Mohamed T. Elnabarawy

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

Prepared by
3M

March 1, 2000

Table of Contents

1.0 Preface

This paper provides an overview of 3M's current knowledge about the sources, dispersion, fate and effects of some of its fluorinated chemical products. It specifically addresses sulfonated perfluoronated chemistry and products, with the major focus on those compounds with an eight carbon chain structure. There are other fluorinated chemical products but these are not covered in this white paper.

The paper presents the past testing of these chemicals for environmentally relevant properties and assesses the quality and adequacy of past testing. It also presents recent results of environmental sampling, estimates of quantities of wastes generated at manufacturing plants and from product use, and new data on physical, chemical and ecotoxicological properties of sulfonated perfluorochemicals. It describes in detail the comprehensive exposure assessment plan currently being implemented. This plan is aimed at providing a better understanding of the transport, fate and effects of these chemicals in the environment and will help the company determine appropriate future actions.

As these studies return data, test plans will be revised to incorporate new information. For this reason, the results of present testing should be treated cautiously. Some data represent first attempts at characterization of complex chemicals in very difficult and dynamic environmental test matrices. The program incorporates new analytical technology, complex models and many variables. These initial findings are subject to change as results from currently planned testing on degradation, biological receptors, wastes from manufacturing facilities and other exposure data are obtained.

This paper should be read in conjunction with previous submittals about the health and environmental issues associated with 3M's sulfonated perfluorochemical product line. In January 1999, 3M submitted to the Environmental Protection Agency (EPA) a report, Perfluorooctane Sulfonate: Current Summary of Human Sera, Health and Toxicology Data, that provided details of analyses of pooled blood sera samples that demonstrated the presence of perfluorooctane sulfonate (PFOS) at very low levels. In February 1999, 3M provided a comprehensive review, The Science of Organic Fluorochemistry, describing the health effects and background chemistry associated with PFOS. Another report submitted to EPA in May 1999, Fluorochemical Use, Distribution, and Release Overview, describes how 3M produces sulfonated perfluorochemicals, which product lines incorporate them, and the uses for these products. Finally, various Section 8(e) submissions have been forwarded to EPA relative to these sulfonated perfluorochemicals.

2.0 Executive Summary

3M produces sulfonated perfluorochemicals by an electrochemical fluorination process. This process creates a complex and variable mix of chemicals in which fluorine atoms replace hydrogen atoms on the organic feedstock and carbon-carbon bonds are rearranged. Because of the carbon-fluorine bond formed by this process, the compounds created are considered to be very stable. Perfluorochemicals have complete substitution of fluorine for hydrogen. Fluorochemicals can repel both water and oils, reduce surface tension dramatically, act as catalysts for oligomerization and polymerization, and function under extreme conditions. Major uses for sulfonated perfluorochemicals are surface protectors and surfactants.

Fluorine's high electronegativity confers a strong polarity to carbon-fluorine bonds, contributing to the stability and nonreactive character of perfluorochemical molecules. They are unusual as that perfluoroalkyl chains are both oleophobic and hydrophobic. The addition of charged moieties to the chain may affect the water solubility of the shorter chains.

The highest volume sulfonated perfluorochemical produced by 3M is perfluorooctanesulfonyl fluoride (POSF). After synthesis, it is used to create several product lines. During their life cycles, POSF and POSF-based products may degrade. If degradation occurs, current research suggests perfluorooctane sulfonate, (PFOS) and a few other perfluorinated forms are degradation products. Timeframes for degradation are variable, with some polymeric products apparently stable for very long periods of time.

The identification and quantification of sulfonated perfluorochemicals pose difficult analytical challenges. Reliable methods for extraction, separation and identification of sulfonated perfluorochemicals in tissues and environmental matrices have evolved and have been developed only in the last few years. New analytical technology is providing capabilities of detection in wide varieties of matrices at parts per trillion (ppt) levels and identification of metabolites and breakdown products.

As fully described throughout this paper, completion of a comprehensive exposure assessment and related scientific studies will require many years of intensive research. 3M is pursuing an aggressive program to reduce releases to the environment while that scientific research is being conducted. It is not the purpose of this paper to describe the nature and extent of that undertaking. Readers should be made aware, however, that 3M has initiated a wide range of activities to utilize available opportunities for reductions in releases. These have included installation of new controls to reduce waste streams in 3M manufacturing facilities. They have also included product stewardship efforts to communicate to customers and downstream users, information regarding fluorochemicals and the need to exert careful management over these substances. In addition, 3M has undertaken major efforts to reinvent its products through the use of alternative chemistry to reduce the volume of fluorochemicals used in those products. All of these efforts will

be continued with intensity while the scientific research described in this paper is being carried out.

3M is examining the life cycle of its sulfonated perfluorochemical products to identify releases to the environment from manufacturing processes, supply chains, product use and disposal. First it is determining waste streams generated throughout the life cycle. This information will be used to estimate environmental releases. This approach is necessary since not all waste produced is released to the environment. Manufacturing waste studies are underway at the 3M plant in Decatur, Alabama on POSF-based processes. PFOS-based waste streams generated from these manufacturing processes are conservatively estimated to be about 1.1 million pounds per year, about 90% as solid waste, most of which is incinerated and destroyed. Recent wastewater controls have reduced amounts of PFOS actually discharged to the river by half since 1998.

Data from business units have identified key products that contain the majority of the fluorochemical solids sold in the United States in 1997. Using this sales information, 3M estimated customer and end user waste streams. Most of the waste generated from these sources is in the form of solid waste. Releases to the environment from product disposal to landfills, wastewater treatment plants and incineration are all being investigated.

Several different fate and transport mechanisms have been identified as important to study. Initially models are being used for screening-level assessments of potential fate mechanisms. Multi-media fugacity models are under development to incorporate the unique properties of fluorochemicals.

Sulfonated perfluorochemicals have been detected at low levels in some species of eagles and wild birds. Low levels were detected in bird plasma and bird livers. 3M believes that these sets of data are insufficient to draw conclusions with any statistical merit. In screening sampling of the river and sediments near the Decatur manufacturing plant, PFOS was present in a few samples collected near the outfall. All this information was used in the design of a more comprehensive program of biosphere sampling. The goal of the biosphere sampling plan is to screen for PFOS across a range of species, habitats and geographic locations and to identify areas on which to focus scientific investigation to develop a better understanding of any potential environmental effects.

A multi-cities study will determine environmental distribution and potential sources of human and ecological exposure. The multi-cities study pairs cities with significant manufacturing or commercial use of fluorochemical products with cities of the same size without significant use. Levels of PFOS and its precursors will be measured in food, air, water, sediment, and disposal facilities. Additionally, levels are being measured arising from carpet use, product uses and potential migration into food from packaging.

The role of hydrolysis, photolysis and biological processes in the degradation of sulfonated perfluorochemicals is being studied. Research suggests that the biodegradation of fluorinated sulfonates requires the presence of hydrogen at the alpha

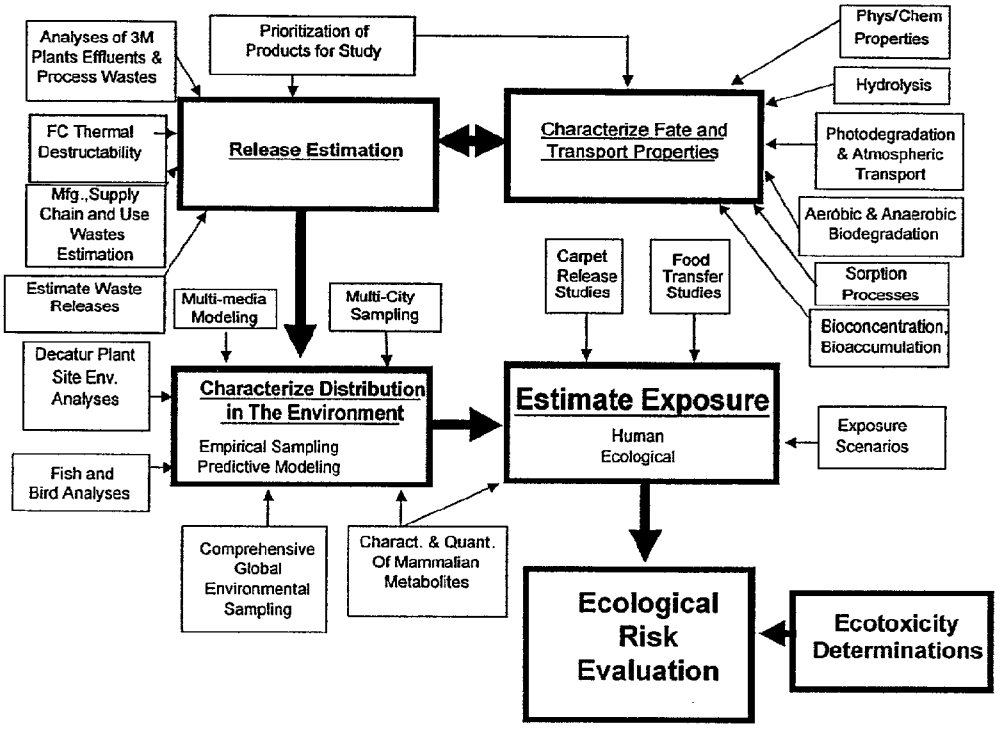
carbon on the fluorinated chain and that perfluorinated molecules are susceptible to breakdown only at non-fluorinated side chains. Degradation of sulfonated perfluorochemicals is not complete but results in production of other fluorochemicals. Studies suggest that compounds made from POSF, a commercially important perfluorochemical product and intermediate, are transformed during metabolism to another sulfonated perfluorochemical, PFOS. PFOS does not appear to further degrade except by incineration.

