DRAFT

ECOTOXICOLOGY AND ENVIRONMENTAL FATE TESTING OF SHORT CHAIN PERFLUOROALKYL COMPOUNDS RELATED TO 3M CHEMISTRIES

XXX XX, 2008

Prepared by

3M

TABLE OF CONTENTS

DRAFT

Introduction to Environmental White Papers on Perfluoroalkyl acids related to 3M chemistries

---

Perfluorochemicals have been commonplace in chemical industry over 50 years but until recently there has been little information on environmental fate and effects avialble in open literature. The following chapters summarize the findings of "***list specific C4 intermediates PFBS, PFBSI, PFBA, PFPA, MeFBSAA, TFA, MeFBSE, FBSA, HxFBSA, FBSE, PBSF, NFB*** ".

As background, 3M announced on May 16, 2000 the voluntary manufacturing phase out of perfluorooctanyl chemicals which included perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and PFOS-related chemistries. The United States Environmental Protection Agency (U.S. EPA) has subsequently issued one final Significant New Use Rule[1], or SNUR, that regulates the production and import of (193??) perfluorooctanyl chemicals followed by an amended SNUR with additional FCs[2]. Canada recently banned[3] the use and importation of a number of long chain perfluorinated carboxylic acids because of concerns over potential adverse human and environmental effects. In January 2006, the U.S. EPA announced a voluntary 2010/15 PFOA Stewardship Program[4] to eliminate emissions and product content of PFOA and related chemicals[5]. In addition, the EU has placed into force a PFOS Marketing and Use Restrictions Directive in 2008.

Starting in 2000, industry began the development of unique, new technologies to replace perfluorooctanyl based technologies which are currently under regulatory scrutiny worldwide. 3M, and other companies, are now developing and selling perfluorobutanyl based technology into applications previously dominated by perfluorooctanoyl, or C8 technology. These areas include fabric and leather protection, carpet anti-soiling protection, fiber water and oil repellency, hard surface treatment, drug synthesis, and industrial surfactants.

The importance of this summary is that these chemicals are part of the degradation pathway for one of the alternative new technology based on perfluorobutanyl (PBSF), or C4 chemistry. Like its longer-chain homolog, PBSF based moieties can break down, through a series of degradants, to the corresponding sulfonic acid, perfluorobutane sulfonate (PFBS). In this series of white papers, the available environmental fate and effects data on the various degradants will be summarized. The ultimate degradation product, PFBS, has a very low potential to bioaccumulate[5] and, as will be discussed in this paper, has a very different environmental profile as compared to perfluorooctanyl compounds [6, 7].

Degradation of Perfluorobutanesulfonamide Based Materials

1.0 Introduction

When assessing environmental fate, one important consideration is the transformation of those materials in the environment. Abiotic transformation consists of two distinct decomposition routes: hydrolysis and photolysis. Biological degradation processes are classified as anaerobic and aerobic and depend on the properties of the media and the activity of the native microbial populations. This summary examines known degradation mechanisms of multiple N-Methylperfluorobutanesulfonamide functionalized polymers. Physical, chemical and environmental toxicological properties of the degradation products are addressed as part of this document in the Degradants & Intermediates section.

2. Abiotic Transformations

2.1. Hydrolysis

2.1.1 Introduction

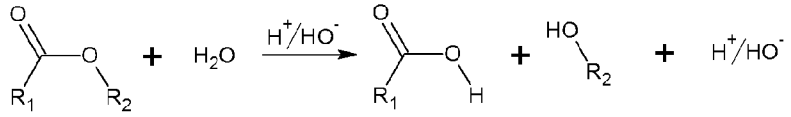
Hydrolysis is a reaction between a target species and water that results in a chemical change in the target.[1] Known reactions include substitution, elimination, addition, and condensation mechanisms. Electronic effects, steric effects, solution pH and ambient temperature determine both hydrolytic reaction rates and products.[2] Essentially, hydrolysis reactions are the chemistry of functional groups as influenced by surrounding substituents and solvation effects.[3] When the material is a polymer, steric effects slow the reaction. Hydrolytic degradation of substituents can be compared with studies from the literature on small molecules with the realization that the reaction is often slower. Kinetic data is given in terms of the rate constants k_A, k_N and k_B at a specific temperature and can be converted into half-lives or a range of half-lives.[1] When the material under investigation is a polymer, half-lives can be calculated based on the appearance of a specific degradation product or group of products.[4] In this situation, the half-life is defined as the time it takes to produce a quantity of product material equal to one-half of the total amount of product available in the polymer. This definition applies when the targeted degradation products are stable over the time-frame of the study or when the kinetics of any product decomposition is known. This half-life convention is followed in all studies referenced in this document.

2.1.2. Acrylates

Acrylate polymers are polyolefin chains with pendant ester substituents. The mechanism of acrylate/ester hydrolysis is illustrated in Figure 1.[D3] As

a general rule, rate constants for ester hydrolysis of hydrocarbon based polymers do not vary much due to steric or electronic effects and are in the range of 10^4k=1.0±0.5 at 25°C (minutes to hours) although measured half-lives have been observed to range from 10 min < Half-Life <100 yr.[5] Exceptions to this general rule are: extensive branching (such as a t-butyl group) alpha to the ester functionality and strong electron withdrawing groups in either position at R_1 or R_2.[D2,D3] While most acrylate polymers do not contain either electron withdrawing groups or t-butyl type functionality, less extensive branching can slow the reaction down by up to two orders of magnitude[3] (1 mo < Half-Life < 10 yr).

Figure 1. Ester/Acrylate Hydrolysis



Many recent 3M acrylate and methacrylate polymers contain a perfluorobutane-sulfonamide based (N-MeFBSE or $C_4F_9SO_2N(CH_3)CH_2CH_2O$-) attached to the polymer in the R_2 position shown in Figure 1.

PM-4800 Acrylate Polymer (NB#128463-22)

"Preliminary Test: Hydrolytic Degradation of an Acrylate Polymeric Ester NB#128463-22 in Aqueous Buffered Solutions" 3M Environmental Laboratory Report #E02-0194. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 04/11/02.

Experimental Summary: Using EPA guidance document OPPTS 835.2110 "Hydrolysis as a Function of pH" for the design of this study, the polymer was suspended into two sets of buffers of pH's 4, 7, and 9 at a nominal concentration of 270 ppm. The first set was cooled to 0 ± 4°C and the second set was allowed to react in/with the buffer solutions for 5 days at 50°C. Once the 5-day reaction period was over, both buffer sets were analyzed by HPLC/MS for perfluorobutanesulfonate (PFBS), N-MeFBSE, 2-*N*-methyl-perfluorobutanesulfonamide (N-MeFBSA) and perfluorobutanesulfonamide (FBSA).

Result: The primary findings established that the polymer NB#128463-22 will hydrolytically degrade to form N-MeFBSEl with the half-life determined to be greater than 48.54 years at pH 7 at 25°C. There was evidence of both acid and base catalysis at pH's 4 and 9 although the

determined half-life didn't change significantly. Degradation to form the three remaining targets (PFBS, N-MeFBSA and FBSA) was not observed.

FC-4430 and FC-4129

"Aqueous Hydrolysis of FC-4430, FC-4171 and FC-4129" 3M Environmental Laboratory Report #E01-0131. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 05/03/01

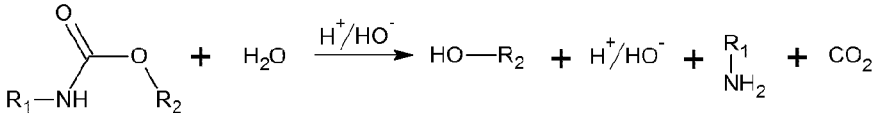
Experimental Design: Using EPA guidance document OPPTS 835.2110 "Hydrolysis as a Function of pH" for the design of this study, each polymer was suspended into three sets of buffers of pH's 4, 7, and 9 and two sets in pH 1.2 at a nominal concentration of 100 ppm. One set of buffers of pH's 1.2, 4, 7, and 9 were cooled to 0 ± 4°C, a second set of buffers of pH's 4, 7, and 9 was allowed to react in/with the buffer solutions for 30 days at 25°C and the third set of buffers of pH's 1.2, 4, 7, and 9 was allowed to react in/with the buffer solutions for 30 days at 37°C. Once the reaction period was over, all buffer sets were analyzed by HPLC/MS for PFBS, FBSA, N-MeFBSA, N-MeFBSE Alcohol and perfluorobutyric acid (PFBA).

Results: The measured half-lives of hydrolysis for formation of N-MeFBSE Alcohol for each FC4430 (pH 9 and 37°C) and FC4129 (pH 1.2 and pH 9 at 37°C and pH 9 and 25°C) were 284 hours, 542 hours, 277 hours and 308 hours respectively. No discernible hydrolysis was observed for either FC-4430 or FC-4129 at pH 5 and 7. Degradation to form the remaining targets was not observed under any condition.

2.1.3 Urethanes

Urethane polymers are essentially long chains of carbamates either forming or connected to a polymeric backbone. Carbamates hydrolyze via the reaction scheme shown in Figure 2.[D2] Hydrocarbon carbamates of are moderately reactive and show wide variations in hydrolysis rates dependant upon the identity of the substituents R_1 and R_2.[D3] A carbamate with R_1 and R_2 being either aliphatic or aromatic (but not both) will have rate constants centered around 10^5k=3.0±0.5 at 25°C (1 min < Half-Life < 2000 yr).[D5] As is the case with acrylates, extensive branching next to the carbamate functionality in a polymer (a urethane) could slow the reaction rate down by two or more orders of magnitude[D3] (1 yr < Half-Life < 200 yr).

Figure 2. Carbamate/Urethane Hydrolysis



Many recent 3M urethane polymers attach the perfluoroalkane-based sulfonamidoethyl alcohol (N-MeFBSE) to the polymer in the R_2 position shown in Figure 2.

PM-1396 (L-18105)

"Preliminary Test: Hydrolytic Degradation of the Urethane Polymer L-18105 in Aqueous Buffered Solutions" 3M Environmental Laboratory Report #E02-1141. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 04/10/03
Experimental Summary: Using EPA guidance document OPPTS 835.2110 "Hydrolysis as a Function of pH" for the design of this study, the polymer was suspended into two sets of buffers of pH's 4, 7, and 9 at a nominal concentration of 19.8 ppm. The first set was cooled to 0 ± 4°C and the second set was allowed to react in/with the buffer solutions for 6 days at 50°C. Once the 6-day reaction period was over, both buffer sets were analyzed by HPLC/MS for PFBA, PFBS, FBSA, N-MeFBSA and N-MeFBSE.
Result: The polymer showed no evidence of degradation. Table 1 gives the calculated half-lives based upon the experimental precision of the analysis or upon the limits of quantitation for the degradation of L-18105 at 25°C to form each specific target.

Table 1. Calculated Half-Lives for Hydrolytic Degradation of L-18105

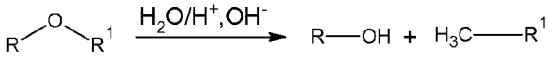
Compound	Half-Life at 25°C
N-MeFBSE	≥32.2 years
N-MeFBSA	≥65.1 years
FBSA	≥62.2 years
PFBS	≥62.4 years
PFBA	≥44.5 years

2.1.4. Polyethers

Polyether polymers

Polyethers are polymers that contain an ether group R-O-R' where R can be a simple or complex organic functionality. Polyether based polymers are known to be highly resistant to hydrolysis, only degrading in the presence of strong acid or base. When a polyether undergoes acid/base catalysed hydrolysis, it occurs by the addition of water across the ether linkage, as shown in Figure 3.[6]

Figure 3 Polyether Hydrolysis



Many recent 3M polyether polymers contain a perfluorobutanesulfonamide based alcohol (N-MeFBSE) attached to the polymer in the R position with polyethylene functionality attached in the R^1 position shown in Figure 1.

FC-4171

"Aqueous Hydrolysis of FC-4430, FC-4171 and FC-4129" 3M Environmental Laboratory Report #E01-0131. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 05/03/01
Experimental Design: Using EPA guidance document OPPTS 835.2110 "Hydrolysis as a Function of pH" for the design of this study, each polymer was suspended into three sets of buffers of pH's 4, 7, and 9 and two sets or pH 1.2 at a nominal concentration of 100 ppm. One set of buffers of pH's 1.2, 4, 7, and 9 were cooled to 0 ± 4°C, a second set of buffers of pH's 4, 7, and 9 was allowed to react in/with the buffer solutions for 30 days at 25°C and the third set of buffers of pH's 1.2, 4, 7, and 9 was allowed to react in/with the buffer solutions for 30 days at 37°C. Once the reaction period was over, all buffer sets were analyzed by HPLC/MS for PFBS, FBSA, N-MeFBSA, N-MeFBSE Alcohol and perfluorobutyric acid (PFBA).
Results: No detectable hydrolysis was observed for FC-4171 under any test condition.

2.1.5 2-(*N*-methylperfluorobutanesulfonamido) ethyl acrylate

Study results which determined the hydrolytic half-life of 2-(*N*-methylperfluorobutanesulfonamido) ethyl acrylate (N-MeFBSEA), the monomeric precursor to all 3M perfluorobutanesulfonamide based acrylates, were included in the report #E02-0194. "Preliminary Test: Hydrolytic Degradation of an Acrylate Polymeric Ester NB#128463-22 in Aqueous Buffered Solutions" 3M Environmental Laboratory Report #E02-0193. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 04/11/02
Experimental Summary: Using EPA guidance document OPPTS 835.2110 "Hydrolysis as a Function of pH" for the design of this study, N-MeFBSEA was suspended into two sets of buffers of pH's 4, 7, and 9 at a nominal concentration of 27 ppm. The first set was cooled to 0 ± 4°C and the second set was allowed to react in/with the buffer solutions for 5 days at 50°C. Once the 5-day reaction period was over, both buffer sets were

analyzed by HPLC/MS for PFBS, N-MeFBSE Alcohol, N-MeBBSA and FBSA.

Result: The primary findings determined the half-life of N-MeFBSEA to be 0.6048 years at pH 7 at 25°C based on the appearance of the N-MeFBSE. The measured half-life was longer under both acidic and basic conditions. Degradation to form the three remaining targets was not observed.

2.1.6. Hydrolysis Conclusions

These studies establish that the hydrolysis rates for hindered hydrocarbon-based materials closely track with the hydrolysis rates observed in studies of perfluorobutanesulfonamide based materials. It is believed that electron-withdrawing effects of the fluorochemical tail on the sulfonamidoethyl alcohol functionality are minimal due to the number of bonds between the two portions of the molecule. Where degradation was observed, the only degradation product was N-MeFBSE Alcohol.

2.2. Photolysis

2.2.1 Introduction

Photolytic decomposition reactions in the environment occur by three distinct mechanisms: direct photolysis, indirect photolysis and photochemical redox reactions.[7] Direct photolysis is defined as absorption of a photon by a target species that leads to a chemical change.[8] Indirect photolysis can be described as a chemical or electronic excitation transfer from a light absorbing species to the test substance, which then undergoes some type of chemical change.[9] Photochemical redox reactions occur when the target species interacts with a metal catalyst in such a way that there is a ligand-to-metal charge transfer upon excitation of the complex by a photon followed by release of the target species as an electron deficient radical.[10,11]

When the material under investigation is a polymer that does not contain a chromophore, the standard definitions become blurred. Commercial polymers often trace amounts of photoinitiators, transition metal catalysts, photostabilizers, residual monomers or even transition metals from aqueous washings that, when excited by a photon of proper the proper frequency, will initiate the photochemical degradation process.[D11, 12] Regardless of which impurity initiates radical formation, the result is the formation of a radical on the polymeric backbone that may lead to photolytic degradation.

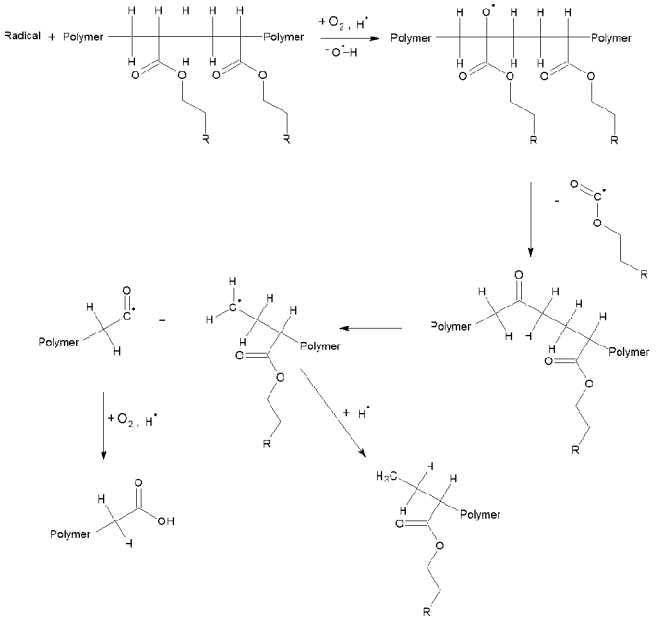
This technical discussion examines what is known about photolytic decomposition reactions of acrylate and urethane-based polymers in the environment. The discussion focuses on aqueous and surface-based photolytic decomposition as it is anticipated the polymeric materials would

predominantly reside in these two compartments. Atmospheric photolytic decomposition is not addressed due to the high molecular weights and low vapor pressures characteristic of polymeric materials. Literature studies typically do not calculate half-lives but instead report the time it takes to degrade polymer performance. The measured time is then referenced to one or more "standard" situations encountered in the environment. In this discussion, a half-life is defined as the time it takes to produce a quantity of a specific degradation product equal to one-half of that total amount of potential product available in the polymer. For this definition to be valid, the degradation product(s) must be stable during the time-frame of the study or the kinetics of any product decomposition must be known. Reports from the 3M Environmental Laboratory reference against light intensity measurements of the sun at noon in Miami Florida, USA or against the ASTM Standard of a 12 hour day on a 30° hemispherical tilted surface.

2.2.1 Acrylates

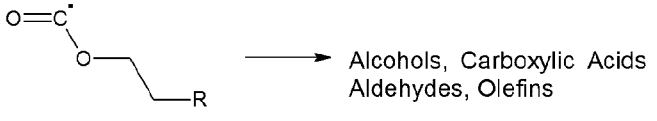
Polyacrylates are simply long chains of esters and are often synthesized in a similar fashion to monomeric esters. Aliphatic-based acrylates typically do not show absorbance above 277 nm.[13 D13] Impurities in or resulting from the polymerization process will initiate radical formation upon excitation by a photon as shown in Figure 4.[D14]The first step in photodegradation results in cleavage of the polymer into two molecules and formation of a small molecule radical. The kinetics of the initial reaction is dependant upon the flux of light at the proper frequency, concentration of the radical initiator, and steric effects.[D15] Continued photolytic decomposition results in additional formation of small radical species and carboxylic acids.[D16]

Figure 4. Photolytic Decomposition of an Acrylate Based Polymer



The small molecule radical generated as a result of photolysis is expected to form the products shown in Figure 5.[D14]

Figure 5. Formation of Small Molecule Degradation Products from Photolytic Degradation of an Acrylate Polymer.



FC-4430

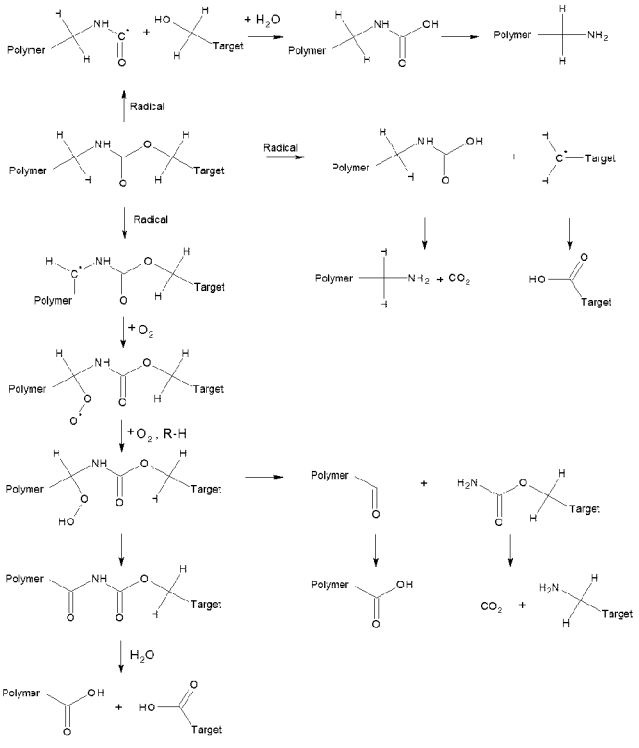
"Photolysis Study for the Polymer FC-4430" 3M Environmental Laboratory Report #E01-0264. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 03/30/01 Experimental Summary: Using EPA guidance document OPPTS 835.5270 "Indirect Photolysis Screening Test" for the design of this study, the polymer was suspended into two sets of vials containing synthetic humic material. One set was cooled to 0 ± 4°C and the second set was allowed to react in/with the matrix for 5.3 days in an Atlas Suntest photoreactor (light filtered to mimic natural sunlight, equivalent 128 12-hour days). Once the reaction period was over, all sample sets were analyzed by HPLC/MS or GC/MS for PFBS, N-MeFBSE Alcohol, N-MeFBSA, FBSA, PFBA, 1,1,2,2-tetrafluoroethane, pentafluoroethane, 1,1,1,2,2,3,3-heptafluoropropane,

1,1,1,2,2,3,3,4,4-nonafluorobutane (C-4 hydride) and Octafluoro-2-butene (*cis and trans*).
Result: The polymer degraded to form N-MeFBSE Alcohol and N-MeFBSA with the measured half-life determined to be greater than 1.06 years.

2.2.3 Urethanes (and Urethane-Ester Hybrids)

Urethanes are simply long chains of carbamates and are typically synthesized from isocynates[D12, D16] Aliphatic-based urethanes do not show absorbance above 280 nm.[D23] Impurities in or resulting from the polymerization process will initiate radical formation via the degradation pathway shown in Figure 5. [D16, D17]
In figure 6, published degradation pathways of hydrocarbons illustrate that a urethane polymer will degrade to form amines, carboxylic acids, alcohols and olefins. Published studies on other fluorochemical containing urethanes propose the same net degradation pathway.[D16,D17]
Urethane polymers may contain other functional groups within the polymeric backbone. In the case of Urethane-Ester hybrids, there are both urethane and ester linkages within the polymer. Photolytic degradation of urethane-ester hybrid polymers track closely with the degradation routes of the two functionalities.

Figure 6. Photolytic Decomposition of a Urethane Based Polymer



P-04-174 in Water, Synthetic Humic Material, Water with Dissolved Fe(III) and Water containing 10% Suspended Sediment.

