indicates that the effect of the effluent from the 3M Facility on TFA water concentration was limited to a small area near the 3M Outfall.

Table 4. Mean concentration of fluorocarbons in surface waters of the Tennessee River in the Decatur, Alabama area. Concentrations in means and standard deviations

Location	PFOS (µg/L)	FOSA (µg/L)	PFOA (µg/L)	PFHS (µg/L)
Guntersville	0.009 (0.002)	0.004 (0.002)	0.008[1]	0.003[1]
DWTP	0.053 (0.013)	0.016 (0.025)	0.028 (0.006)	0.006 (0.006)
Outfall	150.50* (7.778)	7.985* (0.148)	1900.00* (0.00)	42.70* (1.697)
Bakers Creek-1	82.260* (56.672)	5.424* (3.074)	1023.60* (712.64)	22.374* (14.665)
Bakers Creek-2	13.838 (2.351)	1.191 (0.244)	129.375 (31.892)	4.034 (0.575)
Fox Creek-1	0.54 (0.05)	0.169 (0.022)	2.647 (0.614)	0.566 (0.102)
Fox Creek-2	0.179 (0.110)	0.055 (0.033)	1.001 (0.441)	0.168 (0.114)

* Significantly different from Guntersville Reservoir at $\alpha = 0.05$

[1] Limit of quantitation for all fluorochemicals water is 0.025 µg/L. All fluorochemical concentrations reported below the LOQ are estimates.

Additional statistical analyses were conducted on fluorochemicals in surface waters to further examine the difference between sample locations (GTVL, DWTP, BCR2, FCR1, and FCR2) located within the Tennessee River. Results from the first analysis showed that both the 3M Outfall and BCR1 could be influencing the results of the statistical analyses by acting in a manner similar to that of an outlier. For instance, the concentration of PFOS at the 3M Outfall and BCR1 were approximately 17,000-fold and 9,700-fold, greater, respectively, than the concentration observed at the Guntersville location. Removal of the 3M Outfall and BCR1 samples from the analysis allowed for the evaluation of the hypothesis that there were no statistically significant differences in

fluorochemical concentrations within the main channel and near shore locations within the river.

Results from the second analysis (Table 5) show that for water concentrations of PFOS and PFOA, only BCR2 was statistically greater than Guntersville Reservoir concentrations. Furthermore, while the concentrations of FOSA and PFHS at BCR2 and FCR1 were significantly greater than Guntersville, they were not significantly different from the furthest downstream location. Thus, at FCR2, the furthest downstream location, the concentration of targeted fluorochemicals was not significantly different from that observed at Guntersville Reservoir, which was selected as an upstream reference location.

Table 5. Tukey's range test results for surface water fluorochemicals taken from within or near the main channel of the Tennessee River[a]

Site	PFOS	FOSA	PFOA	PFHS
BCR2	A	A	A	A
FCR1	B	B	B	B
FCR2	B	B,C	B	C
WWTP	B	C	B	C
GTVL	B	C	B	C

[a] Sites with the same letter are not significantly different at $\alpha = 0.05$

From these results, it can be concluded that the 3M Outfall does not significantly effect concentrations of fluorochemicals farther downstream than FCR2. In addition, there were no statistically significant differences in the concentrations of fluorochemicals within the main channel of the river immediately below Bakers Creek as compared to those measured at the reference location.

7.3 Sediment concentrations of fluorocarbons

Fluorocarbons were detected in all sediments collected from the study sites (wet weight: Appendix F-figures 3a, b, c, d and dry weight: Appendix F-figures 4a, b, c, d).

Table 6. Mean concentration of fluorochemicals in sediments taken from the Tennessee River in the Decatur Alabama area[a]

Location	Wet weight sediment concentrations				Dry weight sediment concentrations			
	PFOS (µg/kg)	FOSA (µg/kg)	PFOA (µg/kg)	PFHS (µg/kg)	PFOS (µg/kg)	FOSA (µg/kg)	PFOA (µg/kg)	PFHS (µg/kg)
Guntersville	0.18 (0.07)	0.08 (0.01)	0.08 (0.01)	0.08[b]	0.43 (0.20)	0.19 (0.04)	0.19 (0.04)	0.19 (0.04)
DWTP	0.98 (0.42)	0.15 (0.06)	0.09 (0.02)	0.08 (0.01)	1.72 (0.83)	0.26 (0.11)	0.16 (0.04)	0.14 (0.04)
Outfall	5930.00* (254.56)	1200.00* (42.43)	1855.00* (106.07)	135.00* (4.24)	12600.00* (565.69)	2555.00* (91.92)	3950.00* (226.27)	287.50* (9.19)
Bakers Creek 1	1298.67* (751.89)	283.30* (176.21)	892.00* (345.80)	42.10* (22.05)	2275.67* (142.76)	503.17* (364.31)	1548.17* (774.63)	74.6* (48.57)
Bakers Creek 2	192.00 (191.27)	54.09 (36.33)	237.61* (283.01)	11.46* (8.08)	272.64 (279.05)	75.91 (53.03)	338.43* (410.79)	16.18 (11.91)
Fox Creek 1	2.58 (1.37)	1.70 (1.09)	1.81 (0.77)	0.22 (0.11)	4.51 (2.88)	2.99 (2.21)	3.11 (1.68)	0.38 (0.23)
Fox Creek 2	0.93 (0.10)	0.44 (0.05)	0.80 (0.22)	0.08[b]	2.02 (0.22)	0.95 (0.10)	1.73 (0.46)	0.17[b]

* Significantly different form Guntersville Reservoir at $\alpha = 0.05$

[a] Concentrations given as means with standard deviations in parenthesis

[b] Limit of quantification of all fluorocarbons in sediment is 0.20 µg/kg wet weight. All values reported below the LOQ are estimates.

