3M Internal Correspondence

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From: R. D. Howell - Environmental Lab - 2-3E-09 (8-7540)

Subject: Fluorochemicals in the Environment

Date: February 5, 1992

Enclosed is a draft proposal for studying the environmental effects of fluorochemicals. I want to emphasize that it is a draft or preliminary proposal. The intent is to help you prepare your presentation to management. Please keep in mind that the costs are very speculative since the analytical methods are not yet worked out.

Also enclosed is a separate document which contains summaries of some of the previous technical reports dealing with fluorochemical issues. Most of the reports are from the late 1970s, so they are a bit dated.

I look forward to your comments on the draft proposal.

Enclosure

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Fluorochemicals in the Environment

I. Introduction

Fluorochemicals are an important class of compounds to three 3M divisions. The fate and effects of these materials in the environment are not completely understood. 3M needs to develop a more detailed understanding to respond to customer concerns and mounting governmental regulations. Recent advances in analytical methods provide an opportunity to address many of the long-standing questions surrounding fluorochemicals in the environment. A variety of projects are suggested which address environmental issues of fluorochemicals with a focus on model fluorochemical compounds which represent the major classes of 3M fluorochemicals.

II. Background

There is no question that environmental issues will increasingly affect virtually all areas of 3M business. From permits for manufacturing plants to recycling, composting, and incineration of waste products, the future will bring continued concern about the environmental effects of 3M products from customers and from government regulatory authorities.

3M now enjoys a positive environmental image and has been recognized on many occasions for its pollution prevention programs. In order to protect the corporation's positive image, avoid regulatory encumbrances, and reduce costs over the long-term, the leadership role must be maintained. This need is definitely true for 3M's operating units which make and use fluorochemicals. It is essential that answers be found to the long-standing questions on the environmental fate and effects of 3M perfluorinated materials.

For the most part, 3M Environmental Laboratory studies have concentrated on the environmental effects of 3M products that contain fluorochemicals. This product-oriented approach has served and continues to serve 3M and its customers well. However, the environmental effects data on products is of limited value in increasing our understanding of the effects of fluorochemicals for several reasons. First, products are usually complex mixtures of solvents, emulsifiers, surfactants, and inorganic salts so that the environmental effects of the fluorochemical components are obscured by the other ingredients in the product. Second, there is rarely a single fluorochemical present in the product. Instead, products may contain a variety of fluorochemicals and their isomers which makes generalizations about the environmental properties of individual fluorochemicals quite difficult. Third, the tests have focused on short-term effects. Common tests include 96-hour fish or algae toxicity, 48-hour *Daphnia* toxicity, and 30-minute or 3-hour activated sludge respiration inhibition. [These short-term tests aren't intended to measure long-term effects like bioaccumulation or chronic toxicity.]

In addition to the environmental testing on 3M products that contain fluorochemicals, a number of studies have been done to evaluate the environmental properties of fluorochemicals.

Those studies have included aerobic biodegradation, photodegradation, soil sorption, short-term toxicity, and bioaccumulation as well as development of analytical methods for quantifying fluorochemicals.

Perhaps the most important conclusion from previous studies is the stability of fluorochemicals. Although stability is one of the most desirable properties fluorochemicals possess for many applications, from an environmental perspective, "stability" connotes "persistence" which can be the cause of concern especially when coupled with other properties. For example, some fluorochemicals have a tendency to accumulate in biological tissues. Moreover, some fluorochemicals have biological activity. This is most seriously demonstrated by the use of some fluorochemicals as pesticides. This is not to say that all fluorochemicals accumulate or that all have biological activity. But taken together, stability, the tendency to bioaccumulate, and biological activity are a potentially troublesome combination.

Fluorochemical stability has been demonstrated in environmental tests conducted in the 3M Environmental Laboratory. Those tests have shown that fluorinated materials are much more resistant than their hydrogen, chlorine or bromine analogues to degradation through chemical, biological, or photochemical means. This stability may in large part be due to the strength of the carbon-fluorine bond. It is likely that the hydrophobicity of the perfluorinated moieties. Moreover, it is believed that fluorocarbon chains are more "rigid" than analogous hydrocarbon chains [1], perhaps because of the greater size of the fluorine atoms. All of these factors undoubtedly influence the stability of the perfluorinated portions of the molecules, but the stability may extend to the non-fluorinated portions of the molecules as well.

One favorable point about 3M fluorochemicals is that they generally exhibit low orders of toxicity to aquatic organisms in both acute and subchronic tests. There are exceptions though, primarily with fluorochemical surfactants. For example, FC-95 was moderately toxic to fathead minnows in critical life-stage studies[2]. It should be noted, however, that many commonly used non-fluorinated surfactants have similar or greater toxicity[3], but since non-fluorinated surfactants are more likely to degrade in wastewater treatment systems or in the environment, the toxicity of non-fluorinated surfactants is not as great an issue as the fluorochemical surfactant toxicity. Once more, the persistence of fluorochemicals increases the concern caused by their toxicity. It should be kept in mind that the acute toxicity tests for which the greatest amount of data exists are usually a few days in duration and do not reveal long-term effects such as bioaccumulation or chronic toxicity.

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1 Guo, W., Brown T. A., and Fung, B. M. "Micelles and aggregates of fluorinated surfactants." *J. Phys. Chem.* **1991** *95* 1829-1836.