"Aqueous Photolytic Degradation of P-04-174" 3M Environmental Laboratory Report #E05-0664. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 11/16/05

Experimental Summary: Design of this study used EPA guidance document OPPTS 835.2210 "Direct Photolysis Rate in Water By Sunlight", OECD Draft Document "Phototransformation of Chemicals in Water - Direct and Indirect Photolysis", August 2000 and OPPTS 835.5270 "Indirect Photolysis Screening Test" and was augmented by procedures developed in the 3M Environmental Laboratory based on literature studies of related materials. In this study, five matrices containing approximately 51 ppm polymer each were tested for photolytic decomposition: pure water, water containing added hydrogen peroxide, a synthetic humic material matrix, a solution of Fe_2O_3 in water and natural lake water containing well characterized suspended sediment. Multiple sample time points were examined for each matrix. In general, once the reaction period was over, all sample sets were analyzed by HPLC/MS or GC/MS for PFBS, N-MeFBSE Alcohol, N-MeFBSA, FBSA, PFBA, PFBSI, C4 Hydride and Octafluoro-2-butene (*cis and trans*). Both direct photolysis (the interaction

of light with the target molecule leading to a chemical change) and indirect photolysis (the interaction of light with the sample matrix to produce radical species that subsequently reacts with the target material) were examined.
Result: The study established that P-04-174 will degrade by a photolytic decomposition mechanism in all matrices studied. Quantitative screening data from the hydrogen peroxide matrix confirmed the proposed degradation targets. Based on data obtained from all matrices, the primary degradation products are N-MeFBSE Alcohol, N-MeFBSA, C4 Hydride, and PFBA. Small quantities of PFBSI, N-MeFBSAA, FBSA and very low quantities of PFBS were also observed. Half-lives of P-04-174 at 37° South Latitude Solar Spectral Direct Irradiance in each matrix under experimental laboratory conditions are shown in Table 2. Kinetic calculations were not carried out in the hydrogen peroxide matrix.
Table 2. Half-Lives of P-04-174 at 37° South Latitude (12-hour days)

Matrix	Exposure Equivalents (Days)	Conversion of P-04-174 to Products (Percent)*		Half-Life (Years)**	
		Measured	Range	Measured	Range
Pure Water	344	8.86	7.76 - 9.96	7.03	6.23 - 8.08
Water Containing Dissolved Humic Material	25.9	9.65	8.91 - 10.4	0.485	0.449 - 0.527
Water Containing Dissolved Fe(III)	616	19.4	13.3 - 25.6	5.12	3.45 - 9.04
Water Containing 10% Suspended Sediment	43.4	8.90	6.07 - 11.7	1.09	0.772 - 1.81

***Calculated based on the quantity of observed low molecular weight fluorochemical containing degradation products divided by the quantity of fluorochemical containing functionalities initially present in the polymer. **Measured half-lives were calculated using applicable first-order kinetic equations based on production of low molecular weight fluorochemical containing degradation products and the quantity of fluorochemical containing functionalities initially present in the polymer.**

P-04-174 Absorbed to Moist Soil

"Photolytic Degradation of P-04-174 on Soil Surfaces" 3M Environmental Laboratory Report #E05-0665. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 11/03/06
Experimental Summary: This study was based on guideline requirements listed in OECD Draft Document "Phototransformation of Chemicals on Soil Surfaces", January 2002 and was augmented by procedures developed in the 3M Environmental Laboratory based on literature studies of related materials. Three soils types representing the general classes of loam, clay and a sandy loam were studied. The soil thin-layers were prepared by applying a 5µL aliquot of approximately 100 ppm P-04-174 in THF to approximately 5 grams soil spread evenly an 11 in^2 glass plate and was dried in an oven at 70°C for 10-30 minutes to remove solvent. Once dry, the glass plate was placed into an FTIR cell modified with a quartz window to allow light to pass into the cell. The cell was then filled with a simulated

atmosphere of water saturated laboratory air. For selected samples, 1.8 ppm ozone was added to the cell, giving a final simulated atmospheric concentration of approximately 100 ppb ozone. The light source (xenon, filtered to give light over the range of 290-800 nm) was then turned on for a measured amount of time and the intensity was correlated to the actinic solar intensity at 37° south latitude. Multiple sample time points were examined for soil type. In general, once the reaction period was over, all sample sets had a portion of the atmosphere removed for analysis by GC/MS and all soil samples were extracted for analysis by HPLC/MS. Targeted degradation products were PFBS, N-MeFBSE Alcohol, N-MeFBSA, FBSA, PFBA, PFBSI, N-MeFBSAA, C4 Hydride, and Octafluoro-2-butene (*cis and trans*).
Result: From samples exposed to simulated sunlight from an artificial light source equivalent to 95.95 days at 37° South latitude, it was determined that P-04-174 will photolyze on all soil types tested. Table 3 shows the distribution and relative percentages of degradation (assuming 100% total conversion of the polymer to each specific degradation product). Degradation to form the C-4 Hydride and the C-4 Olefin was not observed. Samples exposed to an atmosphere containing ozone showed no appreciable difference compared to those samples exposed without ozone.

Table 3. Distribution and Relative Percentages of Degradation of the Polymer P-04-174 Coated onto Soil Surfaces

Soil Type	PFBA	FBSA	PFBS	N-MeFBSA	N-MeFBSE-Alcohol	PFBSI	N-MeFBSAA	Total Degradation
Sandy Loam	1.32%	0.189%	0.279%	1.24%	5.79%	0.333%	0.035%	9.19%
Loam	2.64%	0.174%	0.382%	0.590%	5.36%	0.414%	0.022%	9.59%
Clay	2.22%	0.155%	0.280%	0.372%	8.54%	0.554%	0.028%	12.15%

Half-lives of P-04-174 at 37° South Latitude Solar Spectral Direct Irradiance (12-hour days) were: Loam, 1.81 years (1.41-2.50), Sandy Loam, 1.89 years (1.51-2.51) and Clay 1.41 years (1.01-2.23).

F-12286 (SRC-220) Coated on to Porours Brick Material

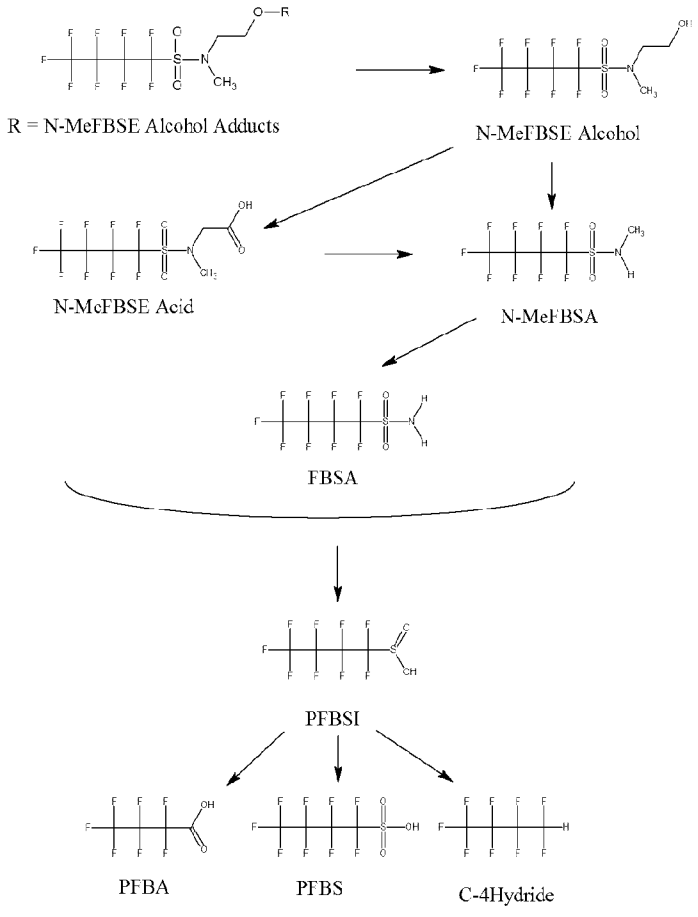
"Photolysis Studies on the Fluorochemical Formulation FC-12286 Coated Onto Porous Brick Material". 3M Environmental Laboratory Report #E03-0733. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 05/20/04
Experimental Summary: The methodology used in this report followed a procedure developed in the 3M Environmental Laboratory based on

literature studies of related materials. Samples of FC-12286 were coated onto bricks of known surface area and exposed to simulated sunlight in a reaction chamber for 36 hours in the reactor or approximately 57 days of Southeast USA sunshine. Humidity was controlled in the reaction cell to duplicate environmental conditions. Real time Fourier Transform Infrared Spectroscopy (FTIR) analysis of the atmosphere in the reaction chamber for volatile degradation products was conducted with samples pulled at the end of the exposure period for analysis of volatile degradation products by GC/MS. Surface Reflectance FTIR (SR-FTIR) analysis was conducted on the bricks before and after exposure. Bricks were extracted post exposure with THF for analysis by HPLC/MS. Targeted degradation products were PFBS, N-MeFBSE Alcohol, N-MeFBSA, PFBA, FBSA, PFBSI, C4-Hydride and Octafluoro-2-butene (*cis and trans*).
Result: It was determined that F-12286 will photolyze to form N-MeFBSA with a half-life of 12.0 years. This study also showed formation of two large but unidentified molecules (1500+ AMU) that contained the C_4F_9-functionality.

Photolysis Conclusions

3M manufactured polymers functionalized with N-Methylperfluorobutanesulfonamide groups fall into the four general classes of acrylates, ethers, urethanes or urethane-ester hybrids. Studies using slight modifications to existing standard OECD/EPA methods (necessary to study polymers rather than small molecules) have shown little differences in the degradation route of these polymers as compared to standard hydrocarbon based polymers. Beginning with the acrylate/urethane functionality, there is oxidative bond cleavage resulting in formation of an alcohol. These studies indicate that the alcohol is in turn degraded by successive oxidations that ultimately lead to formation of perfluorobutanesulfonite, with the rate of formation being matrix dependant. Only at this point does the photolysis of these polymers differ from the hydrocarbon cousins. Once the carbon-sulfur bond of perfluorobutanesulfonite is ruptured, it is believed the reactive C_4F_9 radical anion may react to form PFBS, PFBA or 1H nonafluorobutane. The sequences for these reactions are shown in Figure 7.

Figure 7. Photolytic Decomposition Pathway of N-Methylperfluorobutane-sulfonamide Functionalized Polymers



3.0 Biodegradation

Introduction

Biodegradation (or Catabolism) is the breakdown of organic materials by microbial organisms into smaller compounds through metabolic or enzymatic process in order to produce energy and/or salvage components.[D18] The organic material can be degraded aerobically (with oxygen, ultimately forming CO_2 and H_2O) or anaerobically (without oxygen, ultimately forming methane and water). Biodegradation of water-soluble or water-immiscible materials is necessary because they will eventually enter streams or ground water which can neither be recycled nor incinerated. Tests for biodegradation are used to aid in predicting how quickly and completely chemicals will break down in the environment. However, most tests underestimate a chemical's ability to biodegrade if they do not examine real-world factors, such as the effects of wastewater treatment or microorganism acclimation. Because biodegradability is widely recognized as an indicator of environmental safety, it is crucial that realistic test conditions be used to determine biodegradability.

There have been numerous studies on the biodegradation of polymers. However, many of the studies located in the literature have focused on polymers that are polyhydroxalkyl based materials or were conducted on polymer blends which contained naturally occurring polymers such as starch.[D19] There have been few reported studies on acrylates or urethanes. In all published cases, it was noted that only part of the polymer was biologically available. Due to the lack of studies and difficulties in obtaining relevant results, there are no standard methodologies. Given this, all studies noted in this document were based on standard OECD or EPA methodologies used to study small molecule degradation. Modifications to these methods were made to accommodate the nature of the material such as limited solubilities or relatively slow degradation. Sufficient documentation of these changes are noted in this document to establish study validity. Complete details of any modifications are available in the archived report and/or raw data.

3.1 Aerobic

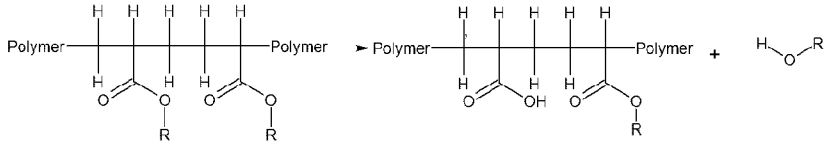
Introduction

Biodegradation is the process that living organisms use to break down organic substances. The organic material can be degraded aerobically, with oxygen or anaerobically, without oxygen. In aerobic biodegradation, the ultimate biodegradation products are carbon dioxide and water although there can be a myriad of intermediates in route to the final products and a number of organisms may be involved. This type of biodegradation occurs mostly in areas where there is oxygen available for use such as lakes, rivers, soils and certain parts of a waste treatment facility. Most polymeric substances are aerobically degraded by one of four common mechanisms; hydrolysis (esterase enzymes), oxidation (H_2O_2 generating enzymes), redox mediators and detoxification by methylation.[D19] Microbial degradation of polymers is dependent on the properties of the polymer such as molecular orientation, crystallinity, cross-linking and chemical groups present in the molecular chains which determine the accessibility to degrading-enzyme systems.[D19] Many microbes are unable to degrade materials with a molecular weight exceeding 1000 AMU, thus limiting degradation to small polymers or smaller polymer fractions within a large polymer.

3.1.1 Acrylates

Based on literature studies of acrylate based polymers, biotic and/or abiotic mediated hydrolysis of the ester linkage with formation of an alcohol would be the first step in degradation as shown in Figure 8.[D20] Biodegradation of the resulting carboxylic acid and the alcohol then follows normal degradation mechanisms and pathways.[D21]

Figure 8. Aerobic Biodegradation Pathway of Acrylate based Polymer



Polymers manufactured by 3M that are addressed in this paper contain N-MeFBSE Alcohol in the R position shown in Figure 8.

Inherent Aerobic Biodegradability of FC-4430

"Inherent Aerobic Biodegradability of the Fluoroaliphatic Polymeric Ester FC-4430" 3M Environmental Laboratory Report E02-0913. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 01/31/03

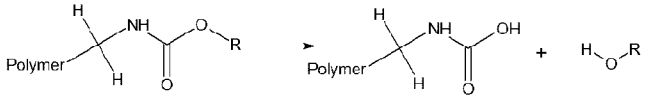
Experimental Summary: The polymeric substance FC-4430 (a fluoropolymer ester) was tested in cultures containing sewage sludge in a mineral salts medium at a concentration of 85 mg/L. Abiotic (no sludge) control cultures and inhibited cultures (containing the antibiotic Chloramphenicol) were included in the study design, as were positive controls containing the biodegradable test substance sodium dodecyl sulfate. Cultures were incubated for 28 days, with sample analysis on days 0, 7, 14 and 28. Cultures were extracted by SPE and analyzed for anticipated products as MeFBSE Alcohol, MeFBSAA, MeFBSA, FBSA, PFBS and PFBA. The analyte MeFBSAA was quantified using of a surrogate standard curve and was considered semi-quantitative results.

Result: Cultures containing the positive control substance sodium dodecyl sulfate showed rapid degradation as expected, demonstrating the viability of the culture. Abiotic control cultures and inhibited cultures showed no generation of low molecular weight components. Cultures containing the fluoropolymer ester FC-4430 demonstrated biodegradation based on the quantities of measured anticipated degradation products. Residual MeFBSE Alcohol was present at day-0 as 26% of the theoretical yield based on fluorine content of the dosed polymer. The major product formed at day-28 was MeFBSAA at 63% of the theoretical yield based on fluorine content of the dosed polymer. Other products observed at low levels were MeFBSA, FBSA, PFBS and PFBA. PFBA was determined to be 0.37% of the theoretical biotransformation yield at day 28.

3.1.2 Urethanes

Based on literature studies of urethane based polymers, biotic and/or abiotic mediated hydrolysis of the ester linkage with formation of an alcohol would be the first step in degradation as shown in Figure 9.[D21,D22] Biodegradation of the resulting carboxylic acid then follows normal degradation mechanisms and pathways.[D20]

Figure 9. Aerobic Biodegradation Pathway of Urethane based Polymer



Polymers manufactured by 3M that are addressed in this paper contain N-MeFBSE Alcohol in the R position shown in Figure 7.

Inherent Aerobic Biodegradability of L18105

"Inherent Aerobic Biodegradability of the Fluoroaliphatic Urethane Polymer L18105" 3M Environmental Laboratory Report E02-1139. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 06/03/03

Experimental Summary: The polymeric substance L-18105 was tested in cultures containing sewage sludge in a mineral salts medium at a concentration of 85 mg/L. Abiotic (no sludge) control cultures and inhibited cultures (containing the antibiotic Chloramphenicol) were included in the study design. A positive control containing the biodegradable test substance sodium dodecyl sulfate was used to demonstrate viability of the culture. Cultures were incubated for 28 days, with collections on days 0, 7, 14 and 28. Cultures were extracted by SPE and analyzed for anticipated products as MeFBSE Alcohol, MeFBSA, MeFBSA, FBSA, PFBS and PFBA.

Result: Cultures containing the test substance sodium dodecyl sulfate showed rapid degradation of that control substrate. Abiotic control cultures and inhibited showed no degradation. Cultures containing the fluoropolymer urethane L-18105 demonstrated less than 1% total biodegradation based on the measured anticipated products versus the theoretical yields as determined from fluorine content of the polymer. The products observed to form at low levels were MeFBSE Alcohol, MeFBSAA, FBSA, PFBS and PFBA. PFBA was 0.0422% of theoretical biotransformation yield at day 28.

Aerobic Biodegradability of P-04-174 with Sewage Sludge

"Aerobic Biodegradability of Fluorochemical Polymer P-04-174 with Sewage Sludge". Environmental Laboratory Report E05-0628. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 10/31/06

Experimental Summary: The fluoropolymer based test substance P-04-174 was added at a nominal concentration of 1.50 mg/L (ppm) to 10 mL of microbiological test cultures that contained municipal wastewater treatment sludge in a mineral salts medium. Cultures were prepared as a multiple shake flask batch-style study. Samples from individual cultures were collected post-incubation on days 0, 3, 7, 14, 20, 29 and 41. Equivalently prepared control cultures containing sterile-sludge or no-sludge (abiotic controls) were included and incubated in parallel with active-sludge test cultures. A positive-control substance sodium dodecyl sulfate (SDS; 10 mg/L) was also tested. A rapid preparation procedure coupled to a sensitive liquid chromatography tandem mass spectrometric (LC/MS/MS) analytical method was used to analyze cultures for the predicted and potentially stable degradation products N-MeFBSE Alcohol, N-MeFBSAA, MeFBSA, FBSA, PFBS, PFBSI, PFBA and the SDS.

Result: A small percentage of the P-04-174 mixture was inherently biodegradable and formed quantifiable amounts of the anticipated end-products. Based on calculated theoretical molar yields of C4F9 equivalents, determined from total fluorine data for P-04-174, a maximum of 9.20 mole-% of the P-04-174 was biotransformed under aerobic conditions over 41 days, forming PFBS as the ultimate end-product. The majority of the biodegradation of P-04-174 occurred within the first 2 weeks of the study and two transient intermediates were formed (PFBSI and N-MeFBSAA). Both of the transient intermediates eventually were further biotransformed to PFBS. N-MeFBSE alcohol was measured in some cultures, but was not consistent with being a biodegradation product. Other potential biodegradation products were not measured in any cultures. Biodegradation had ceased by day-29 based on a leveling off of PFBS formed.
An effort to force biodegradation of the remaining non-degraded P 04-174 fluoropolymer in those cultures, was attempted by adding an 18X sludge addition to a small subset of cultures at day 29. That subset of replicate cultures was incubated for 0, 7 and 12 additional days, and incubated in parallel with non-modified cultures from the original study design for comparability. This resulted in a small increase of ~ 20% in PFBS concentration, with a maximum of 9.20 mole-percent PFBS in sludge-modified cultures, versus a maximum of 7.90 mole-percent measured in cultures that did not receive fresh sludge. The degradation of P-04-174 was definitively the result of microbiological activity in the sludge and likely the result of biodegradation of only a fractional component(s) of the polymer mixture. The bulk of the P-04-174 fluoropolymer (~90 %) appeared to be recalcitrant to microbiological degradation Under the identical test conditions employed for testing P-04-174 biodegradability, the positive control substance SDS was readily biodegraded with complete loss of the SDS in active cultures by day-3 of incubation, proving that the test conditions were adequate for evaluating biodegradability. SDS was rapidly biodegraded when co-incubated with the test substance P-04-174, demonstrating P-04-174 did not significantly inhibit biodegradation activity. The biodegradation of P-04-174 and SDS were not observed in any of the abiotic or sterile-sludge control cultures, demonstrating that the degradation of P-04-174 in active-sludge cultures was biological in nature. Additionally, the penultimate biodegradation product PFBS, and transiently formed PFBSI and N-MeFBSAA, were not observed in the blank control cultures during the course of the study, demonstrating they were derived from P-04-174 biodegradation, and not from any other component of the test system.

Aerobic Biodegradability of P-04-174 with Freshwater Sediment

"Aerobic Biodegradability of Fluorochemical Polymer P-04-174 with Freshwater Sediment". Environmental Laboratory Report E05-0629. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 12/08/06

Experimental Summary: The fluoropolymer based test substance P-04-174 was added at a nominal concentration of 1.50 mg/L (ppm) to 10 mL of microbiological test cultures that contained freshwater lake sediment in a microbiological mineral salts medium. Cultures were prepared as a multiple shake flask batch-style study. Cultures were collected on post-incubation days of 0, 6, 13, 20, 34, 47 and 61. Equivalently prepared control cultures containing sterilized-sediment or no sediment (abiotic controls) were included and incubated in parallel with active-sediment cultures. Additionally, a positive-control substance sodium dodecyl sulfate (SDS; 10 mg/L) was tested to verify the efficacy of the test system. A rapid preparation procedure coupled to a sensitive liquid chromatography tandem mass spectrometric (LC/MS/MS) analytical method was used to analyze the cultures for the predicted and potentially stable degradation products N-MeFBSE Alcohol, N-MeFBSAA, MeFBSA, FBSA, PFBS, PFBSI, PFBA and the SDS.

Result: A small percentage of the P-04-174 mixture was inherently biodegradable and underwent primary biodegradation (e.g. biotransformation) to form quantifiable amounts of anticipated perfluorinated end-products. Based on calculated theoretical molar yields of C4F9 equivalents as determined by total fluorine data for P-04-174, between 6.78 mole-% (day 61) and 9.23 mole-% (day 20) of the P-04-174 was biotransformed under aerobic conditions. The majority of the biodegradation of P-04-174 happened within the first week of the study with formation of two transient intermediates PFBSI and N-MeFBSAA. Both of the transient intermediates eventually were further biotransformed to PFBS, the primary end-product at day-61. The analyte N-MeFBSE alcohol was measured in abiotic cultures, but not in active-sediment or sterile-sediment cultures, and was consistent with being a P-04-174 hydrolysis product. This hydrolysis occurred within the first week with 1.64 mole-% of P-04-174 hydrolyzed at day-6 and a maximum of 2.01 mole% of P-04-174 hydrolyzed by day-47. Other potential degradation products were not detected in any cultures as biological or abiotic degradation products. Biodegradation of P-04-174 appeared to cease by day-6 based on total molar concentration of fluorochemical products formed. The majority of the degradation of P 04-174 was definitively the result of microbiological activity in the active-sediment and likely the result of biodegradation of only a fractional component(s) of the polymer mixture. The bulk of the P-04-174 fluoropolymer (> 90 %) appeared to be recalcitrant to microbiological degradation with freshwater sediment as the microbial inoculum. Under the identical test conditions, the readily biodegradable positive control substance SDS was completely degraded in active cultures by day-6 of incubation, but was not degraded in sterile-sediment or abiotic controls, establishing that the test conditions were adequate for evaluating biodegradability. The SDS was also rapidly biodegraded when co-incubated with the test substance P-04-174, demonstrating that P-04-174 did not significantly inhibit biodegradation activity. The biodegradation of P-04-174 and SDS were not observed in equivalent sterile-sediment control cultures, demonstrating that the degradation of P-04-174 in active-sediment cultures was biological in nature. Additionally, the penultimate biodegradation product PFBS, and transiently formed PFBSI and MeFBSAA, were not observed in blank control cultures during the course of the study, demonstrating they were derived from P-04-174 biodegradation, and not from any other component of the test system. Based on these results, less than 10% of P-04-174 mixture undergoes primary biodegradation over 61 days of incubation with aerated freshwater lake sediment as the microbial inoculum, and biodegradation occurs with penultimate formation of the stable end-product PFBS. P-04-174 appears to contain a small percentage of material at approximately 2.01 mole-% that is susceptible to hydrolysis in this media and liberates N-MeFBSE Alcohol as a product.

3.2 Anaerobic

Introduction

Anaerobic biodegradation, in contrast to aerobic biodegradation does not utilize oxygen in the transformation process. In anaerobic biodegradation, the final products are water and methane and as with aerobic biodegradation, the can be a myriad of intermediates in route to the final product and there are often more than one organism involved in the transformations. This type of biodegradation occurs in landfills, deep underground, deep in sediment and in certain parts of compost composts and soils.

3.2.1 Urethanes

Only one reference on anaerobic biodegradation was located that specifically deals with polymers.[D23] In that reference, only general pathways were discussed, target specific information beyond CO_2 and CH_4 generation was not available. Studies noted below therefore represent the only target specific anaerobic degradation studies conducted to date on urethane polymers.