Several sulfonated perfluorochemicals have been subjected to basic screening tests for environmental toxicity. Different species varied significantly in their response to the same chemical even when using the same laboratory procedure. New testing is underway using purified sulfonated perfluorochemicals, measured test concentrations, and a wide variety of test organisms. Results of these studies are reported in this white paper.

The research projects that are yielding new information on sulfonated perfluorochemicals are part of a comprehensive plan to assess the potential pathways of environmental exposure associated with the manufacture, use and disposal of sulfonated perfluorochemical products. Figure 1 portrays the plan components. Work on the plan is now underway using a combination of 3M resources and outside experts. Recent analytical advances and this extensive research effort are expected to contribute significantly to a better understanding of environmental fate and effects.

The findings resulting from the comprehensive plan, along with new ecotoxicological test data, will be used to evaluate ecological risk. While this evaluation is underway, 3M is implementing actions to reduce generation of waste in manufacturing processes and to reduce releases of sulfonated perfluorochemicals into the environment through process improvements, waste reduction and engineering redesign.

Figure 1. Diagram of Fluorochemical Assessment Plan.



3.0 Introduction to Fluorochemicals

Fluorochemicals are components of several important 3M product lines due to their unique and useful properties. They are stable, chemically inert and generally nonreactive. As components of products, they repel both water and oil, reduce surface tension much lower than other surfactants, act as catalysts for oligomerization and polymerization, and function where other compounds would rapidly degrade.

3M has produced fluorochemicals commercially for over 40 years. 3M produces fluorochemicals by combining anhydrous hydrogen fluoride with hydrocarbon stock in the presence of electrical energy. The highest volume sulfonated fluorochemical produced by 3M is perfluorooctanesulfonyl fluoride (POSF).

$$C_8H_{17}SO_2F + 17\,HF \xrightarrow{4.5\text{-}7.0\ V} C_8F_{17}SO_2F + 17\,H_2$$

1-Octanesulfonyl fluoride Perfluorooctanesulfonyl fluoride **(POSF)**

The fluorination process overall yields about 35-40% straight chain (normal) POSF, and a mixture of byproducts and waste of uncharacterized and variable composition containing:

-higher or lower straight chain homologues, n-$C_nF_{2n+1}SO_2F$, of various chain lengths (7% of process output)

e.g. $C_6F_{13}SO_2F$, $C_7F_{15}SO_2F$, $C_9F_{19}SO_2F$

-branched chain perfluoroalkyl products of various chain lengths (18-20% of output)

e.g. $CF_3CF_2CF_2CF_2CF_2CF(CF_3)CF_2SO_2F$ $CF_3CF(CF_3)CF_2CF_2CF(CF_3)CF_2SO_2F$

- straight chain, branched and cyclic perfluoroalkanes and ethers (20-25% of output) e.g. CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{12}, cC_4F_8

-"tars" (high molecular weight fluorochemical byproducts) and other byproducts, including molecular hydrogen (10-15% of output).

Because of slight differences in process conditions, raw materials, and equipment, the mixture produced by the electrochemical fluorination process varies somewhat from lot to lot and from plant to plant. Numerous process steps are used to convert the fluorinated mixture into final products.

The largest production of fluorochemicals occurs at the 3M manufacturing plant in Decatur, Alabama, and this plant is the focus of current studies. During production, many byproducts and waste products are formed. The volatile waste products have been vented to the atmosphere in the past but improvements are underway to capture and destroy these releases by thermal oxidation. The tars are disposed at hazardous waste landfills or treated by incineration. The byproducts, many of which are incompletely fluorinated with hydrogen atoms still present, are recycled back into processes or partially degraded in stabilization processes and discharged to wastewater treatment systems. The treatment sludge is landfilled. Some of the non-POSF-based byproducts are recovered and sold for secondary uses.

The product of the electrochemical fluorination process is thus not a pure chemical but rather a mixture of isomers and homologues. Perfluorochemicals have complete substitution of fluorine for hydrogen. The commercialized POSF derived products are a mixture of approximately 70% linear POSF derivatives and 30% branched POSF derived impurities. POSF is used as a product and is also an important intermediate in the synthesis of substances used in many other 3M products. To a lesser extent, homologues of POSF, [$C_nF_{(2n+1)}SO_2F$ where n= 2-9, exclusive of 8], are also components used in the formation of other 3M products.

Some of the POSF derived products are surface active materials and monomers of relatively low molecular weight (~500 daltons). These monomers are used as low molecular weight surfactants or are joined with other monomers to form higher molecular weight oligomers and polymers with a mix of fluorinated and unfluorinated portions. Fluorochemical monomers can also be joined to phosphates, to polymeric and oligomeric urethane, or to acrylate backbones through ester and other linkages. The majority of 3M's sulfonated perfluorochemicals produced are used in polymeric form for treatment of surfaces and materials. For example, fluorochemical containing polymers (urethanes, acrylics and esters) can provide soil, stain, and water resistance to personal apparel and home furnishings.

Some products synthesized from POSF and its homologues are sold as raw materials to customers who use them as intermediates or components of their products. The intermediates can be covalently bound to a variety of polymeric hydrocarbon backbones.

The 3M product lines that use sulfonated perfluorochemicals are summarized below. (Product lines using fluorochemicals that contain no sulfonyl groups are not listed.)

Surface Treatments

Fabric/Upholstery Protector (High molecular weight (MW) polymers)
Carpet Protector (High MW polymers)
Leather Protector (High MW polymers)
Paper and Packaging Protector (High MW phosphate esters or high MW polymers)

Surfactants (Low MW chemical substances)

Specialty surfactants
Household additives
Electroplating and etching bath surfactants
Coating and coating additives
Chemical intermediates
Carpet spot cleaners
Fire Extinguishing Foam Concentrates
Mining and Oil Surfactants

Other Uses

Insecticide Raw Materials (Low MW chemical substances)

Typically a fluorochemical product contains a small amount of fluorochemical residuals: unreacted or partially reacted starting materials or intermediates. Residuals which are common to formulations of sulfonated perfluorochemical products include: perfluorooctane sulfonate (PFOS), N-ethyl (or N-methyl) perfluorooctane sulfonamide (N-EtFOSA or N-MeFOSA) , N-ethyl (or N-methyl) perfluorooctane sulfonamidoethyl alcohol (N-Et FOSE alcohol or N-MeFOSE alcohol) and perfluorooctanoic acid (PFOA). Table 1 identifies some sulfonated perfluorochemicals, their acronyms, chemical name, and formulas.