2 J. Dean, "The effects of continuous aqueous exposure to 14C-78.02 (FC-95) on hatchability of eggs and growth and survival of fry of fathead minnow (*Pimephales promelas*)," Report No. BW-78-8-263, EG&G Bionomics, Wareham, MA, August 1978.

3 Goyer, M. M. *et al.* Human Safety and Environmental Aspects of Major Surfactants. A report by Arthur D. Little, Inc., to the Soap and Detergent Association, May 31, 1977.

The greatest limitation to the previous studies was a lack of quantitative analytical methods applicable to fluorochemicals. Recently acquired equipment and advances in analytical methods development in the 3M Environmental Laboratory show great promise in overcoming the difficulties in detecting and quantifying fluorochemicals in environmental matrices such as groundwater, soil, sediment, compost, wastewater, and plant and animal tissues. These advances in analytical methods make this proposal possible.

The proposed studies will require cooperation from all aspects of 3M's fluorochemical community, including manufacturing facilities, product development laboratories, and marketing groups. The studies will also require confidentiality by all members of the 3M community involved in them. Confidentiality will be especially important until the studies are completed so as to avoid false conclusions. On the other hand, EPA regulations require notification of the Agency within specific time constraints if significant effects are discovered. This adds considerable importance that the studies are correct in their findings and completed in a timely fashion. To ease these concerns, outside reviewers, preferably noted academicians in the field, should be retained to aid in the design and interpretation of the studies.

Following are descriptions of proposed projects that will expand 3M's knowledge of the environmental fate and effects of fluorochemicals. The emphasis is on projects with broad applicability that will, as much as possible, overlap the environmental concerns of various product lines. In fact, in most cases, specific products are not mentioned in this proposal. Instead, the emphasis is on specific fluorochemical compounds.

III. Proposed Projects

Proposed projects are given in a more or less chronological and prioritized order. The intent is to give an idea of the kinds of studies we believe are needed along with a rough idea of estimated costs. Lab studies are given first because they will give an opportunity to develop and refine the analytical methods. The proposed field studies are described last since they would likely be done after completion of the lab studies.

A. Degradation Studies

1. Aerobic Microbial Degradation of Non-fluorinated Moieties

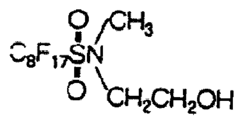
Previous degradation studies have included photochemical and aerobic biodegradation studies. [Those studies have shown conclusively that the perfluorochemical moieties are persistent to degradation by those mechanisms.] There is some evidence from previous studies, however, that the non-fluorinated moieties of 3M fluorochemicals may be degraded by microbial mechanisms. For example, tests on FC-128 using oxygen uptake[4] showed 37% degradation in 6.25 hours at 30°C. Tests on FC-171 showed 25% to

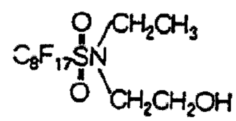
(4) "Biodegradation Studies of Fluorocarbons", 3M Technical Report by E. A. Reiner, Project 75-6398-29, August 12, 1976.

33% of the dissolved organic carbon (DOC) were removed in the first 2 days [5]. The recent study by RCC Notox for the European PMN for the acrylic foamer showed biodegradation of approximately 6% after 5 days [6]. The extent of biodegradation in that study was determined by CO_2 measurements.

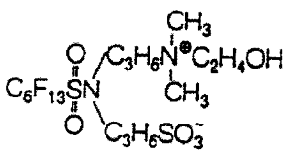
Previous tests used gross measurements such as gas pressure or DOC to determine biodegradation. More definitive answers to the extent of biodegradation and the products of degradation are now believed possible because of the advances in analytical methods.

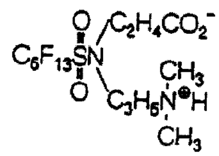
A study is proposed to determine if degradation of hydrocarbon moieties takes place and if so, at what rate and with what degradation products. Proposed compounds of the perfluorosulfonamino class include the methyl or ethyl FOSE alcohol,



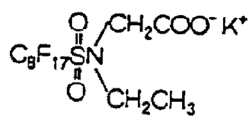


the sultone or acrylic foamer,

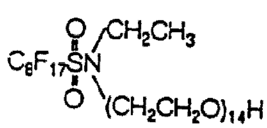


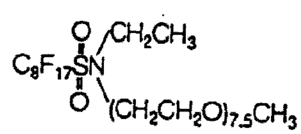


FC-128/129,



or a fluoroaliphatic oxyethylene adduct, such as FC-170C or FC-171





5 FC-171 PED.

6 "Ready Biodegradability: Modified Strum Test with T-2816 (L-4640)" RCC Notox Project 048149, May 17, 1991.

Perfluorosulfonamino compounds are believed to degrade to perfluorooctanesulfonate at which point aerobic degradation ceases. If this is found to be true in this study, it will direct the focus of other projects to that single compound rather than an extensive collection of other materials.

Another material proposed for study is $C_8F_{17}CH_2CH_2OH$ (1H, 1H, 2H, 2H-perfluorodecanol). In spite of the fact that it is not a 3M material, this material is proposed because it is known to biotransform in mammalian systems with $C_7F_{15}COO^-$ (perfluorooctanoate) as a metabolite[7]. The ammonium salt of perfluorooctanoate is a 3M product. Interestingly, elevated inorganic fluoride concentration in plasma and urine in the cited study suggests defluorination of the CF_2 group adjacent to the CH_2 group in the parent compound. Further investigation of this material is warranted because of the apparent degradation of the fluorinated methylene group in the cited study. If perfluorooctanoate is found to be an end product of the biodegradation of $C_8F_{17}CH_2CH_2OH$, it may show that products from other companies contribute to the presence of perfluorooctanoate in the environment.

