

**A SURVEY OF SELECTED FLUOROCHEMICALS  
IN THE DECATUR ALABAMA AREA  
2002 SAMPLING**

**Revised Report 11/3/03**

*Prepared for:*

**3M**

St. Paul, Minnesota

*Prepared by:*

**Entrix, Inc.**

John P. Giesy, Ph.D.

John L. Newsted, Ph.D.

East Lansing, Michigan

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## 1 EXECUTIVE SUMMARY

A monitoring study was conducted to determine the concentrations of selected fluorochemicals in fish, water and sediments within the Tennessee River in the vicinity of the 3M facility in Decatur Alabama. Samples were analyzed for five fluorochemicals: perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (FOSA), perfluorooctanoate (PFOA), perfluorohexanesulfonate (PFHS), and perfluorobutanesulfonate (PFBS). Three primary locations were sampled during the survey. These included a location upstream of the 3M facility (LOC-3) near river mile 307.5, a location across the River from the 3M facility near river mile 301 (LOC-2), and a location downstream of the 3M facility near river mile 296 (LOC-1). All surface water, sediment and fish samples were collected according to standard procedures and analyzed for fluorochemicals according to 3M Environmental Laboratory methods. The results presented in this report have been revised from a previous report.

Conductivity and pH were greater in surface waters from the downstream location (LOC-1) when compared upstream locations (LOC-3 and LOC-2). However, these differences were minor and fell within the range of water quality parameters previously measured in the Tennessee River near Decatur, AL. Surface water concentrations of targeted fluorochemicals were less than limits of quantitation (<LOQ) at LOC-2 and LOC-3. In contrast, PFOS, FOSA, PFOA, PFHS and PFBS were detected in surface water collected downstream of the 3M facility (LOC-1) but were less than 0.6 µg/L. In sediments, PFOS concentrations ranged from 0.42 µg/kg to 3.1 µg/kg (wet weight) for LOC-3 and LOC-1, respectively. In addition, concentrations of FOSA, PFOA, PFHS and PFBS in sediments were also greater at the downstream location (LOC-1) when compared to measured concentrations at LOC-2 and LOC-3. However, due to the small sample size (N=1), statistical analyses were not conducted to evaluate the differences between sample locations. In general, concentrations of fluorochemicals in water and sediment were greater downstream of the 3M facility as compared to concentrations measured across (LOC-2) or upstream (LOC-3) of the 3M facility. The concentration of fluorochemicals in surface waters remained relatively constant or decreased slightly between the 2000 and 2002 sampling seasons. However, due to differences in sample locations, small sample

sizes, and analytical methods, no conclusions about temporal trends for surface water could be made. While differences were observed in sediment fluorochemical concentrations between 2000 and 2002, these changes were not great (less than 2-fold) and due to differences in sample size, analytical methods and variability in the data, conclusions concerning temporal trends could not be made.

Fish collected from LOC-1 contained quantifiable levels of PFOS and FOSA in fillets while at LOC-2 and LOC-3, the only quantifiable fluorochemical in fish fillets was PFOS. The least concentration of fluorochemicals were observed in fish fillets from LOC-2 and LOC-3, across from and upstream of the 3M facility while the greatest concentrations were observed in fish fillets collected downstream of the facility, at LOC-1. For instance, in fish fillets from LOC-3, the average concentration of PFOS was 7.6 µg/kg while FOSA, PFOA, PFHS, PFBS concentrations were <LOQ (wet weight). For fish collected at LOC-1, average fillet concentrations for PFOS and FOSA were 305 µg/kg and 32 µg/kg (wet weight), respectively. However, concentrations of PFOA, PFHS and PFBS in fish fillets from LOC-1 were <LOQ (wet weight). While differences in the concentrations of fluorochemicals were observed between catfish and largemouth bass at the different locations, due to among individual variability and small sample sizes, these differences were not statistically significant. While fish previously have been sampled in the Tennessee River near the 3M facility, a comparison between the previous monitoring study could not be done due to differences in sampling locations, fish age and size, and the types of fish tissues analyzed in each of the studies. Therefore, a trend analysis was not conducted with the fish fluorochemical data

## 2 INTRODUCTION

Entrix, Inc. (ENTRIX) is providing a report on activities to assess the distribution of fluorochemicals in the Tennessee River in the Decatur Alabama area. The results of this study are part of a larger effort to ascertain the spatial and temporal behavior of fluorochemicals in the Tennessee River that may have been discharged from the 3M Decatur Alabama Facility. The results of the 2002 sampling season were compared qualitatively to the results the 2000 sampling season to examine any potential trends in the distribution and magnitude of the fluorochemicals in water, sediment and biota. Water, sediment, and fish were collected from three locations upstream, across and downstream of the 3M Facility. Fluorochemicals selected for evaluation in this study included: perfluorooctanesulfonate (PFOS), perfluorooctanesulfonamide (FOSA), perfluorooctanoate (PFOA), perfluorohexanesulfonate (PFHS) and perfluorobutanesulfonate (PFBS) (see Appendix A).

## 3 FIELD SAMPLING

### 3.1 *Site Description*

The sampling locations selected as part of the 2002 sampling program were representative of areas used by recreational and commercial fishermen. At each of three locations selected for this field investigation, water, sediment, and fish samples were collected. Sampling areas consisted of a location across the River from the 3M point of discharge, a location downstream of the 3M facility, and a location upstream of the 3M facility. The Riverwalk Marina (Marina) located on the northeast side of the river at approximately river mile 305 was used for river access. The downstream sampling location (LOC-1) was in the vicinity of Fox Creek (approximately river mile 296). The sampling location across the river from the 3M facility (LOC-2) was located approximately at river mile 301 while the upstream location (LOC-3) was at river mile 307.5 (upstream of the 3M discharge, the city of Decatur, and the Highway 31 bridge) (Figure 1; also see Appendix B).



### **3.2 Field Sampling Logistics**

Sampling at selected sites on the Tennessee River was initiated on April 15, 2002 by ENTRIX. Collection of water and sediment samples continued until April 16, 2002. Fish collection was initiated on April 15 and continued through April 18, 2002. Water, sediment, and fish were collected as outlined in the General Project Outline (GPO) provided by 3M.

### **3.3 Sample Collection**

#### **3.3.1 Water and Sediment Collection**

Water samples were collected using standard sampling protocols from a total of 3 locations (Table 1: also see Appendix C). At each location, water quality parameters were measured using YSI Model 63 and 95 meters. One sample was collected from each of the locations. All sampling locations were documented using TRIMLBE PRO-XRS Global Positioning Satellite technology and these locations were recorded on topographic maps. Samples were labeled, stored on ice at 4°C, and delivered to the 3M Environmental Laboratory, St. Paul, MN.

Sediment samples were collected from the same locations as the water samples (Table 1). A total of 3 grab samples were collected from the Tennessee River. Sediments were collected by use of a PONAR dredge following standard protocols (Appendix C). Sediments were placed into labeled 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     | River Mile | Code  |
|--------------|-----------------|--------------|------------|-------|
| SW-01        | SED-01          | Downstream   | 296        | LOC-1 |
| SW-02        | SED-02          | Across River | 301        | LOC-2 |
| SW-03        | SED-03          | Upstream     | 307.5      | LOC-3 |



### 3.3.2 *Fish Collection*

Fish were collected from three locations (Figure 1). These three locations were in close proximity to where water and sediments were collected. Fish were collected using a boat mounted Smith-Root type VI-A electroshock device (Appendix G). According to the GPO, a minimum of six bass (preferably largemouth) and six catfish were to be collected from each of the three sites. For this investigation, only the desired fish species caught at each of the sampling locations were retained for analysis. Collected fish were measured (total length), weighed, and immediately wrapped in aluminum foil and placed in Ziplock® storage bags (Table 2). Samples were labeled, placed on ice, and shipped via overnight FedEx to the ENTRIX office in East Lansing, Michigan, and then transported immediately to freezer facilities in the Aquatic Toxicology Laboratory (ATL) at Michigan State University. Upon completion of sampling activities, the Alabama Department of Wildlife and Freshwater Fisheries was notified that sampling was complete and their required notification form was completed and mailed to them.

### 3.3.3 *Fish Fillet Processing and Sample Preparation*

ENTRIX conducted the fish processing and preparation of fillets. Procedures described in the 3M GPO and the Alabama Department of Environmental Management Standard Operating Procedures Volume III were followed in fish fillet preparation (USEPA 2000). Fillets included the tissue from behind the head to the tail on both sides of each fish. Each fillet was removed from the fish and the skin removed using a fillet knife. The rib bones were either avoided during filleting or removed from each fillet so that only edible portions of the fillet remained. The carcass of each fish, the skin, and rib bones from each fillet were then wrapped in aluminum foil (dull side to fish), labeled with its sample location and ID number, placed in a pre-labeled Ziploc® bag and stored at -20°C. The fillet was cut into small pieces to expedite the grinding process. A hand grinder was used for the larger fish and a stainless steel blender for samples with less tissue. In all cases, the ground tissues were thoroughly mixed with stainless steel spatulas and mortar and pestle to ensure adequate homogenization. Once homogenized, the tissue was massed to the nearest hundredth gram and placed in Nalgene HPDPE containers. A label detailing the sample location, ID number, date processed, sample identity (bass or catfish) and

mass of the tissue was placed on each container. All containers were placed in pre-labeled Ziploc® bags and stored in coolers at -20°C. All tools and homogenizers were washed with detergent and warm water, then rinsed with methanol followed by a de-ionized water rinse to avoid cross contamination between each fish sample.