Table 1. Perfluorochemical Glossary

Designation	Name	Formula
POSF	perfluorooctanesulfonyl fluoride	$C_8F_{17}SO_2F$
PFOS	perfluorooctane sulfonate	$C_8F_{17}SO_3^-$
PFOSH	perfluorooctanesulfonic acid	$C_8F_{17}SO_3H$
PFOS.NH_4 salt	ammonium perfluorooctanesufonate	$C_8F_{17}SO_3NH_4$
PFOS.DEA salt	Perfluorooctanesulfonate diethanolamine salt	$C_8F_{17}SO_3NH(CH_2CH_2OH)_2$
PFOS.K salt	potassium perfluorooctanesulfonate	$C_8F_{17}SO_3K$
PFOS.Li salt	lithium perfluorooctanesulfonate	$C_8F_{17}SO_3Li$
FOSA	perfluorooctanesulfonamide	$C_8F_{17}SO_2NH_2$
PFOSAA	perfluorooctane sulfonylamido (ethyl)acetate	$C_8F_{17}SO_2N(CH_2CH_3)CH_2COO^-$
PFDS	perfluorodecanesulfonate	$C_{10}F_{13}SO_3^-$
PFHS	perfluorohexane sulfonate	$C_6F_{13}SO_3^-$
N-EtFOSA	N-ethyl perfluorooctanesulfonamide	$C_8F_{17}SO_2NHC_2H_5$
N-MeFOSA	N-methyl perfluorooctanesulfonamide	$C_8F_{17}SO_2NHCH_3$
N-EtFOSE alcohol	N-ethylperfluorooctane sulfonamidoethanol	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$
N-MeFOSE alcohol	N-methylperfluorooctane sulfonamidoethanol	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$
N-EtFOSEA	N-ethylperfluorooctanesulfonamidoethyl acrylate	$C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OCOCH=CH_2$
N-EtFOSEMA	N-ethylperfluorooctanesulfonamidoethyl methacrylate	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OCOC(CH_3)=CH_2$
N-MeFOSEA	N-methyl-perfluorooctanesulfonamidoethyl acrylate	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OCOCH=CH_2$
PFOA	perfluorooctanoic acid	$C_7F_{15}CO_2H$

4.0 Physical-Chemical Properties of Fluorochemicals

Fluorinated organics are less well described in the science literature than organic molecules bearing other halogens, i.e. bromine and chlorine, which have been more thoroughly investigated by many researchers in published reports. To understand the properties of fluorinated organics, it is necessary to describe the properties of fluorine. Fluorine has several characteristics that differ from the other halogens and contribute to the unusual properties of fluorochemicals.

Fluorine has a van der Waals radius of 1.35 Å, more comparable to that of oxygen than other halogens, and isosterically similar to a hydroxyl group. Fluorine has the highest electronegativity (4.0 -Pauling scale) of all the halogens, indeed the highest in the periodic table. This confers a strong polarity to the carbon-fluorine bond. The carbon-fluorine bond is one of the strongest in nature (~110 kcal/mol). This very strong, high energy bond contributes to the stability of fluorochemicals.

The high ionization potential of fluorine (401.8 kcal/mole) and its low polarizability leads to weak inter- and intramolecular interactions. This is demonstrated by the low boiling points of fluorochemicals relative to molecular weight, and their extremely low surface tension and low refractive index. The partitioning behavior of perfluoroalkanes is unusual. Some perfluoroalkanes when mixed with hydrocarbons and water form three immiscible phases, demonstrating that perfluorinated chains are both oleophobic and hydrophobic. A charged moiety, such as carboxylic acid, sulfonic acid, phosphate or a quaternary ammonium group, when attached to the perfluorinated chain, makes the molecule more water soluble because of the hydrophilic nature of these charged moieties. Therefore, such functionalized fluorochemicals can have surfactant properties. Typically, the presence of these charged groups on short chain perfluorinated compounds (<C6) noticeably increases the solubility of the compound in water.

Physical data available on fluorochemicals at 3M have been principally those parameters needed for quality control use and material handling. Table 2 summarizes the physical data for low molecular weight, POSF-based fluorochemical products that have been developed for use on Material Safety Data Sheets (MSDS).

Some of these perfluorochemical products are primarily used as surfactants; others are primarily used as intermediates in the formation of polymeric or oligomeric products. Some of these low molecular weight fluorochemicals are also likely intermediates in the degradation of polymeric compounds. Some can also result from environmental transformation of other low molecular weight fluorochemical products. It is important to remember that these data were obtained using products that were not highly refined, and products may have more than one fluorochemical component. Some may have nonfluorochemical components that enter into determination of the values. Because of improvements in analytical techniques and product refinement, these data are in the process of being replaced by better quality data.

Table 2. Physical Data on Fluorochemical Products (Developed for Use on MSDS Sheets)

Source: MSDS Sheets
Abbreviations: N/D: not determined; N/A: not applicable; ~: approximately
*measured at 1mm Hg #measured at 2 mm Hg

Product Use	Principal Fluorochemical	boiling pt (b) melting pt, (m) °C	vapor pressure mmHg calc. @20°C	vapor density calc. @20°C Air=1	evap rate BuOAc =1	solubility in water	Specific Grav. Water=1	pH
Intermed.	POSF	154 b	<10	>1.0	<1.0	neglig	~1.8	N/A
Intermed.	N-MeFOSE alcohol	75-95 m	N/D	N/D	N/D	neglig	~1.7	N/A
Intermed.	N-EtFOSE alcohol	~118 b*	<10	>1.0	<1.0	neglig	~1.7	N/A
Surfactant	N-EtFOSA	~110 b# ~ 90 m	<10	>1	N/D	neglig	~1.6	N/A
Intermed.	N-EtFOSEA	~150 b*	<10	>1.0	<1.0	nil	~1.5	N/A
Intermed.	N-EtFOSEMA	~150 b*	<10	>1.0	<1.0*	neglig	~1.5	N/A
Surfactant	PFOS NH_4^+ salt	~ 82 b	~34	~1.0	<1.0	moderate	~1.1	~7
Surfactant	PFOS Li salt	~100 b		N/D	<1	complete	~1.1	6-8
Surfactant	PFOS K salt	N/A	N/A	N/A	N/A	slight	~0.6	7-8
Surfactant	PFOS DEA salt	~ 98 b	~31	~0.62	<1.0	complete	~1.1	~7
Surfactant	PerfluoroC10 sulfonic acid, NH_4^+ salt	~ 96 b	~16	~1.08	<1	moderate	1.08	8.5-9.5
Surfactant	Glycine derivative of FOSA	~100 b	~18	~0.87	<1.0	complete	~1 3	~11
Surfactant	N-EtFOSE alcohol, ethylene oxide adduct	210 b	~18	0.64	<1	apprec	1.31-1.34	5.5-8.4

Additional physical data were developed in the mid-1970s and early 1980s on a few, high volume products. Typically these data are related to developing an understanding of environmental fate, e.g. data on soil mobility and partitioning coefficients. They are summarized in Table 3. 3M has evaluated these data for reliability and the reliability codes are included as part of the table. Progress in analytical techniques has significantly improved the reliability of current data compared to the reliability of these historical data. Current physical/chemical data are found in Table 4.

Table 3. Historical Physical/Chemical Data on Fluorochemical Products Related to Environmental Fate

The reliability code which follows the test value in parentheses is interpreted as follows:
(1A) Study used published test guidelines or well-documented procedures. Where applicable, concentrations were measured. All quality control data were acceptable.
(1B) Results were obtained by mathmatical estimation.
(2) Study meets all the criteria for quality testing, but has one or more deficiencies.
A. Concentrations NOT measured--parameter determined via indirect measurement.
B. Analytical methodology questionable.
(3) Study does not meet criteria for quality testing due to
A. Demonstrated weaknesses in experimental procedures.
B. Insufficient methodology description.
C. Unacceptable quality control.
(4) Study data are available only as summaries. Original reports unavailable.

N/D= not determined

Product Principle FC	Solubility in water mg/L	octanol/water partition coefficient	log n-octanol/water partition coefficient	soil adsorption coefficient (K)	organic carbon adsorption coefficient (K_{oc})	Vapor pressure
PFOS K^+ salt	1080 (2A)	10 (2B)	1 (2B)	0.99 (2B)	66 (2B)	N/D
N-MeFOSE alcohol	0.82 (2B)	56,800 (2B)	ND	77 (2B)	3,500 (2B)	N/D
N-EtFOSE alcohol	0.05 (2B)	6,600,000 (4)	3.60 (1B)	330 (2B)	17,800 (2B)	1.22 mmHg (1B) 0.5Pa@20°C (1A)
N-EtFOSEA	0.89 (2B)	N/D	>6 (2B)	N/D	N/D	6.0×10^{-3} Pa (1A)
POSF	1 est (2A)	N/D	N/D	N/D	N/D	1.6 torr@20°C (4)
N-EtFOSA	N/D	N/D	N/D	N/D	N/D	0.16 Pa@20°C (1A)

Historically, formulated products containing other components and residuals rather than pure perfluorochemicals were used to collect physical/chemical data. While most of the products above consist largely of one active fluorochemical component, the values obtained for the product are not likely those for the purified fluorochemical alone.

Computer models used in conjunction with empirical sampling can be used to predict environmental fate and transport of these substances. Existing models can require the following physical/chemical data for operation: molecular weight, boiling/melting point, pK_a, octanol/water partition coefficient, vapor pressure, solubility, Henry's law constant, density, evaporation rate, heat of vaporization, bioconcentration factor, and degradation mechanisms in air and water (hydrolysis, photolysis, and biodegradation). Precise values for the parent fluorochemical compound, its intermediates, and the end degradation product(s) are essential for comprehensive predictions about environmental fate and transport.