In this study, we will set up aerobic microbial cultures using microbial seeds from the wastewater treatment systems at 3M manufacturing plants. Selected fluorochemicals will be introduced into the cultures and over time, aliquots will be analyzed to assess the degradation of the hydrocarbon moieties and the appearance of recalcitrant fluorochemical end products.

This study is proposed not only for the knowledge it will provide on the fate of the non-fluorinated moieties, but because it will provide an opportunity to perfect the analytical methods for the field studies described below. An estimated cost for this study is $50,000 with 75% of that required for the analytical work.

2. Anaerobic Microbial Degradation

Anaerobic microbial degradation has not been investigated in any previous 3M study. In addition, a thorough search of the literature did not bring up any reports of microbial degradation of perfluorinated materials. The known resistance of perfluorochemicals to aerobic microbial degradation gives this study a high priority.

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(7) Hagen, D. F., *et al.* " Characterization of Fluorinated Metabolites by a Gas Chromatographic-Helium Microwave Plasma Detector - The Biotransformation of 1*H*, 1*H*, 2*H*, 2*H*-Perfluorodecanol to Perfluorooctanoate" *Analytical Biochemistry* 118 (1981) 336-343.

There are many reports of the anaerobic microbial degradation of chlorinated and brominated organics, many of which are resistant to aerobic microbial degradation. There are also reports of microbial degradation of partially fluorinated materials by both aerobic and anaerobic bacteria[8,9,10]. It may be possible for anaerobic microorganisms to degrade perfluorinated materials as well. If anaerobic degradation is found to occur, the knowledge will have important implications for wastewater treatment by 3M and our customers.

In this study, we will investigate the ability of a mixed anaerobic microbial population to degrade perfluorinated materials. Mixed anaerobic population implies commonly occurring populations found in river or lake sediments or municipal anaerobic wastewater treatment systems.

The 3M Environmental Laboratory is equipped to perform anaerobic biodegradation studies following the US EPA/TSCA protocol. In this method, an anaerobic bacterial seed from a municipal wastewater treatment system along with the material being tested is placed in a sealed bottle. The bottle is then incubated at 35°C and the extent of biodegradation is determined by an increase in gas pressure. Besides measuring gas pressure, the fluoride concentration will be measured throughout the test period. An increase in fluoride concentration will occur if degradation of the perfluorinated moiety occurs. Furthermore, the concentration of starting fluorochemicals will be measured, and, as in the aerobic study described above, the fate of non-fluorinated moieties will be determined.

The emphasis in both the anaerobic and aerobic degradation studies will be on specific fluorochemicals rather than products. Several compounds are proposed for subjects of the anaerobic degradation study because they are representative of the major classes of 3M fluorochemicals. It is anticipated that the results of studies on a few model compounds can be extrapolated to other fluorochemicals within the same class, although there is an element of risk with such extrapolations.

The first group proposed for study is the perfluorosulfonamides. This is a large and important class of 3M fluorochemicals. It is proposed that the anaerobic and aerobic degradation studies be performed on the same members of this class since the analytical work will overlap. Suggested compounds and their structures are given above.

The second group is the sulfonic acids, with perfluorooctanesulfonate being the proposed model compound. This is a 3M fluorochemical product, an ingredient in other 3M products, and is believed to be a product of biodegradation of other fluorochemicals.

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8 Walker, J. R. L. and Lien, B. C. "Metabolism of fluoroacetate by a soil *Pseudomonas* sp. and *Fusarium solani*." *Soil Biology and Biochemistry* 13 (1981) 231-5.

9 Linkfield, T. G., Suflita, J. M., and Tiedje, J. M. "Characterization of the acclimation period before anaerobic dehalogenation of halobenzoates." *Applied and Environmental Microbiology* 55 (1989) 2773-8.

10 Rietjens, I. M. C. M., *et al.* "Reaction pathways for biodehalogenation of fluorinated anilines." *European Journal of Biochemistry* 194 (1990) 945-54.

A third group proposed for this work is the phosphate esters. The major material in this class is the ammonium salt of the di-phosphate ester of the ethyl FOSE alcohol (FM-3422). The phosphate esters are important for their use in 3M fluorochemical paper treatment products.

The fourth material proposed for this study is FC-143. It is important not only because it is a 3M material, but because other fluorochemicals may degrade to perfluorocarboxylic acids. FC-143 is a good choice as a model compound for the anaerobic degradation perfluorocarboxylic acids. A fifth compound is $C_8F_{17}CH_2CH_2OH$ (1H, 1H, 2H, 2H-perfluorodecanol). Reasons for studying this material were given above in the discussion of the aerobic degradation study.

This study is estimated to cost $60,000 which includes the analytical method development work and sample analysis.

