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RE: TSCA 8(e) SUPPLEMENTAL NOTICE: Sulfonate-based Fluorochemicals – Docket Nos. 8EHQ-1180-373; 8EHQ-1180-374

To Whom It May Concern:

Enclosed you will find a white paper entitled "Sulfonated Perfluorochemicals in the Environment: Sources, Dispersion, Fate and Effects" prepared by 3M. 3M is submitting this document as a supplement to our original 8(e) submissions on sulfonate-based fluorochemicals.

If you have any questions, please feel free to contact me.

Best regards,

William A. Weppner

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Sulfonated Perfluorochemicals in the Environment: Sources, Dispersion, Fate and Effects

Prepared by
3M

March 1, 2000

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required, along with method validation and oversight at levels comparable to those used in the 3M Environmental Laboratory.

Continual improvements are sought in analytical methods as the ability to detect trace quantities is essential for a number of reasons such as: screening laboratory supplies and environments prior to initiating toxicity testing, for detecting environmental exposure, for determining sources of perfluorochemicals, and for understanding perfluorochemical metabolism kinetics.

6.0 Sources of Fluorochemicals

A few fluorochemicals occur naturally in the biosphere, produced by biological and geochemical processes. Several green plants produce monofluoroacetic acid (CH_2FCOOH). Some fungi produce monofluorinated organics. All fluorochemicals produced biologically contain only one fluorine atom. Volcanoes and other geological processes produce tetrafluoroethylene, sulfur hexafluoride, perfluoromethane and some chlorofluorocarbons in small quantities.

Most fluorochemicals in the environment are present as a result of human manufacture and use. Releases of fluorochemicals into the environment can occur at each stage of the fluorochemical product's life cycle. They can be released when the fluorochemical is synthesized, continue during incorporation of the fluorochemical into a product, during the distribution of the product to users, during the use of the product by consumers, and during disposal practices at all of these stages.

3M is using a two step approach to estimate environmental releases of fluorochemicals. The initial efforts have focused on determining waste generated; the second step will focus on determining releases. This two step approach is necessary since not all waste produced will result in a release to the environment. Much of the waste that is generated is destroyed through treatment or otherwise actively managed to prevent release into the environment. Efforts are also being made to further tighten such controls.

3M has estimated waste generation from each of the following life cycle stages: the manufacturing processes, the supply and distribution chains, customer uses and product/waste disposal.

For ease in comparing waste stream data, wastes are described in term of "PFOS equivalents." PFOS equivalents are the weight of $C_8F_{17}SO_2$ present in a sulfonated perfluorochemical product. It is the mass of PFOS molecules that would be formed in the breakdown of the product. The assumptions of complete breakdown to PFOS of each sulfonated perfluorochemical product, in the year in which the product was sold, are unlikely "worst-case" assumptions. Various degradation testing finds a broad range of product degradation rates. Some polymeric products appear to be quite stable in the environment, with long half-lives; other polymers hydrolyze quickly.

6.1 Manufacturing Waste Streams

The assessment of the release of sulfonated perfluorochemicals into the environment begins with manufacturing waste generation. Some waste streams, such as wastewater discharge or disposal of off-spec products, can be anticipated and controls provided. Other waste can be generated during any of the steps required to produce the fluorochemicals and manufacture the product.

The greatest production of the parent fluorochemical product, POSF, occurs at the Decatur, Alabama plant. Here POSF is created in electrochemical cells and undergoes numerous steps to convert it into final products. Salts of PFOS are also manufactured at the facility. Because of its production volume, the Decatur facility has been the focus of manufacturing waste stream studies. Understanding waste generation and how wastes are managed and disposed of provides a better understanding of potential releases into the environment. That understanding will help to identify opportunities for reductions in such releases.

The manufacturing process for sulfonated perfluorochemicals is complicated. There are more than 600 intermediate manufacturing steps associated with the production of POSF and POSF-based products. This translates into hundreds of process steps that require venting or that generate wastewater or solid waste. Although the manufacturing process attempts to capture, reuse, and recycle most fluorochemicals as desired product material, until recently, the unique chemistries created in each step of the process could not be analyzed precisely to confirm composition and to quantify amounts. The manufacturing process is dynamic, with rapidly changing matrices and many process steps. Ongoing process optimization activities continuously change the waste stream profile.