Anaerobic Biodegradability of P-04-174 with Anaerobic Digester Sludge

"Anaerobic Biodegradability of Fluorochemical Polymer P-04-174 with Anaerobic Digester Sludge". Environmental Laboratory Report E05-0627. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 12/07/06

Experimental Summary: During this study the fluoropolymer test substance P-04-174 was added at a nominal concentration of 1.50 mg/L to 4 mL of municipal anaerobic digester sludge and 1 mL of sterile 10 mg/mL aqueous yeast extract solution in sealed 40 mL vials. Equivalently prepared control cultures containing either sterilized-sludge or no sludge (abiotic controls) were similarly prepared and incubated in parallel with the active-sludge cultures. A set of cultures with 2,4,6-trichlorophenol (TCP; 2.5 mg/L) were prepared to evaluate the efficacy of the anaerobic biodegradation test system. All cultures were prepared and incubated within a sealed glove box under an atmosphere of pure N_2 and held at 25°C. Cultures were collected on post-incubation days of 0, 7, 14, 21, 35, 57 and 121. All cultures were incubated static, but with light mixing at each collection time to ensure homogeneity of the cultures over the course of the study. Gas production within culture headspaces was monitored throughout the study and at day-21 the headspace gas of several test and control cultures was analyzed by static gas-phase FTIR to verify methane and carbon dioxide formation. A rapid preparation procedure coupled to a sensitive liquid chromatography tandem mass spectrometric (LC/MS/MS) analytical method was used to prepare cultures and to measure for the predicted and potentially stable degradation products N-MeFBSE Alcohol, N-MeFBSAA, MeFBSA, FBSA, PFBS, PFBSI, PFBA and to measure the control substance TCP and its anticipated anaerobic biotransformation product 4-chlorophenol (4-CP). Additionally, at day-121, the headspaces of several cultures were analyzed by a sensitive GC/MS method for any potential volatile fluorochemical products.

Results: This study demonstrated that methanogenic anaerobic cultures were established, as evidenced by methane and carbon dioxide production in the active cultures. Analysis of culture extracts by LC/MS/MS showed that P-04-174 underwent primary anaerobic biodegradation with formation of N-MeFBSE Alcohol as a transient intermediate. By the conclusion of the 121 day study, 7.71 mole-% of P-04-174 was biodegraded to two end-products, N-MeFBSAA (3.87 mole-%) and PFBSI (3.84 mole-%). Other anticipated fluorochemical products not observed. P-04-174 biodegradation was definitively the result of microbiological activity since it did not occur in sterile-sludge controls or in abiotic control cultures. However, a low level non-biological formation of N-MeFBSE Alcohol was observed in sterile-sludge and abiotic controls after 35 days of incubation, demonstrating that some hydrolysis of P-04-174 likely occurred. This hydrolytic degradation was calculated at less than 2 mole-% of theoretical P-04-174 degradation.

Biodegradation of the control substrate TCP was complete by day 35 and was coincident with equimolar formation of the anticipated dechlorination product 4 CP, thus demonstrating the efficacy of the anaerobic biodegradation test system for testing biodegradability. The TCP was similarly biotransformed when co-incubated with P-04-174, and methanogenic activity appeared unaffected based on gas formation, suggesting that P-04 174 did not

significantly inhibit anaerobic microbiological activity. Additionally, PFBSI and N-MeFBSAA were not produced in blank control cultures during the course of the study, establishing that the were anerobic biotransformation products and not part of the test system.

Anaerobic Biodegradability of P-04-174 with Anaerobic Sediment

"Anaerobic Biodegradability of Fluorochemical Polymer P-04-174 with Anaerobic Sediment". Environmental Laboratory Report E05-0630. Study conducted in accordance the TSCA Good Laboratory Practices Standards, 40 CFR 792. Completed on 12/08/06

Experimental Summary: During this study the fluoropolymer test substance P-04-174 was added at a nominal concentration of 1.50 mg/L to anaerobic cultures which consisted of 4 mL of < 0.250 mm sieved lake sediment suspended in water and with 1 mL of sterile 10 mg/mL aqueous yeast extract solution under an atmosphere of pure N2 at 25°C. Equivalently prepared control cultures containing either sterilized-sediment or no sediment (abiotic controls) were similarly prepared and incubated in parallel with active-sediment cultures. Additionally, a set of cultures with a control substance 2,4,6-trichlorophenol (TCP; 2.5 mg/L) added was prepared to evaluate the efficacy of the anaerobic biodegradation test system. The cultures were collected on post-incubation days of 0, 11, 22, 43, 78, 103 and 119. All cultures were incubated static, but with light mixing at each collection time to ensure homogeneity of the cultures over the course of the study. Gas production within culture headspaces were monitored throughout the study and at day-103 the headspace gas of several test and control cultures was analyzed by static gas-phase FTIR to verify methane and carbon dioxide formation. A rapid preparation procedure coupled to a sensitive liquid chromatography tandem mass spectrometric (LC/MS/MS) analytical method was used to prepare cultures and to measure the predicted and potentially stable degradation products N-MeFBSE Alcohol, N-MeFBSAA, MeFBSA, FBSA, PFBS, PFBSI, PFBA and to measure the control substance TCP and its anticipated anaerobic biotransformation product 4-chlorophenol (4-CP). Additionally, at day-78 the headspaces of several cultures were analyzed by a sensitive GC/MS method to monitor for potential volatile fluorochemical products.

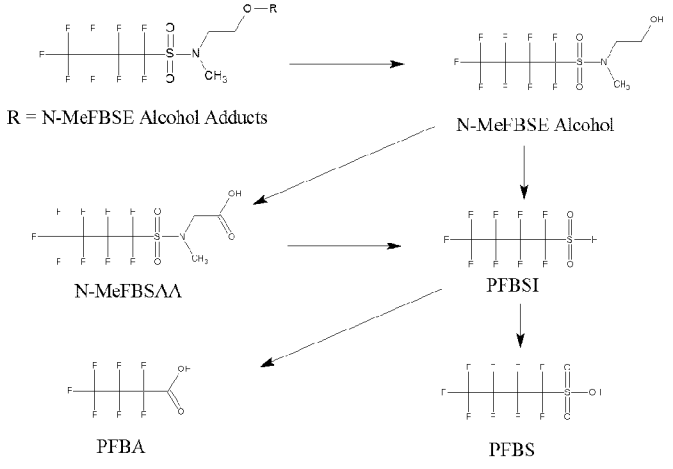
Results: This study demonstrated that methanogenic anaerobic cultures were successfully established, as evidenced by methane and carbon dioxide production in active cultures. The analysis of culture extracts by LC/MS/MS showed that P 04 174 was inherently biodegradable under anaerobic conditions and underwent primary biodegradation to form N-MeFBSE Alcohol (2.87 mole-%). No other predicted degradation product was observed during the coarse of this study. N-MeFBSE alcohol was not formed in abiotic or sterile-sediment cultures. GC/MS analysis of culture headspaces at day-78 showed no volatile fluorocarbon formation from the sediment incubations.

Biodegradation of the control substrate TCP occurred completely by day 11 in active-sediment cultures and was coincident with equimolar formation of the anticipated dechlorinated biotransformation product 4 CP, thus demonstrating the efficacy of the anaerobic biodegradation test system. Unexpectedly, the 4-CP that formed thru day-43 disappeared after 78 days, indicating it too had biodegraded further. The TCP was similarly biotransformed in sediment cultures when co-incubated with P-04-174, and methanogenic activity appeared unaffected by the presence or absence of P-04-174 based on similar amounts of gas formation. Additionally, MeFBSE alcohol did not form in blank control cultures during the course of the study, demonstrating that it was derived from P-04-174 biodegradation and not from the test system.

3.3 Biodegradation Conclusions

Biodegradation of polymers functionalized with N-MeFBSE Alcohol occurred in all media tested. In a matrix dependent fashion, the products were: N-MeFBSE Alcohol, N-MeFBSAA, PFBSI and PFBS. Based on these studies, there appears to be limited availability of biodegradable substrates within the polymers. As a hypothesis, it appears that a significant portion of each polymer is simply to large to undergo biological degradation.

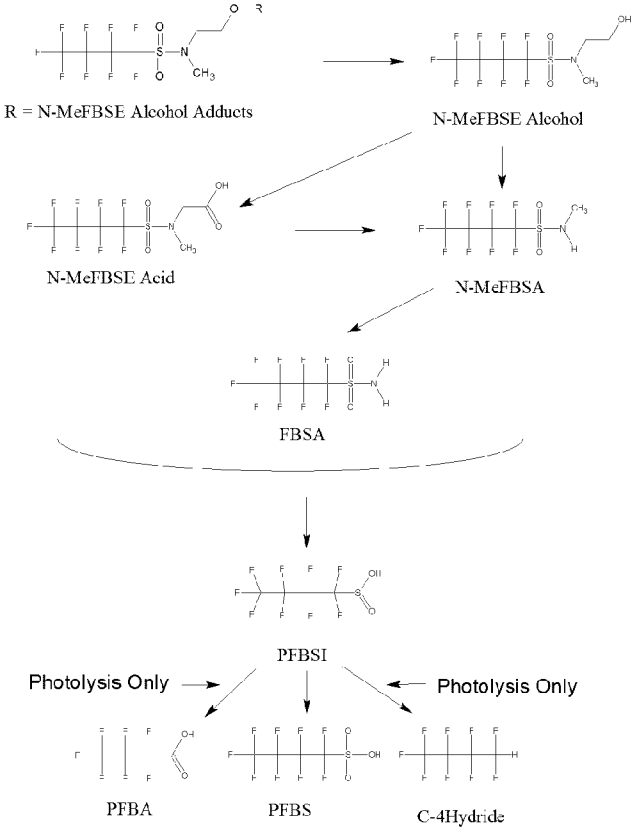
Figure 10. Biodegradation pathway of Perfluorobutanesulfonamide Based Materials



4.0 Conclusions

This chapter has examined studies for all major degradation pathways of N-MeFBSE Alcohol functionalized polymers. While there are a large number of these studies used to determine the extent of degradation of these unique materials, the results are not a t all unanticipated. Known and established degradation pathways of hydrocarbon-based materials have been examined and compared with those of fluorochemical-containing polymers. Evaluation of the data shows that the first degradation step for hydrocarbon and fluorochemical containing polymers is the same - generation of large polymer fragments and small polar molecules. It is only in degradation of the smaller molecules that the two pathways differ: hydrocarbons may be ultimately degraded to form water, carbon dioxide and methane while the functionalized polymers will form predominantly PFBS but also small amounts of C-4 hydride and PFBA. A generalized degradation pathway of perfluorobutanesulfonamide functionalized polymers is shown in Figure 11 based on hydrolysis, photolysis, aerobic and anaerobic degradation studies.

Figure 11. Degradation Pathway of Perfluorobutanesulfonamide Based Materials



The rate of degradation and the distribution of small molecule degradants depends upon the polymer type, the size of the polymer, the mode of release to the environment and the compartment of the environment in which it partitions.

Fluorinated Sulfonic acids and derivatives (PFAS):

PFAS Section 1 - PFBS

EXECUTIVE SUMMARY

Introduction

This document describes the physical and chemical properties, degradation, and ecotoxicology information generated for perfluorobutane sulfonate (PFBS). PFBS is a chemical that is the potential degradation product of certain substances based on perfluorobutane sulfonyl fluoride chemistry. PFBS is a fully fluorinated four-carbon organic molecule produced synthetically by electrochemical fluorination, other processes, and from the degradation or metabolism of other four-perfluorocarbon products or derivatives.

PFBS is not metabolized but is excreted rapidly and has very low toxicity in acute and repeat-dose tests. Further, it does not affect reproductive function or prenatal development. Although it is persistent in the environment, PFBS does not accumulate in organisms. As a chemical with low toxicity that does not bioaccumulate, PFBS does not meet the criteria for designation of a PBT chemical under the USEPA PBT Chemical policy.

PFBS-based products fall into the broad category defined by PFAS (Perfluoro Alkyl Sulfonates, carbon chain length from C1 to C20 or greater). Because properties vary significantly depending on the carbon number or chain length, the environmental, health and safety characteristics of members of this class of substances must be reviewed on an individual basis. 3M has studied the potential hazards of perfluoroalkyl sulfonates with higher carbon numbers or chain lengths (e.g., C_6 and C_8), and this information has enabled 3M to focus its research with respect to PFBS.

Environmental Characteristics

PFBS is non-volatile and highly soluble in water. Thus, any PFBS in water would be expected to remain in the water column rather than volatilizing to air. PFBS does not partition to sediment. It does not bioconcentrate; the steady-state bioconcentration factor in bluegill sunfish was found to be less than 1. It is not degraded by hydrolysis or photolysis, although it is degraded by high-temperature incineration.

Acute and chronic ecotoxicology studies with a number of aquatic species show no or minimal toxicity at quite high concentrations (> 100 mg/L). Acute NOEC values for all species evaluated for ecotoxicity ranged from 127 to 5,620 ppm, while chronic NOEC values ranged from 200 to 502 ppm. Aquatic organisms tested include two invertebrate species and two fish species, as well as algae and wastewater treatment bacteria. The most sensitive aquatic species tested was the mysid shrimp, with the 96-hour acute no-observed-effect concentration (NOEC) determined to be 127 mg/L. Fifty percent clearance from fish was estimated at 1 to 3 days.

In acute avian feeding studies, no mortality was seen with mallard duck or bobwhite quail after exposures as high as 10,000 mg PFBS/kg feed. In a six-week pilot reproduction feeding study with five pairs of bobwhite quail, a NOEC concentration of 200 mg PFBS/kg feed for six weeks was determined based on egg production. A 21-week definitive reproduction study with 16 pairs of Bobwhite Quail determined the NOEC to be 900 mg/kg feed, which is

equivalent to an average daily dose of 87.8 mg PFBS/kg body weight/day. No treatment-related mortalities, overt signs of toxicity, histopathology, or treatment-related effects upon body or liver weight or feed consumption were seen at any of the concentrations tested. There were no treatment-related effects upon any of the reproductive parameters measured. The difference in egg production between the pilot and definitive studies is thought to be an artifact of length of exposure, sample size and the replacement of a hen during the pilot study.

Given the fact that PFBS did not bioconcentrate in organisms to levels greater than the concentrations to which they were exposed and the very low toxicity to aquatic and avian species, no adverse effects on the environment or biota are expected.

Conclusion

This report is a technical summary of the ecological toxicity and fate data accumulated for PFBS as of July 2008. Although PFBS is resistant to degradation and is persistent in the environment, results from environmental testing demonstrate that PFBS is not acutely or chronically toxic to aquatic or avian organisms at concentrations less than 100 ppm. The acute NOEC values for all species evaluated for ecotoxicity ranged from 127 to 5,620 ppm, while chronic NOEC values ranged from 200 to 900 ppm. PFBS does not bioconcentrate and does not bioaccumulate. Thus, adverse ecological effects are not expected. Results from numerous mammalian toxicity studies indicate that PFBS has low toxicity in both acute and repeat dose studies. Further, it does not affect reproductive function or prenatal development. PFBS is cleared from the body in fish and primates within days. Exposures are expected to be low. The data indicate the potential toxicity and ecological impacts of PFBS are minimal.

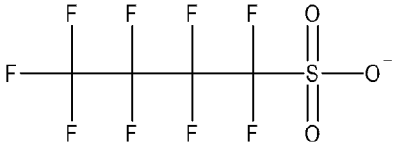
PHYSICAL/CHEMICAL PROPERTIES

Testing described in this document, except where noted, was conducted utilizing the potassium salt of PFBS (CAS No. 29420-49-3). Because the salt is transformed immediately to the anion when dissolved, the results describe the anion as well.

Identity:

Molecular formula: $C_4F_9SO_3^-$

Structural formula:



Synonyms: 1-Butanesulfonate, 1,1,2,2,3,3,4,4,4-nonfluoro

Vapor Pressure

Vapor pressure was evaluated in the laboratory utilizing the Spinning Rotor Gauge method, following OECD guideline 104. Hexachlorobenzene and DDT were successfully used as method reference substances. The vapor pressure of the potassium salt of PFBS was below the method detection limit, and was reported as $<1.22 \times 10^{-5}$ Pa @ 20°C.[1]

Dissociation constant

Perfluoroalkyl sulfonic acids are considered to be strong acids (super acids) and will exist at 100% dissociation when dissolved in aqueous media. A literature citation and Hammett acidity value ($H_o = -13.2$) for PFBS have been reported for the acid dissociation value measured in non-aqueous media by UV spectrophotometry at 22° C.[2]

Solubility

The shake flask method (OPPTS 830.7840 and OECD 105) was used to determine the water solubility of the same lot of PFBS, potassium salt at two different laboratories. Both studies were conducted following Good Laboratory Practice guidelines. Preliminary and definitive tests were conducted at both laboratories, and the concentration of PFBS in the water was measured. At 20° C, solubility was reported as 46,200 mg/L, and at 22.5 – 24° C as 52,600 – 56,600 mg/L.[3,4]

The solubility of PFBS in methanol and acetone was also estimated using the shake flask method. These studies were conducted in one laboratory, and only the preliminary test was conducted. A sample of 10 mg of PFBS was visually determined to be dissolved in 100 µL of each solvent after shaking, vortexing, and sonicating.[4]

Surface Tension

Static surface tension measurement of PFBS in water, was measured at 37 dynes/cm using standard Wilhelmy Plate methodology (1 x 2 cm plate) on a Krüss K12 at ambient pressure and 21° C[5].

Critical Micelle Concentration

A critical micelle concentration for PFBS was determined to be 50,000 mg/L from a graph of the surface tension versus the log of the concentration. The measurements were made using standard methodology at ambient pressure and 21° C using a Krüss K12 and Dosimat 665[6].

PHYSICAL PROPERTIES

Table 1-1 Physical and Chemical Properties

Parameter	Report Date	Results
Vapor Pressure[14]	4/29/02	< 1.22 x 10^{-5} Pa @ 20 °C
Dissociation Constant[15]	1976 (lit. value)	Hammett Value H_o = -13.2
Solubility in Pure Water[16,17]	8/30/00, 3/28/01	46,200 mg/L at 20°C 52,600 - 56,600 mg/L at 22.5 – 24° C
Solubility in Methanol[4]	3/28/01	> 10%
Solubility in Acetone[4]	3/28/01	> 10%
Surface Tension[18]	1/14/2002	37 dynes/cm
Critical Micelle Concentration[19]	1/14/2002	50,000 mg/L

ENVIRONMENTAL FATE

Degradation

Laboratory studies of hydrolysis, photolysis and biodegradation were not carried out to evaluate the degradability of PFBS. PFBS is expected to be stable under environmental conditions based on its chemical structure and by analogy to the stability of longer chain perfluoroalkyl sulfonates. Given the strength of the chemical bonds in the molecule and the complete fluorination, PFBS is not expected to biodegrade or to undergo hydrolysis or photolysis[7,8].

Incineration studies were conducted utilizing a laboratory-scale simulation of a hazardous waste incinerator to evaluate the destruction of two perfluorobutanesulfonyl polymers and PFBS salt at temperatures of up to 900° C. Quantifiable amounts of PFBS were not formed during the combustion of the polymers. Results of chemical analyses indicated that, with the exception of stable C_1 and C_2 fluorocarbons, fluorinated organic intermediates are unlikely to be emitted during the incineration of PFBS or perfluorobutane sulfonamides. Thermal

degradation under high temperature conditions, such as those occurring during incineration is the only known degradation mechanism for PFBS[9].

Table 2-1 Degradation of PFBS

Parameter	Report Date	Results
Hydrolysis[20]	7/22/02	Half life estimate > 41 years
Photolysis[21]	7/22/02 (amended 3/24/04)	Half life estimate ≥ 3.7 years
Biodegradation	Not Tested	Non-biodegradable
Thermal Degradation[22]	1/7/03	No PFBS was formed during combustion studies of two perfluorobutanesulfonyl polymers. Results suggest the C-S bond was completely destroyed and did not reform.

Partitioning

The air/water partition coefficient (K_{AW}) was calculated using the laboratory-generated vapor pressure and water solubility data (see Table 1-1). The result from the water solubility study conducted at 20° C was used in this calculation. The log K_{AW} was found to be < -10.4.[10]

A soil adsorption/desorption study was conducted following OECD Guideline 106. Three soils (loam, clay loam, and clay), one sediment and one washed, powdered, lyophilized NIST sludge were used in the study. Results from the Tier 1 and 2 testing demonstrated that PFBS did not adsorb to the walls of the test vessels. In Tier 3 testing, the three soils and one sediment were tested at a solid to solution ratio of 1:1, while the sludge was tested at a ratio of 1:5. Study results demonstrated no adsorption of PFBS to soils or sediment and minimal adsorption to sludge. Freundlich isotherm calculations were performed using the sludge results only. The sludge adsorption K_f was found to be 0.3 and the desorption K_f was 0.001. The initial PFBS concentration in solution was found to be independent of the determined sorption value. The study results indicate that PFBS tends not to sorb to soils, sediments, and sludge.[11]

An objective of study (3M Environmental Lab Study E07-0521) was to evaluate the adsorption of PFBS from water to a number of different mineral surfaces that are summarized in Table 2-2. The tests were done to determine the adsorption capacity of the mineral surfaces as a function of the equilibrium concentration of each fluorochemical in water and may also be used to assess the equilibrium adsorption coefficient of each fluorochemical on the given mineral surface. The test water used was a groundwater that contained a mixture of fluorochemicals and had a nominal pH between 7 and 8. Several of the mineral surfaces had known pH_{zpc} values, below this pH value the mineral surface has a net positive charge, and above this value the mineral surface has a net negative charge. At the pH used in this study PFBS would be present in the solutions as an anion. Solutions of each mineral surface in the test water were prepared from nominally from 0.1 to 100 gm/L.

The initial concentration of PFBS in the groundwater prior to the addition of the mineral surfaces was nominally 20 ng/mL. As summarized in Table 2-3, except for adsorption on diatomaceous earth, less than 5% of the total mass of fluorochemical was associated with the mineral phase. For PFBS, and only at the highest solids loading, 30% of the total mass was associated with the mineral phase. Overall these data indicate that the adsorption capacity of these surfaces for PFBS is minimal, and it is not expected that these surfaces would greatly retard the transport of these compounds in the subsurface. In this regard these data should be used to more formally assess the aqueous/solid distribution of these compounds at an actual field location by considering the actual solids/water ratio and the aqueous concentration of the fluorochemical.

Table 2-2. Summary of Adsorbents and their pH_{zpc}

Adsorbent	**pH_{zpc}**
Iron Oxide (Fe_2O_3) (Hematite)	6.9
Iron Oxide (FeO(OH) (Goethite)	9.4
Aluminum Oxide (α-Al_2O_3)	8.3
Mississippi River Sand	Likely Between 1 and 3
Silica Gel	Likely Between 1 and 3
Bentonite	
Diatomaceous earth	

Table 2-3 Summary of isotherm experiments conducted using PFBS in groundwater.

		PFBS		
Adsorbent	Dry Mass of Adsorbent Placed into 30 mL vial	Equilibrium Aqueous Concentration Cw (ng/mL)	Equilibrium Solid Concentration Cs (ng/gm)	Fraction of Total Mass Associated with Solid Phase
Bentonite	0.0048	19	3,397	2%
Bentonite	0.0289	19	N/A	<1%
Bentonite	0.3184	18	80	4%
Diatomaceous Earth	0.0026	18	8,773	3%
Diatomaceous Earth	0.0342	19	N/A	<1%
Diatomaceous Earth	0.2922	17	199	10%
Diatomaceous Earth	3	13	61	32%
Fe2O3 (Hematite)	0.0012	18	18,788	3%
Fe2O3 (Hematite)	0.0275	18	1,251	5%
Fe2O3 (Hematite)	0.3158	20	N/A	<1%
Fe2O3 (Hematite)	3.1	19	N/A	<1%

FeO(OH) (Goethite)	0.0066	18	4,730	5%
FeO(OH) (Goethite)	0.0315	18	1,109	5%
FeO(OH) (Goethite)	0.3191	20	N/A	<1%
FeO(OH) (Goethite)	3	20	N/A	<1%
Mississippi Sand	0.0052	19	2,385	2%
Mississippi Sand	0.0263	19	555	2%
Mississippi Sand	0.3253	20	N/A	<1%
Mississippi Sand	3	20	N/A	<1%

A flow-through biocencentration study following OECD Guideline 305 was conducted using juvenile bluegill sunfish (*Lepomis macrochirus*) at exposure concentrations of 0.53 and 5.2 mg/L. The uptake and depuration periods were 28-days and 16-days, respectively. Water, edible, and non-edible fish tissues were analyzed for PFBS concentration. Concentrations in whole fish were calculated based on concentrations in edible and non-edible portions. Calculations of bioconcentration factor (BCF) at apparent steady state and BCFK (kinetic bioconcentration factor) were completed using concentrations of PFBS in edible tissue, non-edible tissue, and whole fish, for both exposure concentrations. BCF values at apparent steady state in edible tissues ranged from 0.16 – 0.21, in non-edible tissues from 0.43 – 0.51, and in whole fish from 0.30 – 0.38. BCFK values in edible tissues ranged from 0.18 – 0.73, in nonedible tissues from 0.50 – 0.86, and from 0.36 – 1.1 in whole fish. Time to 50% clearance was estimated to be from 1.3 – 2.9 days, using BIOFAC computer software.[12]

Table 2-4 Partitioning Test Results

Parameter	Report Date	Results
Log Air-Water Partition Coefficient (log K_{AW}), calculated from water solubility and vapor pressure[23]	6/18/02	< -10.4
Soil and Sediment Adsorption/Desorption[(a)24]	3/08/01	No adsorption to any soil or sediment seen. (K_f = 0.0) Highly mobile
Activated Sludge Adsorption/Desorption[(a)11]	3/08/01	Freundlich K_f(ads) = 0.3 Freundlich K_f(des) = 0.001 Highly mobile
Bioconcentration (Bluegill Sunfish, steady-state BCF) Exposed to 0.53 mg/L[25]	5/09/01	Edible Tissue BCF: 0.21 Non-edible Tissue BCF: 0.51 Whole Fish BCF: 0.38
Bioconcentration (Bluegill Sunfish, steady-state BCF) Exposed to 5.2 mg/L[12]	5/09/01	Edible Tissue BCF: 0.16 Nonedible Tissue BCF: 0.43 Whole Fish BCF: 0.30

[a]Soil types utilized were clay, clay loam, loam, river sediment, powdered and dried activated sludge from NIST.

