A Review of the

Environmental Fate and Effects of Sulfonyl Based Fluorochemicals

3M Environmental Laboratory

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DRAFT

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Executive Summary

Adding fluorine atoms to organic molecules produces fluorochemicals, compounds that are quite stable, chemically inert and nonreactive. Fluorochemicals are produced by an electrofluorination process which creates a complex and variable mix of chemicals in which flurorine atoms replace hydrogen atoms on the organic feedstock and carbon-carbon bonds are rearranged. 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 sulfonyl based 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. Unusually, perfluoroalkyl chains are both oleophobic and hydrophobic. The addition of charged moieties to the chain can affect the water solubility of the shorter chains. Reliable methods for extraction, separation and identification of perfluorochemicals in tissues and environmental matrices have been developed only in the last five years. New analytical technology is aiding in identification of metabolites and breakdown products.

Perfluorochemicals resist degradation by most chemical, physical and biological processes. Research suggests that the transformation of fluorinated sulfonates requires the presence of hydrogen at the alpha carbon on the fluorinated chain. Perfluorinated molecules are attacked at non-fluorinated side chains and are transformed into new fluorochemicals. Studies suggest that compounds made from perfluorooctanesulfonyl fluoride, POSF, a commercially important perfluorochemical product and intermediate, are transformed during vertebrate metabolism and probably by microorganisms to another perfluorochemical, perfluorooctane sulfonate, PFOS. PFOS does not appear to further degrade except in combustion.

While progress has been made in identifying metabolites and degradation products, uncertainties remain about the intermediate forms that may exist in the environment in addition to the final degradation product, PFOS. Degradation studies are now focusing on fluorochemicals with hydrocarbon portions to see if conditions can be optimized to favor the degradation of partially perfluorinated chemicals and a microorganism developed to alter these compounds. The degradation of polymeric perfluorochemicals through hydrolysis, aerobic and anaerobic bacterial metabolism is being examined.

Many perfluorochemicals have been subjected to basic screening tests for environmental toxicity. Using aquatic organisms, the range of toxicity is from an insignificant hazard to

highly toxic. Different species may vary significantly in their response to the same chemical.

Little is known about the environmental fate of perfluorochemicals. Their persistence, which leads to accumulation in the environment, their unusual behavior in partioning and metabolism, and their significant surface activity raise important research issues for environmental dispersion. Uncertainties about the applicability of existing models due to the unusual properties of perfluorochemicals, and gaps in physical-chemical and environmental data needed for model operation and validation, also complicate characterization of environmental fate. More study is essential to find what accumulates, where it accumulates, how exposure to the living and nonliving components of the environment transforms the molecules and what effects this exposure has on organisms at all levels of the ecosystem.

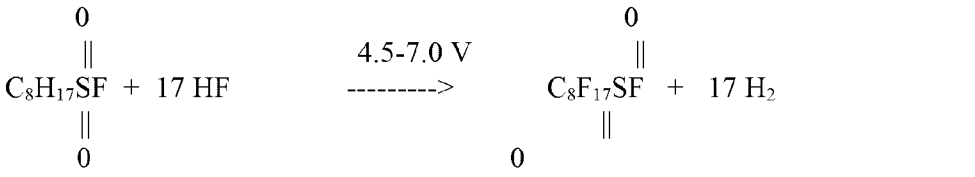
3M has developed a comprehensive plan to gather the necessary information. It will evaluate all releases during the products' life cycles and all routes of exposure to humans and the environment. The plan identifies tasks which will characterize releases from product manufacture and use, characterize the transport and fate of perflurochemicals by addressing the lack of data and validated models, characterize the distribution of perfluorochemicals in the biosphere though sampling of different habitats and species of concern, and estimate the amounts distributed in populations and the environment. Tasks in the plan are underway.

Introduction

Fluorochemicals are components of several important 3M product lines due to their unique and useful properties. They are quite stable, chemically inert and 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 sulfonyl based perfluorochemicals commercially for over 40 years. 3M produces fluorochemicals by combining anhydrous hydrogen fluoride with hydrocarbon stock in the presence of electrical energy (Simons Electrochemical Fluorination Process). [Figure 1.] The highest production volume fluorochemical is principally perfluorooctanesulfonyl fluoride (POSF).

Figure 1. Simons Electrochemical Fluorination Process.

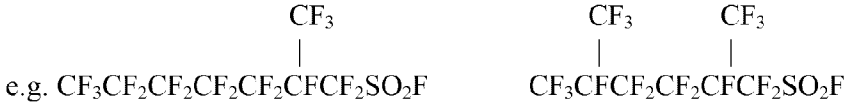


The fluorination process yields about 80% straight chain POSF, and a mixture of unknown and variable composition containing:

-other straight chain perfluoroalkyl products, $C_nF_{2n+1}SO_2F$, of various chain lengths

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



-other straight chain, branched and cyclic perfluoroalkyl compounds

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

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.

Four 3M plants currently produce fluorochemicals. These plants are located in: Cottage Grove MN, Cordova IL, Decatur AL, and Antwerp Belgium. During production, many byproducts and waste products are formed. The volatile waste products, such as perfluoromethane, 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 incinerated. The byproducts, many of which are incompletely fluorinated with hydrogen ions still present, are partially degraded in stabilization processes and discharged to wastewater treatment systems. The treatment sludge is either landfilled or land-incorporated. Some of the non-POSF byproducts are recovered and sold for secondary uses.