Least concentrations of fluorochemicals in sediments were observed at Guntersville Reservoir while the greatest concentrations were observed in sediments collected in the vicinity of the 3M Outfall (Table 6).

Concentrations of fluorochemicals in sediment decreased in the following order: GTVL < DWTP < FCR2 < FCR1< BCR2< BCR1< OUTF. For PFOS and FOSA, only concentrations in sediments at the 3M Outfall and BCR1 locations were significantly greater than those collected from the reference location in Guntersville Reservoir. In addition, concentrations of PFOA and PFHS in sediments at the 3M Outfall, BCR1 and BCR2 were significantly greater than concentrations in sediments from Guntersville Reservoir. However, the fluorochemicals in sediments at BCR2 were not significantly different from concentrations measured at DWTP, FCR1 or FCR2. When sediment concentrations of targeted fluorochemicals were evaluated on a dry weight basis, only concentrations at the 3M Outfall and BCR1 were significantly different from those measured at Guntersville Reservoir.

As was done with the surface water data, statistical analyses were conducted that examined only the Tennessee River channel sample locations (GTVL, DWTP, BCR2, FCR1, and FCR2). Results from the second set of analyses showed that only the BCR2 concentrations of targeted fluorochemicals were greater than those observed at Guntersville Reservoir reference location on both a wet and dry weight basis. Thus, while concentrations at the Outfall and within Bakers Creek were statistically greater than the reference location, concentrations in sediments downstream of the 3M Facility were not statistically greater than those measured at the upstream reference location. The results of both of these analyses indicated that that there is little accumulation of the target fluorochemicals in sediments downstream of the 3M Outfall.

Sediment trifluoroacetic acid (TFA) concentrations were not significantly different between the sampling locations within the main channel of the Tennessee River. TFA concentrations for all sample locations except the 3M Outfall were less than the reporting limit of 500 µg/kg, wet weight. The 3M Outfall sediment TFA concentration averaged

510 µg/kg. This result indicates that the effluent from the 3M Facility only alters sediment concentrations in the immediate vicinity of the 3M Outfall, but does not significantly affect sediment TFA concentrations within Tennessee River.

7.4 Fish

Mean length, whole body weight and liver weight data for all fish species collected from the Tennessee River in the Decatur Alabama area are given (Table 7, Appendix G).

Table 7. Mean length, weight, and liver weight for fish collected from the Tennessee River (Collected on 06/21/00-06/22/00)[1].

Sample ID	Location	Length (cm)	Weight (g)	Liver wt (g)
LM1	Guntersville	26.5	195	1.32
	3M Outfall	32	454	2.92
SHAD	3M Outfall	34 (7.6)	352 (160)	1.95 (0.985)
WP1	3M Outfall	16.8 (0.36)	76 (7.1)	0.42 (0.04)
CAT	Guntersville	32.5 (2.12)	376 (112)	5.6 (0.18)
	3M Outfall	40.5 (12.0)	659.2 (531.2)	6.8 (3.8)
GAR	Guntersville	58.4 (5.25)	765 (170)	6.4 (4.3)
	3M Outfall	48.3 (5.3)	460.7 (170.4)	3.6 (1.9)
SB	Guntersville	23.3 (2.17)	168 (55.6)	1.01 (0.34)

[1] values are means with standard deviations (in parentheses)

Due to the small sample size and large amount of variability in the endpoints, there were no statistically significant different between the sites for species common to both the Outfall and Guntersville locations.

Physiological condition factors were calculated for each species and are given (Table 8, Appendix G). Statistical analysis of both condition factor and LSI showed no significant differences between sites for the species collected from both locations. The lack of any statistical significance was influenced by large amount variability in the data and by the

small sample size. The small sample size was due the fact that only a few species were collected at both locations. Furthermore, replicate fish samples were only collected for catfish and gar at both Guntersville and the Outfall location while largemouth bass, only a single fish was collected at both locations.

Table 8. Species and location specific condition factor (K) and liver somatic index (LSI) for fish collected from the Tennessee River in the Decatur Alabama area.

Species	Location	K[2]	LSI[3]
Largemouth Bass	3M Outfall	1.3855	2.92
Shad	3M Outfall	0.8207 (0.1224)	0.4772 (0.2877)
White perch	3M Outfall	1.6146 (0.0481)	0.5463 (0.0043)
Catfish	3M Outfall	0.8724 (0.0102)	1.1935 (0.3923)
Largemouth Bass	Guntersville	1.0478	0.6769
Catfish	Guntersville	1.0743 (0.1142)	1.5826 (0.5186)
Gar	Guntersville	0.3815 (0.0180)	0.8649 (0.6137)
Striped Bass	Guntersville	1.2094 (0.1207)	0.6241 (0.1902)

[1] Data presented as mean and standard deviation

[2] Condition factor (K) was calculated as $K = (Wt \times 100)/L^3$

[3] Liver somatic index (LSI) was calculated as LSI= (Liver wt/total wt) x100

7.4.1 Concentrations of PFOS, FOSA, PFOA, AND PFHS in fish livers.

Fluorocarbons were detected in all livers removed from fish collected at both the Guntersville and Outfall locations (Table 9, Appendix H). The least liver concentrations for all measured fluorocarbons were observed in fish collected from the Guntersville location while the greatest concentrations were observed in Outfall fish. Average for PFOS, FOSA, PFOA, and PFHS liver concentrations for all fish collected from the Outfall were approximately 19-fold, 340-fold, 109-fold and 710-fold greater than those observed in Guntersville fish, respectively.