The water solubility and soil, sediment, and sludge adsorption/desorption data indicate that any PFBS discharged to a water source would tend to remain in the water column as opposed to binding to sediment.

Bioconcentration test data indicate that PFBS will not partition preferentially from water into fish tissues, and therefore, that PFBS will not bioaccumulate or biomagnify in fish.

The very low vapor pressure and calculated air/water partition coefficient indicate that volatility of the compound is insignificant. Therefore, atmospheric dispersion of PFBS is considered unlikely.

Ecotoxicology Studies

Microbial Systems

PFBS was not toxic to wastewater treatment bacteria at 1,000 mg/L, the highest concentration tested. The study was conducted following OECD guideline 209, and utilized activated sludge from a wastewater treatment plant that receives waste from predominantly domestic sources. After 3 hours of exposure, a concentration-response curve was not evident over 7 nominal test concentrations of PFBS spanning from 1.0 to 1,000 mg/L. The 3-hour EC_{50} was determined to be > 1,000 mg/L, with 8.2% inhibition in respiration seen at 1,000 mg/L. [26]

Algae

PFBS inhibited algal growth only at very high doses (greater than 1,077 mg/L). Testing was conducted using the freshwater green alga, *Selenastrum capricornutum*. Cells were exposed for 96 hours, with microscopic counts taken at 24, 48, 72, and 96 hours. The NOEC and EC_{50} values were calculated using three methods to determine inhibition: 1) cell density; 2) area under the growth curve; and, 3) average specific growth rate. Exposure concentrations were measured at 0, 72 and 96 hours.

The data indicate PFBS was algistatic at the highest level tested; i.e., growth resumed when aliquots of the algae in the maximally inhibited concentration was placed in fresh growth media. Observations of algae cells during the studies found that there were no signs of aggregation, flocculation or adherence of the cells to the flasks after exposure. Calculations utilizing cell density and area under the curve resulted in lower effective concentrations than those using average specific growth rate. However, as the rate of growth, not cell mortality, appeared to be affected in these studies, algae NOEC (1,077 mg/L) and EC_{50} (5,733 mg/L) values reported here were calculated using the average specific growth rate.[27]

Acute Toxicity to Aquatic Invertebrates

The static acute toxicity of PFBS to a freshwater (*Daphnia magna*) and a marine (*Mysidopsis bahia*) aquatic invertebrate were determined. In the daphnid study, two replicates, each containing 10 daphnids, were exposed for 48-hours. Exposure concentrations were determined at 0, 24, and 48 hours. The effect concentrations were calculated using mean measured concentrations. The 48-hour NOEC and EC_{50} were determined to be 886 mg/L and 2,183 mg/L, respectively.[28]

The marine mysid study was also conducted in duplicate, with 10 mysids per vessel exposed for 96 hours. Exposure concentrations were determined at 0, 48, and 96 hours. The mysid 96-hour NOEC and EC_{50} were determined to be 127 mg/L and 372 mg/L, respectively.[29]

Chronic Toxicity to Aquatic Invertebrates

A static-renewal survival, growth and reproduction toxicity study was conducted utilizing *Daphnia magna.* There were no adverse effects on survival, reproduction, or growth at concentrations $\leq$ 502 mg/L after 21 days (NOEC = 502 mg/L). Survival was reduced at 1,876 mg/L, while growth and reproduction were reduced at 995 mg/L. Mean measured concentrations were determined from fresh and previous solutions during each week of the test.

In the course of this study, the young produced by the control, 60, 121, 247, 502 and 995 mg/L exposure groups were removed from the test chambers on Day 14. Due to reduced survival at the 1,876 mg/L concentration, there were insufficient offspring from this treatment group to study. They were exposed to the same concentrations to which the respective first-generation adults were exposed. Survival was monitored for 48 hours. After 48 hours of exposure, survival in all treatment groups (control, 60, 121, 247, 502, and 995 mg/L) was 100%. The results of the daphnid second-generation acute exposure indicated a NOEC of 995 mg/L.[30]

Acute Toxicity to Fish

Two species of fish were evaluated for 96-hour static acute toxicity: fathead minnow (*Pimephales promelas*) and the bluegill sunfish (*Lepomis macrochirus*). The fathead minnow was more sensitive, with an LC_{50} of 1,938 mg/L and a NOEC of 888 mg/L. An LC_{50} of 6,452 mg/L and a NOEC of 2,715 mg/L were reported in the bluegill study. At 96 hours, all surviving fish of both species appeared normal. Exposure concentrations were measured at 0, 48, and 96-hours.[31,32]

Acute Avian Feeding Studies

Study Design

Acute feeding studies were conducted using 8-day-old mallard ducks (*Anas platyrhynchos*) and 10-day-old northern bobwhite quails (*Colinus virginianus*). Each species was offered the dosed feed for 5 days, followed by untreated feed until Day 22. Doses were reported on a nominal concentration basis for five dose levels (1,000; 1,780; 3,160; 5,620; and 10,000 ppm) plus the negative control group. There were 12 animals per PFBS treatment group and 30 for the negative controls. Homogeneity of test substance concentrations in diet was

verified. On Day 8, one-half of the treatment and control bird groups were sacrificed, subjected to gross necropsy, and liver weights were determined. Liver and sera samples were taken from quail exposed to the two highest concentrations (5,620 and 10,000 mg/kg) and were analyzed for PFBS to help determine the concentrations to use in pending reproduction studies. The remaining half of the birds continued without further treatment until Day 22, when the birds were sacrificed, subjected to gross necropsy, and liver weights were obtained.

Results: Mallard Duck (*Anas platyrhynchos*)

There was no mortality from PFBS in mallard ducks at any of the doses tested. The dietary LC_{50} value for mallard ducks was > 10,000 mg/kg feed. Based on a statistically significant ($p < 0.01$) reduction in body-weight gain at the 10,000 mg/kg feed concentration on Day 5 of exposure, the NOEC was 5,620 mg PFBS/kg feed. The mallards exposed to 10,000 mg PFBS/kg feed gained 84 g in weight, while the control birds gained 107 g. There were no overt signs of toxicity or treatment-related effects on feed consumption or liver weights at any of the concentrations tested. No treatment-related necropsy findings were observed. Mallard liver and serum were not analyzed for PFBS.[33]

Results: Bobwhite Quail (*Colinus virginianus*)

There was no treatment-related mortality from PFBS in bobwhite quail at any of the doses tested. The dietary LC_{50} value for quail was > 10,000 mg/kg feed. Based on statistically significant ($p < 0.01$) reductions in body-weight gain after 5 days at the 5,620 and 10,000 mg PFBS/kg feed concentration, the NOEC was 3,160 mg PFBS/kg feed. Quails at the 10,000 mg PFBS/kg feed dose gained 3 grams, those at the 5,620 dose gained 5 grams, while the control quails gained 11 grams after 5 days of exposure. There were no overt signs of toxicity or treatment-related effects on feed consumption or liver weights at any of the concentrations tested. No treatment-related necropsy findings were observed.[34]

PFBS concentrations found in liver and sera taken from the individuals sacrificed on Day 8 are shown in Table 3-1. PFBS did not accumulate to any significant degree in the liver or serum of the bobwhite quail. Doses of 10,000 mg/kg in feed resulted in levels of 1.3 ppm in the serum and liver.[35] Despite a nearly two-fold difference in dose, there does not appear to be any proportional difference in serum and liver PFBS concentrations at the two concentrations studied.

Table 3-1. **Summary of Mean Analytical Results for PFBS in Quail Liver Tissue (mg/kg wet) and Serum (mg/L) at Day 8**

Nominal PFBS Conc., mg/L	Day 8 Percent Mortality	Day 8 PFBS Liver Conc., mg/L	Day 8 PFBS Serum Conc., mg/L
Negative Control	0	<LOQ (0.0256 ppb)	<LOQ (0.0254 ppb)
5,620	0	1.36	2.67
10,000	0	1.34	1.26

Avian Pilot (Range-Finding) Reproduction Feeding Study

Five pairs of adult Northern Bobwhite Quail were each exposed to PFBS at nominal dietary concentrations of 75, 200, 550, or 1,500 mg PFBS/kg in feed for 6 weeks. The birds were observed for mortality, behavior, signs of toxicity, and egg production. At the end of treatment, all birds were euthanized and subjected to gross necropsy. Liver weights were also obtained. Studies demonstrating homogeneity of test substance concentrations in diet were conducted and the results served as verification of test substance concentrations. None of the control diet samples showed any indication of the presence of the test substance.

No treatment-related mortalities or overt signs of toxicity were observed at any of the concentrations tested. All necropsy findings were considered to be unrelated to treatment. There were no treatment-related effects on body weight or feed consumption at the 75, 200, or 550 mg/kg level. There were slight but consistent reductions in male body weight and feed consumption in the 1,500 mg/kg treatment group. There were reductions in mean egg production at the 550 and 1,500 mg/kg test concentrations and reductions in female liver weight at the 1,500 mg/kg test concentrations. The NOEC in this study was determined to be 200 mg/kg based on egg production. It should be noted that the egg production was significantly lower in Pen 322 than that of the other pens in 1500 ppm dose group. In this pen, the female was euthanized on day 3 due to non-treatment related neck injury. This female was replaced with another that had been acclimated with the other birds to the test conditions. However, egg production in this pen consistently lagged behind that of the other pens exposed to 1500 ppm in the diet. Egg production for the other four pens was higher than that than that seen in the 550 ppm dose group. In a study with such a small sample size (n = 5 females per dose), a change in response from one animal can significantly affect statistical evaluation and may not be representative of a true effect. It is uncertain if a true dose-response relationship is demonstrated in this study. The results of this study were used to set feed concentrations for a definitive reproduction study with the Bobwhite Quail.[36]

Avian Definitive Reproduction Feeding Study

Study Design

Sixteen pairs of adult Northern Bobwhite Quail were each exposed to PFBS at nominal dietary concentrations of 0 (control), 100, 300 and 900 mg PFBS/kg feed for 21 weeks. The birds were observed for mortality, behavior, signs of toxicity, eggshell thickness and egg production. Hatching success and hatchling survivability were also monitored. At the end of treatment, all surviving adult birds were euthanized and subjected to gross necropsy. Samples of liver, kidney and gonad from all adult birds and selected offspring from each pen were collected and submitted for histopathological examination. Liver weights were also obtained. Samples of sera and liver were obtained from adults and select offspring at the end of the study and were analyzed for PFBS concentrations. Egg homogenates (at least seven eggs per dose) were also analyzed. Studies demonstrating homogeneity of test substance concentrations in diet were conducted and the results served as verification of test substance concentrations. None of the control diet samples showed any indication of the presence of the test substance.

Results: Bobwhite Quail (*Colinus virginianus*)

No treatment-related mortalities, overt signs of toxicity or treatment-related effects upon body or liver weight or feed consumption were seen at any of the concentrations tested. Except for incidental findings, all birds appeared to be normal in appearance and behavior throughout the study. There were no treatment-related effects upon any of the reproductive parameters measured, including egg production, hatching success and hatchling survivability. All necropsy and histopathological findings were incidental and considered to be unrelated to treatment. The overall estimated daily doses in this study (calculated utilizing feed consumption and body weight) were 0 (negative control), 9.7, 29.7, and 87.8 mg PFBS/kg body weight/day. The NOEC (no-observed-effect concentration) for Northern Bobwhite quail exposed to PFBS in the diet was 900 mg PFBS/kg diet, the highest concentration tested. This corresponds to an average daily dose of 87.8 mg PFBS/kg body weight/day.[37]

PFBS concentrations found in liver and serum samples are shown in Table 3-2. Low levels were detected in negative control liver (range 0.00945 – 0.129 mg/kg) and serum (0.0209 – 2.8 mg/kg). None of the egg samples from the negative control group contained measurable levels of PFBS. Concentrations in the liver, serum, eggs, and offspring tended to increase with increasing dose. Doses at the NOEC of 900 mg/kg in feed resulted in mean PFBS levels of 16 – 30 ppm in adult liver and 68 to 104 ppm in adult serum. Offspring liver and serum values were less than 0.4 ppm at all doses. Mean concentrations in egg homogenates from the 900 ppm dose ranged from 51 to 92 ppm.[38]

Table 3-2. **Summary of Mean (and Range) PFBS Concentrations in Quail Liver Tissue, Serum and Egg Homogenates at Study Termination**

Nominal PFBS Conc., mg/kg feed	PFBS Liver Conc., mg/kg	PFBS Serum Conc., mg/kg	PFBS Egg Conc., mg/kg*
100, male	**3.25** (0.808 – 8.89)	**16.5** (5.81 – 37.7)	
100, female	**3.52** (0.396 – 8.19)	**14.6** (2.49 – 33.1)	**7.65** (lot B), **14.0** (lot G) (4.92 – 10.8 lot B), (8.44 – 26.2 lot G)
100, offspring	**0.0211**** (<0.0137 – 0.0301)	**0.0369**** (<0.0278 – 0.0552)	
300, male	**7.78** (1.42 – 14.2)	**27.9** (14.2 – 42.9)	
300, female	**11.1** 3.57 – 23.5)	**37.8** (12.2 – 102)	**23.6** (lot B), **31.4** (lot G) (13.3 – 36.5 lot B), (16.1 – 73.1 lot G)
300, offspring	**0.0515**** (0.0138 – 0.200)	**0.0567** (0.0245 – 0.119)	
900, male	**15.7** (6.73 – 23.7)	**68.2** (34.3 – 98.8)	
900, female	**29.6** (9.73 – 77.4)	**104** (30.5 – 370)	**50.5** (lot B), **92.6** (lot G) (33.8 – 118 lot B), (52.6 – 137 lot G)
900, offspring	**0.111**	**0.133**	

	(0.0340 – 0.313)	(0.0413 – 0.320)	

*Eggs were collected twice during the study
**The mean was calculated for only those samples in which PFBS was detected.

Table 3-3 Ecotoxicity of PFBS

Organism	Effect/Endpoint[a]	Result
Wastewater Bacteria (OECD 209)	3-hour EC_{50}	> 1,000[b] mg/L
Selenastrum capricornutum (freshwater green algae, now called Pseudokirchneriella subcapitata)	Growth Rate 96-hour NOEC	1,077 mg/L
	Growth Rate 96-hour E_rC_{10}	1,674 mg/L
	Growth Rate 96-hour E_rC_{50}	5,733 mg/L
Daphnia magna (freshwater water flea)		
	Acute 48-hour NOEC	886 mg/L
	48-hour EC_{50}	2,183 mg/L
	21-day Semi-static Life-cycle Test NOEC	502 mg/L
Mysidopsis bahia (mysid shrimp)	Acute 96-hour NOEC	127 mg/L
	Acute 96-hour LC_{50}	372 mg/L
Pimephales promelas (fathead minnow)	Acute 96-hour NOEC	888 mg/L
	Acute 96-hour LC_{50}	1,938 mg/L
Lepomis macrochirus (bluegill sunfish)	Acute 96-hour NOEC	2,715 mg/L
	Acute 96-hour LC_{50}	6,452 mg/L
Anas platyrhynchos (mallard duck)	Dietary (5-days) acute NOEC (body weight gain)	5,620[b] mg/kg[c]
	Dietary (5-days) acute no mortality concentration	10,000[b] mg/kg[c]
	Dietary (5-days) LC_{50}	> 10,000[b] mg/kg[c]
Colinus virginianus (bobwhite quail)	Dietary (5-days) acute NOEC (body weight gain)	3,160[b] mg/kg[c]
	Dietary (5-days) acute no mortality concentration	10,000[b] mg/kg[c]
	Dietary (5-days) LC_{50}	> 10,000[b] mg/kg[c]
	Dietary pilot (6 week) reproduction NOEC (mean egg production)	200[b] mg/kg[c]
	Dietary definitive (21-week) reproduction NOEC (survival, reproduction)	900[b] mg/kg[c]

[a] All results calculated using mean measured concentrations except where noted
[b] Results based on nominal concentrations; sample well characterized
[c] Reported as mg PFBS per kg feed

Summary of Ecotoxicology

PFBS exerted minimal toxicity to the wide range of organisms studied. The most sensitive species tested was the mysid shrimp, *Mysidopsis bahia*, with a 96-hour acute NOEC of 127 mg/L and an acute LC_{50} of 372 mg/L. This acute LC_{50} value is well above 100 mg/L, the concentration threshold above which the USEPA's OPPT classifies chemicals to be of low concern for TSCA 8(e) reporting. This concentration (100 mg/L) is also recommended by the OECD Guidelines for the Testing of Chemicals as the highest to be used in acute aquatic toxicity limit tests.

Environmental Hazard Evaluation

Laboratory data indicate that the environmental hazard of PFBS is low. The most sensitive endpoints in aquatic and terrestrial acute and chronic toxicity testing are at concentrations greater than 100 parts per million.

PFBS does not appear to bioconcentrate, and therefore, exposure through the food chain is unlikely.

Based on the very low to negligible hazard, the rapid clearance as demonstrated in the fish bioconcentration and monkey studies, and the low exposure potential, no adverse environmental or ecological effects are expected from PFBS.

CONCLUSION

This report is a technical summary of the ecological toxicity and fate data accumulated for PFBS as of June 2005. Although PFBS is resistant to degradation and is persistent in the environment, results from environmental testing demonstrate that PFBS is not acutely or chronically toxic to aquatic or avian organisms at concentrations less than 100 ppm. The acute NOEC values for all species evaluated for ecotoxicity ranged from 127 to 5,620 ppm, while chronic NOEC values ranged from 200 to 502 ppm. PFBS does not bioconcentrate and does not bioaccumulate. Thus, adverse ecological effects are not expected. Results from numerous mammalian toxicity studies indicate that PFBS has low toxicity in both acute and repeat dose studies. Further, it does not affect reproductive function or prenatal development. PFBS is cleared from the body in fish and primates within days. Exposures are expected to be low. The data indicate the potential toxicity and ecological impacts of PFBS are minimal.

PFAS Section 2 – PFBSI

Chapter 1 Fluorinated Sulfonates and derivatives

Section 2

Perfluorobutanesulfinic acid (PFBSI)

Summary of Test Results

Introduction and Description of CAS number

Physical Properties

- Melting Point
- Boiling Point
- Vapor Pressure
- Density
- Dissociation Constant
- Refractive Index

Environmental Fate and Pathways

- Degradation
- Partitioning

Ecotoxicity

- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation and aquatic toxicology information in our possession for perfluorobutanesulfinic acid (PFBSI), a metastable intermediate on the final degradation product of many current 3M products. 3M manufactures the ammonium salt of PFBSI as an initiator for fluoropolymerization (CAS# 187480-45-1) and has produced the potassium salt as an internal standard for analytical reference (CAS# 40630-28-2). PFBSI is transient in the environment due to the ease of oxidation of the perfluoroalkyl sulfinate to perfluoroalkyl sulfonate (PFBS). PFBS is persistent but not considered to be PBTs (persistent, bioaccumulative, and toxic) under the USEPA PBT Chemical policy.

As PFBSI is a perfluorinated alkyl derivative it falls into the category of Materials of Public Interest (MPI) and falls in the broad category defined by PFASs (perfluoroalkyl sulfonates with carbon chain length from C1 to C20). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length and functional group.

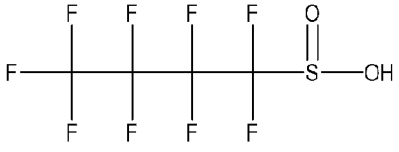
Identity:

Chemical Name: 1-Butanesulfinic acid, 1,1,2,2,3,3,4,4,4-nonfluoro-

CAS Number: 34642-43-8

Molecular formula: $C_4HF_9O_2S$, fwt = 284.1

Structural formula:



Synonyms: **PFBSI, C4 sulfinic acid,**

PHYSICAL/CHEMICAL PROPERTIES (PFBSI)

Physical and Chemical Properties		
Parameter	**Source**	**Results**
Melting Point		Liquid at ambient temperature
Boiling Point[39]	Tetrahedron 2005	**64-65 °C (1 mmHg) (Estimated =212 °C at 760 mmHg)**
Vapor Pressure		**0.04 mmHg @ 25 °C (Estimated)**
Density		**Jay?**
Dissociation Constant		**Jay?**
Water solubility		**1.2 mg/L (Estimated)**
Refractive Index[40]	JLSCBF 1973	**1.332 @ 20 °C**

Fluorinated Carboxylates:

Chapter 2 Fluorinated Carboxylates
Section 1
Trifluoroacetic acid (TFA)
Summary of Test Results

Executive Summary
Physical/Chemical Properties
- Melting Point
- Boiling Point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive Index
- Surface tension
- Dielectric constant
- Heat of vaporization

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

EXECUTIVE SUMMARY

Introduction

This document describes the physical/chemical properties, degradation and aquatic toxicology information currently in our possession for trifluoroacetic acid (TFA), a chemical formerly marketed by 3M as FC-21 (L-2621) as well as the final degradation product of many current 3M products. TFA is highly persistent but not considered to be PBT (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

TFA is a material of public Interest (MPI) and falls in the broad category defined by PFCAs (perfluorocarboxylates with carbon chain length from C1 to C20). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

Environmental Characteristics

TFA is both volatile and highly water soluble. It generally does not sorb strongly to soil. The Henry's Law constant indicates that TFA would exhibit intermediate to low volatility from water to air and will undergo rainout if released to the atmosphere. There is a potential for transport long distances in the atmosphere. At environmental pH (between 5 and 9), the predominant species will be the trifluoroacetate anion (CF_3COO^-) which will tend to remain dissolved in water. TFA does not hydrolyze, photolyze or readily biodegrade although there is evidence that anaerobic biodegradation can occur. Studies with plants found some bioaccumulation potential (BCFs $\leq$27), although it is possible that these values are due to TFA being pulled into shoots due to either transpiration or xylem flow. The aquatic environment is the likely sink for TFA.

There is as yet no agreement about the possibility of natural sources of TFA in the environment. Results from some sampling programs indicate it is possible, while others do not.

Acute ecotoxicology studies with microbes (aerobic, nitrogen-fixing and methanogenic bacteria), fish, daphnia and a number of aquatic plants and algae are available. These demonstrated low to moderate toxicity with the exception of the green alga, *Pseudokirchneriella subcapitata.* There is as yet no accepted explanation as to why this species is so much more sensitive.

Studies with terrestrial plants found sensitivity similar to that seen by *P. subcapitata* in beans, sunflower and wheat. It was found that the most significant route of terrestrial plant uptake is from the soil, not from direct exposure of wet deposition to leaves.