The product that results from electrochemicalfluorination is thus not a pure chemical but rather a mix of isomers and homologues. Perfluorochemicals have complete substitution

of fluorine for hydrogen. 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=anything but 8], principally perfluorohexanesulfonyl fluoride, are also intermediates in the formation of other 3M products.

Some of the POSF derived products are relatively low molecular weight (~500 daltons), surface active materials and monomers. 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 fluorochemicals produced are used in polymeric applications. 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 3M product lines that use sulfonyl based perfluorochemicals are summarized below. (Product lines using fluorochemicals which contain no sulfonyl groups are not listed.)

Surface Treatments

Fabric/Upholstery Protector
Carpet Protector
Leather Protector
Paper Protector

Surfactants

Specialty surfactants
Cleaning applications
Electroplating and Etching Baths
Insecticides
Paints
Inks
Photographic Solutions
Floor Polishes
Fire Extinguishing Foam Concentrates

Some paper protectors are mixtures of mono-, di-, and triphosphate esters of 2-(N-ethylperfluorooctanesulfonamido)ethyl alcohol (N-EtFOSE alcohol). The carpet and textile protectors are based on N-MeFOSE and N-EtFOSE chemistry. The fluorochemicals used in fire extinguishing foams are based on POSF and contain perfluoroalkylsulfonamides, and perfluoroalkylsulfonate salts.

Residuals which are common to all the formulations of perfluorochemical products are perfluorooctane sulfonate (PFOS), N-ethyl (or N-methyl) perfluorooctane sulfonamide (N-EtFOSA or N-MeFOSA) and N-ethyl (or N-methyl) perfluorooctane sulfonamidoethyl alcohol (N-Et FOSE alcohol or N-MeFOSE alcohol). Table 1 identifies some 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	$C_8F_{17}SO_3^-$
PFOS acid	perfluorooctylsulfonic acid	$C_8F_{17}SO_3H$
PFOS NH_4 salt	ammonium perfluorooctylsulfonate	$C_8F_{17}SO_3NH_4$
PFOS DEA salt	Perfluorooctylsulfonate diethanolamine salt	$C_8F_{17}SO_3H{\cdot}HN(C_2H_4OH)_2$
PFOS K salt	potassium perfluorooctylsulfonate	$C_8F_{17}SO_3K$
PFOS Li salt	lithium perfluorooctylsulfonate	$C_8F_{17}SO_3Li$
PFOSA	perfluorooctanesulfonamide	$C_8F_{17}SO_2NH_2$
PFOSAA	perfluorooctane sulfonylamido (ethyl)acetate	$C_8F_{17}SO_2N(CH_2CH_3)CH_2COO^-$
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	2-(N-ethylperfluorooctane sulfonamido)-ethyl alcohol	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$
N-MeFOSE alcohol	2-(N-methylperfluorooctane sulfonamido)-ethyl alcohol	$C_8F_{17}SO_2N(CH_3)\ CH_2CH_2OH$
N-EtFOSEA	2-(N-ethylperfluorooctanesulfonamido)-ethyl acrylate	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OCOCH{=}CH_2$
N-EtFOSEMA	2-(N-ethylperfluorooctanesulfonamido)-Methyl acrylate	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OCOC(CH_3){=}CH_2$

Physical-Chemical Properties

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 their properties, it is necessary to describe the properties of fluorine. Fluorine has several characteristics which differ from the other halogens and contribute to the unusual properties of fluorochemicals.

Fluorine, the most abundant halogen, has a van der Waals radius of 1.47 Å, more comparable to that of oxygen than other halogens, and isosterically similar to a hydroxyl group. Fluorine has the highest electronegativity (4.0) 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 implies weak inter- and intramolecular interactions. This is demonstrated in the low boiling points of perfluorochemicals 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. Typically, the presence of these charged groups on short chain perfluorinated compounds (<C6) noticably increases the solubility of the compound in water.

Physical data available on fluorochemicals at 3M are 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. Some of these products are primarily used as surfactants; others are primarily used as intermediates in the formation of polymeric or oligomeric products. It is important to remember that these data have been obtained using products that are not highly refined, and that products may have more than one fluorochemical component. Some may have nonfluorochemical components which enter into determination of the values.

Additional physical data are available on a few products. These additional data are typically related to determination of environmental fate e.g. data on soil mobility and partioning coefficients. They are summarized in Table 3.

Table 2. Physical Data on Fluorochemical Products

Abbreviations: N/D: not determined; N/A: not applicable; ~: approximately

Product Use	**Principle Fluorochemical**	boiling pt (b) @ 1mmHg 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/A	N/A	N/A	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	~18	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	K salt of carboxylic acid analogue of N-Et-FOSE alcohol	~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

Table 3. Physical Data Related to Environmental Fate

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	10	1	0.99	66	
N-MeFOSE alcohol	0.82	56,800		77	3,500	
N-EtFOSE alcohol	0.05	6,600,000		330	17,800	1.22 mmHg
N-EtFOSEA	0.89		>6			6.0×10^{-3} Pa
POSF	1 est					1.6 torr@20°C
PFOS Li salt						18 mmHg

The tables illlustrate the wide range in values for physical parameters among low molecular weight, POSF based, fluorochemical products. Typically these low molecular weight products tend to have higher water solubility and lower vapor pressure, and tend to be more mobile in the environment, than polymeric products containing them. In addition to being intermediates in the formation of 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.