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

| Sample Id  | Location                    | Fish Type       |
|------------|-----------------------------|-----------------|
| SL01-LM01  | Downstream (Near Fox Creek) | Largemouth Bass |
| SL01-LM02  | Downstream (Near Fox Creek) | Largemouth Bass |
| SL01-LM03  | Downstream (Near Fox Creek) | Largemouth Bass |
| SL01-LM04  | Downstream (Near Fox Creek) | Largemouth Bass |
| SL01-LM05  | Downstream (Near Fox Creek) | Largemouth Bass |
| SL01-LM06  | Downstream (Near Fox Creek) | Largemouth Bass |
| SL01-CAT01 | Downstream (Near Fox Creek) | Catfish         |
| SL01-CAT02 | Downstream (Near Fox Creek) | Catfish         |
| SL01-CAT03 | Downstream (Near Fox Creek) | Catfish         |
| SL01-CAT04 | Downstream (Near Fox Creek) | Catfish         |
| SL01-CAT05 | Downstream (Near Fox Creek) | Catfish         |
| SL01-CAT06 | Downstream (Near Fox Creek) | Catfish         |
| SL02-LMB01 | Across River from 3M        | Largemouth Bass |
| SL02-LMB02 | Across River from 3M        | Largemouth Bass |
| SL02-LMB03 | Across River from 3M        | Largemouth Bass |
| SL02-LMB04 | Across River from 3M        | Largemouth Bass |
| SL02-LMB01 | Across River from 3M        | Largemouth Bass |
| SL02-CAT01 | Across River from 3M        | Catfish         |
| SL02-CAT02 | Across River from 3M        | Catfish         |
| SL02-CAT03 | Across River from 3M        | Catfish         |
| SL02-CAT04 | Across River from 3M        | Catfish         |
| SL02-CAT05 | Across River from 3M        | Catfish         |
| SL02-CAT06 | Across River from 3M        | Catfish         |
| SL02-CAT07 | Across River from 3M        | Catfish         |
| SL03-LMB01 | Upstream                    | Largemouth Bass |
| SL03-LMB02 | Upstream                    | Largemouth Bass |
| SL03-LMB03 | Upstream                    | Largemouth Bass |
| SL03-LMB04 | Upstream                    | Largemouth Bass |
| SL03-LMB05 | Upstream                    | Largemouth Bass |
| SL03-LMB06 | Upstream                    | Largemouth Bass |
| SL03-LMB07 | Upstream                    | Largemouth Bass |
| SL03-SM01  | Upstream                    | Smallmouth Bass |
| SL03-CAT01 | Upstream                    | Catfish         |
| SL03-CAT02 | Upstream                    | Catfish         |
| SL03-CAT03 | Upstream                    | Catfish         |
| SL03-CAT04 | Upstream                    | Catfish         |
| SL03-CAT05 | Upstream                    | Catfish         |
| SL03-CAT06 | Upstream                    | Catfish         |

#### **4 IDENTIFICATION AND QUANTIFICATION OF FLUOROCHEMICALS**

Water and sediment collected from the Tennessee River were analyzed by the 3M Environmental Laboratory (Study No. E02-0443). The analytical methods used for the analysis of water samples were validated by the 3M Environmental Laboratory. HPLC-Electrospray/Mass Spectrometry (HPLC/ES/MS) characterization of fluorochemicals was conducted at the 3M Environmental Laboratory. Summaries of each protocol are given:

##### ***4.1 Water Analysis***

Solid phase extraction was used to prepare the samples for HPLC/ES/MS analysis. A forty-milliliter portion of river water was passed through a preconditioned C<sub>18</sub> SPE cartridge and the column was allowed to dry for at least 3 min. The cartridge was eluted with 2 ml of methanol into autovials. The eluate was collected for analysis by LC/MS. Water extracts were analyzed by use of a Hewlett-Packard HP1100 HPLC system coupled to a Hewlett-Packard Series 1100 API/Mass Spectrometer Detector. HPLC conditions and ES/MS methods were based on ETS-8-155.1 "Analysis of waste stream, water extracts or other systems using HPLC-Electrospray/Mass Spectrometry".

##### ***4.2 Sediment Analysis***

For sediment samples, a 20 g portion was extracted into 35 ml of 1% acetic acid in capped centrifuge tubes. The samples were shaken for 60 min and then centrifuged. The aqueous solutions then passed through pre-conditioned SPE cartridge and the eluate was discarded. Methanol was then added to the sediment and the mixture was shaken for 30 min and centrifuged. The methanol was passed through the SPE cartridge and the eluate was discarded. The SPE cartridge eluted with 4 ml methanol and the collected methanol was then added to approximately 200ml of ASTM Type I water. This solution was then passed through a new pre-conditioned SPE cartridge and the aqueous eluates were discarded. The analytes were eluted from the SPE cartridge with 2.0 ml methanol into autovials for analysis. The extracts were analyzed by use of a Hewlett-Packard HP1100 HPLC system coupled to a Hewlett-Packard Series 1100 API/Mass Spectrometer Detector. HPLC conditions and ES/MS methods were based on ETS-8-155.1 "Analysis of waste stream, water extracts or other systems using HPLC-Electrospray/Mass Spectrometry".

### 4.3 *Fish Fillet Analysis*

Fluorochemicals were extracted from fish fillets using a solid phase extraction (SPE) method. Briefly, 2 g homogenized fillet tissues were diluted with ASTM Type I, mixed and aliquoted into triplicate samples. Matrix spikes were prepared and each sample was spiked with 10  $\mu\text{L}$  of a 100  $\mu\text{g/mL}$  spike solution of each targeted fluorochemical. Acetonitrile was used to extract the fluorochemicals and to precipitate proteins that can interfere with the analysis. After mixing and centrifugation, the supernatant was then passed through a pre-conditioned  $\text{C}_{18}$  SPE cartridge. Finally, the analytes were eluted from the SPE cartridge with methanol into autovials. The extracts were analyzed by HPLC-ES/MS. Details of the analytical procedure have been outlined in the 3M Environmental Laboratory (St. Paul, MN) standard operating procedures (ETS-8-231.1) for the analysis of fluorochemicals in tissues.

## 5 QA/QC

Standard operating procedures for sample collection and preparation were maintained during the entire project. QA/QC samples were collected in the field as required by 3M (Appendix D). Field blanks and trip blanks were collected and shipped with the samples. Field matrix spikes and field control samples were collected at each location along with a field duplicate. Field matrix spike solutions were prepared by collecting one liter of site water and spiking with a stock solution containing PFOS, FOSA, PFOA, PFHS and PFBS. 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. Photographs of all locations were taken to provide a visual record of the conditions of the site during the sampling events. Since the method detection limit (MDL) and lowest limit of quantification (LLOQ) 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. Data quality objectives were also established for each sample matrix (river water, sediment, and fish). In general, the Data Quality Objectives were: (1) all samples were analyzed in triplicate and the %RSD should be  $\leq 25\%$ , (2) matrix spikes should be  $\pm 30\%$  of expected value, (3) water blanks should be less than  $< \frac{1}{2}$  LLOQ for each analyte, and (4) extraction blanks should be  $< \frac{1}{2}$

LLOQ. Water and sediment concentrations were not corrected for either matrix spike recoveries or for purity of the fluorochemical standards. In addition, ambient water quality parameters, such as temperature, conductivity, salinity, pH and dissolved oxygen were measured at each location during each sampling event.

## **6 STATISTICAL ANALYSES**

Statistical analyses were performed with SAS<sup>®</sup> (Version 8, SAS Institute, Cary NC, USA). Where relevant, General linear models (PROC GLM) were used to test for differences among locations for all analyte concentrations in fish 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. All fish samples were included in the statistical analysis. For samples where fluorochemicals concentrations were less than their limit of quantitation, the limit of quantitation was substituted as a conservative estimate of the fish fluorochemical concentrations.

## **7 RESULTS**

A letter report summarizing field activities associated with the Tennessee River field sampling effort in 2002 was provided to 3M by ENTRIX, Inc (see Appendix F). The letter report included information relative to sample locations and a photograph log of sampling activities on the Tennessee River. The result sections below summarize this information along with analytical results from water, sediment and fish that were collected from the Tennessee River.

### ***7.1 Water quality parameters***

Surface water quality parameters from each location are reported (Table 3). Dissolved oxygen, pH, conductivity, and temperature were relatively constant for the Upstream (LOC-3) and Across (LOC-2) locations. However, at the downstream location (LOC-1), pH and conductivity were slightly greater than those recorded at the other locations. These minor differences may be due to the fact that sampling locations LOC-2 and LOC-3 were within or near the Tennessee River channel whereas LOC-1 was located in the mouth a small bay at the mouth of Fox Creek. As result, LOC-1 most likely was influenced by the water quality of the creek. Regardless, all values fell within historical

water quality parameters measured in the Tennessee River in the Decatur Alabama area (Giesy and Newsted, 2001).

**Table 3.** Water quality parameters for samples collected from the Tennessee River, in the Decatur Alabama area. Values are reported as a single value <sup>a</sup>

| Location             | DO<br>(mg/L)    | Conductivity<br>( $\mu$ S) | Temperature<br>(°C) | pH<br>(s.u) |
|----------------------|-----------------|----------------------------|---------------------|-------------|
| Upstream (LOC-3)     | 10.7            | 139.4                      | 18.1                | 7.2         |
| Across River (LOC-2) | 9.36            | 138.9                      | 21.0                | 7.3         |
| Downstream (LOC-1)   | NC <sup>b</sup> | 162.3                      | 21.8                | 9.4         |

<sup>a</sup> Means and standard deviations could not be determined since only a single sample was collected from each location.