Progress has been made in analytical techniques. In 1997, analytical laboratory techniques and methods could quantitatively identify the presence of only one fluorochemical analyte in a wastewater matrix. In 1999, improved analytical techniques and methods were developed for additional fluorochemical analytes in a wastewater matrix.

Advanced field monitoring technology has been developed based on Fourier Transform Infrared spectroscopy (FTIR). This field tool has been used to detect where emissions to air are occurring during the manufacturing process and to evaluate whether a process change or a control technology can decrease the release.

As better analytical techniques become available, efforts are being made to:

- characterize the major manufacturing processes generating fluorochemical waste streams;
- evaluate the effectiveness of fluorochemical removal technologies; and
- provide better estimates of the amounts and kinds of fluorochemicals released to the environment from manufacturing processes and from waste treatment and disposal.

Information currently available on waste streams generated during manufacturing processes at Decatur is derived from engineering calculations, air emissions modeling, and limited testing. An overall site materials balance was developed in the mid- 1990's using the amount of POSF-based solids initially created in the electrochemical cell and the amount of POSF contained in final products sold. The difference was an estimate of *total* waste streams generated during processing. The emission factors derived from this balance are used to calculate waste streams from production throughput. They are the basis for the estimates in Table 5. These estimates derived from the material balance are not precise, as this methodology can produce only rough approximations.

The estimates in Table 5 reflect the most current information available and combine data derived from several sources: information from the mid-90s site balance, wastewater testing, waste disposal records, process models and supplemental information from 1997, 1998 and 1999. Several changes in waste disposal and processing have been implemented since the mid-1990s in order to reduce potential releases to the environment. Wastewater sludges that were once land applied on site are now sent to a municipal landfill for disposal. Off-spec materials that were discharged to wastewater are now shipped off-site to be incinerated.

Table 5 helps to demonstrate the vast difference between volumes of wastes generated and volumes of releases to the environment, since the vast majority of wastes sent to incineration are destroyed in the incineration process and most material sent off-site to landfills will be effectively managed to prevent release to the environment.

Table 5. Estimated 1998 Wastes Generated (in PFOS Equivalents) at the Decatur Manufacturing Plant

Waste Type	Estimated PFOS Equivalents, lbs
Air Emissions	19,000
Wastes sent off-site to Incineration	657,000
Wastes sent off-site to Landfills	380,000
Discharge to River after Wastewater Treatment	10,000
Total Wastes	1,066,000

Note: The 10,000 lbs/yr of PFOS equivalents in the discharge to the river are estimated releases to the environment after wastewater treatment, not the lbs/yr generated prior to treatment.

More explanation of the estimates and efforts currently underway in air, wastewater and waste management follows.

6.11 Waste Stream Characterization

Updating material balances for the manufacturing process is an ongoing effort. Today process engineers use a model of process steps to calculate air emissions. New information is being compiled to aid with model operation and waste calculations. The effort to determine physical/chemical properties for sulfonated perfluorochemicals will improve model inputs and waste stream calculations. Analytical technology is improving understanding of process chemistry

Data from the process engineers' available material balances in the plant's reporting system have been used to supplement the earlier site balance in estimating air emissions. Initial reports from this system indicate that most site waste and air emissions result from fewer than 10 key steps in the early stages of POSF production. Process experts are examining these steps for ways to reduce or eliminate the impurities and wastes generated in the steps.

In 1999, the Decatur plant installed a discotherm unit which heats the process materials, vaporizing and capturing the fluorochemicals. It will significantly reduce the organofluorides in the wastewater. This technology will operate to reduce emissions and waste at the source. It will make it easier to segregate waste streams and recycle fluorochemical wastes back into the process.