Evident from the tables are the deficiencies in existing data. Formulated products containing other components in addition to these fluorochemicals have been the focus of data collection. 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.

Prediction of environmental fate and transport requires the use of computer models. Existing models require at a minimum the following physical 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 are essential for comprehensive predictions about environmental fate and transport.

The 3M Environmental Laboratory is developing the missing physical data on individual fluorochemicals using Guidelines for the Testing of Chemicals developed by the Organisation for Economic Co-operation and Development (OECD). Guidelines exist for the determination of: boiling points, vapour pressures, water solubility, n-octanol/water partition coefficients, soil adsorption/desorption, and hydrolysis as a function of pH. These methods will provide values reported in a consistent format that is internationally familiar and accepted. This standardization will aid in the review and comparison of data on individual fluorochemicals and in model operation and prediction.

Analytical Test Methods

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 detection levels require selective extraction and diverse analytical techniques.

Each fluorochemical requires a unique analytical methodology. Reliable methods for extraction, separation and identification have been developed only within the last five years. Prior to that, analysis usually was for "total organic fluoride," which was nonspecific.

The analytical techology used in extraction, separation and identification includes combinations of : high performance liquid chromotography (HPLC), high pressure solvent extraction (HPSE), electrospray (ES), mass spectrometry (MS), gas chromotography (GC) using a Flame Ionization Detector (FID), a Photo Ionization Detector (PID), or Electron Capture Detector (ECD) and Fourier Transform Infrared spectroscopy (FTIR). For example, analysis of PFOS extracted from tissues requires HPLC-MSMS analysis. This technique focuses quantitation on five secondary ions of one primary ion at a specific HPLC retention time.

3M now has in place Good Laboratory Practice (GLP) methods for several fluorochemicals in several matrices including blood, liver, and several animal tissues and in soil. These methods are summarized in Table 4. It has non-GLP analytical methods in place for several fluorochemicals in several matrices such as wastewater sludge, drinking water, and air. Using a combination of these methods, the 3M Environmental Laboratory now can detect many fluorochemicals in a variety of matrices.

To reach extremely low analytical levels in complicated matrices, the Environmental Laboratory plans to expand its analytical technology with the addition of a tandem time-of-flight mass spectrometer. This LC/MSMS instrument will enhance sensitivity for the target fluorochemical compounds by eliminating most interfering ions and reducing background noise. The instrument provides high mass resolution (to 0.0001 amus) and so will be useful in identifying fluorochemical metabolites and intermediates for which standards are not available.

To futher investigate flurochemical degradation/metabolic pathways, particularly those of polymers, additional new technology will also include a multi-inlet MS/MS system. This system will improve characterization of semi-volatile degradation products.

Table 4. GLP Methods for Extraction and Analysis of Fluorochemicals

Method Type	FC Analyte	Matrix	Equipment	Detect Limits ppb
Thermal Extraction	Fluoride	Rabbit Liver	Modified Dohrmann DX2000 Organic Halide Analyzer; Orion EA 940 Expandable Ion Analyzer	50
Extraction	Et-FOSE Me-FOSE Me-FOSEA Adducts	Corn Oil	Gas Chromatography (GC), Electron Capture (EC) Detector	10
Analysis	Fluoride	Thermal Extract Samples	Skalar Segmented Flow Analyzer with Ion Selective Electrode (ISE)	15
Extract Prep, Analysis	Me FOSE Et-FOSE Me FOSEA Adducts	Food Simulating Liquid ethanol extracts	Gas Chromatography with Electron Capture (EC) Detector	5
Extraction, Analysis	Heptafluoro-butyric acid	Human serum Rabbit serum Bovine serum	ES/MS	20
Extraction, Analysis	PFOS, K salt, other FCs	Fish Livers	ES/MS	50
Analysis	PFOS, other FCs	Fish Serum	ES/MS	120
Extraction, Analysis	FCs	Fish Fillets	ES/MS	100
Extraction, Analysis	PFOS, other FCs	Chicken Serum Bovine Serum	ES/MS	120
Extraction, Analysis	PFOS, other FCs	Soil (eg. clay, loam, sandy loam, sand)	High Pressure Solvent Extraction (HPSE) ES/MS	25
Extraction, Analysis	PFOS, other FCs	Soil supernatant-0.01M $CaCl_2$ solution exposed to soil (clay, loam, sandy loam, sand)	ES/MS	25
Extraction, Analysis	FCs	Chicken Livers	ES/MS	300
Extraction, Analysis	FCs	Chicken gizzards	ES/MS	50
Extraction, Analysis	PFOS,K salt, other anionic FC surfactants	Rabbit liver Rat livers Bovine livers Monkey livers	HPLC-ES/MS HPLC-ES/MSMS	30 10 60 60

Extraction, Analysis	PFOS, other anionic FC surfactants	Rabbit serum Rat serum Bovine serum	HPLC-ES/MS/MS	25 25 50
Analysis	Et-FOSE alcohol EtFOSE-Cl PFOS-DEA	Extracts from corn oil	GC/MS Selected-ion-monitoring (SIM) Thermal desorption autosampler coupled to GC for analyte separation; MS detection and quantitation	0.16 0.26 0.5
Analysis	PFOSA PFOSEA	Extracts from corn oil	HPLC-ES/MS	0.5 0.07

Degradation

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. 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. Photodegradation of the carbon-fluorine bond and the carbon-carbon bonds within perfluorinated portions has not been demonstrated. Combustion does destroy fluorochemicals and degradation is found in high temperature TOC analyzers.