Average liver concentrations for PFOS, FOSA, PFOA, and PFHS for all fish collected at the Guntersville site were 1036, 22.0, 22.1 and 3.79 µg/kg wet weight, respectively.

Table 9. Liver concentrations of selected fluorocarbons in fish collected from the Tennessee River in the Decatur, Alabama area. [a]

Species	PFOS (µg/kg)	FOSA (µg/kg)	PFOA (µg/kg)	PFHS (µg/kg)
Guntersville				
Catfish	87.3 (22.2)	20.3 (5.0)	18.8[b]	3.75[b]
Gar	249.3 (185.9)	20.95 (16.4)	18.8[b]	4.58 (1.65)
Striped Bass	1330.0 (763)	23.19 (10.0)	24.7 (17.6)	3.75[b]
Largemouth Bass	643	18.8[b]	18.8[b]	3.75[b]
Outfall				
Catfish	10093.5 (5,777.8)	14521.5 (2090.9)	252.9 (277.3)	30.2 (28.6)
Gar	13892.0 (3073.1)	5,089.0 (3,739.2)	1,934.5 (652.7)	256.5 (89.9)
Shad	9195.2 (13252.2)	4,420.0 (4047.3)	96.9 (49.0)	129.1 (145.3)
White perch	49285.0 (37657.7)	17403.0 (14679.5)	1628.5 (1228.2)	2069.5 (1941.0)
Largemouth bass	27143.0	2456.0	3.75[c]	11.6

[a] Concentrations are reported as means and standard deviations.
[b] Results was reported as the limit of quantitation: 18.8 µg/kg for PFOS, FOSA, PFOA and 3.75 µg/kg for PFHS
[c] Estimated value.

Differences in liver fluorocarbons concentrations were also observed between fish species collected at the site. Liver concentrations for the selected fluorocarbons increased in the following manner:

PFOS: Catfish < Gar < Largemouth bass < Striped bass

FOSA: (Largemouth bass)< Catfish < Gar < Striped bass

PFOA: (Catfish = Largemouth bass) < Gar < Striped bass

PFHS: (Striped bass = Catfish < Largemouth bass) < Gar

The fish in parentheses indicate liver fluorochemical concentration below the LOQ. Except for PFOS, there were no statistically significant differences in fluorochemical liver concentrations between fish species collected at Guntersville. For PFOS, there was a 160-fold difference between catfish that had the least concentration and striped bass with the greatest liver concentration. FOSA, PFOA, and PFHS liver concentrations in fish from Guntersville were all less than their respective LOQs. The significance of these results and a true understanding of the magnitude of the observed differences at this site are unknown at this time due to the variability in the data and small sample size.

Average liver concentrations for PFOS, FOSA, PFOA, and PFHS for all fish collected from the Outfall location were 15,692, 7,195, 581, and 384 µg/kg wet weight, respectively. As was observed at the Guntersville site, differences in liver fluorochemical concentrations were also observed between fish species collected at the site. Liver concentrations of the selected fluorochemicals at Outfall site increased as follows:

PFOS: Shad < Catfish < Gar < Largemouth Bass < White Perch

FOSA: Largemouth Bass <Shad< Gar < Catfish < White Perch

PFOA: Largemouth Bass < Shad < Catfish < White Perch < Gar

PFHS: Largemouth Bass < Catfish < Shad < Gar < White Perch

Except for PFOA, there were no statistically significant differences in species specific liver concentrations of the selected fluorocarbons for fish from the Outfall. For PFOS, FOSA, and PFHS there were 5.4, 7.1 and 178-fold differences between the least and greatest liver concentrations. However, due to the small sample size and large amount of variability observed in the data, these differences were not statistically significant. For PFOA liver concentrations, there was a 516-fold difference between the least and greatest concentration. However, only shad and gar liver concentrations were significantly different. Largemouth bass was not included in the analysis due to the fact that there was

only a single value for this species. The magnitude and significance of these differences is unknown at this time due to the variability in the data and small sample size.

7.4.2 Whole fish concentrations of PFOS, FOSA, PFOA, and PFHS

Fluorochemicals were detected in all fish collected from both the Guntersville and Outfall locations (Table 10, Appendix I).

Table 10. Whole body concentrations (wet weight) of selected fluorochemicals in fish collected from the Tennessee River in the Decatur Alabama area. [a]

Species	PFOS (µg/kg)	FOSA (µg/kg)	PFOA (µg/kg)	PFHS (µg/kg)
Guntersville				
Catfish	7.5[b]	7.5[b]	20.1[b]	7.5[b]
Gar	15.1 (15.2)	7.5[b]	20.1[b]	7.5[b]
Striped Bass	65.6 (23.2)	10.4 (0.96)	8.03[b]	7.5[b]
Largemouth Bass	230	8.76	8.03[b]	7.5[b]
Outfall				
Catfish	1190 (170)	ND	119.6 (140.6)	11.4 (5.52)
Gar	1863 (1679)	ND	154.5 (40.3)	35.5 (25.0)
Shad	ND	ND	54.0 (48.2)	38.9 (60.2)
White perch	ND	ND	278 (69.3)	405.5 (129.4)
Largemouth bass	ND	557	20.1[b]	7.5[b]

[a] Concentrations are reported as means and standard deviations.