6.12 Air

3M engineers have reviewed specific process steps to determine what air emissions testing is feasible and appropriate. Testing of complex batch-processing systems is difficult due to quickly changing process conditions, venting pressures, and difficulty in isolating processes; however, characterization testing may be possible. The technical feasibility of performing this testing for two major processes is now under evaluation. Any emissions testing will require modifications to process vents and mitigation of potential safety hazards. About 80 separate venting points are associated with the equipment used to make sulfonated perfluorochemicals.

6.13 Wastewater

Analytical methods have been developed during the past year to better characterize the wastewater discharge from the site. The first testing of wastewater before and after treatment for specific fluorochemicals occurred at Decatur early in 1998. The testing was limited and reflected operating conditions for a relatively short period of time (24 hour composite samples of influent and effluent for one week.) Some of the compounds that were identified in the wastewater were: a diester of EtFOSE alcohol, EtFOSE alcohol, MeFOSE alcohol, PFOS, FOSA, PFOSAA, PFOA and PFHS.

In 1998 an interim carbon adsorption treatment system was installed as part of wastewater treatment. Data for the effluent estimate in Table 5 reflects this change. This treatment system treats the largest single source of fluorochemical-containing wastewater in order to remove PFOS and other sulfonated perfluorochemicals from the wastewater. Comparison of the results from sampling done in February 1998 with sampling done in the end of 1998 indicates the quantity of PFOS discharged to the Tennessee River declined by about half. In addition to the carbon adsorption system, in-process operational changes were made in off-spec product discharge procedures that also contributed to the reduction in PFOS content of the discharge to the river.

The carbon system has been incorporated as a permanent upgrade of the wastewater treatment system. Monitoring indicates that with proper operation, carbon adsorption removes better than 99% of PFOS. Removal efficiency of other sulfonated perfluorochemicals varies, but the treatment appears to provide a high degree of removal for most. A number of wastewater streams currently going to sewers are in the process of being diverted to thermal treatment facilities for disposal. This will result in a reduction in the values listed in Table 5. 3M has conducted an extensive review of state-of-the-art technology for wastewater treatment. Various upgrades are currently being evaluated. The long term goal of wastewater treatment at the plant is to utilize source control and end-of-pipe treatment to remove nearly all sulfonated perfluorochemicals from wastewater prior to discharge to the river.

6.14 Solid Waste

An effort to identify all waste streams and their disposal methods is underway. Existing waste tracking is done on a site basis, so it is difficult to distinguish the particular streams with POSF chemistry. The mid-1990s emission estimates did not distinguish final disposal of the material lost from production, so site records were used in combination with the existing emission estimates to create the current picture of potential releases resulting from disposal.

A review of plant records for 1998 has been completed to determine primary waste disposal locations for the site. According to Decatur plant records, 63% of the fluorochemical containing wastes are sent to incinerators, 33% of the wastes are disposed in hazardous waste landfills and 4% in non-hazardous waste landfills.

6.2 Supply Chain Waste Streams

Using sales data, 3M identified key products that contain a majority of the fluorochemical solids used in products. These products represent 89% of PFOS-equivalents sold by 3M in 1997 in the United States. Most commonly, these products were sold to commercial users who applied them or incorporated them into their products.

Using the information developed from sales, 3M estimated customer and end user waste streams (Table 6). These estimates are imprecise and based on several assumptions, but provide qualitative information. Using the chemical formula for PFOS, the fluorochemical solids were converted to "PFOS equivalents" for ease in estimating and comparing total losses of sulfonated perfluorochemicals and in comparing losses. The assumptions of complete breakdown to PFOS of each sulfonated perfluorochemical product, in the year in which the product was sold, are unlikely "worst case" assumptions. Product waste stream estimates are based on conservative, worst case assumptions about the generation of waste streams at supply chain facilities. These are often based on operator experience or engineering estimates rather than laboratory tests and can result in wide ranges in waste stream calculations. In estimating wastes, these data do not include loss of product residuals in the waste streams because information on the properties of residuals and processes at supply chain facilities and end user locations is inadequate to estimate this loss.