3M is developing the missing physical/chemical data on individual fluorochemicals with the assistance of several consultants. While 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. The data are being determined using the Guidelines for the Testing of Chemicals developed by the Organization for Economic Co-operation and Development (OECD) for physical/chemical testing (3) where available. Where possible, melting points, boiling points, vapor pressures, dissociation constants, water solubility, n-octanol/water partition coefficients, air/water partition coefficients, and soil adsorption/desorption will be determined. This information is needed for both environmental fate models and manufacturing emission models. Current modeling efforts are hampered by lack of data on physical/chemical properties.

Data are being collected according to Good Laboratory Practice (GLP) standards. The air/water partition test is non-standard. This test protocol was developed jointly by 3M and an outside expert. Results will be reviewed by several technical experts, both within the 3M Environmental Laboratory, and outside the company.

3M is generating the information on soil sorption/desorption characteristics as non-GLP, screening studies. These data will aid in the evaluation of the transport process and partitioning. For example, will a fluorochemical be retained by the soil matrix or remain in the water phase? The bioconcentration potential of PFOS and EtFOSE alcohol will be examined through empirical testing that determines the extent of the uptake of these chemicals by fish. Work on degradation including hydrolysis, photodegradation and biodegradation is described in another section. (See Environmental Transformation/Degradation.)

The physical/chemical testing is proceeding in order of PFOS, EtFOSE alcohol, and MeFOSE alcohol. The results to date are reported in Table 4. The inability to determine an octanol/water partition coefficient makes it difficult to do predictive modeling.

Table 4. New Physical/Chemical Testing Results on PFOS, potassium salt

Parameter	Results
Solubility: pure water	570 mg/L
Solubility: fresh water	370 mg/L*
Solubility: unfiltered sea water	4-5 mg/L* estimated
Solubility: filtered sea water	25 mg/L*
Vapor Pressure	3.31×10^{-4} Pa @20°C
Melting Point	$\geq$ 400°C
Boiling Point	not calculable
Octanol/Water Partition (K_{ow})	not calculable; three phases
Air/Water Partition Coefficient	0($<2 \times 10^{-6}$)

*Data developed in support of other studies; not developed using GLP standards.

The methods used in these current physical/chemical tests will provide values reported in consistent formats that are internationally familiar and accepted. This standardization will aid in the review and comparison of data on individual fluorochemicals and in model operation and prediction. The data will contribute to analytical method development and overall improvements in sample handling, shipping and storage as well as manufacturing.

5.0 Analytical Test Methods for Fluorochemicals

Procedures for detecting and identifying fluorochemicals in the environment require a very high level of technical expertise. Most general analytical methods do not provide enough sensitivity or selectivity. The complex mixture of possible components in a product, the multiple matrices in which they could reside (e.g. the atmosphere, soils, surface water, groundwater, wastewater, different animal tissues, different animal species, plant species, foods, etc.), and trace level detection require selective extraction and diverse analytical techniques.

Each fluorochemical requires a unique analytical methodology. Separate methods may be needed for every matrix. Validation of each method is time intensive. Often, standards are not available. Reliable quantitative methods for extraction, separation and identification have been developed only within the last few years. Prior to that, relatively insensitive and non-specific analytical methods, such as "total organic fluoride (TOF)," were used.

The analytical technology used in extraction, separation, identification and quantitation includes combinations of:

- High Performance Liquid Chromatography (HPLC);
- High Pressure Solvent Extraction (HPSE);
- ElectroSpray Tandem Mass Spectroscopy (ESMSMS);
- Gas Chromatography (GC) with a Flame Ionization Detector (FID),
  a Mass Spectrometer (MS),
  a Photo Ionization Detector (PID), or
  an Electron Capture Detector (ECD)
- HPLC-Quadrapole- Time Of Flight-mass spectrometer (QTOF)

For example, analysis of PFOS extracted from tissues requires ESMSMS analysis. This technique focuses quantitation on three secondary ions of one primary ion at a specific HPLC retention time.

To provide positive identification of target analytes in complicated matrices, the 3M Environmental Laboratory uses a quadrapole time-of-flight mass spectrometer. The instrument provides high mass accuracy (to 0.0005 amu) and so is useful in identifying

fluorochemical metabolites and intermediates for which standards are not available. Compound identification is based on reasonable HPLC retention time as compared to standard compounds of similar structure, reasonable interpretation of fragment ions associated with the primary ion, interpretation of the accurate mass spectrum, and agreement between the experimental and theoretical molecular weight ($\pm$ 0.0005 amu).

The addition of new technology has permitted 3M analysts to increase the numbers of sulfonated perfluorochemicals that can be identified, expand the matrices in which they can be detected, and lower the levels at which they are detected. The technology has expanded the volumes of analyses that can be done. Nonetheless, capacity limits require analyses to be prioritized. When samples cannot be analyzed soon after collection, care is taken to store the samples appropriately for the matrix and the analytical method, both to prevent sample deterioration and contamination.

3M now has in place several methods for analysis of sulfonated perfluorochemicals in several matrices. The methods produce data of varying quality. They may be used in combination to produce test data. The method performance can be categorized as follows:

1. Quantitative methods that have been validated by studies conducted according to Good Laboratory Practices (GLP). These exist for analyses of samples of blood, liver, and several animal tissues of certain species, drinking water, and certain types of food.

2. Quantitative methods that typically are based on methodologies that have undergone significant analytical characterization during development. These methods are validated by extensive quality control testing, but validation studies may not have been conducted according to GLP requirements. These exist for wastewater, sludge, and air, for example.

3. Semi-quantitative methods that typically are based on the quantitative methods but for which validation studies are lacking or quality assurance cannot be demonstrated because, for example, standards are unobtainable or sample matrix is extremely limited.

4. Screening methods that typically are under development or a result of exploratory studies. These methods yield only qualitative data, i.e. they reliably detect the presence or absence of an analyte.

Method development is continuing, not only at the 3M Environmental Laboratory but also at independent laboratories in consultation with 3M Environmental Laboratory scientists. For some matrices, the detection limits sought are at lower levels. Method validation of low level analyses may be confirmed at a university or other contract laboratories, as appropriate. When samples are sent to consulting laboratories, 3M supplies the methodology or shares expertise to develop the method. Quality assurance is

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.

9.0 Environmental Transformation/Degradation of Fluorochemicals

There are many physical, chemical and biological mechanisms that operate in the environment to transform or degrade molecules. They include abiotic mechanisms, e.g. hydrolysis and photolysis, and biotic mechanisms, especially microbial metabolism. Because the carbon-fluorine bond is one of the strongest in nature, with high bond energies, its cleavage requires large amounts of energy. Most chemical and physical processes naturally occurring in the biosphere lack the required energy. In the laboratory, perfluoroalkyl chains are not degraded in the chemical oxygen demand (COD) test, nor in total organic carbon (TOC) analyzers that use very reactive chemical and ultraviolet degradation mechanisms. Combustion does destroy organic fluorochemicals and degradation is found in high temperature TOC analyzers.

In perfluorinated molecules, the fluorines surround the carbon chain completely, shielding the carbon-carbon bonds from attack. The fluorine atoms confer a "rigidity" to the conformation of the molecule. This rigidity could make it difficult for the molecule to join with enzymes, thereby blocking biological attack of the carbon-carbon bond. As a molecule becomes more fluorinated, carbon-carbon bonds, carbon-hydrogen and carbon-fluorine bonds all typically increase in strength.

Early work with perfluorochemical products using standardized screening tests for degradation found little susceptibility to degradation. (See Table 11.) Fluorochemicals lacking nonfluorinated organic portions produced essentially no biochemical oxygen demand (BOD). Those with ionically bonded organics showed BODs near those expected from their non-fluorinated portion alone. Fluorochemical surfactants with covalently bonded organic portions produced mixed results.

The early data on these degradability studies has been given a reliability code that follows the test results.