A few fluorochemicals occur naturally in the biosphere, produced by biological and geochemical processes. Monofluoroacetic acid (CH_2FCOOH) is produced by several plants. Some fungi produce monofluorinated organics. Tetrafluoroethylene, sulfur hexafluoride, perfluoromethane and some chlorofluorocarbons are produced by volcanoes or other geological processes in small quantities. However, all biologically produced fluorochemicals contain only one fluorine atom. No perfluoro moieties or similar molecules have been found within biological systems.

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 molecule. This rigidity could obstruct the conformation required for a fit 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.

Because fully fluorinated organic molecules have a molecular structure different from anything else known to be present in nature, it is not surprising that no microorganisms as yet have been found that can degrade perfluoroalkyl chains. Work at Michigan State University by Blake Key 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.

Results of standardized degradation tests that have been performed with perfluorochemical products reflect that the products show little susceptibility to biodegradation. (See Table 5.) Fluorochemicals lacking nonfluorinated organic portions have essentially no biochemical oxygen demand (BOD). Those with ionically bonded organics show BODs close to that which would be expected from their organic portion alone. Fluorochemical surfactants with covalently bonded organic portions have mixed results. In aerobic degradation work in the laboratory, a few perfluorochemicals appeared to demonstrate some biodegradation over time but no analysis was done to determine what compounds were present at the conclusion of the tests. See Table 6.

When perfluorinated organic molecules do degrade, it is not the fluorinated portion that is affected. They are only attacked at non-fluorinated side chains. Rather than complete degradation, the molecule undergoes transformation. The transformed product is another fluorinated compound.

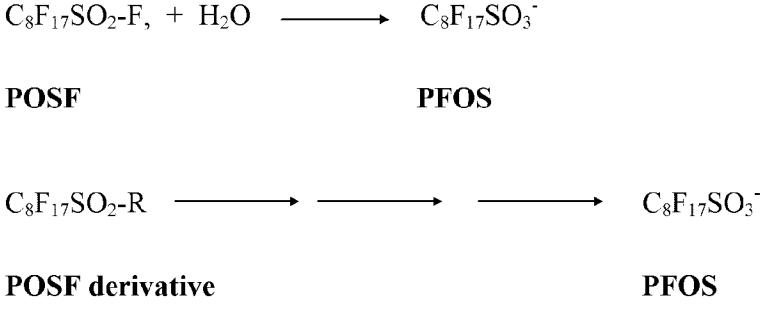


Table 5. Results of Standard Degradation Tests on Fluorochemicals

Product's Principle Fluorochemical	COD mg/Kg	BOD 5-day mg/Kg	BOD 10-day mg/Kg	BOD 20-day mg/Kg	Photo-degrade	Other
POSF	500-720	nil	nil	nil		
N-MeFOSE alcohol	163,000			nil	nil	
N-EtFOSE alcohol	260,000	nil			nil	O2 uptake= 3% of ThOD; No deg in 6 month shake flask studies or 7 day activated sludge studies
N-EtFOSA	1,800	nil	nil	nil		
N-EtFOSEA	240,000	12,000	19,000	23,000		not readily biodegradable
N-EtFOSEMA	80,000	800	2,000	11,000		
PFOS Li^+ salt	54,000					
PFOS K salt	4,000	nil	nil	nil	nil	no degradation in Warburg 3 hr study or 2.5 month shake flask study
PFOS DEA salt	78,000	44,000		82,000		
N-EtFOSE alcohol ethylene oxide adduct	1,070,000	0		107,000		40% removal BiAS

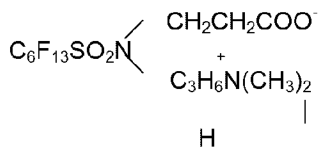
COD means Chemical Oxygen Demand. It is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant such as potassium dichromate.

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.

Table 6. Aerobic Biodegradation Test Results on Sulfonate-based Perfluorochemicals.

Chemical	Biodegradation Test, Result
$C_8F_{17}SO_2N(C_2H_5)(CH_2COO^-K^+)$	O_2 uptake 37% of Theoretical Oxygen Demand in 6.25 hrs.
$C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_{7.5}CH_3$	Dissolved Organic Carbon Removal 25 - 33% in 2 days
$C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_{14}H$	Bismuth Active Substance 40% removal
	CO_2 production 6% of theoretical in 5 days

From studies of vertebrate metabolism using rats, 3M researchers have found that derivatives of POSF breakdown to perfluorooctane sulfonate (PFOS). Exactly how derivatives of POSF are attacked and what intermediates are formed in the transformation process to produce PFOS is not completely known, but significant progress has been made in identification.

In rats it appears N-EtFOSE-OH is metabolized to PFOSA and PFOSAA and other intermediates as it is degraded to form PFOS. The elimination of metabolites via urine and feces is very slow. Intravenous administration of potassium ^{14}C-PFOS showed ^{14}C present in liver and plasma of male rats for several weeks. Concentrations in fat and other tissues were lower (<5% of liver.) Chromatographic analysis showed no biotransformation of PFOS. After a single oral dose of PFOS, 25% was in the liver 89 days post dose.