Initial estimates associate waste streams generated from uses and disposal of the products by customers of each business unit. These estimates are helping to focus efforts in improving customer stewardship practices and 3M product reengineering. As is evident, most of the waste generated is in the form of solid waste.

Table 6. Customer and End User Waste Stream Estimates, PFOS equivalents, lbs in 1997

Waste Stream	Supply Chain	Use	Disposal
Air	2,600	3,300	0
Wastewater	112,000	181,000	0
Solid Waste	59,000	377,000	1,262,000

6.3 Releases from Waste Treatment and Disposal Methods

3M and its consultant are gathering information on treatment and waste handling at several landfills and wastewater treatment plants which receive wastes containing sulfonated perfluorochemicals from the supply chain facilities and 3M manufacturing facilities. Information is also being compiled on some of the largest wastewater treatment facilities and landfills in the United States in order to estimate the potential perfluorochemical releases to the environment from municipal disposal facilities not associated with the supply chain or manufacturing.

Incineration is a favored disposal method because of its high rates of destruction of sulfonated compounds. 3M and its consultant are further evaluating the effectiveness of incineration for this purpose. The basic bond breaking chemistry of thermal destruction of POSF-based fluorochemicals, the destruction efficiencies of various technologies/situations such as municipal incinerators, and the products that could result from incomplete combustion are elements of the study. The study involves a review of 3M and external literature to compile information on the formation and properties of thermal transformation products of sulfonated perfluorochemicals.

Modeling will be used to determine to the extent practical, the releases to the environment from the amount of material sent to incineration, wastewater treatment plants, and landfills.

The goals of the life cycle release studies are:

- to identify important fluorochemicals based on volume of release, mode of release and chemistry;
- to provide values for use in modeling the distribution of fluorochemicals in the environment;
- to determine sampling sites and substantiate sampling results;
- to predict which fluorochemical releases may result in exposure to humans and the environment; and
- to identify fluorochemicals that require further study as to their transport, fate and exposure potential.

7.0 Environmental Transport and Distribution

The transport and fate of chemicals in the environment depends on many factors but principally on the interaction between environmental conditions (e.g. water, temperature, sunlight), and chemical properties (e.g. partitioning and reactivity). In the environmental area, eleven important fate and transport mechanisms for sulfonated perfluorochemicals have been identified for further study. These are:

1. Partitioning between air and product, i.e. volatilization from product to air;
2. Indoor air deposition;
3. Accumulation on airborne particulates;
4. Fate and transport to the stratosphere;

5. Accumulation at the surface water microlayer;
6. Degradation (includes hydrolysis, photolysis and biodegradation);
7. Dissociation in water;
8. Uptake in plants;
9. Uptake in fish;
10. Uptake in birds;
11. Efficiency of wastewater treatment systems.

All of these fate and transport mechanisms have been linked to models. Modeling uses mathematical equations to simulate and predict real events and processes. Many types of models will be considered for use in this effort to evaluate sulfonated perfluorochemicals. Simple models of ecosystems, indoor air, and treatment systems (wastewater, landfills) are being used to screen for possible fate mechanisms, possible exposures, and possible sample detection limits. For example, one preliminary screening model suggests that top trophic level species such as fish eating birds and sea mammals should be examined. This finding was incorporated into the design of the biosphere sampling plan.

Chemicals differ greatly in their behavior. The major differences in behavior of organic chemicals in the environment are due to physical-chemical properties. Although laboratory studies are underway on physical/chemical properties of PFOS, EtFOSE alcohol and MeFOSE alcohol, models are being developed to estimate the physical/chemical properties of other sulfonated perfluorochemicals. This will reduce the time and testing required to gather these data for use in environmental fate models.