Conclusion

This report is a technical summary of the available ecotoxicological and environmental fate data found for TFA as of July, 2008. Although TFA is generally resistant to degradation (except possibly for anaerobic biodegradation), studies indicate that it is not acutely toxic to fish, daphnia, microbes, aquatic plants and most algae. The green alga, *Pseudokirchneriella*

subcapitata and three terrestrial plants were shown to be sensitive to acute exposures to TFA at concentrations between 1 and 10 ppm. Bioconcentration values for plants, soil invertebrates and microbes were found to be low (<30). Although TFA has the potential for long-range transport, bioavailability does not appear to be as high from wet deposition to plant leaves as it does to soil. Water column sampling indicate concentrations of 200 ng/L (parts per trillion), well below effect concentrations for green plants.

DRAFT

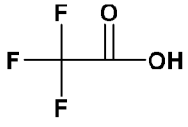
Identity:

Chemical Name: 1,1,1-trifluoroacetic acid

CAS Number: 76-05-1

Molecular formula: $C_2HF_3O_2$, fwt = 114

Structural formula:



Synonyms: TFA , Perfluoroacetic acid, trifluoroacetic acid, trifluoroethanoic acid, HTFA

PHYSICAL/CHEMICAL PROPERTIES (HTFA)

Physical and Chemical Properties		
Parameter	**Source**	**Results**
Melting Point	**Tech. Bull. 10Jan60**	**-15.6 °C**
Boiling Point	Tech. Bull. 10Jan60	**71.1 °C (734 mmHg)**
Vapor Pressure	Tech. Bull. 10Jan60 Tech. Bull. 10Jan60 Boutonnet et al 1999	**191 mmHg @ 37 °C,** **625 mmHg @ 66.7 °C,** **110 mmHg @ 20 °C**
Density	Tech. Bull. 10Jan60	**1.4890 @ 20 °C** **1.4224 @ 50 °C**
Dissociation Constant	Boutonnet et al 1999	**0.23**
Water solubility ***(need to add endnotes)***	Boutonnet et al 1999	**> 10 g/mL; miscible in all proprotions**
Viscosity	Tech. Bull. 10Jan60	**0.622 cps @ 20 °C** **0.427 cps @ 50 °C**
Refractive Index	Tech. Bull. 10Jan60	**1.2850 @ 20 °C**
Surface tension	Tech. Bull. 10Jan60	**15.0 dynes/cm @ 20 °C**
Dielectric constant	Tech. Bull. 10Jan60	**42.1 @ 25 °C**
Heat of vaporization	Tech. Bull. 10Jan60	**8300 cal/mole at b.p.**

Environmental Fate and Pathways

Trifluoroacetic acid is considered to be a strong acid, with a $pK_a = 0.23$[41]. At any pH greater than about 3, the concentration of the acid form will be negligible. Under environmentally significant conditions where the pH is between 5 and 9, the predominant species of

"trifluoroacetic acid" will be as the trifluroacetate anion, TFA^- (CF_3COO^-). It should be understood that under most conditions, the material will be present in the ionic form.

TFA can be transported via atmospheric water. Wet deposition will result in exposure to the aquatic environment. Higher concentrations of TFA have been noted in fog rather than rain, with fog deposition responsible for up to 90% of the total deposition in forests. Dry deposition of atmospheric TFA appears to be the main route of entry to surface areas of arid environments[42].

Several biodegradation studies under both reducing (anaerobic) and oxidizing (aerobic) conditions have been conducted with TFA using sediments, soils and sludge as the inoculum source. One study (cited as Visscher *et al.*, 1994), using anaerobic marine sediment incubated with ^{14}C-labeled TFA showed reductive defluorination and formation of DFA, MFA, acetate and methane under methanogenic and sulfate-reducing conditions. However, this has only been seen one time in one laboratory, in certain samples, and has not been replicated by either the same laboratory or other researchers. Another study showed sustained and long-term loss of 25 – 30% of the incoming [1-^{14}C] TFA in the first (methanogenic) chamber in a sequential column microcosm. However, the researchers were not able to determine what transformation product(s) were formed. It is possible that the lost TFA was actually complexed in a way that it just wasn't recoverable[43].

Kim et al. (2000) evaluated the degradation of TFA in a 90-week continuous flow experiment using laboratory-scale anaerobic reactors containing a mixed culture of naturally occurring microorganisms and ethanol. They observed an increase in fluoride concentration in the effluent after making stepwise increases in the TFA influent concentration. Fluoride was not detected in the influent. When they reached a high (inhibitory) concentration of TFA in the influent, they also saw DFA and MFA in the effluent along with undegraded ethanol. The authors concluded that anaerobic biodegradation of TFA by naturally occurring anaerobic bacteria is possible[44].

Aerobic biodegradation studies were also conducted by several researchers. Evidence for decarboxylation of TFA was seen when pure cultures of microbes were pregrown on very specific substrates (toluene or 4-chlorobenzoate). The cells only demonstrated decaroboxylation after they were harvested from their solvent-enriched media, concentrated and resuspended in fresh media with TFA. They lost the ability to transform TFA very quickly after resting. In an aerobic microcosm inoculated with a composite of soil samples from geographically diverse regions of the globe, no production of $^{14}Co_2$ was seen from [1-^{14}C] TFA. An evaluation of nine strains of bacteria known to contain monooxygenase enzymes capable of inserting oxygen into aliphatic and aromatic hydrocarbons was conducted. The results showed that even with cultures capable of quickly degrading trichloroethylene within 24 hours, there was no detectable decarboxylation or dehalogenation of TFA after 13 days[45].

Benesch et al., 2002, found no degradation of TFA in vernal pool soils held in aerobic microcosms and exposed for three months[46]. Ellis et al., 2001, found no degradation if TFA in field microcosms with exposure for up to one year[47].

TFA is not readily or inherently aerobically biodegradable. A closed bottle test found 0% biodegradation and a modified SCAS test showed 20% loss of TFA after 84 and 27 days, respectively days. However, no fluoride was found in either the SCAS effluent or in the closed bottles[48].

There is some evidence of defluorination and decarobxylation of TFA in a few laboratory studies. It appears possible that there could be some biodegradation of this substance in the environment, particularly under anaerobic conditions. However, to date, this has not been proven.

Some bioaccumulation has been seen in studies with terrestrial plants. It is believed that the TFA is transported into the shoots from the roots via either flow due to transpiration or xylem flow[49] and left behind when the water exited the plant. When plants were removed to clean media, clearance was seen. At concentrations at or below the no effect level of 1 mg/L, literature bioconcentration factors ranged from 5.4 to 27[50]. It should be noted that growth dilution and root excretion will result in the reduction of plant TFA concentrations while leaf fall from deciduous plants is an ultimate removal mechanism. Because TFA will exist in the ionic form at environmental pHs, octanol/water partition coefficient values are not relevant for estimation of bioconcentration potential.

There are contradicting conclusions from studies evaluating the potential for natural sources of TFA in the environment. Ocean sampling found TFA to be homogeneously distributed throughout the water column from water of all ages at a concentration of 200 ng/L. This concentration is much higher than can be accounted for by current and historic anthropogenic production and implies that there is a natural source of TFA within the oceans However, other studies contradict this finding, reporting no detectable TFA in ancient ground water and ice samples[51].

Degradation of TFA		
Parameter	**Report Date**	**Results**
Hydrolysis	Solvay, 1996	No hydrolysis at 95°C, pH 12, 6.5 weeks[a]
Photolysis	Solvay, 1996 Boutonnet, 1999	No photolysis (UV)[a] No absorption at $\lambda > 250$ nm[b]
Biodegradation	Boutonnet, 1999 Solvay, 1996 Benesch et al., 2002 Kim et al. 2000	Not readily or inherently biodegradable.[a,b] Not aerobically biodegradable[c] Evidence of anaerobic biodegradability[d]
Thermal Degradation		
a. Solvay communication[52] b. Boutonnet (Ed)., 1999[53]		

c. Benesch, J.A. et al., 2002[54] d. Kim, B.R. et al. 2000[55]		

Partitioning Test Results		
Parameter	**Report Date**	**Results**
Henry's Law Constant	Boutonnet,1999	K_H = 1.1 x 10^{-2} Pa·m^{-3}·mol^{-1} @ 25°C[a]
Octanol Water	Boutonnet, 1999 Solvay, 1996	Log Kow = -2.1[a] Log Kow = -4.1[b]
Estimated BCF	Boutonnet, 1999	Microbes and soil invertebrates – low BCF range in plants: 5.4 to 27[a]
Soil and Sediment Adsorption/Desorption	Boutonnet, 1999	Varies greatly with soil organic content. Range of Kd from <2 (highly mobile) to 20 (60% retention). The highest Kd was seen in a peat core which contained 93% organic matter.[a]
a. Boutonnet (Ed)., 1999[56] b. Solvay communication[57]		

The high water solubility in combination with a low estimated Henry's Law Constant and generally low soil adsorption means that trifluoroacetic acid will undergo rainout when released to the atmosphere. This suggests that TFA is capable of being dissolved in water droplets, transported long distances in the atmosphere, and being deposited in precipitation at destinations distant from its point of origin. The aquatic environment is the likely sink for TFA.

ECOTOXICOLOGY STUDIES

Monosodium TFA exerted low to moderate toxicity to the range of organisms studied with the exception of the green alga, *Pseudokirchneriella subcapitata*. This species (formerly called *Selenastrum capricornutum*) was found to be the most sensitive with a 72-hour E_bC_{50} (biomass integral) and NOEC of 1.5 mg/L and 0.12 mg/L, respectively.

Organism	Effect/endpoint	Result
Bacteria – Mixed aerobic heterotrophs	Respiration rate – 25-day NOEC	10 mg/L[a]
Bacteria - Mixed methanogens	Methane generation/effect	> 1114 mg/L[b]
Bacteria - Mixed nitrifiers	Nitrogen fixation/effect	> 100 mg/L[c]
Freshwater green algae – *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*)	Growth rate 72-hr NOEC	1.2 mg/L[c,d]
	Biomass 72-hr NOEC	0.12 – 0.30 mg/L[c,d]

	Growth rate 72-hour E_RC_{50}	7.7-160 mg/L[c,d]
	Biomass 72--hour E_bC_{50}	1.5 – 4.8 mg/L[c,d]
Freshwater green algae – *Chlorella vulgaris*	Biomass 72-hr NOEC	1200 mg/L[c,d]
	72-hr E_rC50 and E_bC50	>1200 mg/L[c,d]
Freshwater green algae – *Scenedesmus subspicatus*	72-hr E_rC50 and E_bC50	> 120 mg/L[c,d]
Freshwater green algae – *Chlamydomonas reinhardtii*	Biomass 72-hr NOEC	120 mg/L[c,d]
	72-hr E_rC50 and E_bC50	>120 mg/L[c,d]
Freshwater euglena – *Euglena gracillis*	Biomass 192-hr NOEC	112 mg/L[c,d]
	192-hr E_rC50 and E_bC50	>112 mg/L[c,d]
Oraganism/species	**Effect/endpoint**	**Result**
Marine green algae – *Dunaliella tertiolecta*	Biomass 72-hr NOEC	124 mg/L[c,d]
	72-hr E_rC50 and E_bC50	>124 mg/L[c,d]
Blue green algae – *Anabaena flos-aquae*	Biomass & growth rate 120-hr NOEC	600 mg/L[c,d]
	120-hr E_rC50 and E_bC50	>2400 mg/L[c,d]
Blue green algae – *Microcystis aeruginosa*	Biomass 144-hr NOEC	117 mg/L[c,d]
	144-hr E_rC50 and E_bC50	>117 mg/L[c,d]
Freshwater diatom – *Navicula pelliculosa*	Biomass & growth rate 96-hr NOEC	600 mg/L[c,d]
	Biomass 96-hrE_bC50	1200 mg/L[c,d]
	Growth rate 96-hrE_rC50	2400 mg/L[c,d]
Marine diatom – *Skeletonema costatum*	Biomass & growth rate 96-hr NOEC	2400 mg/L[c,d]
	96-hr E_rC50 and E_bC50	>2400 mg/L[c,d]
Marine diatom – *Phaeodactylum tricornutum*	Biomass 72-hr NOEC	117 mg/L[c,d]
	72-hr E_rC50 and E_bC50	>117 mg/L[c,d]
Duckweed – *Lemna gibba*	168-hr NOEC (frond and weight increase)	300 mg/L[c,d]
	168-hr EC50 (frond increase)	1100 mg/L[c,d]
Mung Bean	Soil application NOEC	1 mg/kg[e]
	Soil application EC/LC_{50}	5.7 mg/kg[e]
Helianthus annuus (annual sunflower)	Soil application NOEC	< 1 mg/kg[e]
	Soil application EC/LC_{50}	12 mg/kg[e]
	Foliar application NOEC	100 mg/L[e]
Triticum aestivum (wheat)[e]	Soil application NOEC	1 mg/kg[e]
	Soil application EC/LC_{50}	12 mg/kg[e]
	Root exposure (var. Katepwa) NOEC	1 mg/L[e]
	Root exposure var. Hanno NOEC	5 mg/L[e]
	Foliar application NOEC	50 mg/L[e]
Plantago major (plantain)	Root exposure NOEC	32 mg/L[e]
Maize, rice, plantain, sunflower, oilseed rape	Foliar application NOEC	100 mg/L[e]
Soya	Root exposure NOEC	1 mg/L[e]
	Foliar application NOEC	10 mg/L[e]
Ponderosa pine	Morphological or photosynthetic effects NOEC	10 mg/L[e]
	Root exposure NOEC	1 mg/L[e]
Aquatic macrophtytes (*Lemna gibba*, *Myriophyllum sibiricum* and *Myriophyllum spicatum*)	Growth and pigment effects EC50	222 – 10,000 mg/L[f]

Daphnia magna (freshwater water flea)	48-hour NOEC	1200 mg/L[e]
	48-hour EC_{50}	>1200 mg/L[e]
Brachydanio rerio (zebrafish)	96-hour NOEC	1200 mg/[e]L
	96-hour LC_{50}	>1200 mg/L
a. Benesch, J.A. et al., 2002. [58] b. Emptage et al., 1997.[59] c. Boutonnet (Ed)., 1999. [60] d. Berends et al. 1999.[61] e. Benesch and Gustin. 2002.[62] f. Hanson and Solomon. 2004.[63]		

MICROBIAL SYSTEMS

Benesch et al., 2002 studied the effect of TFA exposure on aerobic respiration rate of microbial cultures obtained from the soil from vernal pools. Microcosoms containing samples from differing locations/soil types were exposed to 0, 10, 100, 1000, and 10,000 ug/L TFA solutions, which were added to the soils to achieve an 80% by weight saturation level. No significant consistent difference (reduction) in respiration rates at any TFA exposure level in any soil type was observed when compared to control soils during or after 25 days of exposure[64].

Evidence from some biodegradation studies indicate that it is possible to inhibit aerobic microbial processes, but the concentrations used in the studies were not provided.

Nitrogen-fixing and methanogenic bacteria appear to be rather insensitive to TFA at relatively high concentrations. No adverse effects were seen when three species of free-living nitrogen-fixing bacteria, *Azobacter vinelandii* (common aerobic soil microorganism), *Rhodobacter capsulatus* (freshwater photosynthetic bacterium) and *Clostridium pasteruianum* (common anaerobe) were exposed to concentrations as high as 1 nM (~100 mg/L) TFA[65]. Methanogen populations from an anaerobic digester, rumen, freshwater sediments and marine sediments were not impacted at concentrations of 10 nM TFA[66]

ALGAE

Only one species of algae, *Pseudokirchneriella subcapitata* was very sensitive to TFA. It should be noted that the effect was algistatic and growth resumed when cells were transferred to fresh media. Some evidence exists that exposure to TFA or to monofluoroacetate, a potential degradation product of TFA, results in the inhibition of the citric acid cycle. *P. subcapitata* exposed to TFA showed a recovery of growth when citric acid was added[67]. However, this hypothesis is disputed by Hanson due to the apparent lack of either inorganic or organic means of degrading TFA, which would be required to produce the necessary halocitrate to inhibit the enzyme aconitase. A study where concentrations of citrate were measured after aquatic plants were exposed to a TFA and TCA mixture showed no elevation in citrate levels in the plants, as would be expected if aconitase was being inhibited by either TCA or TFA[68].

ACUTE TOXICITY TO AQUATIC INVERTEBRATES

TFA was not toxic (48-hr EC50 > 1200 mg/L) to *Daphnia magna*, the only invertebrate studied. Another study, showing a 24-hour EC50 of 55 mg/L was conducted using TFA acid (HTFA) without pH adjustment (Solvay, 1996). The results reflect toxicity due to pH, not TFA.

ACUTE TOXICITY TO FISH

Acute toxicity to freshwater fish was evaluated on the Zebra fish (*Brachydanio rerio*). The zebra fish 96 hour LC_{50} was > 1200 mg/L with an NOEC of 1200 mg/L.

TOXICITY TO TERRESTRIAL PLANTS

Several terrestrial crop plants were studied because of the potential for exposure to TFA via wet and dry deposition from the atmosphere.

Benesch and Gustin (2002) evaluated uptake and toxicity to Ponderosa Pine via foliar spraying concentrations of 0, 150 and 10,000 ng/L five days each week for four months. It should be noted that the authors state that global TFA rainwater concentrations are predicted to reach 120 – 450 ng/L by 2010. The spray was prevented from reaching the soil so that only foliar uptake could be studied. They found that needles exposed to 150 ng/L had an increased TFA concentration of 10 +/- 5 ng/g from the starting needle concentration. Needles exposed to 10,000 ng/L had increased foliar concentrations of 300 +/- 150 ng/g over initial. However, neither TFA application had any apparent visual morphological or photosynthetic effects on the trees even after 4 months of exposure.[69]

The most significant route of exposure for terrestrial plants is uptake from the soil. Benesch et al., 2002, exposed plants known to grow in vernal pools (*Polypogon monspeliensis, Deschampsia elongate, Lasthenia californica, and Oryza sativa*) to hydroponic (soiless) concentrations of TFA at 0, 100 and 1000 ug/L. There were no noted toxic effects on germination or growth for up to 150 days after germination. Studies on the germination of seeds produced by the initial (first generation) of these TFA-exposed plants also showed no obvious effects. [70]

It is hypothesized by some that the TFA is carried from the soil via transpiration to the shoots and leaves, where it can concentrate as the water evaporates[71]. Benesch et al., 2002, feel that TFA is not carried in the transpiration stream in a plant, but travels with the mass flow of water up the xylem or is transported across the plasma membrane into the phloem. Their studies also showed that TFA was found to accumulate in foliar tissue as a function of concentration and time, but that concentrations leveled off and/or declined with time. This suggests that plants may have a mechanism for excluding TFA at high but nontoxic exposure concentrations[72].

Section 2
Pentafluoropropanoic acid (PFPA)
Summary of Test Results

Introduction and Description of CAS number
Physical Properties
- Melting point
- Boiling point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive index

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation and aquatic toxicology information in our possession for pentafluoropropanoic acid (PFPA), a chemical formally marketed by 3M as FC-22 as well as the final degradation product of current 3M product(s). PFPA is highly persistent but not considered to be a PBT (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PFPA is a material of public Interest (MPI) and falls in the broad category defined by PFCAs (perfluorocarboxylates with carbon chain length from C1 to C20). Environmental, health and

safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

.

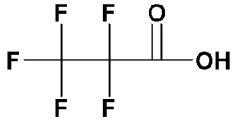
Identity:

Chemical Name: 2,2,3,3,3-pentafluoropropanoic acid

CAS Number: 422-64-0

Molecular formula: $C_3HF_5O_2$ fwt = 164

Structural formula:



Synonyms: Perfluoropropionic acid, perfluoropropanoic acid, PFPA

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Source**	**Results**
Melting Point		
Boiling Point	Tech. Bull. 10Jan60	**96 °C @ 740 mmHg** **50 °C @ 112-113 mmHg**
Vapor Pressure	Tech. Bull. 10Jan60	**40 mmHg @ 20 °C,**
Density	Tech. Bull. 10Jan60	**1.561 @ 20 °C**
Dissociation Constant		
Water solubility		
Viscosity		
Refractive Index	Tech. Bull. 10Jan60	**1.2838 @ 25 °C**

Environmental Fate and Pathways

Degradation of PFPA		
Parameter	**Report Date**	**Results**
Hydrolysis		
Photolysis		
Biodegradation	T.R. Wilbury, 2001	Not readily biodegradable (mean of 3% after 28 days). [73]

	CERI, 2003	1% BOD, 3% TOC, 0% HPLC.[74]
Thermal Degradation		

Partitioning Test Results		
Parameter	**Report Date**	**Results**
Log Air-Water Partition Coefficient (log K_{AW}), calculated from water solubility and vapor pressure		Calculated Log K_{aw} =
Octanol Water – calculated		Log K_{ow} =
BCF in Carp	CERI, 2002	BCFss = >4.8 (0.1 mg/L exp.) [75] BCFss = 1.2 (1.0 mg/L exp.)

PFPA is not readily biodegradable and is likely to persist in the environment. Testing data indicate that PFPA will not accumulate in high concentrations in fish. Other data is not available for the evaluation of fate and transport in the environment.

ECOTOXICOLOGY STUDIES

All ecotoxicology studies, except for that with killifish, were conducted using the hydrolysis product of C6 Ketone. The earlier studies (E01-0605) were conducted using a solution of hydrolyzed C6 ketone prepared by the division lab. Studies under E02-0319 were dosed with C6 ketone (T-7479) by the contract laboratory. PFPA concentrations in the test solutions were measured in both projects.

Organism	Effect/endpoint	Result
Bacteria - Mixed hetrotrophs	3-hr EC_{50}	> 10,000 mg/L[a]
Freshwater green algae – *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*)	Growth rate 96-hr NOEC	3.71 mg/L[a]
	Biomass 96-hr NOEC	1.59 mg/L[a]
	Growth rate 96-hr E_rC_{50}	10.6 mg/L[a]
	Biomass 96-hr E_bC_{50}	
	Growth rate or Biomass 96-hr NOEC	3.5 mg/L[b]
	Growth rate and Biomass 96-hr E_RC_{50} and E_bC_{50}	>6.8 mg/L[b]
Blue green algae – *Anabaena flos-aquae*	Growth rate and Biomass 96-hr NOEC	44 mg/L[b]
	Growth rate 96-hr E_rC_{50}	> 87 mg/L[b]
	Biomass 96-hr E_bC_{50}	80 mg/L[b]
Freshwater diatom – *Navicula pelliculosa*	Growth rate and Biomass 96-hr NOEC	14 mg/L[b]
	Growth rate and Biomass 96-hr E_rC_{50} and E_bC50	> 14 mg/L[b]
Duckweed – *Lemna gibba*	7-day NOEC (# fronds & dry wt)	18 mg/L[b]

	7-day EC_{50} (# fronds & dry wt)	> 18 mg/L[b]
Water flea – *Daphnia magna*	48-hr NOEC	1080 mg/L[a]
	48-hr EC_{50}	> 1080 mg/L[a]
Fathead minnow – *Pimphales promelas*	96-hr NOEC	1070 mg/L[a]
	96-hr LC_{50}	> 1070mg/L[a]
Orange-red Killifish (Medaka) *Oryzias latipes*	96-hr NOEC	333 mg/L[c]
	96-hr LC_{50}	408 mg/L [c]
a. Data is from E01-0605[76] b. Data is from E02-0319[77] c. Data is from CERI BCF Study[78]		

MICROBIAL SYSTEMS

PFPA was not toxic to wastewater treatment bacteria at 10,000 mg/L, the highest concentration tested. The study was conducted following OECD guideline 209, and utilized activated sludge from a wastewater treatment plant that receives waste from predominantly domestic sources. After 3 hours of exposure, no inhibition in respiration rate was observed for any concentrations tested.

ALGAE

The green alga, *Pseudokirchneriella subcapitata* was the most sensitive species tested. Blue green algae, *Anabaena flos-aquae,* was the next most sensitive species, with a No Observed Effect Concentration greater than ten times that of *P. Subcapitata.* PFPA was apparently not acutely toxic to fish, daphnia and wastewater treatment bacteria. This agrees with studies conducted using other perfluorinated acids.

ACUTE TOXICITY TO AQUATIC INVERTEBRATES

No significant effects were seen on *Daphnia magna* at 1080 mg/L, the highest concentration tested.

ACUTE TOXICITY TO FISH

The killifish was apparently slightly more sensitive than fathead minnow. A 96-hour LC50 of 408 mg/L was reported for killifish and > 1070 mg/L for fathead minnow.