3. Fungal Degradation

As with the anaerobic microbial degradation described above, degradation of perfluoro compounds specifically by fungi has not been considered in any previous 3M study. Fungi, however, are widespread in the environment so there were probably some fungi present in the previous aerobic biodegradation studies. Fungi are aerobic organisms and although aerobic microbial degradation is not known to occur, fungi differ from bacteria in that they can thrive in more acidic conditions. No references to degradation of perfluoro compounds by fungi were found in a search of the literature, but fungi have recently been found to break down recalcitrant chlorinated compounds such as dichlorophenol[11]. As with the anaerobic degradation study, this study would address concerns regarding the persistence of fluorochemicals.

Fungal degradation is a new area. We propose as a first step identifying prominent university workers in the field of fungal degradation of recalcitrant materials and contacting them for guidance as well as their research interests in this area. At that point, we would decide whether to have the fungal work done by university workers or within 3M's Corporate Research Analytical Laboratory. In either case, the analytical work would be done within the 3M Environmental Laboratory. The materials described above in the aerobic and anaerobic sections would be the subject of this study as well because of the overlap in the analytical work. Consequently, the analytical method development work is not included in the cost estimate which is to be $30,000.

B. Laboratory-Scale Wastewater Fate Studies

In this study, a bench-scale wastewater treatment system would be set up to evaluate the possible fates of fluorochemicals in manufacturing plant wastewater. These fates include sorption to bacterial solids, vaporization, and passage out of the system with treated wastewater. The main purpose of the lab-scale study is to gain an understanding of the mass balance of fluorochemicals

11 *Chemical and Engineering News*, January 7, 1991, p 22.

in wastewater. The bench-scale model would be based on the wastewater treatment systems at 3M manufacturing plants so as to provide insight into processes taking place at those plants. Mass balance of fluorochemicals in the plants' wastewater treatment systems will be difficult since most fluorochemical production is by batch processes. This study would be preliminary to the manufacturing wastewater treatment system field studies described below. Another motivation for this study is that a lab-scale wastewater treatment system could provide samples of sludge and wastewater for the analytical method development needed for field studies.

This study would be done together with the aerobic degradation studies described above, but the present study would consider a broader range of fluorochemicals that are likely to be pass from the manufacturing processes into the plant wastewater treatment systems. Recall that the aerobic degradation study is limited to the perfluorosulfonamides. A first step in this study is for the manufacturing plant process engineers and EE&PC Environmental Engineering Services (EES) plant environmental contacts to specify fluorochemicals being manufactured and discharged to the wastewater treatment system. In addition, the manufacturing wastewater would be sampled on a limited basis and analyzed for fluorochemicals.

Estimated cost is $60,000.

C. Incineration Studies

Incomplete combustion of fluorochemicals may lead to the formation of acutely toxic by-products such as carbonyl fluoride and perfluoroisobutylene in addition to the HF normally formed. Recently, the German UBA, which is equivalent to the US EPA, has asked for information on the decomposition products from incineration of Fluorinert™ foam blowing agents[12]. Also, questions arise from time-to-time about the production of fluorinated dioxins from the combustion of 3M fluorochemicals. There is also interest from customers regarding the combustion of fluorochemical treated paper, fabric, and carpet.

Recent studies on incineration of non-fluorochemical 3M products have been moderately successful. The work was done for 3M by Southwest Research Institute and was successful in identifying the presence or absence of certain key compounds from an EPA list that includes HCN, chlorinated organics, and metals. To date, no fluorochemical containing products have been studied.

The biggest shortcoming of the Southwest studies is that the apparatus used in those studies was a primary combustion model. This failed as a "real world" incinerator model since it did not include a secondary combustion chamber. Southwest is currently developing laboratory models that include secondary combustion. Those incinerator models are expected to be available this summer. The next generation models will allow for sampling after primary combustion, after secondary combustion, and after cool-down of the secondary combustion emissions.

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12 D. Reese, 3M Germany, personal communication.

Incinerator models are quite difficult to develop since the operational parameters of incinerators are extremely variable and difficult to scale down. The expensive part of the studies is not sample collection, however, but sample analysis, which is about 70% of the cost. Previous studies involving sampling of primary combustion and analytical work ranged from $3,000 to $4,500 per product. Current estimates for sampling three stages (primary, secondary, and cool-down) including the analytical work for all three stages range from $10,000 to $15,000 per material.

A second possibility for this work is the University of Dayton Environmental Sciences Group. They have done considerable work for the EPA and have published extensively. Their focus is on secondary combustion. Their lab-scale apparatus allows for varying residence time, temperature, reactant concentration, and waste/oxygen ratio. The cost would range from $5,000 to $10,000 per material including analytical work.

The recommended scheme for the proposed incineration studies includes studies of model compounds and studies of 3M products that contain fluorochemicals. In each study, analytical work would include scanning for toxic organics from the EPA list as well as fluoroorganics, but the focus would be on verifying that complete combustion occurs with complete conversion of fluorinated materials to CO_2 and HF. It is important to point out that these studies are not intended to address issues of unintentional combustion such as fires. Instead, they will address issues of incineration in municipal or industrial incinerators.

Following are suggested compounds for an incineration study. The final choice of compounds would be determined by the division laboratories.