Fugacity is a concept that is used to describe the tendency of a compound to migrate in and between one environmental medium and another. Different media include air, water, soil, sediment, and biota, all of which together compose a dynamic, interactive system--an *eco*system. Predictions about movement of a chemical must incorporate both its physical/chemical properties and the environment the chemical is in. For example, a low vapor pressure does not mean a chemical is not present in air. It may evaporate appreciably from water despite a low vapor pressure if it has low solubility in water. By entering the physical-chemical property data on a chemical into a fugacity model of a generic or specific environment, it is possible to estimate general features of a chemical's likely behavior and fate. The output of these calculations can be presented numerically and pictorially. (6)

Fugacity models will be used to predict fate and transport of sulfonated perfluorochemicals. Existing fugacity models typically are based on experience with chlorinated organics. An internationally recognized modeling expert is developing/ adapting models to consider the unique properties of fluorochemicals. The goal of this modeling effort is to have a multimedia model or models to predict the fate of sulfonated perfluorochemical products and associated byproducts in a variety of ecosystems.

8.0 Environmental Sampling for Fluorochemicals

8.1 Environmental Levels

8.11 Historical Data

In the late 1970s, 3M conducted a very limited number of studies to assess the distribution of fluorochemical constituents in the environment. Several freshwater fish species were tested for a number of fluorochemical compounds. In reviewing the data obtained from these studies in context of the current knowledge of the behavior of these materials, 3M has concluded that these historical data are highly questionable and may be misleading. Therefore, they are not included in this paper. The sections following present more reliable data and information collected using validated sampling and analytical methodologies.

8.12 Recent Analyses of Wild Birds and Fish

In analysis in 1999 of the plasma of ten fish eating birds, albatross nestlings at Midway Island in the Pacific Ocean and eagle nestlings in Minnesota and Michigan, PFOS was detected in each of the samples from eagles. The samples were collected in 1989, 92, and 93 by Dr. John Giesy of Michigan State University as part of other surveys. Three of the albatross adults showed no detectable levels of PFOS (< 1 ppb detection level). Detectable, but not quantifiable levels of PFOS were found in the remaining albatross samples, both collected from birds less than a year old. All albatross samples were collected in 1992-93. See Table 7. These data are semi-quantitative, screening quality. As only a small amount (< 1mL) of plasma was available to conduct the analyses, no matrix spikes were possible to estimate the method's recovery efficiency, but the methods used have been characterized in other, similar matrices.

After the initial screening results on wild bird plasma, the plasma from a second set of wild birds was examined for the presence of PFOS. (See Table 7.) The source of the plasma was three sea eagles collected from the Baltic Sea and seven bald eagles collected from North America. The samples were collected in 1992-93 and again by Dr. John Giesy. PFOS was detected in all of the eagle plasma screened. These data are semi-quantitative, screening quality. Two matrix spikes (250 ppb) prepared from eagle plasma were extracted and analyzed. Both showed >80% recovery.

Table 7. Levels of PFOS in the Plasma of Wild Birds

Species	Collection Date	Location	Age, Gender	PFOS, ppb
Bald Eagle	5 Jun 93	Lower Penn, MI	163 days, F	30
Bald Eagle	3 Jun 93	Lower Penn,MI	228, F	34
Bald Eagle	1989	Upper Penn, MI	unknown	77
Bald Eagle	1989	Upper Penn, MI	unknown	31
Bald Eagle	17 Jun 92	Voyageurs,MN	82 days, M	34
Albatross	13 Dec 92	Midway atoll	6 years	BLD
Albatross	18 May 93	Midway atoll	0	BLQ
Albatross	13 Dec 92	Midway atoll	8 years	BLD
Albatross	13 Dec 92	Midway atoll	15 years	BLD
Albatross	18 May 93	Midway atoll	0	BLQ
Sea Eagle	28 May 93	Baltic, Sweden	nestling	125
Sea Eagle	27 May 93	Baltic, Sweden	nestling	93
Sea Eagle	23 May 93	Baltic, Sweden	nestling	215
Bald Eagle	26 Jun 92	North America	nestling	165
Bald Eagle	28 Jun 93	North America	nestling	198
Bald Eagle	23 Jun 92	L. Superior ONT	nestling, F	494
Bald Eagle	5 Jun 92	North America	Adult, F	1047
Bald Eagle	26 Jun 92	Devil's Is., WI	nestling, F	226
Bald Eagle	22 Jun 92	Mud Creek,OH	nestling,	371
Bald Eagle	8 Jun 92	Carroll Twp, OH	nestling	374