<sup>b</sup> NC means not collected

## 7.2 Fluorochemicals in Surface waters

Fluorochemicals were quantifiable in surface waters collected from one sample location in the Tennessee River (Table 4) (Ellefson, 2003). At LOC-2 and LOC-3, surface water concentrations of PFOS, FOSA, PFOA, PFHS, and PFBS were less than the limit of quantitation. In contrast, PFOS, FOSA, PFOA, PFHS, PFBS were quantified in surface waters collected from LOC-1, downstream of the 3M facility. However, in samples where fluorochemicals were quantified (LOC-1), the concentrations were less than 0.6  $\mu$ g/L. Due to the small sample size (N=1), statistical analyses of the data was not conducted to evaluate differences among the sample locations.

**Table 4.** Concentration of fluorochemicals in surface waters of the Tennessee River in the Decatur, Alabama area. <sup>a</sup>

| Location                | PFOS<br>( $\mu$ g/L) | FOSA<br>( $\mu$ g/L) | PFOA<br>( $\mu$ g/L) | PFHS<br>( $\mu$ g/L) | PFBS<br>( $\mu$ g/L) |
|-------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Upstream<br>(LOC-3)     | < 0.13 <sup>b</sup>  | < 0.025              | < 0.05               | <0.025               | < 0.05               |
| Across River<br>(LOC-2) | < 0.13               | < 0.025              | < 0.05               | <0.025               | < 0.05               |
| Downstream<br>(LOC-1)   | 0.49                 | 0.025                | 0.55                 | 0.20                 | 0.08                 |

<sup>a</sup> Since only a single sample was collected from each location, no statistics are reported.

<sup>b</sup> All values denoted with (<) are reported as less than their limit of quantitation

### 7.3 Sediment concentrations of fluorochemicals

Some targeted fluorochemicals were quantified in sediments collected from all three locations within the study site (Table 5). Least concentrations of fluorochemicals in sediment were observed at LOC-3, upstream of the 3M Facility while the greatest concentrations were observed in sediments collected at LOC-1, downstream of the 3M facility. While there was insufficient data to conduct a statistical comparison among the sampling locations, these data indicate that concentrations of fluorochemicals in sediments were greater downstream of the 3M facility as compared to the upstream or across the river locations in the Tennessee River.

**Table 5.** Concentration of fluorochemicals in sediments of the Tennessee River in the Decatur, Alabama area. <sup>a</sup>

| Location                | PFOS<br>(µg/kg) | FOSA<br>(µg/kg) | PFOA<br>(µg/kg)      | PFHS<br>(µg/kg) | PFBS<br>(µg/kg) |
|-------------------------|-----------------|-----------------|----------------------|-----------------|-----------------|
| Upstream<br>(LOC-3)     | 0.42            | 0.068           | 0.13                 | < 0.10          | 0.45            |
| Across River<br>(LOC-2) | 0.46            | 0.14            | < 0.025 <sup>b</sup> | < 0.10          | 0.44            |
| Downstream<br>(LOC-1)   | 3.13            | 1.44            | 0.73                 | 0.13            | 0.58            |

<sup>a</sup> Means and standard deviations could not be determined since only a single sample was collected from each location. All concentrations reported on a wet weight basis.

<sup>b</sup> All values denoted with (<) are reported as less than their limit of quantitation

### 7.4 Fish

The fish species that were targeted in this study included largemouth bass (*Micropterus salmoides*) and channel catfish (*Ictalurus punctatus*). However, two other fish species were collected during the field sampling from LOC-3 and included one smallmouth bass (*Micropterus dolomieu*) and one yellow catfish, also known locally as a flathead catfish (*Pylodictis olivaris*). Statistical analysis of fish weight, length and condition factor was conducted using only the data for largemouth bass and channel catfish. There were no significant differences in weight or length of either fish species among the three locations (Table 6; also see Appendix E). Condition factors were calculated for each species and are given (Table 6). The condition factor is a measure of the overall physiological health of a fish that is measured as a ratio of weight to length. Statistical analysis of the

condition factors showed no significant differences in fish health between the three locations for either fish species.

**Table 6.** Mean length, weight, and condition factor for fish collected from the Tennessee River (Collected on 04/15/02-04/18/02).<sup>a</sup>

| Sample ID          | Location                      | Length<br>(cm) | Weight<br>(g) | Condition<br>Factor <sup>b</sup> |
|--------------------|-------------------------------|----------------|---------------|----------------------------------|
| Largemouth<br>Bass | Upstream (LOC-3)              | 36.3           | 639           | 1.305                            |
|                    |                               | (4.77)         | (219)         | (0.228)                          |
|                    | Across (LOC-2)                | 35.4           | 647           | 1.432                            |
|                    |                               | (6.89)         | (302)         | (0.208)                          |
|                    | Downstream (LOC-1)            | 34.5           | 591           | 1.416                            |
|                    |                               | (4.08)         | (170)         | (0.126)                          |
| Catfish            | Upstream (LOC-3) <sup>c</sup> | 55.1           | 2386          | 1.468                            |
|                    |                               | (11.7)         | (1099)        | (0.598)                          |
|                    | Across (LOC-2)                | 56.5           | 1942          | 1.049                            |
|                    |                               | (4.43)         | (623)         | (0.103)                          |
|                    | Downstream (LOC-1)            | 61.4           | 2920          | 1.166                            |
|                    |                               | (7.30)         | (1644)        | (0.192)                          |
| Smallmouth<br>Bass | Upstream (LOC-3)              | 32.5           | 563           | 1.640                            |

<sup>a</sup> Values are means with standard deviations (in parentheses).

<sup>b</sup> Condition factor calculated as  $(\text{Weight} \times 100) / \text{Length}^3$

<sup>c</sup> Catfish data from this site includes both channel and yellow catfish

#### 7.4.1 Fish Fillet concentrations of PFOS, FOSA, PFOA, PFHS and PFBS

Some fluorochemicals were quantified in some fish fillets collected at all three locations (Table 7). The least concentrations of fluorochemicals were observed in fish collected from the upstream location (LOC-3) while the greatest concentrations were observed in fish collected from the downstream location (LOC-1). For all three locations, the fish fillet concentrations of PFOA, PFHS and PFBS were less than the LOQ. PFOS was quantified in fillets of some fish collected from all three locations. However, FOSA was quantified only in catfish which were collected from the downstream location (LOC-1). The mean concentration of PFOS for fish fillets collected at LOC-1 was approximately 3.5-fold greater than that measured in fillets collected from LOC-2 and 40-fold greater than that measured in fillets from LOC-3. In the smallmouth bass collected at LOC-3, all monitored fluorochemicals were less than their limit of quantitation (LOQ). Since there



was no apparent difference between the concentration of fluorochemicals in channel and yellow catfish collected from LOC-3, the data for both species was combined.

**Table 7.** Fillet concentrations (wet weight) of selected fluorochemicals in fish collected from the Tennessee River in the Decatur Alabama area. <sup>a</sup>

| Species                   | N <sup>b</sup> | PFOS<br>(µg/kg)             | FOSA<br>(µg/kg)    | PFOA<br>(µg/kg) | PFHS<br>(µg/kg) | PFBS<br>(µg/kg) |
|---------------------------|----------------|-----------------------------|--------------------|-----------------|-----------------|-----------------|
| <b>UpStream (LOC-3)</b>   |                |                             |                    |                 |                 |                 |
| Catfish                   | 6              | 15.2 <sup>c</sup><br>(14.0) | < 2.5 <sup>d</sup> | < 5.0           | < 2.5           | < 5.0           |
| Largemouth Bass           | 7              | < 5.0                       | < 5.0              | < 5.0           | < 1.0           | < 2.5           |
| Smallmouth Bass           | 1              | < 2.5                       | < 5.0              | < 5.0           | < 1.0           | < 2.5           |
| <b>Across (LOC-2)</b>     |                |                             |                    |                 |                 |                 |
| Catfish                   | 7              | < 2.5                       | < 2.5              | < 5.0           | < 2.5           | < 5.0           |
| Largemouth Bass           | 4              | 169<br>(255)                | < 5.0              | < 5.0           | < 1.0           | < 2.5           |
| <b>Downstream (LOC-1)</b> |                |                             |                    |                 |                 |                 |
| Catfish                   | 6              | 113<br>(48.1)               | 61<br>(20)         | < 5.0           | < 2.5           | < 5.0           |
| Largemouth Bass           | 6              | 553<br>(231)                | < 5.0              | < 5.0           | < 1.0           | < 2.5           |

<sup>a</sup> Concentrations are reported as means and standard deviations. Means calculated with LOQ values.

<sup>b</sup> Number of fish analyzed

<sup>c</sup> Catfish data from this site includes both channel and yellow catfish

<sup>d</sup> All values denoted with (<) are reported as less than their limit of quantitation

PFOS concentrations were significantly greater ( $p < 0.05$ ) in both catfish and largemouth bass fillets collected from LOC-1 (downstream) as compared to fish from collected from across the river (LOC-2) or upstream (LOC3) of the 3M facility. While largemouth bass from LOC-2 had PFOS concentrations that were greater than those measured in fish from LOC-3, the difference in concentration was not statistically significant due to the variability in the measured concentrations in fillets from LOC-2 (Coefficient of variation =152%). The relatively great variability observed at LOC-2 was due to PFOS concentrations in largemouth bass fillets that ranged from <LOQ to 550 µg/kg, wet weight. Similarly, there was an apparent difference in catfish concentrations between

LOC-2 and LOC-3 but it wasn't statistically significant because of the variability in the measured concentrations in catfish fillets from LOC-3 (<LOQ to 37.4 µg/kg, wet weight).

In catfish, FOSA concentrations were significantly greater ( $p < 0.05$ ) in fish from LOC-1 than in catfish collected from LOC-2 or LOC-3. The mean concentration of FOSA in catfish from LOC-3 was not statistically different from those measured in catfish from LOC-2. Concentrations of FOSA in largemouth bass were not statistically different among any of the locations. Since all fillet concentrations were less than the LOQ for each analyte, no statistically significant differences were observed for PFOA, PFHS or PFBS concentrations in either catfish or largemouth bass among LOC-1, LOC-2, LOC-3 sampling locations.