[b] Results was reported as the limit of quantification:7.5 µg/kg for PFOS, FOSA, PFHS, 8.03 µg/kg for PFOA

ND signifies that the compound is present but not quantified due to the data not meeting quality control criteria.

The least fluorocarbon concentrations were observed in fish collected from the Guntersville location while the greatest concentrations were observed in fish from near the Outfall. Mean PFOS, FOSA, PFOA and PFHS concentration for all fish collected from the Outfall were approximately 23-fold, 2-fold, 9-fold and 12-fold greater than those measured in Guntersville fish, respectively.

Mean whole body concentrations for PFOS, FOSA, PFOA and PFHS for all fish collected from the Guntersville site were 59.1, 9.43, 11.7 and 7.50 µg/kg wet weight, respectively. Species differences in whole body concentration at the site were also observed with concentrations increasing as follows:

PFOS:	Catfish < Gar < Striped bass < Largemouth bass
FOSAA:	Catfish = Gar < Largemouth bass < Striped bass
PFOA:	Largemouth bass = Striped bass < Catfish < Gar
PFHS:	All species equal due to being at LOQ

Due to the small sample size, there were no statistically significant differences between whole body concentrations for the species collected at this site. Furthermore, except for PFOS, there was less than a 3-fold difference between the least and greatest fluorochemical concentration in the species being evaluated in this study. For PFOS, there was a 30-fold difference between the least (catfish) and the greatest (largemouth bass) concentrations indicating that there is a potential for differences in the bioaccumulation of PFOS by fish species at this site.

Mean whole body concentration for PFOS, FOSA, PFOA and PFHS for fish caught at the Outfall were 1332.0, 20.1, 106.4, and 86. 9 µg/kg wet weight, respectively. As observed at the Guntersville location, differences in whole body fluorochemical concentrations were also observed between species caught on site. Whole body concentrations of fluorochemicals in Outfall site increased as follows:

PFOS:	Gar < Catfish (Shad, White perch, Largemouth bass)
FOSA:	Largemouth bass (Gar, Catfish, Shad, White perch)
PFOA:	Largemouth bass < Shad < Catfish < White perch
PFHS:	Largemouth bass < Catfish = Shad < White perch

The species listed in the parentheses were not quantified during the analyses and could not be evaluated in this report. As with the Guntersville fish, small sample size precluded any statistical analysis of the data to evaluate differences between species at the Outfall location. Thus, while these data show that there are differences between locations and between fish and locations, the small sample size precludes an evaluation of the significance and magnitude of these differences.

7.5 Fluorochemicals in Clam Tissues

Fluorochemical concentrations were also measured in clam tissues collected at both sites (Table 11, Appendix H). PFOS concentrations did not differ between the sites and ranged from 15.6 µg/kg to 14.1 µg/kg wet weight at Guntersville and the Outfall, respectively. In contrast, there was a 42.8-fold difference in FOSA clam tissue concentrations with 25.1 µg/kg and 1074 µg/kg, wet weight, being measured at Guntersville and Outfall locations, respectively. There were no significant differences in the concentration of PFOA and PFHS in clam tissue collected at each of the two sites. The results of the clam analyses reflect the areas from which the samples were collected. Due to substrate problems, Outfall clams were collected at the Fox Creek location. This location had surface water and sediment fluorochemical concentrations that were statistically similar to those observed at the Guntersville location. Thus, these results indicate that for at least clams, the environmental concentrations of fluorochemicals downstream of the 3M Outfall have returned to background levels within in the Tennessee River.

Table 11. Tissue concentrations of selected fluorochemicals in clams collected from the Tennessee River in the Decatur Alabama area. [1]

Location	PFOS (µg/kg)	FOSA (µg/kg)	PFOA (µg/kg)	PFHS (µg/kg)
Guntersville	15.6[2]	25.1	4.38[2]	0.946[2]
Outfall	14.1[2] (13.7)	1074 (1358)	8.42[2] (7.18)	0.37[2] (0.53)

[1] Concentrations presented as means and standard deviations.
[2] Limits of quantitation: 18.8 µg/kg for PFOS, FOSA, PFOA, 3.75 µg/kg for PFHS. Concentrations reported below LOQs are estimated values

8 REFERENCES

Hansen, K.J. and H.O. Johnson. 2000. Determination of perfluorooctanoate sulfonate (PFOS), perfluorooctane sulfonylamide (FOSA), and perfluorooctanoate (PFOA) in water by liquid-solid extraction and high-performance liquid chromatography/tandem mass spectrometery (HPLC/MS/MS). 3M Environmental Laboratory method. Number ETS-8-154.0.

3M Environmental Laboratory, St. Paul, MN. LIMs Report numbers: E00-2361, E00-1958, E01-0520.

9 APPENDICES

Appendix A. Structure and chemical characteristics of selected fluorochemicals monitored in water, sediment and biota of the Tennessee River in the Decatur Alabama area.

Appendix B. Water and Sediment locations within the Tennessee River study areas

Appendix C. Water, sediment, clams, and fish sampling protocols

Appendix D. Centre Analytical Laboratories analytical report for the characterization of fluorochemicals in water and sediment.

Appendix E. Water quality data collected at sample locations.

Appendix F. Topographic maps of sample locations in the Tennessee River study area. Maps include water quality data, water or sediment fluorochemical concentrations for sample locations.