In the degradation of Me-FOSE-based compounds, several metabolites have been confirmed in tissue samples of test animals. These include: PFOS, PFOSA and Me-FOSE-OH. These were identified using HPLC coupled to electrospray MS and verified against standard material. (See Analytical Methods.) Other metabolites have been tentatively identified but not yet confirmed due to a lack of standards. In other studies, animals dosed with PFOS showed no metabolites other than PFOS.

Thus PFOS appears to be the end product of vertebrate metabolism of POSF based products. It is also the likely final product of degradation by microorganisms. PFOS

therefore enters the environment in multiple ways: as a product, as a residual in another fluorochemical product, as a metabolite, as a degradation product resulting from hydrolysis or microbial breakdown of other fluorochemicals.

Once in the environment, PFOS has not been shown to degrade any further under any natural conditions except combustion. Resistant to chemical and biological attack, PFOS persists and accumulates, but exactly in what amounts, and where is not well understood. Whether PFOS is the form that is most important in the dispersal of perfluorochemical compounds in the environment or it is other intermediates that are mobile and are converted to PFOS over time is unknown.

Although some fluorochemicals with hydrocarbon portions have demonstrated resistance to biodegradation under standard test conditions, i.e. aerobic microbial degradation using a wastewater inoculum, existing studies did not examine all combinations of conditions which could be optimized to favor the degradation of partially perfluorinated chemicals. These include slowly preacclimating microorganisms to the fluorochemical and using these acclimated microbes in degradation testing and using longer biodegradation test periods.

New studies initiated at the Environmental Laboratory are now exploring the possibility that a microorganism could eventually be enriched that could metabolically alter these low molecular weight fluorochemicals. These studies are investigating anaerobic as well as aerobic degradation. Additionally, a program of studies has been initiated to examine how polymeric perfluorochemicals, the most common perfluorochemical products, degrade. This program includes studies of polymer hydrolysis, photolysis, and aerobic and anaerobic biodegradation.

Ecotox

Perfluorochemicals produce a variety of responses in aquatic organisms. Different species may vary significantly in their response to the same chemical. Typically, polymeric forms do not cause significant toxic effects. Surfactants as a class, both fluorinated and unfluorinated, tend to be likely to demonstrate aquatic toxicity.

Basic environmental toxicity screening data are available for many sulfonated perfluorochemicals (see Table 7). In considering the toxicity testing, it is important to note the year of the test. Older test protocols are not comparable to current bioassays which follow accepted, standardized test methods (OECD/USEPA). Almost all testing used products and not purified perfluorochemicals. In old tests, the fluorochemical product used was likely more variable, with more impurities because manufacturing processes and product purity have significantly improved overtime. Several tests were hampered by the insolubility of the perfluorochemical and results are expressed as greater than the measured solubility.

In describing environmental toxicity data, the 3M Environmental Laboratory uses six levels of descriptors on its Product Environmental Data Sheets. These levels are similar to definitions used by the National Institute for Occupational Safety and Health (NIOSH).

Definitions of Toxicity

where X= the lowest LC50, EC50 or IC50 in mg/L (ppm)

Environmental Lab		**NIOSH**
Insignificant hazard	X> 1000	Insignificant hazard
Minimal	100< X<1000	Practically nontoxic
Harmful	10< X <100	Slightly toxic
Toxic	1< X<10	Moderately toxic
Very Toxic	0.1< X <1	Highly toxic
Extremely Toxic	X< 0.1	

Two perfluorocompounds 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. The manufacturer of the insecticide using PFOS Li salt, in addition to the aquatic toxicity data, supplied data on wildlife toxicity. These are:

Mallard:	Acute Toxicity	LD50= 81 mg/kg NOEL<12.5 mg/kg
	Subacute Toxicity,	LC50=324 ppm NOEC<94 ppm
Northern:	Acute ToxicityLD50=42 mg/kg	
Bobwhite		NOEL<11.7 mg/kg
	Subacute Toxicity	LC50=220 ppm NOEC<94 ppm

The insecticide N-EtFOSA and its metabolite PFOSA have been reported to be potent uncouplers of oxidative phosphorylation in rabbit renal mitochondria.

Table 7. Aquatic Toxicity Testing on Perfluorochemical Products

Product's Principle Fluorochemical	Test Organism	Study Type	Results mg/L	Year
POSF	*Pimephales promelas*	96 hr LC50	>1000	84
N-MeFOSE alcohol	*Lepomis macrochirus*	96 hr LC50	>solubility	79
	Daphnia magna	48 hr LC50	>solubility	79
N-EtFOSE alcohol	*S. capricornutum*	14 day EC50	>1800	81
	Pimephales promelas	30 day NOEC hatch, grow, survive	.020	78
		30 day LOEC histopathology	>.020	78
N-EtFOSA	*Daphnia magna*	24 hr EL50	24.6	98
		48 hr EL50	14.5	98
		48 hr EL10	7.3	98
		48 hr NOEL	5.8	98
	Pimephales promelas	24 hr LL50	308	98
		48 hr LL50	216	98
		72 hr LL50	216	98
		96 hr LL50	206	98
		96 hr LL10	115	98
		96 hr NOEL	130	98
	Ceriodaphnia dubia	24 hr EL50	380	98
		48 hr EL50	328	98
		48 hr EL10	184	98
		48 hr NOEL	216	98
	Pimephales promelas	96 hr LC50	0.189	92
		96 h NOEC	0.086	92
	Lepomis macrochirus	96 hr LC50	>6.6	90
		96 hr NOEL	1.6	90
	Salmo gairdneri	96 hr LC50	>10	88
		96 hr NOEC	10	88
	Daphnia magna	48 hr EC50	>10	88
		48 hr NOEL	10	88
	Daphnia magna	48 hr EC50	3.2	84
		96 hr LC50	34	84
N-EtFOSEA	*Pimephales promelas*	96 hr LC50	>1000	84
N-EtFOSEMA	*Pimephales promelas*	96 hr LC50	>1000	84
PFOS NH_4 salt	*Pimephales promelas*	96 hr LC50	85	74
	Pimephales promelas	96 hr LC50	100	74