### ***7.5 Comparison to 2000 Decatur Monitoring Study***

To evaluate trends in fluorochemical concentrations in the Tennessee River, data from the 2000 and 2002 sampling programs were compared (Giesy and Newsted, 2001). However, while fluorochemical concentrations in sediment and surface water can be directly compared among years, concentrations in fish could not be compared due to differences in experimental design. In 2000, the study design was intended to evaluate the distribution and magnitude of fluorochemicals in biota of the vicinity of the 3M facility and as a result fish concentrations were measured in whole body homogenates. In 2002, the objective of the study was to provide information on the potential exposure to humans consuming sport-caught fish and as a result, fish concentrations were measured only in homogenized fillets. Thus, a direct comparison of fluorochemicals in fish can not be made based on the different tissue targeted for analysis.

#### ***7.5.1 Surface water***

The concentration of fluorochemicals in surface waters remained relatively constant or decreased slightly between the 2000 and 2002 sampling seasons. (Table 8). For locations where a direct comparison could be made, WWTP to LOC3 and Fox Creek 1 to LOC1, the concentrations of fluorochemical in surface waters in 2002 were equal to or less than

those measured in 2000. For instance, concentrations of PFOS, FOSA, PFOA and PFHS were 9%, 85%, 80% and 65% less at in surface water collected at LOC-1 than that collected at Fox Creek 1, respectively. However, a direct comparison of fluorochemical concentrations between 2000 and 2002 was complicated by the fact that in 2000, the LOQs for all target analytes were approximately 2-fold less than those reported in 2002. This was due to the fact that different analytical methods were used in each sampling event to quantitate fluorochemicals in river water. Thus, if one used the greater LOQs from 2002, a decreasing trend in fluorochemical concentrations is observed for surface waters above and below the 3M facility in Decatur. However, due to the small sample size in 2002, a statistical comparison could not be made for surface water fluorochemical concentrations in the Tennessee River. Finally, it is important to note that all concentrations of fluorochemicals in surface water collected in 2002 were less than 1.0 µg/L (ppb).

**Table 8.** Mean concentration of fluorochemicals in surface waters of the Tennessee River near Decatur, Alabama.<sup>a</sup>

| Year | Station      | River Mile | PFOS (µg/L)         | FOSA (µg/L) | PFOA (µg/L) | PFHS (µg/L) |
|------|--------------|------------|---------------------|-------------|-------------|-------------|
| 2000 | Guntersville | 370        | <0.025 <sup>b</sup> | <0.025      | <0.025      | <0.025      |
| 2000 | WWTP         | 303.5      | 0.053               | <0.025      | 0.028       | <0.025      |
| 2000 | Bakers Cr.-2 | 301-302    | 14                  | 1.2         | 130         | 4.0         |
| 2000 | Fox Cr.-1    | 296        | 0.54                | 0.17        | 2.7         | 0.57        |
| 2000 | Fox Cr.-2    | 296        | 0.18                | 0.055       | 1.00        | 0.17        |
| 2002 | LOC-3        | 307.5      | < 0.13              | < 0.025     | < 0.05      | < 0.025     |
| 2002 | LOC-2        | 301        | < 0.13              | < 0.025     | < 0.05      | < 0.025     |
| 2002 | LOC-1        | 296        | 0.49                | <0.025      | 0.55        | 0.20        |

<sup>a</sup> All surface water concentrations reported as mean value.

<sup>b</sup> Concentrations given as less than (<) are less than their limit of quantitation (LOQ).

#### 7.5.2 Sediment

Concentrations of fluorochemicals in sediments upstream of the 3M facility (LOC3, WWTP and LOC2) did not differ greatly between the 2000 and 2002 sampling events. PFOS and FOSA concentrations at LOC-3 were approximately 0.42 -fold less than those measured at WWTP. In contrast, sediment PFOA concentrations at LOC-3 were 1.4-fold

greater than those measured at WWTP. While differences in sediment fluorochemical concentrations of FOSA, PFOA and PFHS were observed between the three upstream sites (WWTP, LOC-3 and LOC-2), these differences were less than 1.5-fold and most likely are indicative of the variability in fluorochemical concentrations in the Tennessee River in the Decatur Alabama area. However, downstream of the 3M facility, concentrations of fluorochemicals in sediments were more variable. The mean concentration of PFOS and FOSA was approximately 2-fold greater at LOC-1 than that measured at Fox Creek 2 but were similar to those measured at Fox Creek 1. In contrast, no trend was evident for concentrations of PFOA or PFHS in sediment among these three down stream locations. Overall, the temporal differences in sediment fluorochemical concentrations did not differ greatly and due differences in sample locations, analytical methods, and small sample size in 2002 (1 sample per location), a trend in fluorochemical concentrations could not be statistically evaluated upstream or downstream of the 3M facility.

**Table 9.** Mean fluorochemical concentrations in sediments of the Tennessee River near Decatur, Alabama. <sup>a</sup>

| Year | Station      | River Mile | PFOS (µg/kg)       | FOSA (µg/kg) | PFOA (µg/kg) | PFHS (µg/kg) |
|------|--------------|------------|--------------------|--------------|--------------|--------------|
| 2000 | Guntersville | 370        | <0.20 <sup>b</sup> | <0.20        | <0.20        | < 0.20       |
| 2000 | WWTP         | 303.5      | 0.98               | <0.20        | <0.20        | <0.20        |
| 2000 | Bakers Cr.-2 | 301-302    | 192                | 54.1         | 238          | 11.5         |
| 2000 | Fox Cr.-1    | 296        | 2.58               | 1.70         | 1.81         | 0.22         |
| 2000 | Fox Cr.-2    | 296        | 0.93               | 0.44         | 0.80         | < 0.20       |
| 2002 | LOC-3        | 307.5      | 0.42               | 0.068        | 0.13         | < 0.10       |
| 2002 | LOC-2        | 301        | 0.46               | 0.14         | <0.25        | < 0.10       |
| 2002 | LOC-1        | 296        | 3.13               | 1.44         | 0.73         | 0.13         |

<sup>a</sup> All sediment concentrations reported as mean value.

<sup>b</sup> Concentrations given as less than (<) are less than their limit of quantitation (LOQ). All data reported on a wet weight basis.

### 7.5.3 Fish

Concentrations of fluorochemicals were less in fish collected upstream of the 3M facility as compared to fish collected at the two downstream locations. However, comparisons

between sampling events is difficult due to differences in the tissue type analyzed each year and to the fact that fish were collected from different locations in the Tennessee River. Taking these differences into consideration, the mean concentration of PFOS was less in fish collected from Guntersville, LOC-3 and LOC-2 than that observed in fish from the Outfall or LOC-1. This same general trend was also observed for FOSA, PFOA and PFHS where concentrations in fish downstream of the 3M facility were greater than those measured in fish upstream of the facility. However, in largemouth bass collected in both years, concentration of PFOA and PFHS were less than their LOQ while FOSA was only quantified in fish collected from the Outfall in 2000. In catfish, PFOA and PFHS were not quantified in fish collected from Guntersville, LOC-3, LOC-2 and LOC-1. In addition, PFOS and FOSA were not quantified in fish collected from Guntersville, LOC-3, and LOC-2. Only the Outfall had quantifiable concentrations of all targeted fluorochemicals in catfish (2000) while LOC-1 had quantifiable concentrations of PFOS and FOSA (2002). The statistical significance of these differences can not be determined due to the fact that whole body homogenates were analyzed in 2000 while fillet homogenates were analyzed in 2002. Finally, for both 2000 and 2002, some concentrations of fluorochemicals were different between species sampled at all locations. For PFOS, the concentrations in largemouth bass were greater than those measured in catfish. However, for FOSA, PFOA and PFHS no species differences were discerned due several factors including variability in the data, small sample size and the fact that for PFOA and PFHS, all concentrations were less than the LOQ.

**Table 10.** Mean tissue fluorochemical concentrations in fish sampled from the Tennessee River near Decatur Alabama.

| Species         | Location                  | PFOS<br>(µg/kg)    | FOSA<br>(µg/kg) | PFOA<br>(µg/kg) | PFHS<br>(µg/kg) |
|-----------------|---------------------------|--------------------|-----------------|-----------------|-----------------|
| Largemouth Bass | Guntersville <sup>a</sup> | 230                | 8.8             | < 8.0           | < 7.5           |
|                 | LOC-3 <sup>b</sup>        | < 5.0 <sup>d</sup> | < 5.0           | < 5.0           | < 1.0           |
|                 | LOC-2 <sup>b</sup>        | 170                | < 5.0           | < 5.0           | < 1.0           |
|                 | Outfall <sup>a</sup>      | NQ                 | 560             | < 20            | < 7.5           |
|                 | LOC-1 <sup>b</sup>        | 550                | < 5.0           | < 5.0           | < 1.0           |
| Catfish         | Guntersville <sup>a</sup> | < 7.7              | < 7.5           | < 20            | < 7.5           |
|                 | LOC-3 <sup>b,c</sup>      | < 5.0              | < 2.5           | < 5.0           | < 2.5           |
|                 | LOC-2 <sup>b</sup>        | < 2.5              | < 2.5           | < 5.0           | < 2.5           |
|                 | Outfall <sup>a</sup>      | 1200               | NQ              | 120             | 11              |
|                 | LOC-1 <sup>b</sup>        | 110                | 61              | < 5.0           | < 2.5           |

<sup>a</sup> Fish collected in 2000

<sup>b</sup> Fish collected in 2002

<sup>c</sup> Catfish data from this site includes both channel and yellow catfish

<sup>d</sup> All values denoted with (<) are reported as less than their limit of quantitation

NQ is not quantified due to data not meeting quality control criteria.