Table 11. Historical Results of Standard Degradation Tests on Fluorochemicals

Product Principle Fluorochemical	COD mg/Kg	BOD 5-day mg/Kg	BOD 10-day mg/Kg	BOD 20-day mg/Kg	BOD 28-day mg/Kg	Photo degra-dation	Other
POSF	500-720 (4)	nil (4)	nil (4)	nil (4)	N/D	N/D	N/D
N-MeFOSE alcohol	163,000 (1)	N/D	N/D	nil (1)	N/D	nil (1)	N/D
N-EtFOSE alcohol	260,000 (4)	nil (4)	N/D	N/D	N/D	nil (1)	O2 uptake= 3% of ThOD; No deg in 6 month shake flask studies or 7 day activated sludge studies (2B)
N-EtFOSA	1,800 (4)	nil (4)	nil (4)	nil (4)	N/D	N/D	N/D
N-EtFOSEA	240,000 (1)	12,000 (2A)	19,000 (2A)	23,000 (2A)	N/D	N/D	not readily (1) biodegradable
N-EtFOSEMA	80,000 (1)	800 (2A)	2,000 (2A)	11,000 (2A)	N/D	N/D	N/D
Perfluoro C10, sulfonic acid, NH4 salt	1,000,000 (2A)	67,000 (2A)	600,000 (2A)	720,000 (2A)	N/D	N/D	N/D
K salt of carboxylic acid analogue of N-EtFOSE alcohol	462,000 (1)	<39,800 (2A)	172,000 (2A)	179,000 (2A)	289,000 (2A)	N/D	N/D
PFOS Li^+ salt (4)	54,000	N/D	N/D	N/D	N/D	N/D	N/D
PFOS K salt	4,000 (4)	nil (4)	nil (4)	nil (4)	N/D	nil (4)	no degradation in Warburg 3 hr study or 2.5 month shake flask study (2B)
PFOS DEA salt	78,000 (2A)	44,000 (2A)		82,000 (2A)	N/D	N/D	N/D
N-EtFOSE alcohol $(C_2H_4O)_{14}H$ adduct	1,070,000 (1)	0 (4)	N/D	107,000 (4)	N/D	N/D	40% removal BiAS (3A)
PFOS NH_4 salt	412,000 (4)	232,500 (4)	267,500 (4)	292,500 (4)	N/D	N/D	N/D

COD means Chemical Oxygen Demand. It is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant such as potassium dichromate.

BOD means Biochemical Oxygen Demand. It is the amount of oxygen consumed by microbial processes while breaking down a known amount of a test substance.

ThOD means Theoretical Oxygen Demand. It is the theoretical quantity of oxygen used when the test compound is fully mineralized. This value is calculated using the structure of the test chemical.

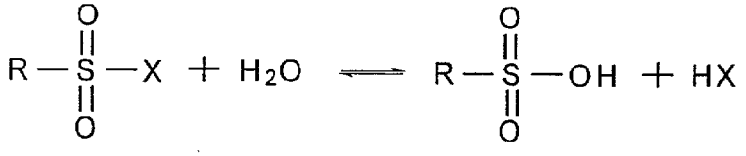
BiAS means Bismuth Active Substances. These are materials, such as water soluble polyethoxylates, that precipitate with barium tetraiodobismuthate.

N/D means Not Determined.

Code meanings are:
(1) Study used published test guidelines or well-documented procedures.
Concentrations were measured, and all quality control data were acceptable.
(2) Study meets all the criteria for quality testing but has a deficiency
A. Concentrations NOT measured.
B. Analytical methodology questionable.
(3) Study does NOT meet criteria for quality testing; data have one or more flaws.
A. Demonstrated weakness in experimental procedures.
B. Insufficient description of method.
C. Unacceptable performance of controls.
(4) Data are available only as summaries; original reports not found.

9.1 Hydrolysis Studies

Hydrolysis is a major mechanism contributing to abiotic degradation of organic molecules, although it rarely is responsible for complete degradation. The hydrolysis of sulfonated compounds is described below.



X = halogen, OR, NR

3M is evaluating the potential for hydrolysis of fluorochemicals using EPA guidance [Fate, Transport and Transformation Test Guidelines, *Hydrolysis as a Function of pH and Temperature*](2), and is conducting pH dependent studies of PFOS and MeFOSE alcohol, as well as on fluorochemical monomers, to estimate half-lives. Selected fluorochemical products are being subjected to a single temperature (50°C), variable pH screening process. For those that demonstrate hydrolysis or a deviation form first order kinetics, multiple pH, multiple temperature studies are planned. Hydrolysis test data are being reviewed by an outside expert.

9.2 Photolysis

Like hydrolysis, photodegradation is a major abiotic mechanism contributing to the transformation of organic molecules, but rarely responsible for complete degradation. Photodegradation occurs primarily in air, in shallow water, on soil and vegetative surfaces. It is likely an important factor in the fate of soluble and volatile compounds, less so for insoluble and sorbed compounds. Products and intermediates most susceptible to photodegradation are those most likely to be used outdoors in sunlight.

Initially, the degradation that might occur in products dissolved or suspended in water is under investigation. The first studies are using the PFOS precursors such as EtFOSE alcohol, MeFOSE alcohol, MeFOSA, EtFOSA, and FOSA. Later studies will use POSF-based polymers. If simple methods can be found, gas phase photolysis of volatile and semi-volatile fluorochemical degradation intermediates will be investigated.

The preliminary results suggest that PFOS is unchanged as a result of light exposure. However, EtFOSE alcohol, MeFOSE alcohol, EtFOSA and MeFOSA as well as a surfactant and foamer product all appeared to undergo photolysis to FOSA, PFOA, a hydride, and olefins. PFOS was not detected. One product, an aromatic perfluorooctane sulfonate, did photodegrade to form PFOS.

9.3 Atmospheric Studies

Although PFOS has a low volatility, several PFOS precursors are volatile. These include: EtFOSE alcohol, MeFOSE alcohol, MeFOSA, EtFOSA, and FOSA. When present as residuals in products, these precursors could evaporate into the atmosphere when the product is sprayed and then dried. Once in the atmosphere, the compounds can remain in the gas phase, condense on particulates present in the atmosphere and be carried or settle out with them, or be washed out with rain. The measured vapor pressure of Et-FOSE alcohol is sufficiently high that essentially all of it is likely to be in the gas phase and not condensed on particulate matter. Gas chromatic data suggest that other precursors are even more volatile. The low water solubility of these compounds makes it unlikely they washout from the atmosphere in rainwater.

Thus the rate of removal of these precursors from the atmosphere will likely depend on their photochemical reactivity, e.g. their reaction with hydroxyl ions in the atmosphere. How widely distributed they are locally, regionally or globally depends on the rate of photochemical transformation to more soluble or less volatile products.

3M is examining atmospheric lifetimes of these PFOS precursors. Initially EtFOSE alcohol and MeFOSE alcohol will be tested for reactivity with the OH radical in the gas phase. Modeling will determine their atmospheric lifetimes and analytical work will determine their gas-phase degradation products. Then those properties of the degradation

products that affect removal rates from the atmosphere, e.g. solubility and vapor pressure, will be determined. This information will be used to predict distribution of these compounds resulting from atmospheric mechanisms.

9.4 Biodegradation Studies

Biodegradation is essential to the functioning of living systems. Natural systems rely on living organisms, especially microbes, to break down complex organic molecules to simple inorganic molecules that can be recycled back into the ecosystem. Some microbial communities have demonstrated the ability to degrade some xenobiotic compounds. During biologically catalyzed degradation of these compounds, the degradation intermediates produced are frequently of a molecular structure that naturally occurs. Particularly important environments for biological breakdown are: sewage treatment systems, soils/sediments, estuaries and wetlands. Both aerobic and anaerobic organisms play important roles in degradation. 3M is studying biodegradation using several approaches.

9.41 Microbial Studies on Perfluorochemicals

Work at Michigan State University by Blake Key (6,7) under the direction of Dr. Craig Criddle used a laboratory isolate of a bacterium, a *Pseudomonas* species, to investigate the potential for biodegradation of fluorinated sulfonates. The researchers used model fluorinated sulfonate compounds: difluoromethane sulfonate (DFMS), trifluoromethane sulfonate (TFMS), 2,2,2-trifluoroethanesulfonate (TES), PFOS and H-PFOS (1H,1H,2H,2H-perfluorooctane sulfonate).

Criddle et al. demonstrated that the microorganism degraded those fluorochemical compounds containing hydrogen and used them as sulfur sources for growth under sulfur-limiting, aerobic conditions. They later found that such degradation occurred in soil even when sulfur was not limiting. The organism completely defluorinated DFMS. It used DFMS as the sole source of sulfur, but not as a source of carbon or energy. TES and H-PFOS were partially defluorinated. Six volatile products were detected for H-PFOS, all containing oxygen and fluorine but not sulfur. Where the carbons were fully fluorinated, i.e. TFMS and PFOS, no degradation was found. Criddle et al. concluded that the transformation of fluorinated sulfonates required the presence of hydrogen at the alpha carbon on the fluorinated alkyl chain. They theorized that when hydrogen is present at the alpha carbon, a site for attack is provided and the carbon-sulfur bond becomes more accessible. Perfluorinated compounds have a rigidity conferred by the fluorine substitution and no structures that are susceptible to electrophilic or nucleophilic attack.