PFOS Li salt	Microtox *P.phosporeum*	30 min EC50	>1000	94
	Daphnia magna	24 hr EC50	330	94
		48 hr EC50	210	94
		48 hr EC50	67	92
		NOEC	34	92
	Pimephales promelas	24 hr LC50	>56	94
		48 hr LC50	>56	94
		72 hr LC50	36	94
		96 hr LC50	19	94
PFOS Li salt continued	*Lepomis macrochirus*	96 hr LC50	49	92
		NOEC	16	92
	Salmo gairdneri	96 hr LC50	4.2	92
		NOEC	2	92
PFOS K salt	Microtox	5 min EC10	49	91
		15 min EC10	59	91
		30 min EC10	45	91
		30 min EC50	>280	91
	Daphnia magna	48 hr EC50	27	84
		28 day NOEC	7	84
	Selenastrum	4 day EC50 ct	82	82
	capricornutum	14day EC50 ct	95	82
	Pimephales promelas	30 day NOEC	1	78
		30 day LOEC	1.9	78
		96 hr LC50	38	77
	Lepomis macrochirus	96 hr LC50	68	78
	Salmo gairdneri	96 hr LC50	11	78
	Daphnia magna	48 hr EC50	50	79
	Pimephales promelas	96 hr LC50	29	74
	Pimephales promelas	96 hr LC50	32	73
PFOS DEA salt	*Lepomis macrochirus*	96 hr LC50	31	79
		96 hr NOEL	18	79
perfluoroC10 sulfonic acid, NH_4^+ salt	*Daphnia magna*	48 hr EC50	44	92
	Pimephales promelas	96 hr LC50	4.8	92
	Microtox	EC50	330	92
K salt of carboxylic acid analogue of N-Et-FOSE alcohol	*Pimephales promelas*	96 hr LC50	97	97
		96 hr NOEC	54	97
	Selenastrum	96 hr EC50	600	97
	capricornutum	96 hr NOEC	216	97
	Daphnia magna	48 hr EC50	9.1	97
		48 hr NOEC	3.9	97
	Microtox	30 min IC50	270	97
	Pimephales promelas	96 hr LC50	518	81
N-EtFOSE alcohol ethylene oxide adduct	*Lepomis macrochirus*	96 hr LC50	285	78
	Daphnia magna	48 hr EC50	1.5	78

Table Key

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

EC50= Median Effective Concentration. It is the concentration of a test substance which 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 wheere growth is measured.

LC50= Median Lethal Concentration. It is the concentration of a substance which 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 which inhibits a biological process of a test organism by 50% (e.g. light production, respiration) after a specified exposure period

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NOEL= No Observed Effect Loading

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.

Environmental Fate

The release of perfluorocarbons into the environment begins with the manufacturing process. Unintentional releases can occur during any of the steps required to produce the fluorochemical and manufacture the product. 3M applies strict industrial hygiene and safety practices to aid in minimizing production releases. Some releases such as disposal of waste products, are expected and controls provided.

Within the last five years, the Environmental Laboratory has developed advanced technology based on Fourier Transform Infrared spectroscopy (FTIR) and applied it to the field monitoring of fluorochemicals at plant sites. Using this technology, perfluorochemical releases can be characterized and quantified. It has been used to minimize releases of fluorochemicals through optimizing the operation of steps in the production process. It has also been used to monitor the effectiveness of pollution control equipment in removal of fluorochemical waste emissions.

In addition to releases during production and at manufacturing plants, perfluorochemicals enter the environment with product usage. After starting with the manufacturing process,

the release of perfluorocarbons into the environment continues through product handling and distribution in the commercial sector, through the application of the perfluorochemical product e.g. textile protection, and during wear, abrasion and use of articles treated with product. The release ends during the final disposition or disposal of perfluorochemically treated products.

The fate of perfluorochemicals released to the environment is largely unknown. The characterization of fate is complicated by uncertainties about the full range of intermediate forms of perfluorochemicals that may exist in the environment in addition to PFOS, the final degradation product. Very little basic physical, chemical and biological data have been collected on the environment near the plants. Gaps in physical, chemical, and environmental monitoring data hinder model prediction and validation.

The quite limited biological data that do exist consist of scattered, one-time testing and pioneer sampling involving very small numbers of organisms. These are reported below.