DRAFT

Section 3

Heptafluorobutanoic acid (PFBA)
Summary of Test Results

Executive Summary
Introduction and Description of CAS number
Physical Properties
- Melting point
- Boiling point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive index

Environmental Fate and Pathways
- Degradation
- Partitioning
- Adsorption to mineral surfaces

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Chronic Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

EXECUTIVE SUMMARY

Introduction

This document describes the physical/chemical properties, degradation and aquatic toxicology information currently in our possession for nonafluorobutanoic acid (PFBA), a chemical formerly marketed by 3M as FC-23 (L-16222) as well as the final degradation product of many current 3M products. PFBA is highly persistent but not considered to be PBT (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PFBA is a material of public Interest (MPI) and falls in the broad category defined by PFCAs (perfluorocarboxylates with carbon chain length from C1 to C20). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

Environmental Characteristics

PFBA is moderately volatile with a relatively high vapor pressure and is miscible with water at 20 degrees C. It generally does not sorb strongly to soil. There is a potential for transport long distances in the atmosphere. At environmental pH (between 5 and 9), the predominant species will be the nonafluorobutyrate anion ($CF_3CF_2CF_2COO^-$) which will tend to remain dissolved in water. PFBA does not hydrolyze, photolyze or readily biodegrade.

Acute toxicity studies were conducted with bacteria, algae, invertebrates, frogs and fish. The freshwater green algae, *Pseudokirchneriella subcapitata* was found to be the most sensitive species tested. The 96-hour EC_{50} values were at least 10 times lower than the effect concentrations found for a wide range of aquatic organisms. This same sensitivity was also seen with TFA and PFPA, and the same mode of action may be responsible. It is not known at this time why this species of green algae is so sensitive to perfluorinated acids.

Conclusion

This report is a technical summary of the available ecotoxicological and environmental fate data found for PFBA as of July, 2008. Although PFBA is generally resistant to degradation (except for thermal degradation), studies indicate that it is not acutely toxic to fish, daphnia, microbes, aquatic plants and most algae. The green alga, *Pseudokirchneriella subcapitata* was shown to be sensitive to acute exposures to PFBA at a concentration of 29 ppm. Bioconcentration value was extrapolated from data on rainbow trout to be less than 1[79].

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation and aquatic toxicology information in our possession for heptafluorobutanoic acid (also known commonly as perfluorobutanoic acid PFBA), a chemical formally marketed by 3M as FC-23 as well as the final degradation product of current 3M product(s). PFBA is highly persistent but not considered to be PBT (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PFBA is a material of public Interest (MPI) and falls in the broad category defined by PFCAs (perfluorocarboxylates with carbon chain length from C1 to C20). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

Identity:

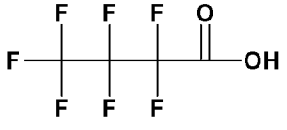
Chemical Name: 2,2,3,3,4,4,4-heptafluorobutanoic acid

CAS Number: 375-22-4

335-10-4 (iso PFBA)

Molecular formula: $C_4HF_7O_2$, fwt = 214

Structural formula:



Synonyms: Perfluorobutyric acid, heptafluorobutyric acid, perfluorobutanoic acid, HFBA, PFBA, C4 acid

Table 3-1 PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Source**	**Results**
Melting Point	Tech. Bull. 10Jan60	**-17.5 °C**
Boiling Point	Tech. Bull. 10Jan60	**120 °C (735 mmHg)**
Vapor Pressure	Tech. Bull. 10Jan60	**44 mmHg @ 56 °C, 455 mmHg @ 107.4 °C, 735 mmHg @ 120 °C**
Density	Tech. Bull. 10Jan60	**1.641 @ 25 °C**
Dissociation Constant		

Water solubility	Tech. Bull. 10Jan60	**miscible @ 20 °C**
Viscosity	Tech. Bull. 10Jan60	**1.622 cps @ 25 °C** **0.828 cps @ 60 °C**
Refractive Index	Tech. Bull. 10Jan60	**1.290 @ 25 °C**
Surface tension	Tech. Bull. 10Jan60	**15.8 dynes/cm @ 30 °C**
Heat of vaporization	Tech. Bull. 10Jan60	**11,200 cal/mole at b.p.**

Environmental Fate and Pathways

Table 3-2

Partitioning Test Results		
Parameter	**Report Date**	**Results**
Log Air-Water Partition Coefficient (log K_{AW}), calculated from water solubility and vapor pressure		Calculated Log K_{aw} =
Octanol Water		Log K_{ow} =
BCF		BCF

An objective of 3M Environmental Lab study E07-0521 was to evaluate the adsorption of PFBA from water to a number of different mineral surfaces that are summarized in Table 3-3. The tests were done to determine the adsorption capacity of the mineral surfaces as a function of the equilibrium concentration of each fluorochemical in water and may also be used to assess the equilibrium adsorption coefficient of each fluorochemical on the given mineral surface. The test water used was a groundwater that contained a mixture of fluorochemicals and had a nominal pH between 7 and 8. Several of the mineral surfaces had known pH_{zpc} values, below this pH value the mineral surface has a net positive charge, and above this value the mineral surface has a net negative charge. At the pH used in this study PFBA would be present in the solutions as an anion. Solutions of each mineral surface in the test water were prepared from nominally from 0.1 to 100 gm/L. The initial concentration of PFBA in groundwater prior to the addition of the mineral

surfaces was nominally 105 ng/mL. As summarized in Tables 3-4, less than 6% of the total mass of PFBA was associated with the mineral phase. Overall these data indicate that the adsorption capacity of these surfaces for PFBA is minimal, and it is not expected that these surfaces would greatly retard the transport of these compounds in the subsurface. In this regard these data should be used to more formally assess the aqueous/solid distribution of these compounds at an actual field location by considering the actual solids/water ratio and the aqueous concentration of the fluorochemical.

Table 3-3. Summary of Adsorbents and their pH_{zpc}

Adsorbent	**pH_{zpc}**
Iron Oxide (Fe_2O_3) (Hematite)	6.9
Iron Oxide (FeO(OH) (Goethite)	9.4
Aluminum Oxide (α-Al_2O_3)	8.3
Mississippi River Sand	Likely Between 1 and 3
Silica Gel	Likely Between 1 and 3
Bentonite	
Diatomaceous earth	

Table 3-4. Summary of isotherm experiments conducted using PFBA in groundwater

		PFBA		
Adsorbent	Dry Mass of Adsorbent Placed into 30 mL vial	Equilibrium Aqueous Concentration Cw (ng/mL)	Equilibrium Solid Concentration Cs (ng/gm)	Fraction of Total Mass Associated with Solid Phase
Bentonite	0.0048	101	26,977	4%
Bentonite	0.0289	100	6,011	5%
Bentonite	0.3184	108	N/A	<1%
Diatomaceous Earth	0.0026	106	N/A	<1%

Diatomaceous Earth	0.0342	102	2,981	3%
Diatomaceous Earth	0.2922	110	N/A	<1%
Diatomaceous Earth	3	98	68	6%
Fe2O3 (Hematite)	0.0012	107	N/A	<1%
Fe2O3 (Hematite)	0.0275	107	N/A	<1%
Fe2O3 (Hematite)	0.3158	106	N/A	<1%
Fe2O3 (Hematite)	3.1	103	23	2%
FeO(OH) Goethite	0.0066	106	N/A	<1%
FeO(OH) Goethite	0.0315	107	N/A	<1%
FeO(OH) Goethite	0.3191	106	N/A	<1%
FeO(OH) Goethite	3	101	44	4%
Mississippi Sand	0.0052	105	3,700	0%
Mississippi Sand	0.0263	99	6,940	6%
Mississippi Sand	0.3253	104	101	1%
Mississippi Sand	3	108	N/A	<1%

ECOTOXICOLOGY STUDIES

Tests were conducted with iso, normal and the potassium salt of perfluorobutyric acid. PFBA exerted minimal toxicity to the wide range of organisms studied. The Green Algae, *Pseudokirchneriella subcapitata* was found to be the most sensitive organism as was seen with other perfluorinated acids.

Oraganism	Effect/endpoint	Result
Bacteria - Mixed hetrotrophs	Respiration effect 3-hr EC_{50}	>1000 mg/L[a]
Freshwater green algae – *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*)	Biomass and Growth Rate 96-hr NOEC	29 mg/L[a]
	Growth rate 96-hour E_RC_{50}	137 mg/L[a]
	Biomass 96-hour E_bC_{50}	50 mg/L[a]
	Biomass approx. 96-hr E_bC50	500 mg/L[b]
Water flea – *Daphnia magna*	Acute NOEC	962 mg/L[a]
	Acute NOEC	1000 mg/L[b]
	Acute NOEC	2425 mg/L[c]
	Acute 48-hr EC_{50}	> 962 mg/L[a]
	Acute 48-hr EC_{50}	> 1000 mg/L[b]
	Acute 48-hr EC_{50}	3475 mg/L[c]
Cladoceran – *Ceriodaphnia dubia*	Acute 48-hr NOEC	1000 mg/L[d]
	Acute 48-hr EC_{50}	3162 mg/L[d]
Midge –*Chironomus tentans*	Acute 96-hr NOEC	10,000 mg/L[d]
	Acute 96-hr LC_{50}	> 10,000 mg/L[d]
Oligochaete – *Lumbriculus variegates*	Acute 96-hr NOEC	1000 mg/L[d]
	Acute 96-hr EC_{50}	3162 mg/L[d]
Scud – *Hyalella azteca*	Acute 96-hr NOEC	61 mg/L[c]
	Acute 96-hr LC_{50}	971 mg/L[c]
Mussel – *Elliptio complanata*	Acute 96-hr NOEC	1000 mg/L[d]
	Acute 96-hr LC_{50}	4815 mg/L[d]

Fathead minnow – *Pimphales promelas*	Acute 96-hr NOEC	933 mg/L[a]
	Acute 96-hr NOEC	1000 mg/L[b]
	Acute 96-hr NOEC	1295 mg/L[c]
	Acute 96-hr LC_{50}	> 933 mg/L[a]
	Acute 96-hr LC_{50}	> 1000 mg/L[b]
	Acute 96-hr LC_{50}	4149 mg/L[c]
	Acute 96-hr LC^{50}	> 2000 mg/L[e]
Rainbow trout – *Oncorhynchus mykiss*	Acute 96-hr NOEC	1000 mg/L[d]
	Acute 96-hr LC_{50}	3162 mg/L[d]
Bluegill – *Lepomis macrochirus*	Acute 96-hr NOEC	2325 mg/L[c]
	Acute 96-hr LC_{50}	5573 mg/L[c]
Green Frog – *Rana clamitans*	Acute 96-hr NOEC	10,000 mg/L[d]
	Acute 96-hr LC_{50}	> 10,000 mg/L[d]

a. Data is for perfluoroisobutyric acid.[80]
b. Data is for normal perfluorobutyric acid[81]
c. Data is for perfluorobutanoic acid, potassium salt; GLP study with measured conc.[82]
d. Toxicity results are from range finder studies and are non-GLP[83]
e. Data is for FC-23, 3M Env Lab, 1981[84]

MICROBIAL SYSTEMS
PFBA did not inhibit the respiration rate of activated sludge even at the extremely high concentration of 10,000 mg/L.

ALGAE
The green algae, *Pseudokirchneriella subcapitata* was found to be the most sensitive species tested. The 96-hour EC_{50} values were at least 10 times lower than the effect concentrations found for a wide range of aquatic organisms.

ACUTE TOXICITY TO AQUATIC INVERTEBRATES
Several aquatic invertebrates were evaluated. The scud (*Hyalella azteca*) was found to be the most sensitive invertebrate. The NOEC was found to be 61 mg/L and the 96-hr EC50 was 971 mg/L. The dose-response curve for the study was unusual in that there was higher mortality at the second lowest concentration that at the second from the highest concentration. It is possible that the animals were somewhat stressed due to test chamber design and/or handling and that the unusual dose-response curve reflects mortality not associated directly with PFPA. All of the other invertebrates tested had NOEC values of 1000 mg/L or greater.

CHRONIC TOXICITY TO AQUATIC INVERTEBRATES
No data available.

ACUTE TOXICITY TO FISH
Three species of fish were studied; fathead minnow, bluegill sunfish and rainbow trout. PFBA was found to be basically non-toxic to these fish. The most sensitive species was rainbow trout with a 96-hr NOEC of 1000 mg/L.

Section 4
MeFBSE acid, perfluorobutyl-methyl sulfonamido glycine acid
Summary of Test Results

Introduction and Description of CAS number
Physical Properties
- Melting point
- Density
- Dissociation Constant
- Solubility
- pH

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Chronic Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation, and aquatic toxicology information generated for perfluorobutyl-methyl sulfonamido glycine acid, a chemical which results from the degradation pathway of Perfluorobutane sulfonamido derivatives to perfluorobutane sulfonate (the ultimate degradation product of many new 3M products). Neither MeFBSE acid (is this correct, do we have enough data?) nor PFBS are considered to be PBTs (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PBSF-based products, including MeFBSE acid, would fall in the broad category defined by PFAS (carbon chain length from C1 to C20 or greater). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length. Note that all testing described in this document, except where noted, was conducted utilizing the non-ionic form of this compound.

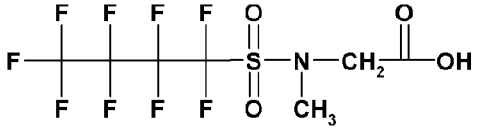
Identity:

Chemical Name: Glycine, N-methyl-N-[(nonafluorobutyl)sulfonyl]-

CAS Number: 159381-10-9

Molecular formula: $C_7H_6F_9NO_4S$

Structural formula:



Synonyms: C4 glycine acid, M370, MeFBSE acid, perfluorobutyl-methyl sulfonamido glycinc acid

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Report Date**	**Results**
Melting Point[85]	**GID**	**94-96 °C**
Boiling Point[86]		
Vapor Pressure[87]	**GID**	
Density[88]		**1.7 (melt)**
Dissociation Constant[89,90]	**GID 70920**	
Water solubility		
pH		**3-4**
Refractive Index[91]		

Environmental Fate and Pathways

Degradation of MeFBSE acid

Partitioning Test Results		
Parameter	**Report Date**	**Results**
Log Air-Water Partition Coefficient (log K_{AW}), calculated from water solubility and vapor pressure		
Octanol Water – calculated		
Estimated BCF		

ECOTOXICOLOGY STUDIES

Screening, non-GLP studies were conducted on this test substance. Test substance concentration was not measured and all results are reported as nominal.

MICROBIAL SYSTEMS
At the highest concentration tested, 1000 mg/L, activated sludge respiration was inhibited by 27% after 3 hours exposure. The EC_{50} could not be calculated.

ALGAE
The green algae *Pseudokirchneriella subcapitata* was slightly more sensitive than the other organisms evaluated against MeFBSE acid.

ACUTE TOXICITY TO AQUATIC INVERTEBRATES
No effect was seen on *Daphnia magna* at 100 mg/L, the highest concentration tested.

CHRONIC TOXICITY TO AQUATIC INVERTEBRATES
No chronic studies have been completed.

16.5 ACUTE TOXICITY TO FISH
There was no effect seen on fathead minnow at 100 mg/L, the highest concentration tested.

Oraganism	Effect/endpoint	Result
Bacteria - Mixed hetrotrophs	Respiration effect 3-hr EC_{50}	> 1000 mg/L[a]
Freshwater green algae – *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*)	Biomass and Growth Rate 96-hr NOEC	50 mg/L[b]
	Growth rate 96-hour E_RC_{50}	77 mg/L[b]
	Biomass 96-hour E_bC_{50}	66 mg/L[b]
Water flea – *Daphnia magna*	Acute NOEC	100 mg/L[b]
	Acute 48-hr EC_{50}	> 100 mg/L[b]
Mysid shrimp – *Mysidopsis bahia*	Acute NOEC	100 mg/L[b]
	Acute 96-hr LC_{50}	> 100 mg/L[b]
Fathead minnow – *Pimphales promelas*	Acute 96-hr NOEC	100 mg/L[b]
	Acute 96-hr LC_{50}	> 100 mg/L[b]

a. Data from Era Laboratories, 2003. LIMS E03-0514[92]
b. Data is from Wildlife International, 2003, LIMS E03-0514[93]

Fluoirnated Non-Ionic Chemicals:

Section 1
N-(2-Hydroxyethyl)-N-Methyl-Perfluorobutane Sulfonamide (MeFBSE) Summary of Test Results

Introduction and Description of CAS number
Physical Properties
- Melting Point
- Boiling Point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive Index

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

Introduction

This document describes the physical/chemical properties, degradation and aquatic toxicology information generated for Nonafluoro-N-(2-ethoxy)-N-methyl-butanesulfonamide, a chemical which is used as an intermediate in the production of functionalized fluorochemical products and is on the degradation pathway to perfluorobutane sulfonate, the ultimate degradation product of many new 3M products. Neither MeFBSE nor PFBS are considered to be PBTs (persistent, bioaccumulative, toxic) under the US EPA PBT Chemical policy.

PBSF-based products, including MeFBSE, would fall in the broad category defined by PFAS (carbon chain length from C1 to C20 or greater). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length. Note that all testing described in this document, except where noted, was conducted utilizing the non-ionic form of this compound.

Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

Environmental Characteristics
The very low vapor pressure of MeFBSE, and calculated air/water partition coefficient, indicate the volatility of the compound is insignificant. Therefore, significant atmospheric dispersion of MeFBSE is considered unlikely. MeFBSE is inherently biodegradable with 97.4 % degradation in 28 days. The primary metabolite was observed from oxidation under biotic conditions to the primary carboxylate ($C_4FSO_2N(CH_3)CH_2CO_2$-).

The water solubility, >100 ppm, suggest that MeFBSE would be fairly mobile in soils and could move into groundwater. MeFBSE does hydrolyze with a half life range of 1.6 to 2.3 years depending on temperature and pH.

MeFBSE exerted low to moderate toxicity to the range of organisms studied. The most sensitive species tested was the mysid shrimp, *Mysidopsis bahia*, with a 96-hour LC_{50} of 4.4 mg/L. Other acute toxicity studies were conducted with bacteria, algae, invertebrates, and fish with toxicity values ranging from 25 to 1000 mg/L..

Conclusion

This report is a technical summary of the available ecotoxicological and environmental fate data found for MeFBSE as of September, 2008. Studies indicate that it is not persistent but it does show some toxicity to mysid shrimp and to a lesser degree to fish, daphnia, and algae. MeFBSE is not considered bioaccumulative because of it's short have life in the biodegradation study. The ultimate degradant of MeFBSE is PFBS, which is persistent but not bioaccumulative.

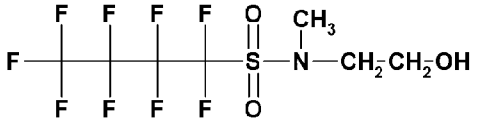
Identity:

Chemical Name: 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-N-(2-hydroxyethyl)-N-methyl-

CAS Number: 34454-97-2

Molecular formula: $C_7H_8F_9NO_3S$

Structural formula:



Synonyms: **MeFBSE alcohol, C4 sulfonamido alcohol, C4 alcohol**

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Report Date**	**Results**
Melting Point[94]	**10-25-01**	**65 °C**
Boiling Point[1]	**10-25-01**	**248 °C**
Vapor Pressure[95]	**11-12-04** **GID 87564**	**3 E-5 mmHg @ 20 °C,** **1.1 E-2 mmHg @ 55 °C** **1.1 mmHg @ 87 °C**
Density[1]	**10-25-01**	**1.56 (melt)**
Dissociation Constant[96]	**9-30-02** **GID 70920**	**~6.6 (by analogy to FBSE)**
Water solubility ***(need to add endnotes)***	**7-26-04** **E02-0094** **Req.# 061466**	**118 ppm @ 20 °C** **141 ppm @ 24 °C** **1250 ppm @ 92.6 °C**
Viscosity[1]	**10-25-01**	**7.6 cps @ 80 °C**
Refractive Index[1]	**10-25-01**	**1.3758**

Environmental Fate and Pathways

MeFBSE is inherently biodegradable with 97.4 % degradation in 28 days. The primary metabolite was observed from oxidation under biotic conditions to the primary carboxylate ($C_4FSO_2N(CH_3)CH_2CO_2$-).[97]

The water solubility and soil, sediment and sludge adsorption/desorption data suggest that MeFBSE would be fairly mobile in soils and could move into groundwater.

The very low vapor pressure and calculated air/water partition coefficient indicate that volatility of the compound is insignificant. Therefore, atmospheric dispersion of MeFBSE is considered unlikely (*want to check this relative to Mabury findings*).

Degradation of MeFBSE		
Parameter	**Report Date**	**Results**
Hydrolysis	E02-0813	*Half life 1.67 years minimum @ 25°C (test conducted at 3 pH levels);* *2.26 years @ 25°C (independent of pH)*
Photolysis		
Biodegradation	12/19/03 E02-1325	Inherently biodegradable 97.4% in 28 days
Thermal Degradation		No PFBS was formed during combustion studies of two perflurorbutanesulfonyl polymers. Results suggest the

		C-S bond was completely destroyed and did not reform.

Partitioning Test Results		
Parameter	**Report Date**	**Results**
Log Air-Water Partition Coefficient (log K_{AW}), calculated from water solubility and vapor pressure		Calculated Log K_{aw} = -4.636
Octanol Water		
Estimated BCF		

ECOTOXICOLOGY STUDIES

McFBSE exerted low to moderate toxicity to the range of organisms studied. The most sensitive species tested was the mysid shrimp, *Mysidopsis bahia*, with a 96-hour LC_{50} of 4.4 mg/L.

Ecotoxicity of MeFBSE		
Organism	Effect/Endpoint	Result[a]
Wastewater Bacteria (OECD 209)	Respiration effect 3-hr EC_{50}	> 1000 mg/L[b, c]
Freshwater green algae - *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*)	Growth Rate 96-hr NOEC	11 mg/L[d]
	Growth Rate 96-hr ErC_{50}	79 mg/L[d]
Water Flea - *Daphnia magna*	Acute 48-hr NOEC	4.7 mg/L[d]
	48-hr EC_{50}	38 mg/L[d]
Mysid shrimp - *Mysidopsis bahia*	Acute 96-hr NOEC	1.3 mg/L[d]
	Acute 96-hr LC_{50}	4.4 mg/L[d]
Fathead minnow - *Pimephales promelas*	Acute 96-hr NOEC	16 mg/L[d]
(95% confidence interval)	Acute 96-hr LC_{50}	25 mg/L[d]

[a] All results calculated using mean measured concentrations except where noted
[b] Results based on nominal concentrations; sample well characterized
[c] Data from E01-1501[98]
[d] Data from E02-0806[99]

MICROBIAL SYSTEMS

The study was conducted utilizing activated sludge from a wastewater treatment plant that receives waste from predominantly domestic sources. After 3 hours of exposure, a concentration-response curve was not evident over 7 test concentrations spanning from 1.0 to 1000 mg/L. The 3-hour EC_{50} was determined to be > 1000 mg/L, with -81.2 % inhibition in respiration seen at 1000 mg/L. Exposure concentrations were not determined analytically.[100]

ALGAE

Testing was conducted using the freshwater green alga, Selenastrum capricornutum. Cells were exposed for 96-hours, with microscopic counts taken at 24, 48, 72 and 96-hours. The NOAEC and EC_{50} values were calculated using three methods to determine inhibition: cell density, area under the growth curve and average specific growth rate. Results are based on growth rate. Exposure concentrations were measured at 0, 72 and 96-hours in all concentrations.

The effects were determined to be algistatic (growth resumed when aliquots of the algae in the maximally inhibited concentrations were placed in fresh growth media). Observations of algae cells during the studies found that there were no signs of aggregation, flocculation or adherence of the cells to the flasks after exposure. Since the rate of growth, and not cell mortality appeared to be affected in these studies, algae NOAEC (11 mg/L) and EC_{50} (79 mg/L) values reported here were calculated using the average specific growth rate.[101]

ACUTE TOXICITY TO AQUATIC INVERTEBRATES

A freshwater (Daphnia magna)[102] and a marine (Mysidopsis bahia)[103] aquatic invertebrate were evaluated for acute toxicity. The marine organism appeared to be more sensitive. The daphnid 48 hour EC_{50} value was 38 mg/L, while the mysid LC_{50} value was 4.4 mg/L. Exposure concentrations were measured at 0, 24, and 48 hours (daphnids) and 0, 48 and 96-hours (mysids) in all concentrations.