9.42 Biological Transformation

When perfluorinated organic molecules do biodegrade, it is not the fluorinated portion that is affected. Enzymes attack at non-fluorinated side chains. Rather than complete degradation, i.e. degradation to inorganic compounds, another fluorinated molecule results from biodegradation processes. Existing studies of metabolism appear to indicate that for POSF-based compounds, the biological degradation halts when PFOS is formed.

$C_8F_{17}SO_2\text{-}F, + H_2O \longrightarrow C_8F_{17}SO_3^-$

POSF **PFOS**

$C_8F_{17}SO_2\text{-}R \longrightarrow \longrightarrow \longrightarrow C_8F_{17}SO_3^-$

POSF derivative **PFOS**

Once formed, PFOS has not been shown to degrade any further under any natural conditions except combustion. Because PFOS is resistant to physical, chemical and biological degradation, it persists in the environment, but the mechanism of accumulation is under study.

9.43 Optimizing Conditions for Biodegradation

Past studies on fluorochemicals with hydrocarbon portions have demonstrated resistance to biodegradation under standard test conditions, i.e. aerobic microbial degradation using a wastewater inoculum. These studies did not examine all combinations of conditions that could be optimized to favor the degradation of partially fluorinated chemicals.

3M is conducting new screening studies for biodegradation. These will determine if aerobic and/or anaerobic degradation of key fluorochemicals occurs using activated sludge, anaerobic sludge, aquatic sediments and soil. If degradation occurs, the studies will determine to what extent it occurs and the nature of degradation products. It will also provide information on the degree of fluorochemical sorption onto microbial sludges and toxicity to microbes. New studies are being designed to promote degradation. They will use enriched environments that support biodegradation, e.g. sewage, soil, sediments, and cultures of microbes selected for biodegradation capabilities.

10.0 Ecotoxicity Testing of Fluorochemicals

Ecotoxicology is the extension of toxicology to the ecological effects of chemicals. Ecotoxicological studies measure the effects of a chemical substance in the environment on indigenous populations of organisms. They provide a mechanism to estimate hazard. Ecotoxicological data are appropriately interpreted with knowledge of the ecosystem where the organisms live. In aquatic ecotox studies, what may be toxic under conditions created in the laboratory, may be more or less toxic in the aquatic environment due to factors present in the aquatic ecosystem which affect bioavailability. Also the chemical itself may be transformed as a result of physical and biological mechanisms, including metabolism. An accurate evaluation of the toxicity of a chemical requires knowledge of these factors.

Sulfonated perfluorochemicals appear to produce a variety of responses in single species tests of aquatic organisms. Different species have varied significantly in their response to the same chemical even when using the same laboratory procedure. In ecotoxicology, environmental concentration often substitutes for knowing the actual amount or dose of a chemical entering an organism, but concentration and dose may not be directly related and their relationship varies from species to species.

Basic environmental toxicity screening data are available for many sulfonated perfluorochemicals (see Table 12), although their quality is variable. In considering the toxicity test results, it is important to note the year of the test. Test protocols typically were developed considering water soluble, stable and well-dispersed compounds. Compounds such as sulfonated perfluorochemicals challenge test protocols due to their insolubility, polymeric, or surface active nature. The older data may reflect these test limitations. Older test protocols are not comparable to recent and current bioassays that follow accepted, standardized test methods (OECD/USEPA).

Almost all previous testing used products which are complex mixtures and not purified perfluorochemicals. In old tests, the sulfonated perfluorochemical product used was likely more variable, with more impurities because manufacturing processes and product purity have significantly improved over time. Several tests were hampered by the insolubility of the perfluorochemical and results are expressed as greater than the measured solubility.

Two sulfonated perfluorochemicals have more toxicity test data than others because of their use as insecticides in ant and roach bait stations. These perfluorochemicals are N-EtFOSA and PFOS Li salt. Toxicity data on these compounds may be found in the disclosures filed by other registrants under the Federal Insecticide, Fungicide and Rodenticide Control Act (FIFRA).

3M has evaluated the reliability of its aquatic toxicity test data base. The numerical descriptor is modeled after the reliability coding used by EPA's Office of Toxic Substances for the AQUIRE (Aquatic Information Retrieval) toxicology data base.

Table 12. Ecotoxicity Testing on Sulfonated Perfluorochemical Products

Pimephales promelas= Fathead minnow
Salmo gairdneri= Rainbow trout
Selenastrum capricornutum= Green algae
Lepomis macrochirus= Bluegill sunfish
Daphnia magna= Water Flea
Microtox=*Photobacterium phosphoreum*

Reliability Codes:

1. Study used published test guidelines or well-documented procedures. Control performance was satisfactory. Toxicant concentration was measured. Test water temperature, pH and dissolved oxygen were measured.
2. Study meets all the criteria for quality testing but has one or more of the following deficiencies:
   - A. Nominal test substance concentration; actual concentration not measured.
   - B. Test water quality variables not reported or incomplete.
   - C. A water accommodated fraction (WAF) was used.
   - D. Analytical methodology was questionable.
3. Study does **not** meet the criteria for quality testing. Characterized by one of the following:
   - A. Demonstrated weaknesses in experimental procedures.
   - B. A static test with unmeasured concentrations was conducted in the presence of precipitate or some undissolved chemical
   - C. Insufficient description of methods.

D. Unsatisfactory control mortality.

Product's Principal Fluorochemical	Test Organism	Study Type	Results mg/L	Year	Reliability Code
POSF	*Pimephales promelas*	96 hr LC50	>1000	84	2A
N-MeFOSE alcohol	*Lepomis macrochirus*	96 hr LC50	>solubiliy	79	3B
	Daphnia magna	48 hr LC50	>solubiliy	79	3B
N-EtFOSE alcohol	*S. capricornutum*	14 day EC50	>1800	81	3B
	Pimephales promelas	30 day hatch,	.020	78	2D
		growth,survival			2D
		histopathology			2D
		NOEC	.020	78	2D
		LOEC	>.020		
N-EtFOSA	*Daphnia magna*	48 hr EL50	14.5	98	2A,C
		48 hr EL10	7.3	98	2A,C
		48 hr NOEL	5.8	98	2A,C
	Pimephales promelas	96 hr LL50	206	98	2A,C
		96 hr LL10	115	98	2A,C
		96 hr NOEL	130	98	2A,C
	Ceriodaphnia dubia	48 hr EL50	328	98	2A,C
		48 hr EL10	184	98	2A,C
		48 hr NOEL	216	98	2A,C
	Daphnia magna	48 hr EC50	3.2	84	3B
	Pimephales promelas	96 hr LC50	34	84	3B

Product's Principal Fluorochemical	Test Organism	Study Type	Results mg/L	Year	Reliability Code
N-EtFOSEA	*Pimephales promelas*	96 hr LC50	>1000	84	3B
N-EtFOSEMA	*Pimephales promelas*	96 hr LC50	>1000	84	3B
PFOS NH_4 salt	*Pimephales promelas*	96 hr LC50	85	74	2A
	Pimephales promelas	96 hr LC50	100	74	2A
PFOS Li salt	Microtox *P.phosporeum*	30 min EC50	>1000	94	2A
	Daphnia magna	48 hr EC50	210	94	2A
		48 hr NOEC	100	94	2A
	Pimephales promelas	96 hr LC50	19	94	2A
PFOS K salt	Microtox	30 min EC10	45	91	2A
		30 min EC50	>280	91	2A
	Daphnia magna	48 hr EC50	27	84	2A
		28 day NOEC	7	84	2A
	Selenastrum capricornutum	4 day EC50 cell count	82	82	2A
		14 day EC50 cell count	95	82	2A
	Pimephales promelas	30 day NOEC	1	78	2D
		30 day LOEC	1.9	78	2D
		96 hr LC50	38	77	2A
	Lepomis macrochirus	96 hr LC50	68	78	2A
	Salmo gairdneri	96 hr LC50	11	78	2A
	Daphnia magna	48 hr EC50	50	79	2A
	Pimephales promelas	96 hr LC50	29	74	2A
	Pimephales promelas	96 hr LC50	32	73	2A
PFOS DEA salt	*Lepomis macrochirus*	96 hr LC50	31	79	2A
		96 hr NOEL	18	79	2A
perfluoroC10 sulfonic acid, NH_4^+ salt	*Daphnia magna*	48 hr EC50	44	92	2A
	Pimephales promelas	96 hr LC50	4.8	92	2A
	Microtox	30 min EC50	330	92	2A
K salt of carboxylic acid analogue of N-Et-FOSE alcohol	*Pimephales promelas*	96 hr LC50	97	97	2A
		96 hr NOEC	54	97	2A
	Selenastrum capricornutum	96 hr EC50	600	97	2A
		96 hr NOEC	216	97	2A
	Daphnia magna	48 hr EC50	9.1	97	2A
		48 hr NOEC	3.9	97	2A
	Microtox	30 min IC50	270	97	2A
	Pimephales promelas	96 hr LC50	518	81	3B
		96 hr LC50	15	74	3A
N-EtFOSE alcohol ethylene oxide adduct	*Lepomis macrochirus*	96 hr LC50	285	78	2A
	Daphnia magna	48 hr EC50	1.5	78	2A