All data reported on a wet weight basis.

## 8 REFERENCES

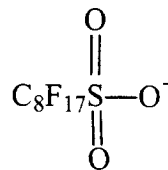
- Ellefson, M.E. 2003. Tennessee River Valley Samples. 3M Environmental Laboratory Study No. E02-0443. p. 276.
- Giesy, J.P. and J.L. Newsted. 2001. Selected fluorochemicals in the Decatur Alabama Area. Report to 3M.
- Reagen, W.K., 2002. Solid phase extraction and analysis of fluorochemical compounds from biological matrices. 3M Environmental Laboratory Method, Number ETS-8-231.1.
- US EPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1: Fish Sampling and Analysis, 3<sup>rd</sup> Edition. United States Environmental Protection Agency, Office of Water. EPA 823-B-00-007.

## **9 APPENDICES**

## 9.1 APPENDIX A

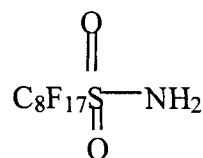
Selected Perfluorocarbons monitored in water, sediment and fish Collected from the Tennessee River, Decatur Alabama.

**Chemical Name:** Perfluorooctanesulfonate  
**Molecular structure:**  $\text{C}_8\text{F}_{17}\text{SO}_3^-$   
**Molecular ion:** 499



PFOS

**Chemical Name:** Perfluorooctanesulfonamide  
**Molecular structure:**  $\text{C}_8\text{F}_{17}\text{SO}_2\text{NH}_2$   
**Molecular ion:** 498



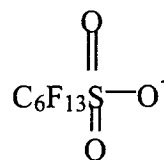
FSOA

**Chemical Name:** Perfluorooctanoate  
**Molecular structure:**  $\text{C}_7\text{F}_{15}\text{COO}^-$   
**Molecular ion:** 413



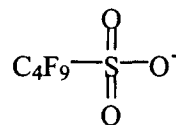
PFOA

**Chemical Name:** Perfluorohexanesulfonate  
**Molecular structure:**  $\text{C}_6\text{F}_{13}\text{SO}_3^-$   
**Molecular ion:** 399



PFHS

**Chemical Name:** Perfluorobutanesulfonate  
**Molecular structure:**  $\text{C}_4\text{F}_9\text{SO}_3^-$   
**Molecular ion:**



PFBS



## 9.2 APPENDIX B

Water, sediment and fish sampling locations for the 2002, 3M Tennessee River Project

| <b>Water and Sediment</b>                             | <b>Easting</b> | <b>Northing</b> |
|-------------------------------------------------------|----------------|-----------------|
| Downstream- Sample Location 1                         | 490208         | 3836096         |
| Across 3M- Sample Location 2                          | 498946         | 38357705        |
| Upstream- Sample Location 3                           | 505470         | 3827825         |
|                                                       |                |                 |
|                                                       |                |                 |
| <b>Fish Locations</b>                                 | <b>Easting</b> | <b>Northing</b> |
| Downstream start                                      | 490601         | 3836210         |
| Downstream end                                        | 491386         | 3834205         |
| Across 3M start                                       | 499043         | 3836283         |
| Across 3M end                                         | 498483         | 3836387         |
| Upstream start (a)                                    | 505306         | 3827660         |
| Upstream end (a)                                      | 504900         | 3824585         |
| Upstream start (b)                                    | 505466         | 3828685         |
| Upstream end (b)                                      | 506967         | 3827705         |
|                                                       |                |                 |
| <b>Coordinate System- UTM- Zone 16 North-NAD 1927</b> |                |                 |

**Water Sampling  
Standard Operating Procedure  
3M Decatur Sampling Trip**

**1.0 PURPOSE**

The purpose of this Standard Operating Procedure (SOP) is to provide details for the collection of water using a MasterFlex® peristaltic pump or some comparable unit. This SOP outlines the general procedures for collection of water samples. Specific sampling details should be outlined in the site-specific work plan and quality assurance project plan for each individual project.

**SCOPE**

Water samples collected under this SOP are to be taken with a MasterFlex tubing pump or some comparable unit. These samplers are fairly simple devices that consist of a peristaltic pump and tubing appropriate for the specific project. The tubing fits within a groove within the pump head. Several rollers are designed within the pump head to roll over the tube in a clockwise fashion. As the rollers move over the tube they create a vacuum that draws the water up through the tubing and dispels it on the other side. These units are optimal for surface water sampling in cases where it is important that only the selected tubing comes in contact with the sample. No portion of the pump comes in contact with the sample. A new portion of pre-cleaned tubing can be used with each sample to minimize any risk of contamination.

**EQUIPMENT**

Equipment and supplies needed may include, but are not limited to the following:

- One boat or sampling barge for the purpose of collecting *in situ* parameters and surface water samples
- Direct-read and properly calibrated water quality sampling instruments capable of recording temperature, DO, pH, conductivity, and salinity (YSI Models 63 and 95)
- MasterFlex tubing pump or some comparable unit
- Sample containers and coolers with wet ice for sample storage
- Field data sheets, COC forms, and related materials
- Items needed to document data collection activities and to label sample jars for shipment, including: camera, film, field notebook, pens, sample labels, custody seals
- Personal Protective Equipment PPE as required by the site Health and Safety Officer,
- Decontamination equipment

Prior to the collection of surface water samples, direct-read field meters will be deployed to measure the water quality parameters at each sample station. The direct read instruments will be calibrated each day. Suggested parameters targeted for measurement at each sampling station may include but are not limited to:

- Water depth (m)
- Temperature (°C)
- Dissolved oxygen (mg/L)
- Conductivity (µmhos/cm)

- Salinity (‰)
- pH (s.u.)

In some instances, the collection of additional water quality parameters may be warranted or required. Water quality meters to collect additional parameters will be added as needed.

## PROCEDURES

1. Obtain the sample location information from either the scope-of-work, work outline, or the Work Plan. This may be in the form of an actual coordinate or a description of the general sampling location.
2. Position the sampling barge or boat over the selected sample location. The field crew should always work from the most downstream location to the most upstream location unless otherwise directed.
3. Once you arrive at the proper location measure and record depth of water and record sample location identification as identified on the sampling log.
4. Make sure that all data sheets correspond to the correct sampling location.
5. Measure the sampling location using the best available technology (e.g., global positioning satellite system) and record sample coordinates on the sampling log.
6. After warm-up and calibration of the field meters, water quality parameters will be measured and recorded. The depth of readings should reflect the depth at which water samples are collected and any other requirements of the site specific work plan.
7. Water samples will then be collected using an appropriate pump with pre-cleaned tubing.
8. The specific type and size of tubing for sampling should be obtained. The length of this tubing depends on the depth of sample to be collected.
9. Weave the tubing through the designated slot on the pump. Make sure that the peristaltic head is correctly situated.
10. Lower the end of the tube into the water to the desired depth. Turn the pump on and wait for it to prime itself.
11. Run water through the tube until you have completed at least three volume additions of the tubing (calculated by taking the radius of the tubing and the length -  $\Pi r^2 l$ ).
12. Once approximately three volume additions have run through the tubing, begin collecting your sample.
13. Sample containers will be sealed with the appropriate caps, labeled, and placed on wet ice in an insulated container or cooler.
14. Appropriate COC documentation will accompany the samples as required by the project-specific QAPP.
15. After collection of the sample, remove the tubing and discard. Obtain a new section of tubing and navigate to the next sampling location.

**Sediment and Soil Sampling  
Petite Ponar® or Eckman Dredge  
Standard Operating Procedure  
For the 3M Decatur Sampling Trip**

## **1.0 PURPOSE**

The purpose of this Standard Operating Procedure (SOP) is to provide details for the collection of surface sediments using either a Petite Ponar or Eckman Dredge. Procedures outlined below detail the general methods required to collect surface sediment samples using either of these sampling devices. Although the details of sample collection will be influenced by site-specific conditions, certain aspects of sample collection can be standardized. These procedures give descriptions of equipment, field procedures, and documentation necessary to collect sediments using either of these methods.

## **2.0 SCOPE**

### ***Petite Ponar***

The Petite Ponar is widely used in both fresh and salt waters for collecting sediments from soft to relatively hard bottoms. It is especially useful in sand, gravel, consolidated marl or clay bottoms where standard dredges will not work. The Ponar is a self-closing sampler that releases when the unit comes in contact with the sediment. The sample area with this unit is 15 x 15 cm and the unit weight is approximately 55 kg.

### ***Eckman Dredge***

The Eckman Dredge is designed to collect samples in soft, finely divided littoral bottoms. In systems that have high amounts of debris or rocky bottoms, these units typically will not work well. The unit is typically lowered to the bottom via a rope and a messenger is sent down the line to release the spring-loaded doors. The doors are designed to close tight, encompassing a 15 x 15 cm area of sediment.

This SOP will cover the equipment required to collect sediment samples using either of these sampling devices and the specific procedures that are followed.