BLQ= Below Limit of Quantitation (10 ppb)
BLD= Below Limit of Detection (approximately 1 ppb)

Following the bird plasma studies, sixty liver samples collected by the U.S. Fish & Wildlife Service from various species of birds were analyzed. The dead birds were collected at a variety of sites across the United States. They were not part of a controlled research study, but were selected for their location and diet. All but sandhill cranes are fish eating species. The sandhill cranes are an insect eating species. The purpose of the analyses was to determine if the presence of PFOS could be detected in these sample matrices. 3M believes that these sets of data are insufficient to draw conclusions with any statistical merit. The PFOS data in Table 8 are semi-quantitative, screening quality, with a margin of error estimated at $\pm$ 30%. The limit of quantitation for PFOS is 6 ppb.

Table 8. Analysis of Wild Bird Livers.

BLQ= Below limit of quantitation (6 ppb)

Sample No.	Species	Location	PFOS ppb
1	Sandhill Crane	Kearney, NE	41
2	Sandhill Crane	Kearney, NE	BLQ
3	Sandhill Crane	Kearney, NE	BLQ
4	Sandhill Crane	Kearney, NE	BLQ
5	Sandhill Crane	Kearney, NE	BLQ
6	Sandhill Crane	Chochise Co., AZ	BLQ
7	Sandhill Crane	Chochise Co., AZ	BLQ
8	Sandhill Crane	Chochise Co., AZ	BLQ
9	Sandhill Crane	Chochise Co., AZ	BLQ
10	Sandhill Crane	Chochise Co., AZ	BLQ
11	White Pelican	Calipatria, CA	35
12	White Pelican	Calipatria, CA	1293
13	White Pelican	Calipatria, CA	29
14	White Pelican	Calipatria, CA	15
15	White Pelican	Calipatria, CA	153
16	Brandt's Cormorant	San Diego, CA	53
17	Brandt's Cormorant	San Diego, CA	46
18	Brandt's Cormorant	San Diego, CA	46
19	Brandt's Cormorant	San Diego, CA	80
20	Brandt's Cormorant	San Diego, CA	2055
21	Dbl. Crested Cormorant	St. Martinville, LA	59
22	Dbl. Crested Cormorant	St. Martinville, LA	145
23	Dbl. Crested Cormorant	St. Martinville, LA	333
24	Dbl. Crested Cormorant	St. Martinville, LA	76
25	Dbl. Crested Cormorant	St. Martinville, LA	170
26	Brown Pelican	Miami, FL	106
27	Brown Pelican	Miami, FL	134
28	Brown Pelican	Miami, FL	125
29	Brown Pelican	Miami, FL	159
30	Brown Pelican	Miami, FL	48
31	Sandhill Crane	Valenica Co., NM	BLQ
32	Sandhill Crane	Valenica Co., NM	BLQ
33	Sandhill Crane	Socorro Co., NM	BLQ
34	Sandhill Crane	Socorro Co., NM	BLQ
35	Sandhill Crane	Valenica Co., NM	BLQ
36	Dbl. Crested Cormorant	Naples, FL	212
37	Dbl. Crested Cormorant	Naples, FL	10
38	Dbl. Crested Cormorant	Naples, FL	52
39	Dbl. Crested Cormorant	Naples, FL	100
40	Dbl. Crested Cormorant	Naples, FL	152
41	Brown Pelican	Calipatria, CA	16
42	Brown Pelican	Calipatria, CA	36
43	Brown Pelican	Calipatria, CA	BLQ
44	Brown Pelican	Calipatria, CA	6
45	Brown Pelican	Calipatria, CA	32