Table Key

EC50= Median Effective Concentration. It is the concentration of a test substance that causes a 50% effect on a specific characteristic of the test organisms (e.g. immobilization of 50% of the Daphnia, reduction in algal cell growth by 50% as compared to the controls) after a specified exposure period. It is the usual endpoint in a toxicity test with Daphnia and other small organisms where death is hard to determine or in tests where growth is measured.

LC50= Median Lethal Concentration. It is the concentration of a substance that kills 50% of the test organisms exposed to it in a specified time. It is the usual endpoint in an acute toxicity test with fish.

IC50= Median Inhibitory Concentration. It is the concentration of a test substance that inhibits a biological process of a test organism by 50% (e.g. light production, respiration) after a specified exposure period

NOEL= No Observed Effect Level

NOEC= No Observed Effect Concentration

EL=Effective Loading, **LL**=Lethal loading. These are used where the test substance is not completely water soluble. A water accomodated fraction (WAF) is prepared. The test substance is loaded into water at different loadings to prepare each test concentration. The solutions are mixed and the liquid fraction is decanted to use as the test water.

Additional studies are underway on ecotoxicity using established OECD/EPA methods. Initially purified PFOS and EtFOSE alcohol are being tested to determine acute and chronic toxicity to a wide range of species. The results to date are found in Table 13.

Table 13. New Ecotox Studies on PFOS, potassium salt

Parameter	Study Type	Results,
Wastewater Bacteria (OECD 209)	3 hr NOEC 3 hr. EC50 Inhibition @ highest conc (1000 mg/L)	1.0 mg/L >1000 mg/L 39%
Senenastrum capricornutu (green algae)	96 hr NOEC (growth rate) 96 hr ErC10 96 hr. ErC50	48 mg/L 65 (59-69) mg/L 138 (125-149) mg/L
Daphnia magna (freshwater flea)	Acute 48 hr NOEC Acute 48 hr EC10 Acute 48 hr EC50 Acute 48 hr EC90 21 day semi-static life cycle NOEC 21 day semi-static life cycle NOEC	36 mg/L 57 (<12->99) mg/L 66 (36-99) mg/L 69 (<12->99) mg/L *13 mg/L* 26 mg/L
Mysidopsis bahia (marine shrimp)	Acute 96 hr NOEC Acute 96 hr EC50 35 day flow thru life cycle NOEC 35 day flow thru life cycle NOEC	1.2 mg/L 4.0(3.3-5.0) mg/L *0.28 mg/L* *0.6 mg/L*
Freshwater mussel	Acute 96 hr NOEC Acute 96 hr LC50	22 mg/L 65 mg/L
Pimephales promelas (fathead minnow)	Acute 96 hr. NOEC Acute 96 hr LC50 47 day early life-stage toxicity NOEC 47 day early life-stage toxicity LOEC	3.6 mg/L 10 (8.8-12) mg/L *0.33 mg/L* 0.65 mg/L
Oyster Shell Deposition	Acute 96 hr NOEC Acute 96 hr EC50 (Solubility limits precluded EC50) Inhibition @ highest conc (3.3 mg/L)	2.1 mg/L >3.3 mg/L 28%
Avian Dietary Toxicity Testing	Acute Mallard Duck LC50 Acute Mallard Duck, no mortality Acute Mallard Duck NOEC Acute Bobwhite Quail LC50 Acute Bobwhite Quail, no mortality Acute Bobwhite Quail NOEC	*730 (532-1059) mg/kg* *160 mg/kg* *40 mg/kg* *214 (163-260) mg/kg* *80 mg/kg* *80 mg/kg*

Data in italics are from draft reports.

All of the results shown in Table 12 suffer from limitations in the reliability of the data, and there is a clear need for high quality ecotoxicity data using established OECD/EPA methods. Testing on purified PFOS and EtFOSE alcohol is in progress. However, the available new data (Table 13) and the historic data are consistent in that almost all toxicity values for PFOS and related sulfonated perfluorochemicals are greater than 1 mg/L and most are greater than 10 mg/L. An exception is the fathead minnow results reported on Table 12 for N-EtFOSE alcohol where apparently there is no acute toxicity at

or above the water solubility level. The available new data on PFOS itself suggest that it has similar aquatic toxicity to that of other anionic surfactants (9). Few other conclusions can be reliably drawn at this time. For instance, ecological risk assessment typically relies on chronic toxicity values, but there are too few data on this to draw any conclusions.

11.0 Comprehensive Plan to Assess Environmental Exposure

The ongoing activities described in the previous sections of this paper are being carried out as part of a 3M developed comprehensive plan using a combination of 3M resources and outside experts. This plan, summarized in Figure 1, is designed to assess the potential pathways of environmental exposure associated with the manufacture, use and disposal of its sulfonated perfluorochemical products.

11.1 Plan Overview

The plan structure consists of four components:

1. Characterize the properties critical to understanding the fate and transport of sulfonated perfluorochemicals.

2. Estimate the releases of sulfonated perfluorochemicals.

3. Characterize the distribution of sulfonated perfluorochemicals in the environment.

4. Estimate human and ecological exposure to sulfonated perfluorochemicals.

Several individual research projects feed information into each component. The early components provide information needed to complete the later ones. Thus the information base expands when one goes from component 1 to component 4.

This section provides an overview of the plan and its research projects. Specific descriptions of how and why the research projects are being conducted can be found in the preceding sections of this document. The results generated by this plan will be combined with the ecotoxicological studies to develop an assessment of risk. A tentative initiation date for each of the research projects is found in Figure 2. It is expected that the studies will continue over several years.

Figure 1. Diagram of Fluorochemical Assessment Plan.

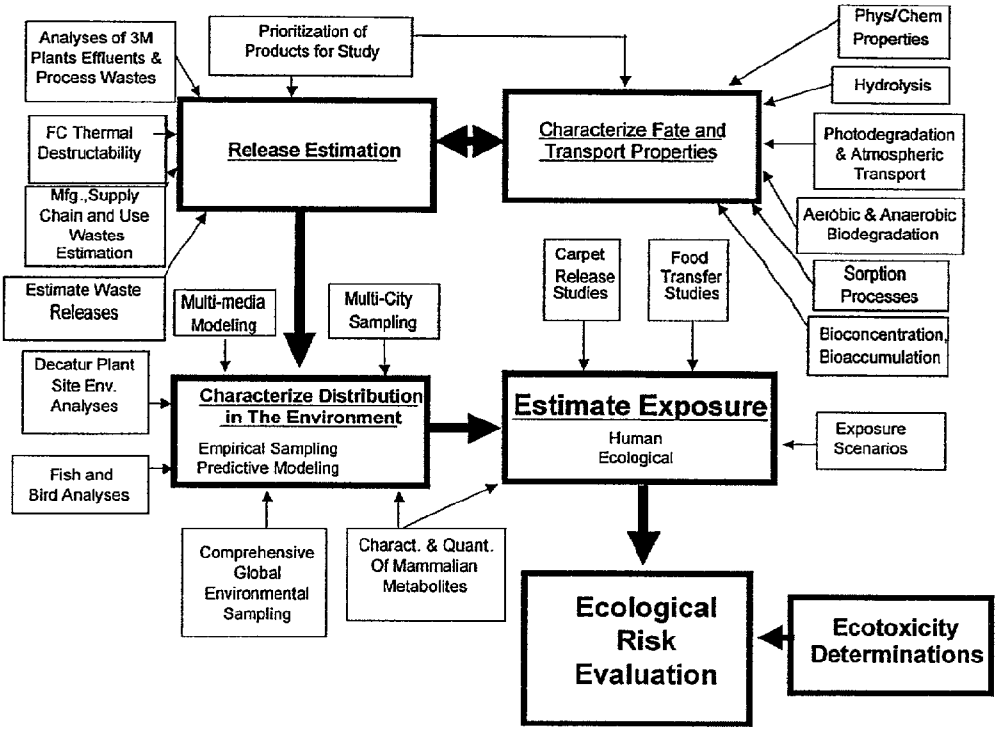


Figure 2. Schedule for FC Exposure Plan Components.