## **3.0 EQUIPMENT**

Equipment and supplies needed may include, but are not limited to the following:

- Petite Ponar and Eckman Dredge
- Stable boat or platform barge
- Stainless steel mixing containers
- Stainless steel spoons for homogenizing sediments
- Sample containers (project specific) and coolers with wet ice for sample storage
- Field data sheets (water quality/chemistry, general data sheets)
- Chain-of-custody forms

- Items needed to document data collection activities and to label sample containers for shipment, including: camera, film, field notebook, pens (write in the rain and Sharpie), sample labels, custody seals
- Personal protection equipment as required by the site Health and Safety Officer, including organic vapor meters (OVMS)
- Decontamination equipment specific for the project

#### **4.0 SAMPLE COLLECTION PROCEDURE**

Surface sediment collection using the Ponar or Dredge samplers will involve the following procedures:

1. Obtain the sample location information from either the scope-of-work, work outline, or the Work Plan. This may be in the form of an actual coordinate or a description of the general sampling location.
2. Position the sampling barge or boat over the selected sample location. When sampling sediments, the field crew should always work from the most downstream location to the most upstream location unless otherwise directed.
3. When sampling sediments in deep waters, attempt to set the barge in place with either a two to three point tie down (e.g., spud poles). This will provide some stability for the platform and ensure that the platform does not drift while sampling.
4. Once you arrive at the proper location measure and record depth of water and record sample location identification as identified on the sampling log.
5. Make sure that all data sheets correspond to the correct sampling location.
6. Measure the sampling location using the best available technology (e.g., global positioning satellite system) and record sample coordinates on the sampling log.
7. Obtain the decontaminated dredge or ponar (depends on the sediment/substrate type).
8. Make sure that the dredge or ponar are in the open position and slowly lower them over the side of the boat. This is to prevent the units from premature closure. Once the units are slightly submerged, release them and let them fall to the bottom of the system you are sampling in. The weight of the units should force them into the sediment bottom.
9. If using the Eckman Dredge, make sure that the unit is upright on the bottom (tug lightly on the line). Pull the line taut and release the messenger. Once the messenger releases the doors, pull the unit off the bottom and slowly through the water to the boat.
10. For the Ponar, the force of the unit hitting the sediment should cause the pin holding the doors open to release. Therefore when you pull the line holding the unit, the doors will close (collecting the sample).
11. Once the unit is in the boat, place all the contents into one of the decontaminated stainless steel mixing containers. Use a decontaminated, stainless steel spoon to homogenize the sediment.
12. Once homogenized, use the stainless steel spoon to place sufficient sample volumes into the proper sample containers. It is critical that the sample label for this sample be placed on the container. At a minimum, this label should contain the sample ID, date, time collected, initials of the persons collecting, and type of analysis for this sample.

13. Collect the appropriate QA/QC samples as outlined in the QAPP attached to the project specific work plan.
14. Complete the chain-of-custody form.
15. Place all samples in the proper sample shipping/storage container, which should contain sufficient wet ice to keep the samples at a temperature of 4°C until receipt by the laboratory.

Slight modifications may be required in the field, depending upon the type of sample that is being collected. The field crew will always have a working knowledge of the equipment prior to sampling, and will be familiar with the specific requirements of the project. Any modifications or changes that are needed for sampling specific systems should be documented in field data sheets and reflected in the final report.

## 9.4 APPENDIX D

| QA/QC samples for the 2002, 3M Tennessee River sampling effort |       |                           |            |         |       |                               |
|----------------------------------------------------------------|-------|---------------------------|------------|---------|-------|-------------------------------|
| Sample ID                                                      | Media | Location                  | River Mile | Date    | Time  | Description                   |
| FB01                                                           | Air   | Tennessee River           | -          | 4/15/02 | 14:30 | Field Blank-Empty             |
| FB02                                                           | Water | Tennessee River           | -          | 4/15/02 | 14:30 | Field Blank-Filled            |
| SW01-DUP                                                       | Water | Downstream near Fox Creek | 296        | 4/15/02 | 14:45 | Field Duplicate               |
| SW01-Low                                                       | Water | Downstream near Fox Creek | 296        | 4/15/02 | 14:45 | Field Matrix Spike-20 ppb     |
| SW01-Med                                                       | Water | Downstream near Fox Creek | 296        | 4/15/02 | 14:45 | Field Matrix Spike-20 ppm     |
| FSC01-Low                                                      | Water | Downstream near Fox Creek | 296        | 4/15/02 | 14:45 | Field Control Sample-20 ppb   |
| FSC01-Med                                                      | Water | Downstream near Fox Creek | 296        | 4/15/02 | 14:45 | Field Control Sample-10 ppm   |
| SW02-DUP                                                       | Water | Across River from 3M      | 301        | 4/16/02 | 10:20 | Field Duplicate               |
| SW02-Low                                                       | Water | Across River from 3M      | 301        | 4/16/02 | 10:20 | Field Matrix Spike-20 ppb     |
| SW02-Med                                                       | Water | Across River from 3M      | 301        | 4/16/02 | 10:20 | Field Matrix Spike-20 ppm     |
| FSC02-Low                                                      | Water | Across River from 3M      | 301        | 4/16/02 | 10:20 | Field Control Sample-20 ppb   |
| FSC02-Med                                                      | Water | Across River from 3M      | 301        | 4/16/02 | 10:20 | Field Control Sample-10 ppm   |
| SW03-DUP                                                       | Water | Upstream                  | 307.5      | 4/16/02 | 8:00  | Field Duplicate               |
| SW03-Low                                                       | Water | Upstream                  | 307.5      | 4/16/02 | 8:00  | Field Matrix Spike- 20 ppb    |
| SW03-Med                                                       | Water | Upstream                  | 307.5      | 4/16/02 | 8:00  | Field Matrix Spike- 20 ppm    |
| Trip Blank #1                                                  | Water | -                         | -          | -       | -     | Shipped with water samples    |
| Trip Blank #2                                                  | Water | -                         | -          | -       | -     | Shipped with sediment samples |

## 9.5 APPENDIX E

| Fish collection information for the 2002 3M Tennessee River sampling effort |                |                |                 |             |            |
|-----------------------------------------------------------------------------|----------------|----------------|-----------------|-------------|------------|
| Sample ID                                                                   | Location       | Date Collected | Fish Type       | Length (cm) | Weight (g) |
| SL01-LM01                                                                   | Downstream     | 4/15/02        | Largemouth Bass | 41          | 872        |
| SL01-LM02                                                                   | Downstream     | 4/15/02        | Largemouth Bass | 36          | 619        |
| SL01-LM03                                                                   | Downstream     | 4/16/02        | Largemouth Bass | 31.4        | 450        |
| SL01-LM04                                                                   | Downstream     | 4/16/02        | Largemouth Bass | 33.2        | 535        |
| SL01-LM05                                                                   | Downstream     | 4/16/02        | Largemouth Bass | 44.5        | 1181       |
| SL01-LM06                                                                   | Downstream     | 4/16/02        | Largemouth Bass | 31.2        | 478        |
| SL01-CAT01                                                                  | Downstream     | 4/16/02        | Catfish         | 61          | 2222       |
| SL01-CAT02                                                                  | Downstream     | 4/16/02        | Catfish         | 62.5        | 3150       |
| SL01-CAT03                                                                  | Downstream     | 4/16/02        | Catfish         | 62.1        | 2785       |
| SL01-CAT04                                                                  | Downstream     | 4/16/02        | Catfish         | 74.1        | 6047       |
| SL01-CAT05                                                                  | Downstream     | 4/16/02        | Catfish         | 55          | 1744       |
| SL01-CAT06                                                                  | Downstream     | 4/16/02        | Catfish         | 53.5        | 1575       |
| SL02-LM01                                                                   | Across from 3M | 4/18/02        | Largemouth Bass | 30          | 450        |
| SL02-LM02                                                                   | Across from 3M | 4/18/02        | Largemouth Bass | 45.5        | 1097       |
| SL02-LM03                                                                   | Across from 3M | 4/18/02        | Largemouth Bass | 33          | 506        |
| SL02-LM04                                                                   | Across from 3M | 4/18/02        | Largemouth Bass | 33          | 535        |
| SL02-CAT01                                                                  | Across from 3M | 4/18/02        | Catfish         | 57          | 2138       |
| SL02-CAT02                                                                  | Across from 3M | 4/18/02        | Catfish         | 51          | 1387       |
| SL02-CAT03                                                                  | Across from 3M | 4/18/02        | Catfish         | 59.5        | 2025       |
| SL02-CAT04                                                                  | Across from 3M | 4/18/02        | Catfish         | 57.5        | 1800       |
| SL02-CAT05                                                                  | Across from 3M | 4/18/02        | Catfish         | 64          | 3206       |
| SL02-CAT06                                                                  | Across from 3M | 4/18/02        | Catfish         | 53.5        | 1519       |
| SL02-CAT07                                                                  | Across from 3M | 4/18/02        | Catfish         | 53          | 1519       |
| SL03-LM01                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 30.5        | 450        |
| SL03-LM02                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 36.5        | 760        |
| SL03-LM03                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 38          | 675        |
| SL03-LM04                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 41.2        | 956        |
| SL03-LM05                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 29.7        | 281        |
| SL03-LM06                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 36          | 619        |
| SL03-LM07                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 42          | 731        |
| SL03-SM01                                                                   | Upstream       | 4/17/02        | Largemouth Bass | 32.5        | 563        |
| SL03-CAT01                                                                  | Upstream       | 4/17/02        | Catfish         | 32.2        | 816        |
| SL03-CAT02                                                                  | Upstream       | 4/17/02        | Catfish         | 57          | 3516       |
| SL03-CAT03                                                                  | Upstream       | 4/18/02        | Catfish         | 64.2        | 3769       |
| SL03-CAT04                                                                  | Upstream       | 4/18/02        | Catfish         | 61.5        | 2081       |
| SL03-CAT05                                                                  | Upstream       | 4/18/02        | Catfish         | 55          | 1856       |
| SL03-CAT06                                                                  | Upstream       | 4/18/02        | Catfish         | 60.5        | 2278       |



## **9.6 APPENDIX F**

Letter Report and Photographs of water, sediment and fish sampling efforts in 2002 on the Tennessee River.