Sample No.	Species	Location	PFOS ppb
46	Great Blue Heron	St. Martinville, LA	188
47	Great Blue Heron	St. Martinville, LA	59
48	Great Blue Heron	St. Martinville, LA	1061
49	Great Blue Heron	St. Martinville, LA	261
50	Great Blue Heron	St. Martinville, LA	173
51	White Pelican	Fallon, NV	141
52	White Pelican	Fallon, NV	362
53	White Pelican	Fallon, NV	927
54	White Pelican	Fallon, NV	133
55	White Pelican	Fallon, NV	291
56	Brown Pelican	Ft. Lauderdale, FL	194
57	Brown Pelican	Ft. Lauderdale, FL	75
58	Brown Pelican	Ft. Lauderdale, FL	71
59	Brown Pelican	Ft. Lauderdale, FL	31
60	Brown Pelican	Ft. Lauderdale, FL	91

In addition to wild birds, some fish from the wild were tested for the presence of PFOS. The fish were collected in 1997-98 from sites in Michigan as part of surveys conducted by Dr. John Giesy. They were stored frozen and analyzed in 1999. Six species were tested. Low levels of PFOS were detected in four of the twelve samples. Since no sample matrices were available for matrix spike studies, these data are of screening quality only. No clear meaning can be drawn from the data. They are being used to develop sampling programs. Table 9 reports the findings.

Table 9. PFOS Screening in Fish.

BLD= Below Limit of Detection (approximately 7ppb)
BLQ=Below Limit of Quantitation (approximately 70 ppb)

Sample No.	Species	Location	Test Matrix	Test Result
1	Carp	Pine River, MI	whole body	BLD
2	Lake Trout	Siskiwit Lake, Isle Royale, MI	whole body	BLD
3	Lake Trout	Siskiwit Lake, Isle Royale, MI	whole body	BLD
4	Lake Trout	Pine River, MI	whole body	BLQ
5	Lake Trout	Lake Superior	whole body	BLD
6	Walleye	Detroit River, MI	whole body	BLD
7	Ciscowet	Lake Superior, Marquette, MI	muscle	BLD
8	Brown Trout	Detroit River, MI	muscle	BLD
9	Brown Trout	Rouge River, MI	liver	BLQ
10	Channel Catfish	Lake St. Claire, MI	muscle	BLD
11	Channel Catfish	Lake St. Claire, MI	egg	BLQ
12	Channel Catfish	Lake St. Claire, MI	egg	BLQ

8.13 Testing of Fishmeal Used in Rat Studies

While performing human health toxicity studies (see Perfluorooctane Sulfonate: Current Summary of Human Sera, Health and Toxicology Data, January 1999), 3M found "endogenous" levels of PFOS in some of the naive rats used in the studies. The levels found in the rat livers ranged from 29 ppb to 300 ppb. Livers of rats from one supplier showed no PFOS above the detection limit of 15 ppb. Further investigation revealed fishmeal to be an ingredient in the rat chow fed to the rats in which PFOS was detected. Fishmeal was not a dietary component of the rats that had no detectable levels of PFOS. 3M developed a complex analytical method to analyze fishmeal samples collected from different fish stock. At a detection limit of 2 ppm, PFOS was detected in three samples of fishmeal and not detected in three samples. At this time, these data are not conclusive.

8.14 Plant Site Analyses

In March of 1998, 3M conducted screening level sampling for PFOS around the Decatur plant. The outfall of the Decatur wastewater treatment plant is at a bay near the mouth of Baker's Creek. Baker's Creek flows into the Tennessee River, a large river that supports barge traffic. About 25 miles downstream is Wheeler Dam. The samples tested were of water surface film, subsurface water and sediment. A goal of the sampling was to experiment with sampling techniques and analytical methods. Therefore, the analytical data are of screening quality only. Data on PFOS from the sampling are in Table 10.