ACUTE TOXICITY TO FISH

Acute toxicity to freshwater fish was evaluated on the fathead minnow (*Pimephales promelas*). The fathead minnow 96 hour LC_{50} was 25 mg/L with an NOEC of 16 mg/L. At 96 hours, all surviving fish appeared normal. Exposure concentrations were measured at 0, 48 and 96-hours in all concentrations.[104]

Section 2
N-Methyl-Perfluorobutane Sulfonamide (MeFBSA)
Summary of Test Results

Introduction and Description of CAS number
Physical Properties
- Melting point
- Boiling point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive index

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation and aquatic toxicology information generated for Nonafluoro-N-methyl-butanesulfonamide, a chemical which is used as an intermediate in the production of functionalized fluorochemical products and is on the degradation pathway to perfluorobutane sulfonate, the ultimate degradation product of many new 3M products. Neither MeFBSA nor PFBS are considered to be PBTs (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PBSF-based products, including MeFBSA, would fall in the broad category defined by PFAS (carbon chain length from C1 to C20 or greater). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length. Note that all testing described in this document, except where noted, was conducted utilizing the non-ionic form of this compound.

Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

Environmental Characteristics
The vapor pressure and calculated air/water partition coefficient, of MeFBSA, indicate that volatility of the compound may not be insignificant. Therefore, atmospheric dispersion of MeFBSA is considered possible. Although official biodegradablility and hydrolysis studies have not been completed on MeFBSA, by analogy with it's C8 analog, it is considered biodegradable versus persistent.

The water solubility, >300 ppm, suggest that MeFBSA would be fairly mobile in soils and could move into groundwater.

MeFBSA shows moderate toxicity to the range of organisms studied. The most sensitive species tested was the mysid shrimp, *Mysidopsis bahia*, with a 96-hour LC_{50} of 2.4 mg/L. Other acute toxicity studies were conducted with algae, invertebrates, and fish with toxicity values ranging from 8.8 to 17 mg/L..

Conclusion

This report is a technical summary of the available ecotoxicological and environmental fate data found for MeFBSA as of September, 2008. By analogy to it's C8 analog, MeFBSA is not persistent nor bioaccumulative. The ultimate degradant of MeFBSA is postulated to be PFBS, which is persistent but not bioaccumulative. Studies show MeFBSA has toxicity to mysid shrimp and to a lesser degree to fish, daphnia, and algae.

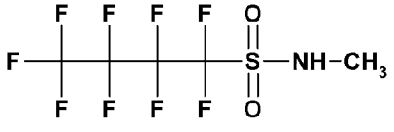
Identity:

Chemical Name: 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-N-methyl-

CAS Number: 68298-12-4

Molecular formula: $C_5H_4F_9NO_2S$

Structural formula:



Synonyms: **MeFBSA amide, C4 sulfonamido amide, C4 amide**

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties

Parameter	Report Date	Results
Melting Point[105]	**GID 58957**	**40 °C**
Boiling Point[1]	**GID 58957**	**206 °C**
Vapor Pressure[1]	**GID 58957**	**3.0 E-2 mmHg @ 20 °C, 4.7 E-1 mmHg @ 55 °C 1.1 mmHg @ 64.2 °C**
Density[106]	**10-25-01**	**1.65 (melt)**
Dissociation Constant[107]	**9-30-02 GID 70920**	**7.52** (RFSO2NHCH3)
Water solubility *(need to add endnotes)*	**7-26-04? Req.# 061466? EDP (25C) OECD 105 on E02-0095**	**434 ppm @ 10 °C 554 ppm @ 20 °C 359 ppm @ 25 °C 1770 ppm @ 41.2 °C 375 ppm @ 92.6 °C**
Viscosity[2]	**10-25-01**	**6.9 cps @ 80 °C**
Refractive Index[108]	**1-5-06 GID 102901**	**1.3407 @ 25 °C**

Environmental Fate and Pathways

MeFBSA is one of the degradation products observed on the pathway from MeFBSE to PFBS in aerobic biodegradation.[109] The primary metabolite was assumed to be to the primary amide ($C_4FSO_2NH_2$).

The water solubility and soil, sediment and sludge adsorption/desorption data suggest that MeFBSA would be fairly mobile in soils and could move into groundwater.*?MeFBSA is relatively mobile in the environment – check this relative to Mabury conclusions on non-ionics.*

The vapor pressure and calculated air/water partition coefficient indicate that volatility of the compound may not be insignificant. Therefore, atmospheric dispersion of MeFBSA is considered possible (*want to check this relative to Mabury findings*).

Degradation of MeFBSA		
Parameter	**Report Date**	**Results**
Thermal Degradation		No PFBS was formed during combustion studies of two perflurorbutanesulfonyl based polymers. Results suggest the C-S bond was completely destroyed and did not reform as

		MeFBSE fragment or residue. This is relevant due to the similarity between the tested polymer and MeFBSE functional groups. Thermal degradation above 500 C is assumed to yield primarily CO2, HF and simple non-functional fluorinated alkanes (C1 & C2 based residues).

Partitioning Test Results		
Parameter	**Report Date**	**Results**
Log Air-Water Partition Coefficient (log K_{AW}), calculated from water solubility and vapor pressure		Calculated Log K_{aw} = -0.664
Octanol Water		
Estimated BCF		

ECOTOXICOLOGY STUDIES

MeFBSA exerted low to *moderate (high?)* toxicity to the range of organisms studied. The most sensitive species tested was the mysid shrimp, *Mysidopsis bahia*, with a 96-hour LC_{50} of 2.4 mg/L.[110]

Ecotoxicity of MeFBSA		
Parameter	Report Date	Result[a]
Wastewater Bacteria (OECD 209)	01/30/02, E01-1502	
3-hour EC50		> 1000[b] Insignificant toxicity
Inhibition at highest concentration tested (1000 mg/L)		No inhibition seen
***Selenastrum capricornutum* (freshwater green algae)**	11/08/02, E02-0807	
96-hour NOAEC (growth rate)		1.9
96-hour ErC_{10} (95% confidence interval)		6.8 (5.7 – 8.2)
96-hour ErC_{50} (95% confidence interval)		13 (12 - 14) Harmful toxicity
***Daphnia magna* (freshwater water flea)**	01/09/04, E02-0807	
Acute 48-hour NOEC		6.0
48-hour EC_{50} (95% confidence interval)		17 (12 – 24) Harmful toxicity
***Mysidopsis bahia* (mysid shrimp)**	01/19/04, E02-0807	

Acute 96-hour NOEC		0.35
Acute 96-hour LC_{50} (95% confidence interval)		2.4 (1.4 – 2.8) Toxic
***Pimephales promelas* (fathead minnow)**	01/19/04, E02-0807	
Acute 96-hour NOEC		16
Acute 96-hour LC_{50} (95% confidence interval)		44 (31 - 62) Harmful toxicity

[a]All results calculated using mean measured concentrations except where noted
[b] Results based on nominal concentrations; sample well characterized

MICROBIAL SYSTEMS
The study was conducted utilizing activated sludge from a wastewater treatment plant that receives waste from predominantly domestic sources. After 3 hours of exposure, a concentration-response curve was not evident over 8 test concentrations spanning from 10 to 1000 mg/L. The 3-hour EC_{50} was determined to be > 1000 mg/L, with -41.5 % inhibition in respiration seen at 1000 mg/L. Exposure concentrations were not determined analytically.[111]

ALGAE
Testing was conducted using the freshwater green alga, Selenastrum capricornutum. Cells were exposed for 96-hours, with microscopic counts taken at 24, 48, 72 and 96-hours. The NOAEC and EC_{50} values were calculated using three methods to determine inhibition: cell density, area under the growth curve and average specific growth rate. Results are based on growth rate. Exposure concentrations were measured at 0, 72 and 96-hours in all concentrations.

The effects were determined to be algistatic (growth resumed when aliquots of the algae in the maximally inhibited concentrations were placed in fresh growth media). Observations of algae cells during the studies found that there were no signs of aggregation, flocculation or adherence of the cells to the flasks after exposure. Since the rate of growth, and not cell mortality appeared to be affected in these studies, algae NOAEC (1.9 mg/L) and EC_{50} (13 mg/L) values reported here were calculated using the average specific growth rate.[112]

ACUTE TOXICITY TO AQUATIC INVERTEBRATES
A freshwater (Daphnia magna)[113] and a marine (Mysidopsis bahia)[114] aquatic invertebrate were evaluated for acute toxicity. The marine organism appeared to be more sensitive. The daphnid 48 hour EC_{50} value was 17 mg/L, while the mysid LC_{50} value was 2.4 mg/L. Exposure concentrations were measured at 0, 24, and 48 hours (daphnids) and 0, 48 and 96-hours (mysids) in all concentrations.

ACUTE TOXICITY TO FISH
Acute toxicity to freshwater fish was evaluated on the fathead minnow (Pimephales promelas). The fathead minnow 96 hour LC_{50} was 44 mg/L with an NOEC of 16 mg/L. At 96 hours, all surviving fish of both species appeared normal. Exposure concentrations were measured at 0, 48 and 96-hours in all concentrations.[115]

Section 3
N-(2-Hydroxyethyl)-Perfluorobutane Sulfonamide (FBSE) Summary of Test Results

Introduction and Description of CAS number

Physical Properties

- Melting point
- Boiling point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive index

Environmental Fate and Pathways

- Degradation
- Partitioning

Ecotoxicity

- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Chronic Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation, and aquatic toxicology information generated for Nonafluoro-N-(2-ethoxy)-butanesulfonamide, a chemical which is used as an intermediate in the production of functionalized fluorochemical products and may be on the degradation pathway from Perfluorobutane sulfonamide derivatives to perfluorobutane sulfonate (the ultimate degradation product of many new 3M products). Neither *FBSE* nor PFBS are considered to be PBTs (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PFBS-based products, including FBSE, would fall in the broad category defined by PFAS (carbon chain length from C1 to C20 or greater). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length. Note that all testing described in this document, except where noted, was conducted utilizing the non-ionic form of this compound.

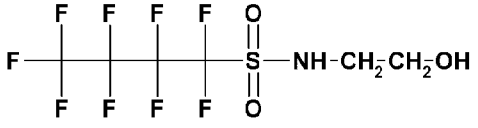
Identity:

Chemical Name: 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro- N-(2-hydroxyethyl)-

CAS Number: 34454-99-4

Molecular formula: $C_6H_6F_9NO_3S$

Structural formula:



Synonyms: FBSE, FBSE alcohol, C4 sulfonamido primary alcohol, T-7868 (ammonium salt)

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Report Date**	**Results**
Melting Point[116]	**GID 59437**	**65 °C**
Boiling Point[117]	**GID**	**120-134 C @ 4-9 torr** **251.4 C @760 torr**
Vapor Pressure[118]	**GID 73379**	**6 mmHg @ 147 °C** **66.2 mmHg @ 197 °C**
Density[119]	**GID 71162**	**1.56 (molten)**
Dissociation Constant[120]	**GID 70920**	**6.57** (RFSO2NHCH2CH2OH)

Environmental Fate and Pathways

FBSE is one of the potential degradation products observed on the pathway from MeFBSE to PFBS in aerobic biodegradation.[121] The primary metabolite is assumed to be to the primary carboxylate ($C_4F_9SO_2NHCH_2CO_2$-) based upon comparison to closely related structural analogs.

Degradation of FBSE		
Parameter	**Report Date**	**Results**
Thermal Degradation[122]		No FBSE was formed during combustion studies of two perflurorbutanesulfonyl based polymers. Results suggest the C-S bond was completely

		destroyed and did not reform as a FBSE fragment or residue. Thermal degradation above 500 C is assumed to yield primarily CO2, HF and simple non-functional fluorinated alkanes (C1 & C2 based residues). TGA in air and N_2 shows an onset of degradation of 155 °C with 98% mass loss by 198 °C.

Boiling point = two temperatures: 97°C (aqueous solution) and ~274°C (not sure where this one is from, will need to research it- jfs)
Freezing Temperature = -7.9°C (aqueous solution)

ECOTOXICOLOGY STUDIES

FBSE has not been characterized for ecotoxicity.

Section 4
Perfluorobutane Sulfonamide (FBSA)
Summary of Test Results

Introduction and Description of CAS number
Physical Properties
- Melting point
- Boiling point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive index

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Chronic Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation, and aquatic toxicology information generated for Nonafluoro-butanesulfonamide, a chemical which is used as an intermediate in the production of functionalized fluorochemical products and is on the degradation pathway from Perfluorobutane sulfonamide derivatives to perfluorobutane sulfonate (the ultimate degradation product of many new 3M products). Neither *FBSA* nor PFBS are considered to be PBTs (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

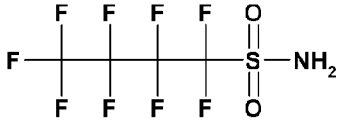
PBSF-based products, including FBSA, would fall in the broad category defined by PFAS (carbon chain length from C1 to C20 or greater). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length. Note that all testing described in this document, except where noted, was conducted utilizing the non-ionic form of this compound.

Identity:

Chemical Name: 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-
CAS Number: 30334-69-1

Molecular formula: $C_4H_2F_9NO_2S$

Structural formula:



Synonyms: **FBSA amide, C4 sulfonamido primary amide, MTDID 603 (ammonium salt)**

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Report Date**	**Results**
Melting Point[123]	**GID 59437**	**67.4-71.1 C**
Boiling Point[124]		**114-115 C @ 11.3 torr**
Vapor Pressure[125]	**GID 71780 & GID 73379**	**3.8 mmHg @ 94.3 °C, 25.8 mmHg @ 131.4 °C 351.4 mmHg @ 196.3 °C**
Density[126]	**10-25-01**	**1.68 (melt)**
Dissociation Constant[127,128]	**GID 70920**	**6.5** (RFSO2N**H**$_2$) 5.98 (RFSO2NH-K+)
Water solubility ***(need to add endnotes)***	***7-26-04? Req.# 061466? EDP (25C) OECD 105 on E02-0095***	***434 ppm @ 10 °C 554 ppm @ 20 °C 359 ppm @ 25 °C 1770 ppm @ 41.2 °C 375 ppm @ 92.6 °C***
Viscosity[2]	***10-25-01***	***6.9 cps @ 80 °C***
Refractive Index[129]	***1-5-06 GID 102901***	***1.3407 @ 25 °C***

Environmental Fate and Pathways

FBSA is one of the degradation products observed on the pathway from MeFBSE to PFBS in aerobic biodegradation.[130] The primary metabolite was assumed to be to the perfluorobutane sulfonate ($C_4F_9SO_3^-$).

Degradation of FBSA		
Parameter	**Report Date**	**Results**
Thermal Degradation		No FBSA was formed during combustion studies of two perflurorbutanesulfonyl based polymers. Results suggest the C-S bond was completely destroyed and did not reform as a FBSA fragment or residue. Thermal degradation above 500 C is assumed to yield primarily CO2, HF and simple non-functional fluorinated alkanes (C1 & C2 based residues).

ECOTOXICOLOGY STUDIES

FBSA has not been characterized for ecotoxicity.

Section 5
N-Hexyl-Perfluorobutane Sulfonamide (HxFBSA)
Summary of Test Results

Introduction and Description of CAS number
Physical Properties
- Melting point
- Boiling point
- Vapor Pressure
- Density
- Dissociation Constant
- Solubility
- Viscosity
- Refractive index

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- Microbial Systems
- Algae
- Acute Toxicity to Aquatic Invertebrates
- Chronic Toxicity to Aquatic Invertebrates
- Acute Toxicity to Fish

Introduction and Description of CAS number

This document describes the physical/chemical properties, degradation, and aquatic toxicology information generated for Nonafluoro-N-hexyl-butanesulfonamide, a chemical which is used as an intermediate in the production of functionalized fluorochemical products and may be assumed to degrade to perfluorobutane sulfonate (the ultimate degradation product of many new 3M products). PFBS is not considered to be PBTs (persistent, bioaccumulative, toxic) under the USEPA PBT Chemical policy.

PBSF-based products, including HxFBSA, would fall in the broad category defined by PFAS (carbon chain length from C1 to C20 or greater). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary

significantly depending on the carbon chain length. Note that all testing described in this document, except where noted, was conducted utilizing the non-ionic form of this compound.

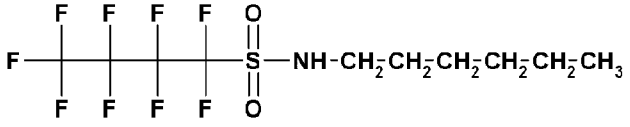
Identity:

Chemical Name: 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro- N-hexyl-

CAS Number: 606966-46-5

Molecular formula: $C_{10}H_{14}F_9NO_2S$

Structural formula:



Synonyms: **HxFBSA, HxFBSA amide, C4 sulfonamido hexyl amide**

PHYSICAL/CHEMICAL PROPERTIES

Physical and Chemical Properties		
Parameter	**Report Date**	**Results**
Melting Point[131]	**GID 79753**	**36 °C**
Vapor Pressure[132]	**GID 79752**	**3 E-6 mmHg @ 55 °C** **0.2 mmHg @ 100 °C** **52.2 mmHg @ 180 °C**
Density[133]	**GID ?**	**1.6 (molten)**
Water solubility[134]	**GID 80024**	**8 ppm @ 20 °C**

Environmental Fate and Pathways

HxFBSA is one of the intermediate materials further reacted to produce 3M products. It may potentially degrade to PFBS in aerobic biodegradation.[135] The ultimate degradant is assumed to be perfluorobutane sulfonate (C_4FSO_3-).

Degradation of HxFBSA		
Parameter	**Report Date**	**Results**
Thermal Degradation[136]		No HxFBSA was formed during combustion studies of two perflurorbutanesulfonyl based polymers. Results suggest the C-S bond was

		completely destroyed and did not reform as a HxFBSA fragment or residue. Thermal degradation above 500 C is assumed to yield primarily CO2, HF and simple non-functional fluorinated alkanes (C1 & C2 based residues).

ECOTOXICOLOGY STUDIES

HxFBSA has not been characterized for ecotoxicity.

Fluorinated Inerts and Volatiles:

Chapter 4 Fluorinated Inerts and Volatiles
Section 1
Perfluorobutanesulfonyl fluoride (PBSF)
Summary of Test Results

Executive Summary ??
Physical/Chemical Properties
- Freezing Point
- Boiling Point
- Vapor Pressure
- Density
- Solubility
- Viscosity
- Refractive Index

Environmental Fate and Pathways
- Degradation
- Partitioning

Ecotoxicity
- ?Microbial Systems
- ?Algae
- ?Acute Toxicity to Aquatic Invertebrates
- ?Acute Toxicity to Fish

EXECUTIVE SUMMARY

Introduction

This document describes the physical/chemical properties, degradation and aquatic toxicology information in our possession for perfluorobutanesulfonyl fluoride (PBSF), a chemical marketed by 3M as FC-51 and FC-202 (L-15676, L-19150). PBSF is the starting raw material for all of 3M's PFBS based products and intermediates. PBSF is marginally reactive, it will degrade in the environment typically yielding perfluorobutane sulfonate under normal hydrolytic (catalyzed), photoxidative and oxidative conditions. It is highly persistent once converted to the sulfonate. EPA does consider it to be a PBT (persistent, bioaccumulative, toxic) based solely upon estimations derived from EPISuite modeling. 3M does not consider this to be a PBT based upon internal testing and assessment.

PBSF is not a material of public Interest (MPI) due in likelihood to its limited marketing and general public awareness. It falls in the broad category defined by PFAS (perfluoroalkyl sulfonates with carbon chain length from C1 to C20). Environmental, health and safety characteristics need to be reviewed on an individual basis as these properties vary significantly depending on the carbon chain length.

Environmental Characteristics

PBSF is both volatile but minimally soluble in water. It does not sorb strongly to soil. The Henry's Law constant indicates that PBSF would exhibit high volatility from water to air and will undergo rainout once hydrolysis and oxidation occurs if released to the atmosphere. There is a potential for transport long distances in the atmosphere.

Conclusion

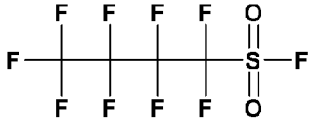
Identity:

Chemical Name: 1-Butanesulfonyl fluoride, 1,1,2,2,3,3,4,4,4-nonafluoro-

CAS Number: 375-72-4

Molecular formula: $C_4F_{10}O_2S$, fwt = 302.1

Structural formula:



Synonyms: **PBSF, perfluorobutanesulfonyl fluoride, C4 sulfonyl fluoride, nonaflyl fluoride**

PHYSICAL/CHEMICAL PROPERTIES (PBSF)

Physical and Chemical Properties		
Parameter	**Source**	**Results**
Freezing Point	**MRD GID 59002 & 59003**	**-75 °C**
Boiling Point[137]	**MRD GID 59002 & 59003**	**66.1 °C (754 mmHg)**
Vapor Pressure	**MRD GID 59002 & 59003** **Env Lab E01-0867**	**131 mmHg @ 21.2 °C,** **217 mmHg @ 30.9 °C,** **406 mmHg @ 48 °C** **734 mmHg @ 64.8 °C** **38.4 Torr @ 0 °C** **65.3 Torr @ 10 °C** **107 Torr @ 20 °C** **136 Torr @ 25 °C** **171 Torr @ 30 °C** **396 Torr @ 50 °C**
Density	**MRD GID 59002 & 59003**	**1.70 @ 25 °C** **14.2 lb/gal @ 25 °C**
Water solubility	**MRD GID 59002 & 59003,** **Env Lab E01-0904**	**14 mg/L** **< 0.3 mg/L,** **< 274 ug/L**
Viscosity	**MRD GID 59002 & 59003**	**1.44 cps @ 25 °C** **1.48 cps @ 20 °C** **1.66 cps @ 0 °C**
Refractive Index[138]		**1.281 @ 25 °C**

Environmental Fate and Pathways

Discuss the hydrolysis study results (Tom H.). Do we want a discussion of nucleophilic susceptibility relative to environmental persistence? (JAY S.)

ECOTOXICOLOGY STUDIES

PBSF has not been characterized for ecotoxicity.

Chapter 4 Fluorinated Inerts and Volatiles
Section 2
Nonafluorobutane (NFB)
Summary of Test Results

Physical/Chemical Properties
- Boiling Point
- Density

Environmental Fate and Pathways
- ?Degradation
- ?Partitioning

Ecotoxicity
- ?Microbial Systems
- ?Algae
- ?Acute Toxicity to Aquatic Invertebrates
- ?Acute Toxicity to Fish

DRAFT

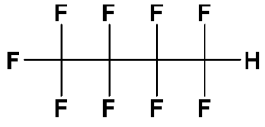
Identity:

Chemical Name: Butane, 1,1,1,2,2,3,3,4,4-nonafluoro-

CAS Number: 375-17-7

Molecular formula: C_4HF_9, fwt = 220.0

Structural formula:



Synonyms: **Perfluorobutane monohydride, C4 hydride L-12585**

PHYSICAL/CHEMICAL PROPERTIES (NFB)

Physical and Chemical Properties		
Parameter	**Source**	**Results**
Boiling Point[139]	**MRD GID 59002 & 59003**	**14 °C (740 mmHg)**
Density	**MRD MSDS L-12585**	**1.8 @ 14 °C (as liquified gas)**

Environmental Fate and Pathways

??

ECOTOXICOLOGY STUDIES

NFB not been characterized for ecotoxicity.