# ENTRIX

ENTRIX, Inc.  
5252 Westchester, Suite 250  
Houston, Texas 77005  
(713) 666-6223  
(713) 666-5227 FAX

*Since 1984 – Environmental Excellence*

April 24, 2002

Mr. Dale Bacon  
3M Environmental Technology and Safety Services  
Building 2-3E-09  
P.O. Box 33331  
St. Paul, MN 55133-3331

Re: 2002 Tennessee River Sampling - Fish, Sediment, and Water,  
Decatur, Alabama (ENTRIX Project 178401)

Dear Dale:

ENTRIX, Inc. (ENTRIX) is providing this letter report summarizing field activities associated with the Tennessee River field-sampling effort conducted April 15 – 19, 2002 in Decatur, AL for 3M. To satisfy project deliverables, surface water, sediment and fish (catfish and largemouth bass) were collected from three locations in the area of the 3M facility on the Tennessee River. The objective of this effort was to collect representative samples for the measurement of selected perfluorinated compounds (PFCs). Samples were collected by Barry Gillespie, Matt Barczyk, Ramsey Redman, and Ryan Holem of ENTRIX. The General Project Outline (GPO) and Sampling Protocols provided by the 3M Analytical Technologies Group were followed by ENTRIX in the conduct of the field investigation.

Sampling locations were determined previously by ENTRIX and 3M personnel and reviewed by the ENTRIX field team prior to sampling. The 2000 sampling event provided the necessary site reconnaissance to allow ENTRIX to familiarize itself with river conditions and specific site locations. The sampling locations were representative of areas used by recreational and commercial fishermen. At each of three locations selected for this field investigation, water, sediment, and fish samples were collected. Sampling areas consisted of a location across the River from the 3M point of discharge, a location downstream of the 3M facility, and a location upstream of the 3M facility. The Riverwalk Marina (Marina) located on the northeast side of the river at approximately river mile 305 was used for river access. The downstream sampling location was in the vicinity of Fox Creek (approximately river mile 296), the sampling location across the river from the 3M facility was located approximately at river mile 301, and the upstream location was at river mile 307.5 (upstream of the 3M discharge, the city of Decatur, and the Highway 31 bridge) (Figure 1).

## FIELD SAMPLING

The ENTRIX field sampling crew arrived at the sampling site the morning of April 15, 2002. Equipment and supplies were loaded on a 16' sampling barge in the morning and testing of field equipment proceeded. Actual sampling commenced the afternoon of April 15, 2002 (Monday) and activities were completed on the evening of April 18, 2002 (Thursday). Collection of water and sediment samples commenced on April 15, 2002 and continued until April 16, 2002. Fish collection was initiated on the evening of April 15 and continued through April 18, 2002.

### Water and Sediment Collection

Water, sediment, and the QA/QC samples for water were collected according to the General Project Outline (GPO) provided by 3M. The boat was navigated to the selected location and a Garmin GPS 12 Global Positioning System was used to document the sampling location (Table 1a). All sampling locations have been recorded on a topographic map (Figure 1). Water quality meters (YSI Model 95 and Model 63) were then calibrated and used to measure pH, dissolved oxygen, temperature, salinity and conductivity (Table 1b). Once surface water and sediment samples were collected according to the 3M GPO, they were properly labeled, stored on ice at 4°C, and delivered to the 3M environmental laboratory in Minnesota via FedEx courier. All water, sediment and accompanying water QA/QC samples were delivered (priority overnight) to 3M in Minnesota on April 16, 2002.

Standard operating procedures for sample collection and preparation were maintained during the entire project. Proper QA/QC samples for water, as required by the 3M GPO, were collected in the field (Table 2). All samples were shipped under ENTRIX chain of custody forms, and a field data book was used to document conditions and activities.

### Fish Collection

Fish were collected from the three sample locations (Table 1a and Figure 1) identified above using a boat mounted Smith-Root type VI-A electroshocking device (see attached Photo Log). According to the GPO, a minimum of six bass (preferably largemouth) and six catfish were to be collected from each of the three sites, if possible. At both the upstream and downstream sampling locations, the minimum number of each species of fish was collected (i.e., six bass and six catfish). However, while the minimum number of catfish across from the 3M facility was captured, only four bass were collected. Repeated attempts to collect the remaining two bass resulted in no capture. For this investigation, only the desired fish species caught at each of the sampling locations were retained for analysis. Collected fish were measured (total length), weighed, and immediately wrapped in aluminum foil and placed in ziplock storage bags (Table 3). Samples were labeled, placed on ice, and shipped via overnight FedEx to the ENTRIX office in East Lansing, Michigan, and then transported immediately to freezer facilities in the Aquatic Toxicology Laboratory (ATL) at Michigan State University.

Upon completion of sampling activities, the Alabama Department of Wildlife and Freshwater Fisheries was notified that sampling was complete and their required notification form was completed and mailed to them.

#### Fish Processing & Sample Preparation

Fish remained frozen in MSU freezer facilities until processing began. ENTRIX personnel (Mr. Ryan Holem) conducted the fish processing and preparation of fillets. Procedures described in the 3M GPO and the Alabama Department of Environmental Management Standard Operating Procedures Volume III were followed in fish tissue preparation.

Prior to processing, all working surfaces in the MSU laboratory were washed with soap and warm water then covered with aluminum foil. Any utensils utilized in the filleting and homogenization process were first washed with soap and warm water, then methanol-rinsed followed by a de-ionized (DI) water rinse. All utensils were decontaminated between fish to avoid cross-contamination. In addition, aluminum foil was wrapped (dull side out) around the handles of both fillet knives. Nitrile gloves were worn throughout the process. This process was repeated before each new fish was started to avoid cross-contamination.

Fillets included the tissue from behind the head to the tail on both sides of each fish. Each fillet was removed from the fish and the skin removed using a fillet knife. The rib bones were either avoided during filleting or removed from each fillet so that only edible portions of the fillet remained. The carcass of each fish, the skin, and rib bones from each fillet were then wrapped in aluminum foil (dull side to fish), labeled with its sample location and ID number and placed in a pre-labeled ziploc bag. When possible, carcasses were kept in their original foil before being placed in ziploc bags. Carcasses were then placed in portable coolers and stored at -20°C. The fillet was cut into small pieces to expedite the grinding process. A hand grinder was used for the larger fish and a stainless steel blender for samples with less tissue. In all cases, the ground tissues were thoroughly mixed with stainless steel spatulas and mortar and pestle to ensure adequate homogenization. Once homogenized, the tissue was massed to the nearest hundredth gram and placed in 3M approved Nalgene containers. A label detailing the sample location, ID number, date processed, sample identity (bass or catfish) and mass of the tissue was placed on each container. All containers were placed in pre-labeled ziploc bags and stored in coolers at -20°C.

Upon completion of processing, samples were removed from the coolers operated at -20°C, placed in portable coolers and covered with wet ice. Original Chain of Custody forms (or copies of originals), a sample summary sheet, and copies of laboratory notebook pages in ziploc bags were placed in each cooler. Tape was used to secure the lids and drains of all coolers. Coolers were shipped priority overnight mail to Sue Beach at 3M's Environmental Laboratory in Minnesota.

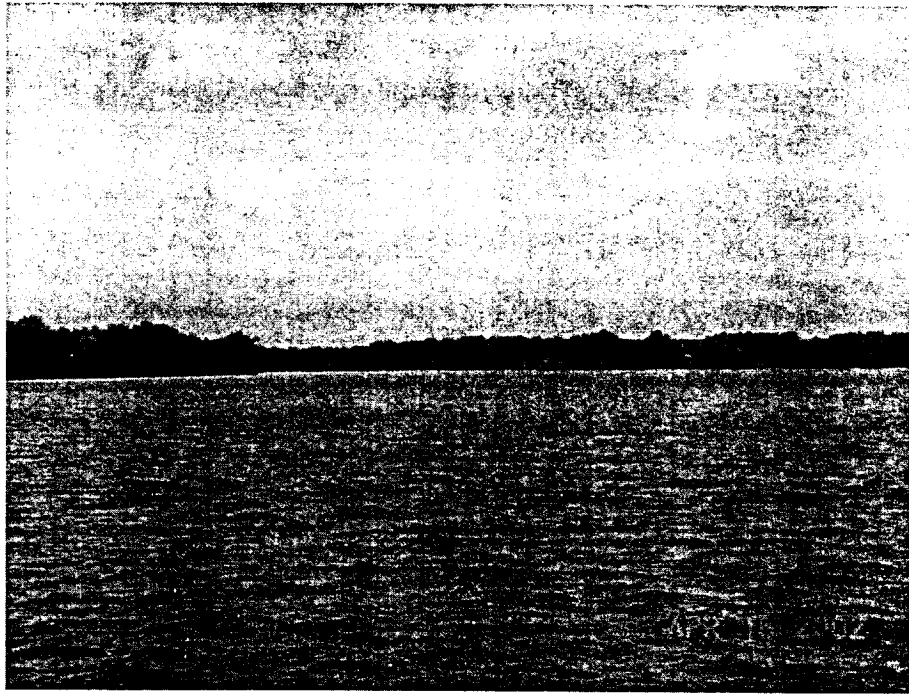
ENTRIX is pleased with the opportunity to conduct this sampling effort for 3M. If you have any questions please contact me at 713-662-1908.