1Q=First Quarter, 2Q= Second Quarter, 3Q=Third Quarter, 4Q=Fourth Quarter

		Initiation Dates
Characterize Fate & Transport Properties	PFOS Phys/Chem Properties	Complete
	EtFOSE alcohol Phys/Chem Properties	1Q 2000
	MeFOSE alcohol Phys/Chem Properties	1Q 2000
	Hydrolysis	1Q 1999
	Photodegradation and Atmospheric Transport	1Q 1999
	Biodegradation (aerobic and anaerobic)	1Q 1999
	Sorption Processes	2Q 1999
	PFOS Bioconcentration	2Q 2000
	EtFOSE alcohol Bioconcentration	4Q 2000
Estimate Releases	3M Plant Effluent & Process Waste Analyses	1Q 1999
	Estimate Mfg, Supply Chain, & Use Waste Streams	Complete
	Estimate Waste Releases	1Q 1999
	FC Thermal Destructability	2Q 1999
Characterize Distribution in Environment	Bird & Fish Analyses	Complete
	U.S.Bird Livers Analyses	Complete
	Biosphere Sampling Pan	1Q 1999
	Multi-media Modeling	1Q 2000
	Multi-cities Study	1Q 1999
Estimate Exposure	Carpet Study	2Q 1999
	Paper and Packaging Studies	1Q 1999
	Exposure Scenarios	2Q 1999
Ecotoxicity Determinations	PFOS Acute Ecotoxicity	1Q 1999
	PFOS Chronic Ecotoxicity	2Q 1999
	EtFOSE alcohol Acute Ecotoxicity	2Q 2000
	EtFOSE alcohol Chronic Ecotoxicity	3Q 2000
	FOSA Acute Ecotoxicity	1Q 2000
	FOSA Chronic Ecotoxicity	2Q 2000

11.2 Component 1: Characterize Fate and Transport Properties

This component was developed in three steps. First, the important fate and transport mechanisms were identified. Next, priorities were set for testing, with the likely degradation products having the highest priority for testing. Finally, methods and laboratories were selected to do the testing. For sulfonated perfluorochemicals not tested, models are being developed that will predict physical and chemical properties. The specific research projects underway are:

1. Physical and chemical properties testing.
2. Hydrolysis testing.
3. Photodegradation and atmospheric transport testing.
4. Anaerobic and aerobic biodegradation testing.
5. Soil and sediment sorption testing.
6. Bioconcentration testing.

11.3 Component 2: Estimate Releases

This component was also developed in several stages. First, product sales data from 1997 were used to identify a study set of products. The study set was based on volume of use and waste streams, mode of release and product chemistry. Next, evaluation efforts of the waste streams generated focused on those study set products sold by 3M in the greatest quantities in the United States. Commercial and residential uses of these products, including transportation, handling and application during the supply chains that lead to product use, were examined. Additionally, the releases likely to result from disposal during these portions of the products' life cycles were also estimated. The estimates included disposal via incineration, landfilling and wastewater treatment.

Waste streams generated at the start of the products' life cycles, i.e. the manufacturing process, were also examined. Better estimates are continuing to be developed of waste streams occurring during the manufacturing process.

11.4 Component 3: Characterize Distribution in the Environment

This component is distinguished by iterative interaction between modeling and field sampling. Models are being used to suggest sampling locations and detection limits. Field sampling is planned to obtain empirical data to validate model output and improve predictions. As new data become available, research projects become more refined and focused. The research projects completed or planned to characterize environmental distribution include:

1. Field sampling of environmental media near the Decatur manufacturing plant.
2. Screening of eagle and albatross plasma and fish tissue from archived samples.
3. Analysis of wild bird livers.
4. Biosphere sampling plan to determine levels in biota of different geographic locations.
5. Development of a multimedia model for predicting distribution.
6. Multi-cities studies in which cities of a similar size are paired, one demonstrating significant manufacturing or commercial uses of sulfonated perfluorochemicals, the other having no identified use of sulfonated perfluorochemicals.

11.5 Component 4: Estimate Exposure

When data from the release and distribution components are available, hypotheses will be developed about important exposure pathways. Iterative sampling and modeling will be used to test these hypotheses and to determine the important exposure pathways to be used in risk assessment. The research projects planned to estimate exposures are:

1. Carpet releases and links to ingestion, inhalation and dermal exposure.
2. Paper and packaging studies and ingestion exposure.
3. Exposure scenarios which combine information from the release, fate, and sampling studies.

12.0 Ecotoxicity Determinations

In conjunction with the studies described in the four component plan described above, 3M is conducting ecotoxicological studies. Ecotoxicological studies are used to estimate hazard. Initial ecotox testing is focusing on PFOS, EtFOSE alcohol, and FOSA. The results of the release, distribution and exposure assessments may provide reasons to test more substances.

The following research projects on ecotoxicity are planned or underway:

1. Aquatic acute toxicity studies: sewage microorganisms, freshwater and marine algae, duckweed, daphnia, mysid shrimp, freshwater mussels, fathead minnows.
2. Terrestrial acute toxicity studies: mallard duck and bobwhite quail dietary exposure studies, earthworm toxicity studies, and green plant growth and uptake studies.
3. Aquatic chronic toxicity studies: oyster shell deposition, daphnia, mysid shrimp, frog embryo development and fish early life stage studies.

4. Terrestrial chronic toxicity studies: mallard duck and bobwhite quail reproduction.

13.0 Ecological Risk Evaluation

Evaluating ecological risk is more complex and more uncertain than assessment of human health risks where a clearer connection can be drawn between dose and response.

As this comprehensive science and exposure assessment program progresses, a framework in which ecological risk can be evaluated will be developed. The evaluation of ecological risks and human risks will both use information about distribution in the environment and exposures generated by this comprehensive exposure plan. Because of the scope and magnitude of the overall program, aspects of the knowledge gained will be compartmentalized into discreet elements to create this framework. For example, as data on ecotoxicological properties, fate and transport mechanisms, and environmental distribution are developed, they will be used to evaluate ecological risk within a certain geographic area or locality. The science data and environmental sampling results will be applied to a very specific area and set of species to evaluate relative risks in that area. Building a number of these compartmental evaluations will result in a much more complete picture of ecological risk. This evaluation will identify additional actions 3M could take to minimize the releases of sulfonated perfluorochemicals.

14.0 References

1. Cohrssen, J.J. and Covello, V.T. Risk Analysis: A Guide to Principles and Methods for Analyzing Health and Environmental Risks, U.S. Council on Environmental Quality, Executive Office of the President, 1989

2. Fate, Transport and Transformation Test Guidelines, Office of Prevention, Pesticides and Toxic Substances (OPPTS) 835.2110, Hydrolysis as a Function of pH and Temperature, EPA 712-C-98-057, January 1998.

3. Flynn, R.L. in "Industrial Applications of Organochlorine Compounds," Proceedings of the Symposium on Electrochemistry in the Preparation of Fluorine and Its Compounds, Childs and Fuchigami, Eds, The Electrochemical Society, Inc.: Pennington, NJ, **1997;** *97-15*: 51.

4. Guidelines for the Testing of Chemicals, vol. 1, Section 1, "Physical Chemical Properties," Organisation for Economic Co-operation and Development (OECD), Paris, France.

5. Guidelines for the Testing of Chemicals, vol. 1, Section 2, "Effects on Biotic Systems," Organisation for Economic Co-operation and Development (OECD), Paris, France.

6. Key, B.L.; Howell, R.D.; Criddle, C.S. "Fluorinated Organics in the Biosphere," *Environ. Sci. Technol*, **1997**, *31*: 2445-2454.

7. Key, B.L.; Howell, R.D.; Criddle, C.S. "Defluorination of Organofluorine Sulfur Compounds by *Pseudomonas* Sp. Strain D2," *Environ. Sci. Technol*, **1998**, *32*: 2283-2287.

8. Mackay, D. Shiu, W.Y., and Ma, K.C., Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume 1: Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs. Lewis Publishers, Chelsea, MI. 1992.

9. Scholz, N., "Ecotoxicology of surfactants," *Tenside Surfactants and Detergents*, **1997**, *34*:229-32.