Figure 1. Water quality parameters
Figure 2. Fluorochemicals in surface waters
Figure 3. Fluorochemicals in sediments, wet weight
Figure 4. Fluorochemicals in sediments, dry weight

Appendix G. Physiological data for fish collected from the Tennessee River.

Appendix H. Fluorochemicals concentrations in fish livers and clam tissues collected from the Tennessee River in the Decatur Alabama area.

Appendix I. Whole body fluorochemical concentrations in fish collected from the Tennessee River in the Decatur Alabama area.

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Analytical Report

Fluorochemical Characterization of Water and Sediment Samples

MSU-Entrix (Tennessee River) FACT-GEN-037 (E00-1958)

Centre Analytical Laboratory Report No. 023-014O (Revision 2)

Revision Date 6/28/01

Testing Laboratory

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1 Introduction

Results are reported for the analysis of a series of water and sediment samples received by Centre Analytical Laboratories, Inc. (Centre) from the 3M Environmental Laboratory. The samples were collected from the Tennessee River and are part of 3M Project E00-1958. The Centre study number assigned to the project is 023-014.

Specific fluorochemical characterization by liquid chromatography / tandem mass spectrometry (LC/MS/MS) was requested for all samples. A total of 66 samples were received for analysis.

The samples were prepared and analyzed by LC/MS/MS for the following list of fluorochemicals:

- Table 1: Target Analysis

Compound Name	Acronym
Perfluorooctane Sulfonate	PFOS
Perfluorooctane Sulfonylamide	PFOSA
Perfluorooctanoate	POAA
Perfluorohexane Sulfonate	PFHS

The analytical methods used for water samples were validated by Centre. The validation protocol and results are on file with Centre. The methods were modified for the sediment samples, however the procedures have not been fully validated for this matrix. Data presented here is the highest quality data available at this time.

2 Sample Receipt

The samples were submitted in individual plastic containers and were not preserved. Sixty-six individual sample containers were received. Samples were received on 7/26/00. The samples were collected between 6/19/00 and 6/22/00. Chain-of-custody information is presented in Attachment C.

3 Holding Times

The analytical method used was validated against a maximum holding time of 14 days. Samples were received after the 14-day holding time. However, it should be noted that field fortifications in water and other matrices have shown acceptable recoveries at 100 and 1000 ng/L for periods longer than 14 days.

4 *Methods - Analytical and Preparatory*

4.1 LC/MS/MS

4.1.1 Sample Preparation for LC/MS/MS Analysis

Water samples were initially treated with 200 uL of 250 mg/L sodium thiosulfate solution to remove residual chlorine. Solid phase extraction (SPE) was used to prepare the samples for LC/MS/MS analysis. A forty-milliliter portion of sample was transferred to a C_{18} SPE cartridge. The cartridge was first eluted with 5 mL of 40% methanol in water solution. The eluate was discarded and the SPE column was then eluted with 100% methanol. A 5 mL portion of methanol was collected for analysis by LC/MS/MS. This treatment resulted in an eight-fold concentration of the samples prior to analysis.

For the sediment samples, a representative portion of sample (5 grams) was first extracted into 5 ml of methanol. The extracts were filtered and diluted to a final volume of 40 mL with Type I water. The diluted extracts were then treated in the same manner as the water samples, beginning with the solid phase extraction.

4.1.2 Sample Analysis by LC/MS/MS

In HPLC, an aliquot of extract is injected and passed through a liquid-phase chromatographic column. Based on the affinity of the analyte for the stationary phase in the column relative to the liquid mobile phase, the analyte is retained for a characteristic amount of time. Following HPLC separation, ES/MS provides a rapid and accurate means for analyzing a wide range of organic compounds, including fluorochemicals. Electrospray is generally operated at relatively mild temperatures; molecules are ionized, fragmented, and detected. Ions characteristic of known fluorochemicals are observed and quantitated against standards.

A Hewlett-Packard HP1100 HPLC system coupled to a Micromass Ultima MS/MS was used to analyze the sample extracts. Analysis was performed using selected reaction monitoring (SRM). Water samples were extracted on 8/2/00 and 8/3/00 and analyzed by MS/MS between 8/3/00 and 8/17/00. Sediment samples were extracted 8/4/00 and 8/10/00 and were analyzed by MS/MS between 8/8/00 and 8/17/00. The HPLC and MS/MS methods used for analysis and instrument parameters can be found in Attachments D and E.

5 *Analysis*

5.1 Calibration

A 7-point calibration curve was analyzed at the beginning and end of the analytical sequence for the compounds of interest. The calibration points were prepared at 0, 25, 50, 100, 250, 500, and 1000 ng/L (ppt). The instrument response versus the concentration was plotted for each point. Using linear regression with 1/x weighting, the slope, y-intercept and correlation coefficient (r) and coefficient of determination (r^2) were determined. A calibration curve is acceptable if $r \geq 0.985$ ($r^2 \geq 0.970$).

Calibration standards are prepared using the same SPE procedure used for samples.

Calibration check standards were analyzed periodically (every three to five sample injections) throughout the analysis sequence. Compliance is obtained if the standard analyte concentrations are within +/-20% of the actual value.

For the results reported here, calibration criteria were met.

5.2 Blanks

Extraction blanks were prepared and analyzed with every extraction batch of samples. The extraction blanks should not have any target analytes present at or above the concentration of the low-level calibration standard. For these samples, the extraction blanks were compliant.

Instrument blanks in the form of clean methanol solvent were also analyzed after every high-level calibration standard, and after known high-level samples. Again, the blanks should not have any target analytes present at or above the low-level calibration standard. For the samples presented here the instrument blanks are compliant.