1. Perfluoroalkanes. Suggested model compound is perfluoropentane (C_5F_{12}).
2. Perfluoroamines. Suggested model compound is perfluorotripentyl amine, $(C_5F_{11})_3N$.
3. Phosphate Esters.
   The phosphate esters are used in 3M fluorochemical paper treatment products. This study would include separate combustion tests of the untreated paper, the fluorochemical paper treatment product, and the paper treated with the fluorochemical treatment. Tests on each of these materials would be done with an appropriate fuel and at reasonable concentrations of paper, fluorochemical paper treatment, or treated paper in the combustion mixture. The intent would be to determine if the fluorochemical treatment causes any measurable effects on the combustion of paper under normal circumstances. This would include analyzing for the presence of additional hazardous combustion products from the fluorochemical treated paper.
4. Fluoroaliphatic Polymer.
   This is a polymeric material used in 3M fluorochemical carpet or fabric treatment products. The study would include separate combustion tests of untreated carpet/fabric, fluorochemical carpet/fabric treatment product, and fluorochemical treated carpet/fabric. As with the testing scheme in item 3, the tests would be done with an appropriate fuel and at reasonable concentrations of the test materials. The intent would be to determine the effects of the fluorochemical treatment on the combustion of carpet or fabric and the presence or absence of additional hazardous combustion products from the fluorochemical treated materials.

- A preliminary estimate for the incineration studies is $150,000.

D. Fate and Effect of Fluorochemicals in Compost

Increasingly, composting is becoming a common method of disposal of solid wastes, particularly paper products such as that used in the fast food industry. 3M's fluorochemical paper treatment products are an important part of that industry. This project is being driven by our customers who want to know if fluorochemicals influence the composting process in any way. Moreover, customers want to know if fluorochemicals cause measurable effects that would limit the salability of the finished compost.

3M Environmental Laboratory personnel have developed a laboratory scale compost apparatus that makes use of modified 55-gallon drums to simulate large-scale compost operations. The method is similar to that in use elsewhere (most notably, Proctor and Gamble) to study the degradability of products in compost and the fate and effects of degradation products. In addition, 3M is sponsoring a post-doctoral fellow at the University of Massachusets at Lowell to develop rapid, reproducible, lab-scale compost testing methods.

The Protective Chemical Products Division has agreed to sponsor studies of paper treated with its Scotchban™ fluorochemical paper treatment products in the 3M Environmental Laboratory. Those studies are beginning at this time. Limited analytical work has been accomplished on FC-807 with the MS/MS, but the details of super-critical extraction of fluorochemicals from compost have yet to be worked out.

We anticipate that the analytical work will be the most expensive part of these studies since the compost apparatus and methodology are already in use in the 3M Environmental Laboratory. This project is estimated to cost $50,000 with 75% of that amount for the analytical work.

Further compost studies should include large scale composting of a food waste/fluorochemical treated paper mixture similar to that produced by a fast food restaurant. Initial inquiries have been made with a commercial municipal waste composting operation located in St. Cloud, Minnesota (RECOMP of Minnesota) for such a study. The estimated cost is $20,000.

E. Bioconcentration

Laboratory-scale bioconcentration studies are proposed to investigate the uptake of fluorochemicals by fish. An important reason for undertaking this study is that wastewater discharges from 3M manufacturing plants enter rivers used for sport and commercial fishing as well as drinking water supplies. Moreover, structure activity computer models currently in use by regulatory authorities may give unrealistic values for the bioaccumulative potential of fluorochemicals. Those models are often based on the octanol/water partition coefficient which may not be an appropriate measure of bioaccumulative potential for fluorochemicals, particularly those with an electronic charge. To successfully counter the predictions of the computer models, defendable bioaccumulation and octanol/water partition data are needed.

Previous studies have shown that some fluorochemicals bioaccumulate in fish [13,14,15,16]. The proposed study would go far beyond previous studies because of the more advanced analytical capabilities available today. This study will not be limited to compounds detectable by gas chromatographic techniques (such as the ethyl FOSE alcohol, FM-3422) but will include charged fluorochemicals as well. Additionally, the improved analytical capabilities will allow better measurement of fluorochemical concentration in specific organs.

Proposed fluorochemicals for this study are: perfluorooctanesulfonate (FC-95), perfluorooctanoate (FC-143), ethyl FOSE alcohol (FM-3422), and a charged perfluorosulfonamide such as FC-128 or the sultone or acrylic foamer. These represent four classes of 3M fluorochemicals: uncharged perfluorosulfonamides, charged perfluorosulfonamides, perfluorocarboxylic acids, and perfluorosulfonic acids. Study of these three classes will also provide insight into the mechanism of bioaccumulation which may be different for charged versus uncharged molecules.

Each material will include two phases: an uptake phase and a clearance phase. In the uptake phase, fish will be placed in aquaria and exposed to the fluorochemicals for several weeks. Individual aquaria will be used for each test material. Fish will be sacrificed during the exposure period to monitor the uptake rate. In the clearance phase, the remaining fish will be placed in aquaria with flowing water that is free of fluorochemicals. At appropriate intervals, fish will be sacrificed and analyzed for fluorochemicals to determine the rate of removal of fluorochemicals.

As with the model wastewater treatment plant study given above, this laboratory bioaccumulation model should be done prior to the field studies described below to provide opportunities for the analytical method development. Estimated price is $150,000 to $250,000 per compound and includes analytical method development for measurement of the fluorochemicals given above in fish tissues.