Sincerely,

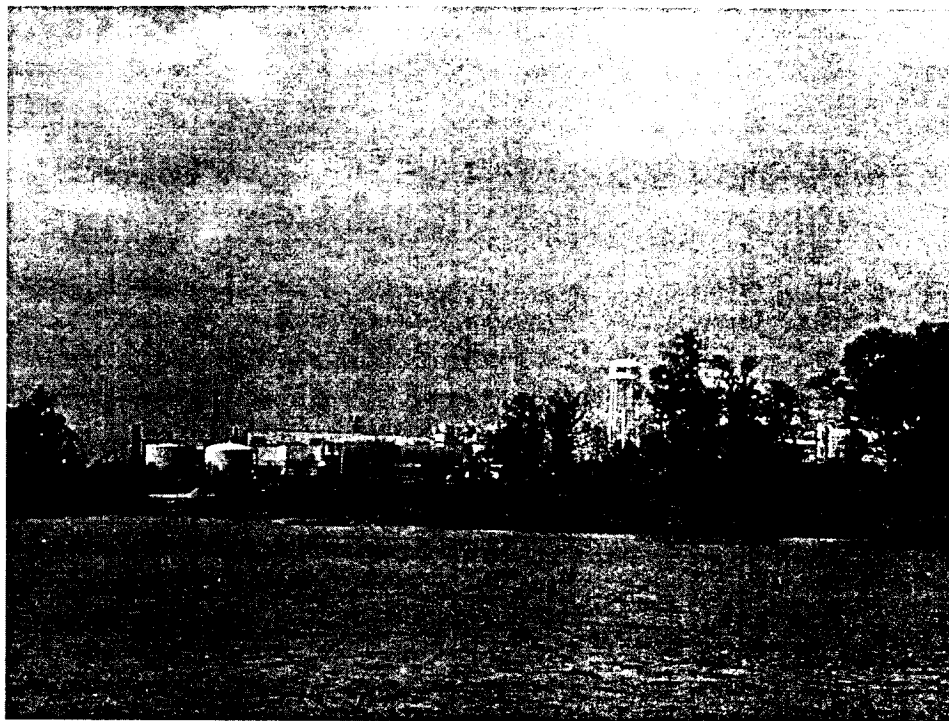
W. Barry Gillespie, Jr.  
Project Scientist

Cc: Dr. John Giesy

Photo Log-2002 3M, Tennessee River Sampling Effort



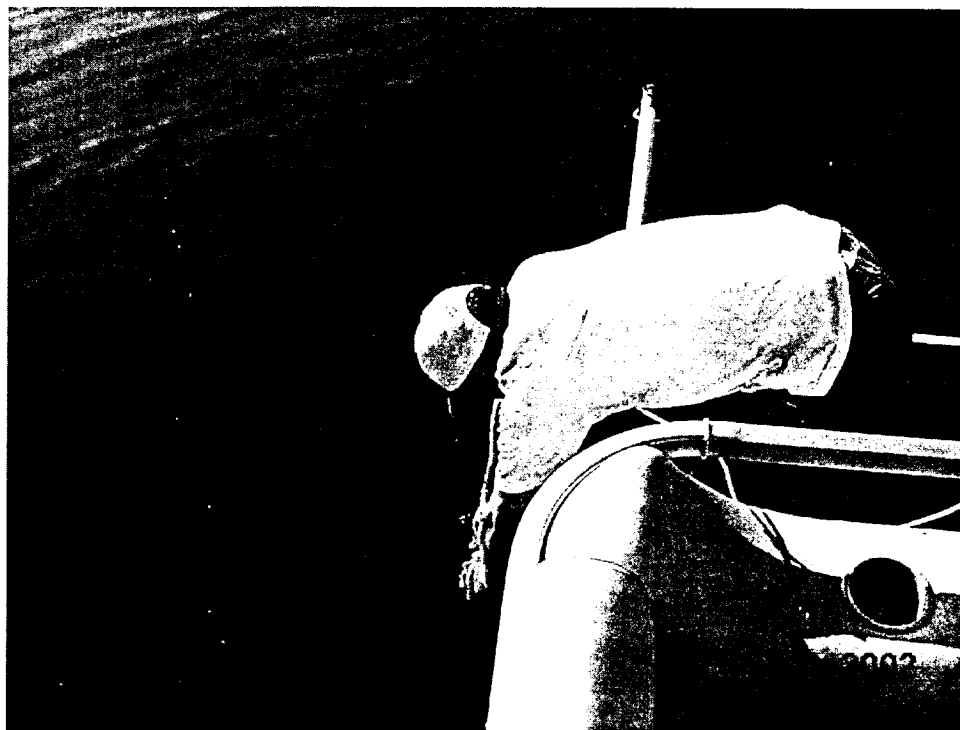
Photograph 1: Downstream sampling location (mouth of Fox Creek).



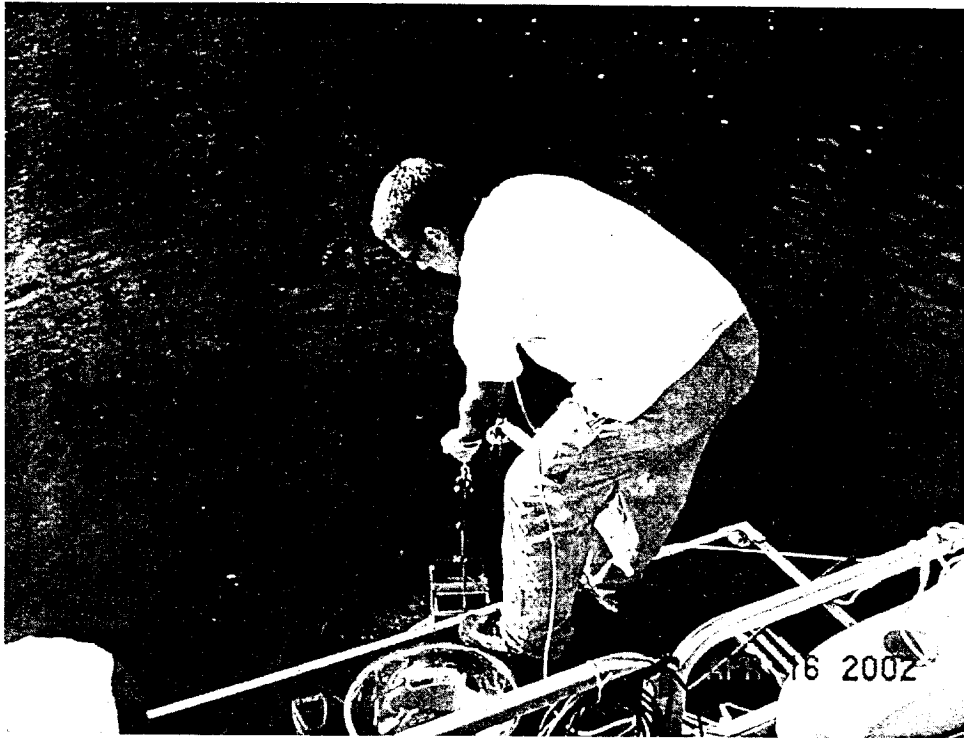
Photograph 2: 3M facility near outfall (sample location across river from this facility).



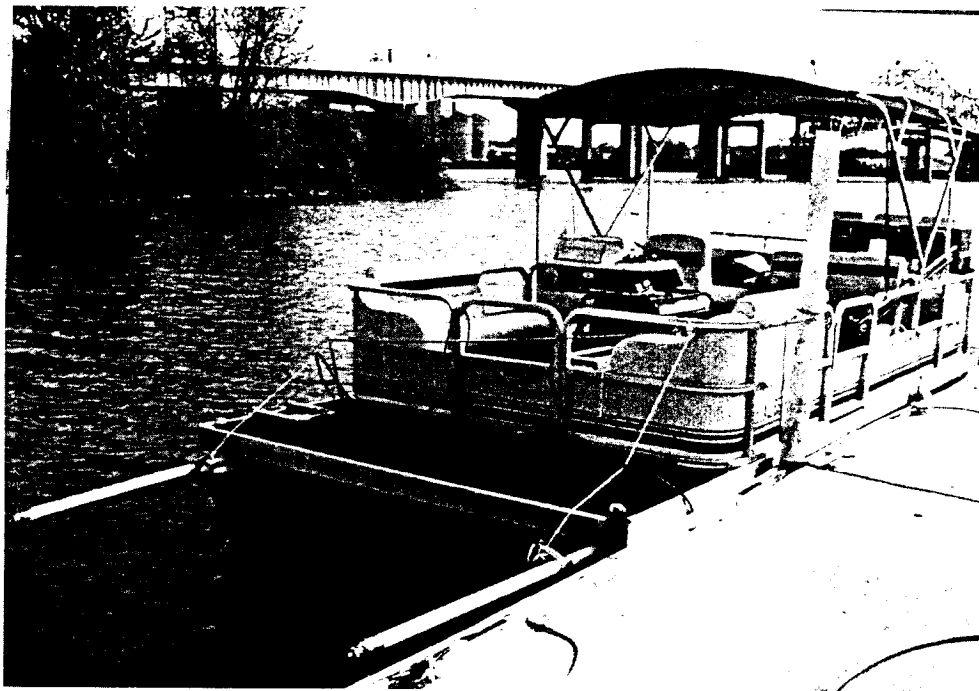
Photograph 3. Upstream sampling location.



Photograph 4: Collection of surface water.



Photograph 5: Collection of sediment using Ponar sampler.



Photograph 6: Electroshocking device mounted onto 16' pontoon boat.





Photograph 7. Site across the river from the 3M facility.

## **9.7 APPENDIX G**

Fish were sampled from each location with a Smith-Root Type VI-A heavy duty 5kW electroshocker. This electroshocker can be used in large bodies of water like lakes and rivers. Electroshock operating procedures followed in the collection of fish from the Tennessee River were taken from the Smith-Root manuals These include the following:

1. Type VI-A Operation Manual. January 1994. pp 4.
2. Type VI-A Parts Identification. December 1994, pp 10
3. Electrofishing Manual. June 1994, pp 9.
4. Electrofishing Safety, January 1994. pp 3

Smith-Root, Inc.  
14014 NE Salmon Creek Avenue  
Vancouver, WA 98686  
Phone: 360-573-0202  
Fax: 503-286-1931