Laboratory studies done in the late 1970s detected the presence of certain fluorochemicals in fish. Early studies used N-EtFOSE alcohol. Aquatic testing was hampered by the insolubility of this material and the actual concentration fish were exposed to was disputed (reported solubility: 50 ppb; reported aquarium concentration: 500 ppb). Both 3 bluegill and 2 channel catfish were found to rapidly take up the chemical and have a whole body burden of N-EtFOSE alcohol up to 400 times that in the water. The amounts in the fish declined rapidly when the fish were placed in clear water. Two channel catfish were dissected to determine concentrations in organs. The gall bladder concentrated the chemical more than any other organ (26,550 ppm). Concentrations in the brain and gastrointestinal tract exceeded 1000 ppm. The skin, skeleton, liver and gills contained the chemical at a level similar to the whole organism

In 1979, thirty bluegill sunfish exposed to effluent from a manufacturing plant were found to contain N-EtFOSA (10 ppm), N-EtFOSE alcohol (7 ppm), and PFOS. Thirty more exposed to water from a nearby river tested negative for fluorochemicals.. When four fish (2 channel catfish, 1 white bass, and 1 white crappie) were collected from the river, initial testing reported the presence of N-EtFOSA, N-EtFOSE alcohol and N-MeFOSE alcohol in the fish. On further examination of test methodology, this finding was reported as incorrect. No volatile fluorochemicals were found. Non-volatile fluorochemicals, e.g. PFOS, appeared to be present, but could not be identified.

In recent tests of the blood of 10 fish eating birds, albatross nestlings in the mid-Pacific and eagle nestlings in the Midwest, PFOS was detected in the eagles at an average of 41 ppb. The albatross showed very little or no detectable levels of PFOS. PFOS has been detected in human blood collected from the general U.S. population (30-40 ppb).

These data support speculation about biological amplification. A reliable method for measuring fluorochemical concentration in fish tissue has recently been developed in the

Environmental Laboratory, but very few data currently exist on amounts present after either laboratory or field exposure to a fluorochemical. Extrapolation from existing physical/chemical data is problematic. Many perfluororganics have quite different properties from other chemicals that are known to bioconcentrate. For example, the hydrophobic and lipophilic properties of chlorinated hydrocarbons differ from perfluorinated chains which are both oleophobic and hydrophobic.

Vertebrates may also metabolize perfluorochemicals differently from the way known bioaccumulative chemicals are metabolized. Metabolic studies at 3M suggest that after ingestion, PFOS is readily adsorbed into the blood from the gut. Once in the blood, it appears to bind to albumin and circulates in the blood until it reaches the liver where it collects. In the liver, PFOS either binds, complexes or becomes a conjugate of newly manufactured bile. The bile is then stored in the gall bladder, being expressed into the duodenal area of the intestine. Here PFOS may again be readsorbed into the blood and recirculated in this loop. This proposed mechanism explains the long half life of fluorochemicals in the vertebrate body.

Models are critical to determining environmental fate, but models currently in use are typically derived from experience with chlorinated hydrocarbons. Model assumptions may not apply to or inadequately consider fluorochemical behavior. For example, do the unusual surface activity and partitioning properties of fluorochemicals lead to concentration in the micro-layer between surface water and air? If so, what does this mean for the community of organisms that routinely inhabit this area? For organisms that feed on surface inhabitants? Will measurements of PFOS in organisms result from a classic biological amplification through trophic levels or be the result of a hitherto unknown bioconcentration mechanism?

Reservoirs and sinks for perfluorocarbons are yet to be documented. The dynamics regulating living systems evolved without the experience of these chemicals, and it is uncertain how they are incorporating these molecules. A substantial amount of additional research is needed to adequately characterize their fate. It will require more direct testing, inference from detected ambient levels, and modeling. More study is essential to find what accumulates, where it accumulates, how exposure to the living and nonliving components of the environment transforms the molecules and what effects this exposure has on organisms at all levels of the ecosystem.

Research Rationale

Assessing the environmental fate and effects of perfluorochemicals is a challenging task. As described above, these chemicals have unusual properties which distinguish them from other perisistent chemicals, e.g. chlorinated hydrocarbons, which now form the basis for understanding and predicting environmental fate. Extrapolations and assumptions based

on historical understandings of fate could introduce error and bias into research designed to evaluate uniquely perfluorochemical behavior. Basic information gathering similar to that gathered in the first studies of environmental fate is required. The physical-chemical, degradative, temporal and geographic nature of releases throughout the fluorochemical products' life cycles must be understood.
Representative questions that must be answered include:

How much human and ecosystem exposure is due to releases from plants, from the application of products, from the use and disposal of products?

What are the major sources of fluorochemical exposure through the natural environment?

What happends to fluorochemicals as they pass through wastewater treatment systems? When discharged to the air?

Do polymeric flurochemical products differ in stability and environmental behavior from the low molecular weight perfluorochemical intermediates?

How and in what forms are perfluorochemicals transported through environmental media e.g. air, soils, ground water, surface water, the surface film of water?

What is the distribution of fluorochemicals throughout the biosphere? near manufacturing plants? in remote areas?

Could the concentrations of fluorochemicals detected in the environment affect the functioning of any part of the ecosystem?

To answer these questions and many others like them, significant additional background information must be generated. After considering the current and historical information available on the physical, chemical and biological behavior of perfluorochemicals, 3M and its consultant, Batelle Memorial Institute, have developed a research plan to gather the necessary data. The plan has four research components. It is diagrammed in Figure 2.