F. Field Studies at 3M Manufacturing Plants

Field studies at 3M manufacturing plants are recommended to measure distribution, transformation, biological uptake, and effects of fluorochemicals. 3M manufacturing plants provide a unique opportunity to investigate the environmental effects of fluorochemicals because they have been sites of fluorochemical manufacture for many years and fluorochemicals are likely to be present in rather high concentrations. Fluorochemicals have been entering the

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13 M. T. Elnabarawy, "Bioconcentration of FM-3422 in Bluegill Sunfish and in Channel Catfish", Project 9970612600 Technical Report No. 1, May 17, 1977.

14 A. N. Welter, "Evaluation of the Bioconcentration Potential of FM-3422", Project 9970612623 Technical Report No. 2, August 16, 1978.

15 G. A. Vraspir and A. Mendel, "Analysis of Fluorochemicals in Bluegill Fish", Project 9970612600 Technical Report No. 14, May 1, 1979.

16 J. E. Gagnon, "Bioaccumulation of Fluorochemicals in Tennessee River Fish", Project 78-2740 Technical Report No. 1, May 22, 1979.

environment via vapor and wastewater discharges from manufacturing processes. Also, tars and wastewater sludges that contain fluorochemicals have been disposed of by incorporation into soil. 3M manufacturing plants are unique in that they are situated on aquatic ecosystems that will enable investigations of fluorochemical accumulation in fish, shellfish, aquatic plants, and sediments.

Important questions which will be addressed by these projects include:

- What fluorochemicals are present in the wastewater from the 3M manufacturing plants and at what concentration?
- What happens to the fluorochemicals in the wastewater as it passes through the treatment system? Are they changed in any way? Are the hydrocarbon moieties degraded by the microorganisms in the treatment system?
- Do fluorochemicals pass through the treatment processes with the effluent and out into the receiving stream or are they adsorbed to the sludge?
- Historically, sludge from the wastewater treatment plants has been applied to land. What has happened to the fluorochemicals in sludge applied to land? Have the fluorochemicals migrated through the soil with the groundwater? If so, what is the extent of their migration?
- What fluorochemicals are present, and at what concentration, in the bottom sediments near the outfall from the wastewater treatment plants? How does the fluorochemical concentration in sediments vary downstream from the plants' outfall?
- Are fluorochemicals present in the biota of the receiving streams? Does the amount or type of fluorochemical vary with the trophic level? What about such factors as the age, size, and species of fishes?
- What are the potentials for human exposure to fluorochemicals from consumption of fish from the streams receiving wastewater from fluorochemical manufacture?

Several studies are proposed to learn the fate of fluorochemicals around 3M manufacturing plants. These studies are now believed possible because of recent analytical advances in the 3M Environmental Laboratory. The analytical method development is not complete for all of the environmental matrices likely to be encountered in these studies.

1. Fluorochemicals in Wastewater

Determine fluorochemical content of manufacturing plant wastewater and determine the fate of fluorochemicals in the wastewater treatment plant. Sampling should include wastewater treatment plant influent, effluent, and sludge. Air near the plant's aeration basins should be sampled to determine the amount of volatilization of fluorochemicals from the treatment system.

As described above, it will be difficult to perform a rigorous mass balance of fluorochemicals in the wastewater treatment plant since fluorochemicals are manufactured in batch processes. Sampling should be done over several months' time and at various times after discharge from specific fluorochemical manufacture to learn their fate in the system.

Samples of wastewater are sent to the 3M Environmental Laboratory for routine analysis related to the operating permits. This study would involve additional analytical work related to fluorochemical measurement. It is anticipated that once they are developed, the analytical methods can be automated using existing equipment. 3M EE&PC Environmental Engineering Services (EES) have expressed interest and willingness to cooperate with this study[17]. Wastewater and sludge sampling for fluorochemical content could become part of the plant sampling program in order to follow the discharge of fluorochemicals over time. Such a program, however, would be under the direction of the EES plant contacts. Presently, funding is needed refine the analytical methods. Estimated cost is $25,000.

2. River Sampling

Sample sediment and river water above and below the wastewater treatment plants outfall and quantify the fluorochemicals present. Sampling would be a function of both distance downstream from the outfall and depth, so a study of the hydraulics of the river or lake would be needed before beginning the sampling.

The analytical methods for extraction and measurement of fluorochemicals from sediments have not been developed and the development work would comprise a portion of this study. For the sediment samples, fluorochemicals bound to particles and fluorochemicals not bound to particles but "free" in interstitial water will be quantified. The bulk of the cost would be sampling and actual analysis. Estimated cost is $250,000 for one plant study.

3. River Biota Sampling

In this study, animals and plants in the receiving streams would be collected the analyzed for the presence of fluorochemicals. If possible, animals will include all trophic levels: plants (algae, rooted plants), invertebrates (worms, mussels, crayfish, *Daphnia*, insect larvae), and fish (carp, catfish, bluegill, crappie). For fish, the fluorochemical content of the major organs and the muscle will be analyzed so that the implications for human consumption can be assessed. Estimated cost is $300,000 for one plant study.

17 Melanie S. Field and Amy E. Short, personal communication.

4. Caged Fish Studies

Caged fish will be placed in the wastewater treatment plant effluent for a period of time, for example, one month, to determine the uptake of fluorochemicals. At the end of the exposure, the fluorochemical content of the fishes' major organs and muscle will be analyzed. Estimated cost is $80,000 for one plant study.