Table 10. Sampling Near the Decatur Wastewater Discharge

Sample Locations:
UP1 & UP2: Tennessee River, upstream of discharge
BC1: Baker's Creek below outfall
Q1 & Q2: Baker's Creek, downstream of discharge, in quiet waters near Tennessee River
WD1 & WD2: Tennessee River below Wheeler Dam

	UP1	UP2	BC1	Q1	Q2	WD1	WD2
Sub-surface water, in ppm							
PFOS	<.010	<.010	0.44	0.025	0.012	<.010	<.010
PFOS homologues	<.010	<.010	0.10	<.010	<.010	<.010	<.010
Surface films, in ppm							
PFOS	N/C	N/C	1.60	1.00	0.28	N/C	N/C
PFOS homologues	N/C	N/C	0.02	<.010	<.010	N/C	N/C
Sediment, in ppm							
PFOS	0.177	<.050	31.1	N/C	N/C	<.050	<.050
PFOS homologues	<.050	<.050	<.050	N/C	N/C	<.050	<.050

N/C = not collected
Surface film samples were skimmed from the top of the water, at the air/water interface.
Sediment samples were collected from the river bed using an Ekman Dredge. Samples were taken at the water collection point or, if sediment was lacking there, as close as possible to it.

Based on this initial sampling, a more extensive sampling was conducted. Sampling locations extended from about 10 miles upstream of the facility to 25 miles below the facility. As a result of analytical techniques being developed to lower detection limits, analyses of these samples is pending.

8.15 Biosphere Sampling

3M is building on recent information with advances in technology to design a program that could detect traces of sulfonated perfluorochemicals across a range of species, environmental habitats and geographic locations, including soil, water and organisms. 3M's approach is to use existing, scientifically recognized, sampling and data collection programs in order to minimize the time needed to obtain information. The goal is to set some bounds on the geographic regions where sulfonated perfluorochemicals are currently found, identify areas that should receive more investigation, and eliminate some general environments from further sampling in the immediate future. Key ecosystems and species of concern surrounding manufacturing plants are being tested as well as ecosystems remote from manufacturing and use locations.

Where possible, synoptic samples of soil, sediment, air or water are also being taken, but the primary focus of initial studies is tissue samples from biological receptors, especially those in upper trophic levels. The information obtained in the initial studies will be used to determine appropriate studies for ascertaining critical pathways.

8.2 Human Exposure Levels

Studies to investigate human exposures take several approaches:

1. Environmental exposure of the general U.S. population will be assessed in phases through a "Multi-Cities Study." This involves field investigation of paired cities, one with significant manufacturing or commercial fluorochemical use, matched with a city without known significant use. The study will involve direct sampling for dietary and environmental presence.

2. Residential exposure will be assessed through a product's use and controlled measurements of the product's releases. This study will measure releases of fluorochemical residuals and total PFOS from carpets.

3. The migration of sulfonated perfluorochemicals used in food packaging to the food is being quantified for several foods.

8.21 Multi-cities Sampling

The multi-cities study pairs a city having significant manufacturing or commercial use of fluorochemical products based on customer sales with a city that does not. Initially six cities, (three pairs) are being examined. This may be expanded, depending on initial results. The multi-cities sampling will yield environmental distribution data as well as data on potential sources of human exposure. The cities were selected to represent urban locations with various levels of fluorochemical releases and various types of municipal water supplies. The samples to be obtained, where possible, are: urban air, surface water column and surface microlayer, sediment, river fish, drinking water intake, treated drinking water, tap water, the influent and effluent to publicly owned waste treatment works, sludge, and municipal landfill leachate. Additionally a "market basket" of several food products will be sampled. These include: beef, pork, chicken, hot dogs, catfish, eggs, milk, bread, green beans, apples from three grocery stores and, if possible, produce from local farmers' markets.

8.22 Carpet Use Studies

The carpet study will estimate any loss of fluorochemical from normal use of carpets. If a pilot study of carpets finds significant releases, then the study will assess human exposure that may occur via inhalation, dermal and ingestion routes.

8.23 Paper and Packaging Studies

Results of past studies on the migration of fluorochemicals from packaging into food have been submitted to the FDA, and FDA has cleared the use of paper and packaging protectors for food as indirect food additives. Current work focuses on the development of new methodologies to extract various fluorochemicals from paper and several foods, then perform quantitative, low level analyses (< 1 ppb).

8.24 Exposure Scenarios

These scenarios will be developed using data from release, fate and distribution studies. Their purpose is to prioritize exposure pathways for further study by developing quantitative estimates of specific exposures under known conditions in a specific location.