5.3 Surrogates

Surrogate spikes are not a component of the LC/MS/MS analytical method.

5.4 Matrix Spikes

Matrix spikes were prepared for every field sample using all compounds of interest. Matrix spike recoveries are given in Attachment B.

Field spikes were submitted with one sediment and one surface water sample. Field spike recoveries are also included in Attachment B. The sediment sample showed no recovery of the field spike, indicating that there was a problem with the sediment field spiking procedure.

Field control samples spiked at 200 ppt and 1000 ppt were submitted. The field control samples showed recoveries between 70 and 130%. The results are also included in Attachment B.

5.5 Duplicates

All field samples were analyzed in duplicate. Results are given along with the sample results in Attachment A.

5.6 Laboratory Control Samples

For LC/MS/MS analyses, Milliq water was spiked with all compounds of interest at 25 and 250 ng/L during each extraction set. All recoveries for all compounds were between 70-130% in each LCS. Results are given along with the raw data in Attachments D and E.

5.7 Sample Related Comments

There are no other sample related comments for this data set.

6 Data Summary

Please see Attachment A for a detailed listing of the analytical results. Surface water results are reported in parts per trillion (ppt) (ng/L). Sediment sample results are reported in parts per billion (ppb) (ug/Kg) on both an as-received and dry-weight basis.

7 *Data/Sample Retention*

Samples are disposed of one month after the report is issued unless otherwise specified. All electronic data is archived on retrievable media and hard copy reports are stored in data folders maintained by Centre.

8 *Attachments*

8.1 Attachment A: Results

8.2 Attachment B: Matrix Spike Recoveries

8.3 Attachment C: Chain of Custody

8.4 Attachment D: LC/MS/MS Raw Analytical Data (Surface Water Samples)

8.5 Attachment E: LC/MS/MS Raw Analytical Data (Sediment Samples)

9 *Signatures*

John M Flaherty 6/28/01

John M. Flaherty, Operations Manager — Date

6/28/01

Kevin J Lloyd, Vice President — Date

Other Lab Members Contributing to Data

Karen Smith

SECTION A

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Analytical Results GEN-037 Surface Waters

3M Sample Identification	Date Collected	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)	PFHS (ng/L)
SW-FB01	6/20/00	NQ	ND	ND	ND
SW-13	6/19/00	60.2	NQ	30.7	NQ
SW-13 Dup	6/19/00	65.2	NQ	32.0	NQ
SW-14	6/19/00	67.0	NQ	30.1	26.4
SW-14 Dup	6/19/00	64.0	NQ	32.1	NQ
SW-15	6/19/00	49.7	NQ	25.6	NQ
SW-15 Dup	6/19/00	59.7	NQ	30.3	NQ
SW-16	6/19/00	53.5	NQ	28.6	NQ
SW-16 Dup	6/19/00	52.9	NQ	29.2	NQ
SW-17	6/19/00	41.2	NQ	NQ	NQ
SW-17 Dup	6/19/00	68.4	NQ	42.0	NQ
SW-18	6/19/00	32.9	NQ	NQ	< 25
SW-18 Dup	6/19/00	33.2	NQ	NQ	< 25
SW-18 Field Duplicate	6/19/00	40.6	NQ	NQ	NQ
SW-25	6/19/00	156000	7880	1900000	43900
SW-25 Dup	6/19/00	145000	8090	1900000	41500
SW-26	6/19/00	77300	6960	58200	12100
SW-26 Dup	6/19/00	78300	6700	57200	11500
SW-01	6/19/00	131000	7930	1700000	35300
SW-01 Dup	6/19/00	154000	8830	1800000	38800
SW-02	6/19/00	66700	4400	748000	17000
SW-02 Dup	6/19/00	67700	4840	753000	17700
SW-03	6/19/00	11900	1120	117000	3070
SW-03 Dup	6/19/00	13300	1160	126000	3460
SW-04	6/19/00	14500	1300	107000	4250
SW-04 Dup	6/19/00	10900	878	102000	3210
SW-05	6/19/00	14800	1430	162000	4130
SW-05 Dup	6/19/00	18200	1610	187000	5030
SW-06	6/19/00	11900	1020	104000	3920
SW-06 Dup	6/19/00	11900	986	104000	3800
SW-06 Field Duplicate	6/19/00	15200	1140	143000	4470
SW-11	6/20/00	565	151	2050	446
SW-11 Dup	6/20/00	497	141	1920	410
SW-11 FMS1	6/20/00	687	316	2040	584
SW-11 FMS2	6/20/00	1350	1050	2470	1090
SW-FSCS1	6/20/00	223	219	192	194
SW-FSCS2	6/20/00	993	717	903	889
SW-12	6/20/00	565	184	2646	637
SW-12 Dup	6/20/00	574	188	3030	654
SW-12 Field Duplicate	6/20/00	588	190	2990	635
SW-27	6/20/00	592	181	3410	658
SW-27 Dup	6/20/00	579	188	3510	658

Limit of Detection (LOD) for the procedure is appoximately 2.5 ng/L for PFOS, PFHS, and PFOSA and 7.5 ng/L for POAA

Limit of Quantitation (LOQ) for the procedure is 25 ng/L for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Surface Waters