5. Soil and Groundwater Sampling

Soil and groundwater at the locations where fluorochemical containing sludge has been disposed of will be sampled and analyzed for fluorochemical content. Fluorochemicals bound to soil particles as well as fluorochemicals moving with groundwater will be measured. Sampling will be done at various levels below the ground to determine if migration of fluorochemicals has taken place.

In addition, columns of soil will be removed from the ground and brought to the laboratory where water will be applied at rates to simulate rainfall. Analysis of soil samples and leached water over time will provide data to determine the potential for further migration of fluorochemicals and data for an assessment of future threats to groundwater. Estimated cost is $100,000 for one plant study.

6. Plant Uptake Studies

The cultivation of crops at the sludge disposal sites presents a unique opportunity to learn if fluorochemicals are taken up by plants. The focus of this study will be the measurement of fluorochemicals in crops. These crops may include cotton, corn, alfalfa, or soybeans that are grown on the sludge disposal site. This study is an important one since customers that use large quantities of fluorochemicals also may be disposing of fluorochemical containing sludges on land used for growing crops. This study may also provide insight into the effects of land disposal of composted fluorochemical treated paper.

The crops are already being grown and analyzed for other parameters such as metals content. This study would include the additional analyses for fluorochemicals. Estimated cost is $20,000.

7. Air Emission Monitoring

Emissions from the electrochemical fluorination cells likely includes a number of perfluorinated and partially fluorinated materials. CF_4, C_2F_6, C_3F_8, and SF_6 have been identified in gas samples[18] and H_2S, octane sulfonyl fluoride, acid chlorides, and organic

18 James D. Johnson, personal communication.

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polysulfides may also be present[19]. Plant personnel are concerned about the emissions and their effects on human health[20]. Another concern is the global warming potential of released materials. Estimated cost is $100,000.

G. Chronic Toxicity

Because of the persistence of perfluorinated materials, knowledge is needed on their long-term effects to aquatic organisms such as algae, *Daphnia*, and fish. The exposure times for these studies are on the order of a few weeks. Standard laboratory test protocols as defined by the US EPA or international organizations such as the OECD would be followed for these studies. Typically, a chronic *Daphnia* or fish study on one compound ranges from $10,000 to $20,000.

It is premature to provide a scope for the these studies since the fluorochemicals in air and wastewater emissions from the manufacturing plants are not known. We also need to know what kinds of biological transformations take place in the wastewater treatment systems and the nature of the end products from biological degradation before planning these studies in detail. In spite of these uncertainties, $100,000 is a rough cost estimate.

IV. Summary

This document contains an overview of projects that are needed to increase our understanding of the environmental fate and effects of fluorochemicals. It should be considered a pre-proposal with the costs given as order of magnitude estimates since the analytical methods have yet to be worked out. The costs in some cases include estimates for analytical method development and in others, the costs assume the methods will have been developed in previous studies.

A. Degradation	
1. Aerobic Microbial Degradation of Non-fluorinated Moieties	$50,000
2. Anaerobic Microbial Degradation	$60,000
3. Fungal Degradation	$30,000
B. Laboratory-Scale Wastewater Fate	$60,000
C. Incineration	$150,000
D. Fate and Effect of Fluorochemicals in Compost	$70,000
E. Bioconcentration	$500,000
F. Field Studies at 3M Manufacturing Plants	
1. Fluorochemicals in Wastewater	$25,000
2. River Sampling	$250,000

19 Charles F. Kolpin, personal communication.
20 Melanie S. Field, personal communication.

3. River Biota Sampling	$300,000
4. Caged Fish Studies	$80,000
5. Soil and Groundwater Sampling	$100,000
6. Plant Uptake Studies	$20,000
7. Air Emission Monitoring	$100,000
G. Chronic Toxicity Studies	$100,000

Internal Correspondence

cc: J. T. Ling - 21-2W-07 (Memo only)
D. L. Bacon - 21-2W-05 (Memo only)
E. A. Reiner - 21-2W-05 (W/Attachment)
W. H. Pearlson/D. R. Ricker - 223-6S-04 (W/Attachment)
F. D. Griffith - 220-2E-02 (W/Attachment)
S. M. Leahy - 220-13E-33 (Memo only)

To: J. D. LAZERTE - COMMERCIAL CHEMICALS DIVISION - 236-1B-21

From: R. L. BOHON - ENVIRONMENTAL LAB/EE & PC - 21-2W-05

Subject: FATE OF FLUOROCHEMICALS PHASE II

Date: MAY 25, 1983

3M

Attached for your review is a proposal from our laboratory to further evaluate selected environmental properties of 3M fluorochemicals. For background purposes, the proposal contains an extensive compendium of all existing, environmentally relevant information on 3M fluorochemicals.

The scientific aspects of this proposal have been reviewed and endorsed by our Environmental Science Advisors (M. Case, W. Pearlson, D. Hagen, W. Perkins, G. Hunt, and S. Bandal).

The Phase I Fate of Fluorochemical Study (1977-79) yielded information which led to the conclusion that although fluorochemicals were extremely persistent, they caused no apparent adverse environmental effects. Since that time, however, new information has been brought to our attention which suggests the need to reassess the validity of this conclusion.

Persistence continues to be a key concern and trigger by environmental agencies in the selection of chemicals for further review and testing, both domestically under TSCA and internationally in Japan and the ten-nation European Community. The regulatory review process is further stimulated when resistance to degradation is coupled with the property to bioaccumulate. In fact, in Japan, these two properties of new chemicals are the key criteria for initiation of extensive bioassay testing.