Glossary

BCF, BCFK	**Bioconcentration Factor** The ratio between the chemical concentration observed in the test organism and the concentration in water. Typically, data is generated using fish with the chemical dissolved in the water. The level of the chemical in the test organism is achieved through passive absorption (through gills and skin) and not through ingestion. BCF can be calculated from kinetic and steady state (dynamic equilibrium) data. Kinetic BCF (BCFK) The bioconcentration factor calculated directly from the ratio of the uptake (k1) and depuration (k2) rate constants (k1/k2), assuming first-order kinetics, is termed the kinetic bioconcentration factor, BCFK. Steady state BCF (BCFSS or KB) The ratio of a chemical's steady state concentration in an organism (CB, wet-weight basis) to the concentration in the organism's media (CR) where uptake occurs through absorption through breathing apparatus (e.g., gills or lungs) and skin, and not through feeding. It is more universally applicable when CR is the concentration of the vapor- or gas-phase chemical concentration, or the aqueous concentration; in neither case should the concentration include that associated with particulate matter. BCF can also be expressed on a lipid weight basis. For hydrophobic compounds, BCF values expressed on a lipid-weight basis are equivalent among different organisms, regardless of the lipid content. **Common and Preferred Units** As a ratio of rate constants or concentrations, the bioconcentration factor is either unitless or expressed as L/kg. **Mathematical Definition** BCFK = k1/k2 BCFSS = CB/CR or BCFSS = Cf/Cw [where Cf = concentration in fish, Cw = concentration in water] or lipid-weight basis: BCFLipid =Cf/(Cw * L) = CB/(CR * L) Where L is the concentration of lipid in the organism (g lipid/ g organism)
EC50	Median Effective Concentration. The experimentally derived 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, etc.) after a specified exposure period. An EC_{50} 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. Other percentages, e.g., 10 or 1%, are often used to show threshold effect levels (or for e.g., EC10, threshold effect level).
FBSA	Perfluorobutane Sulfonamide
FBSE	N-(2-Hydroxyethyl)-Perfluorobutane Sulfonamide
HTFA	Trifluoroacetic acid (see also TFA)
HxFBSA	N-Hexyl-Perfluorobutane Sulfonamide
k_A	Tom – please define
k_B	Tom – please define
k_N	Tom – please define
K_{AW}	The ratio between the concentration of a test substance found in the n-octanol phase and the concentration found in the gas phase after equilibrium when concentrations are expressed in the same units. KOA is measured at a specified temperature, usually 20 or 25 °C. **Definition** K_{OA} is the partition coefficient between octanol and air K_{OA}=[Xoct]/[Xair] **Common and Preferred Units** Unitless (concentrations in octanol and air are in the same units, e.g., Moles/m3) **Comments** Note In K_{OA} the octanol is pure unlike in KOW where the octanol is saturated with water. This can make a large difference for highly hydrophobic compounds.
K_{OW}	The ratio between the concentration of a test substance found in the n-octanol phase and the concentration found in the water phase after equilibrium. Also called P, P_{OW} or K_{OW}. K_{OW} is measured at a specified temperature, usually 20 or 25 °C. K_{OW} or its logarithm (log K_{OW}) is often used in chemical property estimation. **Definition** K_{OW} is the partition coefficient between octanol and water K_{OW}=[Xoct]/[Xwat] **Common and Preferred Units** Unitless (concentrations in octanol and water are in the same units, e.g., mg/L or Moles/m3) **Comments** This is actually the ratio of solute concentration in octanol saturated with water to that in water saturated with octanol.
LC50	Median Lethal Concentration. The experimentally derived concentration of a test substance which kills 50% of the test organisms after a specified exposure period. An LC_{50} is the usual endpoint in an acute toxicity test with fish. Other percentages, e.g., 10 or 1%, are often used to show threshold lethal levels (or for e.g., LC10, threshold lethal concentration).
MeFBSA	N-Methyl-Perfluorobutane Sulfonamide

MeFBSE	N-(2-Hydroxyethyl)-N-Methyl-Perfluorobutane Sulfonamide
MeFBSE acid	Perfluorobutyl-methyl sulfonamide glycine acid
MPI	"Materials of public interest" (MPI) can be defined as substances or classes of substances or physical agents receiving substantial public or customer attention because of alleged or known effects, concerns or characteristics.
NFB	Nonafluorobutane (most commonly used for nonafluoro n-butane H-$CF_2CF_2CF_2CF_3$)
NIST	National Institute of Standards and Technology, founded in 1901, NIST is a non-regulatory federal agency within the U.S. Department of Commerce. NIST's mission is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life. Website: http://www.nist.gov/
NOEC	No Observed Effect Concentration, the highest concentration tested at which the measured parameter(s) show(s) no significant inhibition or other effect relative to control values
OECD	Organization for Economic Cooperation and Development (OECD) A group of more than 20 member countries that gathers information and promotes cooperation with a view to promoting economic development. As a part of this function, it collects and collates data on environmental degradation and spending on environmental protection as well as promoting a number of cooperative ventures aimed at environmental protection. The OECD Guidelines for Testing of Chemicals are followed for ecotox, toxicology, environmental fate and physical/chemical properties testing in many nations, including the USA. The OECD was the first group to devise GLP (Good Laboratory Practice) testing procedures. In addition, it is coordinating an international High Production Volume (HPV) testing program, which is intended to obtain the information necessary to estimate the risks of these chemicals to the environment and human health. OECD Guidelines for Testing of Chemicals can be found at: http://www.sourceoecd.org/rpsv/periodical/p15_about.htm?jnlissn=1607310x
OPPTS	OPPTS - Office of Prevention, Pesticides and Toxic Substances, is an office from the United States Environmental Protection Agency (U.S. EPA) Develops national strategies for toxic substance control and promotes pollution prevention and the public's right to know about chemical risks. Website: http://www.epa.gov/oppts/index.htm
PBSF	Perfluorobutane sulfonyl fluoride
PBT	Persistent, Bioaccumulative, Toxic
PFAS	Perfluoro Alkyl Sulfonate
PFBS	Perfluorobutane Sulfonate
PFBSI	Perfluorobutanesulfinic acid
PFBA	Perfluorobutanoic acid
PFCA	Perfluorocarboxylic acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooactane sulfonate
PFPA	Perfluoropropanoic acid
TFA	Trifluoroacetic acid

Endnotes:

---

[1] Fate, Transport and Transformation Test Guidelines Office of Prevention, Pesticides and Toxic Substances (OPPTS) 835.2110 Hydrolysis as a Function of pH, EPA 712-C-98-057, January 1998.
[2] Harris, Judith C.; Rate of Hydrolysis in *Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds*; Warren J. Lyman, William F. Reehl, David H. Rosenblatt. Eds. McGraw Hill New York **1982**, pp 7-1 to 7-48.
[3] Maybey, W.; Mill, T, *Critical Review of Hydrolysis of Organic Compound in Water Under Environmental Conditions*, **J. Phys. Chem Ref. Data** *2 (7),* **1978** 383-415
[4] See a complete mathematical derivation for calculating half-lives based on appearance of predicted degradation products contained in the appendices of any 3M Environmental Laboratory report on hydrolytic or photolytic degradation. This derivation was based upon the mathematical treatment of rates given in: Benson, S.W.; *The Foundations of Chemical Kinetics*, McGraw-Hill Book Co., New York, **1960**.
[5] An average *k* was calculated from data contained in reference 3. Half-lives were calculated as per reference 1 using data contained in references 2 and 3.
[6] Aquatic and Surface Photochemistry; Helz, G.R.; Zepp, R.G.; Crosby, D.G. Eds. Lewis Publishers Boca Raton 1994, pp3 -172
[7] Whelan, T.; *Polymer Technology Dictionary*; Springer, New York, NY, 1993, pp321-323
[8] United States Environmental Protection Agency. OPPTS 835.2210 Direct Photolysis Rate in Water by Sunlight. *Prevention, Pesticides and Toxic Substances: Tate, Transport and Transformation Test Guidelines.* EPA 712-C-98-060, Pages 1-35, 1998.
[9] United States Environmental Protection Agency. OPPTS 835.5170 Indirect Photolysis Screening Test. *Prevention, Pesticides and Toxic Substances: Tate, Transport and Transformation Test Guidelines.* EPA 712-C-98-099, Pages 1-16, 1998.
[10] Wilhelm, C.; Gardette, J-l *Infrared analysis of the photochemical behavior of segmented polyurethanes: 1. Aliphatic poly(ester-urethane).* Polymer, *38(16),* 1997, 4019-4031
[11] Decker, C.; Zahouily, K. *Photodegradation and photooxidation of thermoset and UV-cured acrylate polymers* Polymer Degrad. and Stab. *64*, 1999, 293-304
[12] Irusta, L.; Fernandez-Berridi, M.J. *Photooxidative behavior of segmented aliphatic polyurethanes*, Polymer Degrad. and Stab. *63*, 1999, 113-119
[13] Gerlock, J.L.; Nichols, M.E. *Rates of photoxidation induced crosslinking and chain scission in thermoset polymer coatings II. Effect of hindered amine light stabilizer and ultraviolet light absorber additives* Polymer Degrad. and Stab. *69*, 2000, 117-207
[14] Wildlife International, Ltd., 2002, "Determination of the Vapor Pressure of Perfluorobutanesulfonate, Potassium Salt (PFBS) Using the Spinning Rotor Gauge Method", Study Number 454C-127

[15] Grondin, Joseph; Sagnes, Rene; Commeyras; 1976; "Perfluorosulfonic acids and their Hammett Acidity Functions"; Bull. Soc. Chim. Fr.; 1779-83

[16] Wildlife International, Ltd, 2000, "Determination of the Water Solubility of Perfluorobutanesulfonate, Potassium Salt (PFBS) by the Shake Flask Method", Study Number 454C-118

[17] 3M Environmental Laboratory, 2001, "Characterization Study PFBS: a.) Primary Standard – Test Control Reference #TCR-99030-023 (Lot 101), b.) Test Control Reference #TCR-00017-071 (Lot 2) Phase: Solubility Determination", Study Number E00-1877

[18] 3M Specialty Materials Laboratory, 2002, "Potassium Perfluorobutane Sulfonate Surface Tension" Internal report and correspondence

[19] 3M Specialty Materials Laboratory, 2002, "Potassium Perfluorobutane Sulfonate Critical Micelle Concentration" Internal report and correspondence

[20] 3M Environmental Laboratory, 2002, "Discussion of the Rate of Hydrolysis Perfluorobutane Sulfonate", Study Number E00-1429

[21] 3M Environmental Laboratory, 2002, "Discussion of the Photolytic Decomposition of Perfluorobutane Sulfonate", Study Number E00-1429

[22] University of Dayton Research Institute; 2003; "Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides" UDR-TR-2002-000153

[23] 3M Environmental Laboratory, 2002, "Determination of the Air-Water Partition Coefficient of Perfluorobutane Sulfonate, Potassium Salt (PFBS) from its Vapor Pressure and Water Solubility", Study Number E00-1429

[24] Centre Analytical Laboratories, Inc., 2001, "Adsorption and Desorption Study to Determine the Mobility and Distribution of Perfluorobutanesulfonic Acid in Soil", Study Number 023-048

[25] Wildlife International, Ltd., 2001, "Perfluorobutane Sulfonate, Potassium Salt (PFBS): a Flow-Through Bioconcentration Test with the Bluegill (*Lepomis macrochirus*)", Study Number 454A-117

[26] Wildlife International, Ltd., 2001, "PFBS: An Activated Sludge, Respiration Inhibition Test", Study Number 454E-102A

[27] Wildlife International, Ltd., 2001, "PFBS: A 96-Hour Toxicity Test with the Freshwater Alga (*Selenastrum capricornutum*)", Study Number 454A-129

[28] Wildlife International, Ltd., 2001, "Perfluorobutane Sulfonate, Potassium Salt (PFBS): A 48-Hour Static Acute Toxicity Test with the Cladoceran (*Daphnia magna*)", Study Number 454A-118A

[29] Wildlife International, Ltd., 2001, "PFBS: A 96-Hour Static Acute Toxicity Test with the Saltwater Mysid (*Mysidopsis bahia*)", Study Number 454A-128

[30] Wildlife International, Ltd., 2001, "PFBS: A Semi-Static Life-Cycle Toxicity Test with the Cladoceran (*Daphnia magna*)", Study Number 454A-130

[31] Wildlife International, Ltd., 2001, "Perfluorobutanesulfonate, Potassium Salt (PFBS): A 96-Hour Static Acute Toxicity Test with the Fathead Minnow (*Pimephales promelas*)", Study Number 454A-115

[32] Wildlife International, Ltd., 2001, "Perfluorobutanesulfonate, Potassium Salt (PFBS): A 96-Hour Static Acute Toxicity Test with the Bluegill (*Lepomis macrochirus*)", Study Number 454A-114

[33] Wildlife International, Ltd., 2003, "T-7485: A Dietary LC50 Study with the Mallard", Study Number 454-113

[34] Wildlife International, Ltd., 2003, "T-7485: A Dietary LC50 Study with the Northern Bobwhite", Study Number 454-112

[35] 3M Environmental Laboratory, 2002. "Quantitative Analysis of Fluorochemicals in Bobwhite Quail Samples Obtained from Wildlife International, Ltd", Study Number E02-0659

[36] Wildlife International, Ltd., 2003, Letter Report 7/11/03, Study Number 454-115

[37] Wildlife International, Ltd., 2005, "T-7485: A Reproduction Study with the Northern Bobwhite", Study Number 454-116

[38] Wildlife International, Ltd., 2005, "T-7485: A Reproduction Study with the Northern Bobwhite", Study Number 454-116

[39] Wang, Xiao-Jin; Liu, Jin-Tao; Tetrahedron; EN; 61; 29; 2005; 6982 - 6987.

[40] Harzdorf, C. et al.; Justus Liebigs Ann. Chem.; GE; 1973; 33-39.
[41] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[42] M. L. Hanson and K. R. Solomon. 2004. Haloacetic acids in the aquatic environment, Part II: ecological risk assessment. Environmental Pollution 130 (2004) 385 – 401.
[43] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[44] Kim, B.R. et al. 2000. Biodegradability of Trifluoroacetic Acid. Environmental Engineering Science. Volume 17, No. 6. PP337 – 342
[45] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[46] Benesch, J.A. et al., 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647.
[47] Ellis et al. 2001. The fate and persistence of trifluoroacetic and chloroacetic acids in pond waters. Chemosphere 42 (2001) 309-318
[48] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124
[49] Benesch, JA, MS Gustin, GR Cramber and TM Cahill, 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647.
[50] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[51] M. L. Hanson and K. R. Solomon. 2004. Haloacetic acids in the aquatic environment, Part II: ecological risk assessment. Environmental Pollution 130 (2004) 385 – 401.
[52] Solvay communication, Commission of the European Communities DG XI on TFA 04.11.96
[53] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[54] Benesch, JA, MS Gustin, GR Cramber and TM Cahill, 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647.

[55] Kim, B.R. et al. 2000. Biodegradability of Trifluoroacetic Acid. Environmental Engineering Science. Volume 17, No. 6. PP337 – 342

[56] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[57] Solvay communication, Commission of the European Communities DG XI on TFA 04.11.96
[58] Benesch, JA, MS Gustin, GR Cramber and TM Cahill, 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647
[59] Emptage, M., J. Tabinowski and J. Martin Odom. 1997. Effects of Fluoroacetates on Methanogenesis in Samples from Selected Methanogenic Environments. Environ. Sci Technol. 1997. *31*, 732 – 734.
[60] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[61] Berends et al. 1999. Toxicity of Trifluoroacetate to aquatic organisms. Environmental Toxicology and Chemistry, Vol. 18, No. 5, pp. 1053 – 1059.
[62] Benesch, J. A. and M. S. Gustin. 2002. Uptake of trifluoroacetate by *Pinus ponderosa* via atmospheric pathway. Atmospheric Environment 36 (2002) 1233 – 1235.
[63] Hanson, M. L. and K. R. Solomon. 2004. Haloacetic acids in the aquatic environment. Part I: macrophyte toxicity. Environmental Pollution Vol. 130, Issue 3, pp 371-383.
[64] Benesch, JA, MS Gustin, GR Cramber and TM Cahill, 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647
[65] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.
[66] Emptage, M., J. Tabinowski and J. Martin Odom. 1997. Effects of Fluoroacetates on Methanogenesis in Samples from Selected Methanogenic Environments. Environ. Sci Technol. 1997. *31*, 732 – 734.

[67] Berends et al. 1999. Toxicity of Trifluoroacetate to aquatic organisms. Environmental Toxicology and Chemistry, Vol. 18, No. 5, pp. 1053 – 1059.
[68] Hanson, ML, PK Sibley, SA Mabury, KR Solomon and DC Muir. 2002. Trichloroacetic acid (TCA) and trifluoroacetic acid (TFA) mixture toxicity to the macrophytes *Myriophyllum spicatum* and *Myriophyllum sibiricum* in aquatic microcosms. Science of the Total Environment, Vol 285, Issues 1-3, pp 247 – 259.
[69] Benesch, J. A. and M. S. Gustin. 2002. Uptake of trifluoroacetate by *Pinus ponderosa* via atmospheric pathway. Atmospheric Environment 36 (2002) 1233 – 1235
[70] Benesch, JA, MS Gustin, GR Cramber and TM Cahill., 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647.
[71] Boutonnet (Ed)., 1999. Environmental Risk Assessment of Trifluoroacetic Acid. Human and Ecological Risk Assessment: Vol. 5, No. 1, pp. 59-124.

[72] Benesch, JA, MS Gustin, GR Cramber and TM Cahill., 2002. Investigation of effects of trifluoroacetate on vernal pool ecosystems. Environmental Toxicology and Chemistry, Vol. 21, No. 3, pp. 640-647.
[73] Perfluoropropionic Acid: Determination of the Ready Biodegradability (Biotic Degradation) using the CO2 Evolution test (Modified Sturm). T.R. Wilbury, 8/27/01. E01-0605
[74] Biodegradation study of T-7701.5 in microorganisms. July 5, 2002. CERI Study number 13858. LIMS E03-0510
[75] Bioconcentration Study of T-7701 in Carp. 09/12/02. Kurume Laboratory Study Number 43859, CERI, Japan. LIMS E03-0510
[76] 3M Environmental Lab LIMS number E01-0605, 2001
[77] 3M Environmental Lab LIMS Number E02-0319 (testing of Hydrolysis product of C6 Ketone), 2002

[78] "Bioconcentration Study of T-7701 in Carp", section Acute Toxicity in Oryzias latipes. Kurume Laboratory (CERI), 2002 LIMS E03-0510
[79] Martin, JW et. al. 2002, Bioconcentration and tissue distribution of Perfluorinated acids in rainbow trout (*oncorhynchus mykiss*); Martin JW, Mabury SA, Solomon KR, Muir DCG. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mukiss). Environ Toxicol Chem 2003a; 22: 196-204.
130; Martin JW, Mabury SA, Solomon KR, Muir DCG. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (Oncorhynchus mukiss). Environ Toxicol Chem 2003b; 22(1): 189-195.
[80] Data is for iso perfluorobutyric acid. All results from AScI laboratory, LR U1613, using mean measured concentrations, 1999
[81] Data is for normal perrluorobutyric acid. All results from AScI Laboratory, LR U1159, 1999
[82] Data is with potassium perfluorobutanoic acid. Wildlife International, LIMS E08-0122, 2008
[83] A hazard assessment of perfluorobutyric acid (PFBA), 2008, Entrix Inc.

Study insertion is incomplete as is the reference table - References need to be updated

[84] FC-23, 3M Env Lab, 1981, Lab Request 7364
[85] 3M Materials Resource Division (MRD) Analytical Lab, 1999, GID #59437
[86] Liebigs Ann. Chem., GE; 3; 1982; 545-563; Bussas, R., et.al.
[87] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #71780
[88] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #
[89] Org. Biomol. Chem.; EN; 3; 2; 2005; 225-226; Blackburn, G. et. Al.
[90] 3M Materials Resource Division (MRD) Analytical Lab, 2002, GID # 70920
[91] 3M Materials Resource Division (MRD) Analytical Lab, 2006, GID #102901
[92] Era laboratories, 2003. LIMS E03-0514
[93] Wildlife International, 2003. LIMS E03-0514
[94] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #
[95] 3M Materials Resource Division (MRD) Analytical Lab, 2004, GID # 87564
[96] 3M Materials Resource Division (MRD) Analytical Lab, 2002, GID # 70920

[97] 3M Environmental Technology and Safety Services, 2003, "Inherent Aerobic Aquatic Biodegradation of MeFBSE", E02-1325
[98] Wildlife International, Ltd. 2002. E01-1501
[99] Wildlife International, Ltd. , 2004. E02-0806
[100] Wildlife International, Ltd., 2002, "Activated Sludge Respiration Inhibition Test ", Study Number 454E-109
[101] Wildlife International, Ltd., 2002, "A 96-hour Toxicity Test with the Freshwater Alga (*Selenastrum capricornutum*) ", Study Number 454A-187
[102] Wildlife International, Ltd., 2004, "A 48 hour Static–Renewal Toxicity Test with Cladoceran, *daphnia magna*", Study Number 454A-184.
[103] Wildlife International, Ltd., 2004, "A 96-hour Static Acute Toxicity test with the Saltwater Mysid (*Mysidopsis bahia*) ", Study Number 454A-186C.
[104] Wildlife International, Ltd., 2004, "A 96-hour Static-Renewal Acute Toxicity Test with the Fathead Minnow (*Pimephales promelas*) ", Study Number 454A-185
[105] 3M Materials Resource Division (MRD) Analytical Lab, 2004, GID #58957
[106] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #
[107] 3M Materials Resource Division (MRD) Analytical Lab, 2002, GID # 70920
[108] 3M Materials Resource Division (MRD) Analytical Lab, 2006, GID #102901
[109] 3M Environmental Technology and Safety Services, 2003, "Inherent Aerobic Aquatic Biodegradation of MeFBSE", E02-1325
[110] Wildlife International, Ltd., 2004, "A 96-hour Static Acute Toxicity test with the Saltwater Mysid (*Mysidopsis bahia*) ", Study Number 454A-182.
[111] Wildlife International, Ltd., 2002, "Activated Sludge Respiration Inhibition Test ", Study Number 454E-110
[112] Wildlife International, Ltd., 2002, "A 96-hour Toxicity Test with the Freshwater Alga (*Selenastrum capricornutum*) ", Study Number 454A-183
[113] Wildlife International, Ltd., 2004, "A 48 hour Static –Renewal Toxicity Test with Cladoceran, *daphnia magna*", Study Number 454A-180A.
[114] Wildlife International, Ltd., 2004, "A 96-hour Static Acute Toxicity test with the Saltwater Mysid (*Mysidopsis bahia*) ", Study Number 454A-182.
[115] Wildlife International, Ltd., 2004, "A 96-hour Static-Renewal Acute Toxicity Test with the Fathead Minnow (*Pimephales promelas*) ", Study Number 454A-181
[116] 3M Materials Resource Division (MRD) Analytical Lab, 1999, GID #59437
[117] Liebigs Ann. Chem., GE; 3; 1982; 545-563; Bussas, R., et.al.
[118] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #71780
[119] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #
[120] Org. Biomol. Chem.; EN; 3; 2; 2005; 225-226; Blackburn, G. et. Al.
[121] 3M Environmental Technology and Safety Services, 2003, "Inherent Aerobic Aquatic Biodegradation of MeFBSE", E02-1325
[122] 3M Materials Resource Division (MRD) Analytical Lab, 2003, GID #7426956
[123] 3M Materials Resource Division (MRD) Analytical Lab, 1999, GID #59437
[124] Liebigs Ann. Chem., GE; 3; 1982; 545-563; Bussas, R., et.al.
[125] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #71780
[126] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #
[127] Org. Biomol. Chem.; EN; 3; 2; 2005; 225-226; Blackburn, G. et. Al.
[128] 3M Materials Resource Division (MRD) Analytical Lab, 2002, GID # 70920
[129] 3M Materials Resource Division (MRD) Analytical Lab, 2006, GID #102901
[130] 3M Environmental Technology and Safety Services, 2003, "Inherent Aerobic Aquatic Biodegradation of MeFBSE", E02-1325
[131] 3M Materials Resource Division (MRD) Analytical Lab, 2003, GID #79753
[132] 3M Materials Resource Division (MRD) Analytical Lab, 2003, GID #79752
[133] 3M Materials Resource Division (MRD) Analytical Lab, 2001, GID #
[134] 3M Materials Resource Division (MRD) Analytical Lab, 2003, GID # 80024
[135] 3M Environmental Technology and Safety Services, 2003, "Inherent Aerobic Aquatic Biodegradation of MeFBSE", E02-1325
[136] 3M Materials Resource Division (MRD) Analytical Lab, 2003, GID #7426956

[137] Gramstad; Haszeldine; Journal of the Chemical Society; 1957; 2640,2642; ISSN: 0368-1769.
[138] Gramstad; Haszeldine; Journal of the Chemical Society; 1957; 2640,2642; ISSN: 0368-1769.
[139] LaZerte et al.; Journal of the American Chemical Society; 75; 1953; 4525,4526; ISSN: 0002-7863.