3M Sample Identification	Date Collected	PFOS (ng/L)	PFOSA (ng/L)	POAA (ng/L)	PFHS (ng/L)
SW-07	6/20/00	509	149	2220	520
SW-07 Dup	6/20/00	464	143	2050	474
SW-08	6/20/00	319	99.4	1630	324
SW-08 Dup	6/20/00	315	96.3	1430	305
SW-09	6/20/00	97.6	36.1	582	86.3
SW-09 Dup	6/20/00	98.8	35.4	559	83.3
SW-10	6/20/00	116	34.4	925	110
SW-10 Dup	6/20/00	109	31.2	882	96.9
SW-19	6/21/00	NQ	ND	ND	ND
SW-19 Dup	6/21/00	NQ	ND	ND	ND
SW-20	6/21/00	NQ	NQ	ND	ND
SW-20 Dup	6/21/00	NQ	NQ	ND	ND
SW-21	6/21/00	NQ	NQ	ND	ND
SW-21 Dup	6/21/00	NQ	NQ	ND	ND
SW-22	6/21/00	NQ	NQ	ND	ND
SW-22 Dup	6/21/00	NQ	NQ	ND	ND
SW-23	6/21/00	NQ	NQ	ND	ND
SW-23 Dup	6/21/00	NQ	NQ	ND	ND
SW-24	6/21/00	NQ	NQ	ND	ND
SW-24 Dup	6/21/00	NQ	NQ	ND	ND
SW-FB02	6/22/00	ND	ND	ND	ND

Limit of Detection (LOD) for the procedure is appoximately 2.5 ng/L for PFOS, PFHS, and PFOSA and 7.5 ng/L for POAA

Limit of Quantitation (LOQ) for the procedure is 25 ng/L for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Sediments

3M Sample Identification	Date Collected	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)	PFHS (ug/Kg) (as received)
Sed-11	6/20/00	1.56	0.816	1.17	NQ
Sed-11 Dup	6/20/00	1.62	0.848	1.18	NQ
Sed-12	6/20/00	3.47	2.48	2.34	0.278
Sed-12 Dup	6/20/00	2.85	2.09	2.31	0.295
Sed-12 Field Dup	6/20/00	4.80	3.50	2.32	0.310
Sed-13	6/19/00	1.62	0.255	NQ	NQ
Sed-13 Dup	6/19/00	1.38	0.225	NQ	ND
Sed-14	6/19/00	0.43	NQ	ND	ND
Sed-14 Dup	6/19/00	0.506	NQ	ND	ND
Sed-15	6/19/00	1.53	0.248	NQ	ND
Sed-15 Dup	6/19/00	1.30	NQ	ND	ND
Sed-16	6/19/00	0.452	ND	ND	ND
Sed-16 Dup	6/19/00	0.574	ND	ND	ND
Sed-17	6/19/00	1.03	NQ	ND	ND
Sed-17 Dup	6/19/00	0.896	NQ	ND	ND
Sed-18	6/19/00	0.824	NQ	NQ	ND
Sed-18 Dup	6/19/00	0.816	NQ	NQ	ND
Sed-18 Field Dup	6/19/00	1.38	NQ	NQ	ND
Sed-25	6/19/00	5750	1170	1930	132
Sed-25 Dup	6/19/00	6110	1230	1780	138
Sed-27	6/20/00	3.63	1.55	2.49	0.330
Sed-27 Dup	6/20/00	3.54	2.90	2.76	0.320

Limit of Detection (LOD) for the procedure is appoximately 0.08 ug/Kg for all compounds

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Sediments

3M Sample Identification	Date Collected	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)	PFHS (ug/Kg) (as received)
Sed-01	6/19/00	1400	270	1010	36.5
Sed-01 Dup	6/19/00	1720	317	862	39.6
Sed-02	6/19/00	1860	431	1270	67.4
Sed-02 Dup	6/19/00	2070	513	1230	69.4
Sed-03	6/19/00	309	73.6	453	16.9
Sed-03 Dup	6/19/00	433	95.2	527	22.8
Sed-04	6/19/00	465	107	654	24.5
Sed-04 Dup	6/19/00	478	96.9	643	21.9
Sed-05	6/19/00	69.9	54.6	105	7.22
Sed-05 Dup	6/19/00	85.5	56.9	135	7.79
Sed-06	6/19/00	64.7	19.3	36.7	5.99
Sed-06 Dup	6/19/00	83.6	23.1	47.7	6.56
Sed-06 Field Dup	6/19/00	97.3	20.8	41.9	6.24
Sed-07	6/20/00	1.01	0.598	0.880	ND
Sed-07 Dup	6/20/00	0.872	0.553	0.848	NQ
Sed-08	6/20/00	0.936	0.491	0.710	ND
Sed-08 Dup	6/20/00	1.12	0.471	0.740	ND
Sed-09	6/20/00	0.92	0.468	1.08	ND
Sed-09 Dup	6/20/00	0.912	0.447	1.07	ND
Sed-10	6/20/00	0.864	0.373	0.582	ND
Sed-10 Dup	6/20/00	0.832	0.393	0.612	ND
Sed-19	6/21/00	NQ	ND	ND	ND
Sed-19 Dup	6/21/00	ND	ND	ND	ND

Limit of Detection (LOD) for the procedure is appoximately 0.08 ug/Kg for all compounds

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Sediments

3M Sample Identification	Date Collected	PFOS (ug/Kg) (as received)	PFOSA (ug/Kg) (as received)	POAA (ug/Kg) (as received)	PFHS (ug/Kg) (as received)
Sed-20	6/21/00	0.217	ND	ND	ND
Sed-20 Dup	6/21/00	0.318	NQ	ND	ND
Sed-21	6/21/00	NQ	ND	ND	ND
Sed-21 Dup	6/21/00	NQ	ND	ND	ND
Sed-22	6/21/00	NQ	ND	ND	ND
Sed-22 Dup	6/21/00	NQ	ND	ND	ND
Sed-23	6/21/00	NQ	ND	ND	ND
Sed-23 Dup	6/21/00	NQ	ND	ND	ND
Sed-24	6/21/00	0.266	NQ	NQ	ND
Sed-24 Dup	6/21/00	0.257	NQ	NQ	ND