1. Characterize releases. The fate and dispersion of perfluorochemicals in the environment is determined by the quantity and rate of their release from processes and products. Quantitative information about releases will be used to estimate environmental burden, both present and historical, and may be used to forcast changes that result from changes to products and processes. The plan provides for measuring the amounts and kinds of perfluorochemicals released during the full life cycle of a perfluorochemical product. Testing will start when the perfluorochemicals are first created, continue through the distribution and conversion stages where perfluorochemicals are sold or made into products, extend to the commercial and residential use of the products and include the final disposal of the product. Several different environmental compartments for releases will be sampled. These include: indoor and outdoor air (3M manufacturing, customer facility, commercial establishment, and residential), floor dust and soil, wastewater, wastewater sludge and municipal landfill. The measurements will come from direct testing, engineering estimates, and simulations.

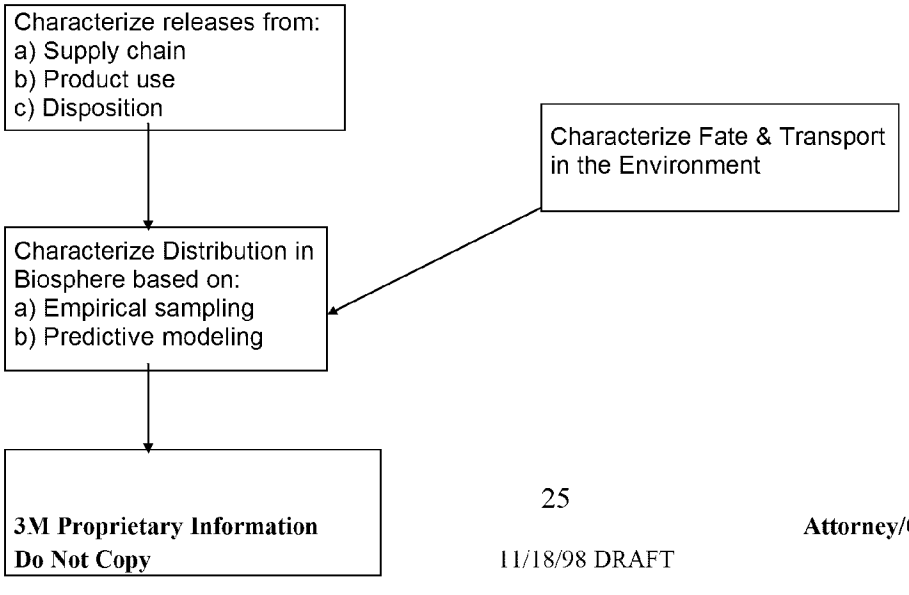
2. Characterize the transport and fate of perfluorochemicals. Full characterization of intermediate forms of perfluorochemicals that may exist in the environment in addition to PFOS will take some time. Initial priorities will be established by:

-reviewing existing studies on multimedia transport;
-investigating how existing compartmental/fugacity models can be adapted to consider the properties of perfluorochemicals;
-developing a set of data needs for physical-chemical properties and environmental parameters to support modeling of fate and transport mechanisms;
-screening available data, both estimated and measured, ambient and laboratory, to develop a plan to address data gaps.

3. Characterize distribution of perfluorochemicals in the biosphere. To determine where perfluorochemicals accumulate in ecological systems, levels will be measured in the soil, water and species of three different kinds of habitat. Key ecosystems and species of concern surrounding a manufacturing plant will be identified and listed. Habitat types and location with respect to the 3M plant and effluent streams will be described. Samples will be collected from representative habitats and biological receptors at different trophic levels. Missing data will be predicted using computer models which have been thoroughly evaluated.

4. Estimate amounts of perfluorochemicals distributed in populations and environments. The methods used to estimate human exposure include collection of samples during scenarios which demonstrate use patterns and exposure pathways, personal monitoring, questionnaires, surveys, and testing of statistically valid subsets of populations. The methods used for ecological exposure assessments will be based on U.S. Environmental Protection Agency (USEPA) ecological risk assessment guidelines.

Figure 2. Overview of Project Plan



Estimate Exposure Distribution:
a) Human
b) Ecological

The plan has been implemented and the needed information is being collected or developed. 3M has for many years been working on reducing and minimizing releases of the products as part of its overall focus on product stewardship and pollution prevention. A corporate policy formalized in 1975 commits the company to safe and environmentally responsible practices in the development, manufacture, distribution, use and disposal of all 3M products. One initiative established under this policy is Product Life Cycle Management (PLCM). This initiative is designed to assure awareness of potential impacts at every stage of a product's life cycle. 3M business units selling fluorochemical products have evaluated their products, listing those of greatest concern, the significant routes of exposure, information gaps and what testing is needed.

In the environmental area, twelve important fate and transport mechanisms have been identified . These are:

1. air/product partitioning
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. toxicity to wastewater treatment systems
12. efficiency of wastewater treatment systems.

All twelve of these fate and transport mechanisms have been linked to three modeling categories: ecosystem, indoor air and wastewater treatment systems. Models and adaptations of models are being evaluated in each of these categories for use in a screening process which will identify areas requiring more detailed modeling. The physical/chemical parameters necessary to support model operation have been identified and are being developed. The degradation testing now underway will aid in determining which chemical species need further examination.

The plan provides a comprehensive approach to answering the questions about perfluorochemical fate and effects. These new exposure studies supplement existing ongoing research at 3M. To provide information quickly, the project components will proceed simultaneously and independently. Giving a high priority to developing the information, the estimated timeframe for completion of these studies is two years.

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