Limit of Detection (LOD) for the procedure is appoximately 0.08 ug/Kg for all compounds

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Sediments

3M Sample Identification	Date Collected	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)	PFHS (ug/Kg) (dry weight)
Sed-11	6/20/00	2.05	1.07	1.54	NQ
Sed-11 Dup	6/20/00	2.13	1.12	1.55	NQ
Sed-12	6/20/00	6.46	4.62	4.36	0.518
Sed-12 Dup	6/20/00	5.31	3.89	4.30	0.549
Sed-12 Field Dup	6/20/00	9.14	6.67	4.42	0.590
Sed-13	6/19/00	2.72	0.429	NQ	NQ
Sed-13 Dup	6/19/00	2.32	0.378	NQ	ND
Sed-14	6/19/00	0.572	NQ	ND	ND
Sed-14 Dup	6/19/00	0.673	NQ	ND	ND
Sed-15	6/19/00	2.35	0.382	NQ	ND
Sed-15 Dup	6/19/00	2.00	0.235	ND	ND
Sed-16	6/19/00	0.657	ND	ND	ND
Sed-16 Dup	6/19/00	0.834	ND	ND	ND
Sed-17	6/19/00	2.78	NQ	ND	ND
Sed-17 Dup	6/19/00	2.42	NQ	ND	ND
Sed-18	6/19/00	1.36	NQ	NQ	ND
Sed-18 Dup	6/19/00	1.34	NQ	NQ	ND
Sed-18 Field Dup	6/19/00	2.28	NQ	NQ	ND
Sed-25	6/19/00	12200	2490	4110	281
Sed-25 Dup	6/19/00	13000	2620	3790	294
Sed-27	6/20/00	6.54	2.79	4.49	0.595
Sed-27 Dup	6/20/00	6.38	5.23	4.97	0.577

Limit of Detection (LOD) for the procedure is appoximately 0.08 ug/Kg for all compounds (as received)

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds (as received)

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Sediments

3M Sample Identification	Date Collected	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)	PFHS (ug/Kg) (dry weight)
Sed-01	6/19/00	2150	415	1550	56.1
Sed-01 Dup	6/19/00	2640	487	1320	60.8
Sed-02	6/19/00	3660	848	2500	133
Sed-02 Dup	6/19/00	4070	1010	2420	137
Sed-03	6/19/00	472	113.0	693	25.8
Sed-03 Dup	6/19/00	662	146	806	34.9
Sed-04	6/19/00	671	154	944	35.4
Sed-04 Dup	6/19/00	690	140	927	31.6
Sed-05	6/19/00	94.6	73.9	142	9.77
Sed-05 Dup	6/19/00	116	77.0	183	10.5
Sed-06	6/19/00	88.9	26.5	50.4	8.23
Sed-06 Dup	6/19/00	115	31.7	65.5	9.01
Sed-06 Field Dup	6/19/00	133	28.3	57.1	8.72
Sed-07	6/20/00	1.36	0.806	1.19	ND
Sed-07 Dup	6/20/00	1.18	0.745	1.14	NQ
Sed-08	6/20/00	2.04	1.07	1.55	ND
Sed-08 Dup	6/20/00	2.44	1.03	1.61	ND
Sed-09	6/20/00	1.96	0.998	2.30	ND
Sed-09 Dup	6/20/00	1.94	0.953	2.28	ND
Sed-10	6/20/00	1.89	0.816	1.27	ND
Sed-10 Dup	6/20/00	1.82	0.860	1.34	ND
Sed-19	6/21/00	NQ	ND	ND	ND
Sed-19 Dup	6/21/00	ND	ND	ND	ND

Limit of Detection (LOD) for the procedure is appoximately 0.08 ug/Kg for all compounds (as received)

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds (as received)

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ

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Analytical Results GEN-037 Sediments

3M Sample Identification	Date Collected	PFOS (ug/Kg) (dry weight)	PFOSA (ug/Kg) (dry weight)	POAA (ug/Kg) (dry weight)	PFHS (ug/Kg) (dry weight)
Sed-20	6/21/00	0.558	ND	ND	ND
Sed-20 Dup	6/21/00	0.817	NQ	ND	ND
Sed-21	6/21/00	NQ	ND	ND	ND
Sed-21 Dup	6/21/00	NQ	ND	ND	ND
Sed-22	6/21/00	NQ	ND	ND	ND
Sed-22 Dup	6/21/00	NQ	ND	ND	ND
Sed-23	6/21/00	NQ	ND	ND	ND
Sed-23 Dup	6/21/00	NQ	ND	ND	ND
Sed-24	6/21/00	0.600	NQ	NQ	ND
Sed-24 Dup	6/21/00	0.580	NQ	NQ	ND

Limit of Detection (LOD) for the procedure is appoximately 0.08 ug/Kg for all compounds (as received)

Limit of Quantitation (LOQ) for the procedure is 0.20 ug/Kg for all compounds (as received)

ND - Compound not detected

NQ - Compound detected at a level between the LOD and LOQ. Result is not quantifiable.

ND < LOD < NQ < LOQ