Recent mammalian studies conducted by Riker Laboratories indicate that in addition to demonstrating strong protein binding properties (a form of bioaccumulation), certain fluorochemicals tend to be excreted extremely slowly. While these studies were conducted in order to estimate the potential impact on humans, they do raise questions regarding the effect on other organisms, especially those near fluorochemical production or processing facilities. An important part of the proposed Phase II study involves an evaluation of field conditions near the 3M Decatur, AL plant.

Our data base on the environmental properties of 3M fluorochemicals has continued to expand since 1979 through routine assessments on new or modified products containing fluorochemicals. Nevertheless, gaps still exist in our basic environmental knowledge. This Phase II study proposes to address this deficiency in an orderly and cost-effective fashion via additional laboratory and field studies plus the selective development and use of valid structure activity relationships (SAR).

Due to the magnitude of the study and our limited manpower, it is proposed that the study be conducted over a three-year period at a total estimated cost of under $500,000. We are prepared to commence work in the 3rd quarter 1983.

If Commercial Chemicals Division cannot fund this study, I would appreciate your guidance and help in identifying an alternate sponsor or cosponsor.

Should you have any questions, please call me at 778-5104. I will contact you shortly to set up a review meeting on this proposal.

RLB/cel

Attachment: Proposal, "Fate of Fluorochemicals - Phase II"

3M "CONFIDENTIAL"

FATE OF FLUOROCHEMICALS - PHASE II

Prepared by:

Environmental Laboratory (EE & PC)
E. A. Reiner, Editor

May 20, 1983

ACKNOWLEDGMENTS

This proposal represents the combined efforts of many persons throughout 3M, particularly past and present members of the Environmental Laboratory Staff.

Special thanks are extended to Commercial Chemicals, Agricultural Products, Riker Laboratories, Central Research Analytical Services, and 3M Toxicology for sharing with us pertinent information from their experience on selected fluorochemicals. We apologize for any misquoted information or incorrect interpretations which may have crept into the final proposal.

3M "CONFIDENTIAL"

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ABSTRACT

This report reviews the Environmental Laboratory's knowledge through the end of 1982 of the environmental behavior of 3M fluorochemicals and proposes areas of further study necessary to resolve important unanswered questions.

ORGANIZATION OF REPORT

The arrangement of the report is as follows:

I. INTRODUCTION. This section covers four areas: A) Background, B) Remaining Environmental Concerns, C) Time, and D) Cost requirements of the proposal.

II. FLUOROCHEMICAL RISK ASSESSMENT. The reader is introduced to the basic approach and thought processes used by the Environmental Laboratory in assessing the environmental risks of fluorochemicals and the need for such study.

III. COMMON CONCERNS WITH 3M FLUOROCHEMICALS. This section is divided into 3 parts:

A. Structure-Activity Relationship. This part addresses the need to develop capabilities which will enable prediction of the environmental behavior of fluorochemicals from structure and physical properties measurements rather than expensive laboratory and field testing.

B. Field Studies. This part discusses a proposal to perform on-site studies to evaluate actual environmental concentration and fate of selected fluorochemicals. The section emphasizes the need to compare field study data with laboratory data predictions.

C. Incineration. This part describes the need to determine experimentally whether fluorochemicals produce toxic combustion by-products at levels that could have significant effects on the surrounding environment.

IV. ENVIRONMENTAL PROPERTIES OF FLUOROCHEMICAL CLASSES. This extensive section reviews existing environmental data and assessment needs for each of the following fluorochemical groups: A. Inert Liquids; B. Low Molecular Weight Acids and Their Salts; C. Surfactants; D. Phosphates; E. Alcohols; F. Acrylates; G. Urethanes; H. the FLUOREL® and Kel-F® polymers; and I. Catalysts.

Each of the above fluorochemical groups (A through I) are further divided into two parts entitled:

1. Background: An examination of current understanding of physical properties, degradability, and bio-effects for each fluorochemical group.

2. Recommended Testing: Proposals for further studies needed in order to fill important gaps in present knowledge. Decision points, expected test output, and priorities are included.

V. SUMMARY. This section reviews in tabular form the proposed work and cost for this Part II of the Fate of Fluorochemicals Study.

VI. REFERENCES. A list of cited 3M internal reports and published literature reports.

Four appendixes follow the report:

Appendix I: The NIOSH Aquatic Toxicity Ranking System.

Appendix II: "Key to Chemical Products Discussed in the Report." This appendix provides the class, chemical code name, and structure or formulation of chemical products mentioned in the report text.

Appendix III: "Needs For ^{14}C-Radiolabeled Fluorochemicals." It lists the proposed tests which require, or would be simplified by, using radiolabeled fluorochemicals. The section addresses test priorities, the preferred placement of the radiolabel on the fluorochemical, and the importance of having radiolabeled material for each recommended test. The appendix also references the location of the proposed test in the report.

Appendix IV: Article from the Chemical Regulation Reporter showing the importance of structure activity relationships to the U.S. EPA chemical assessment program.

I. INTRODUCTION

A. Background

The Environmental Laboratory has a considerable amount of environmental test data on 3M fluorochemicals. This work consists primarily of environmental screening tests on Commercial Chemicals Division products and a previous (Part I) "Fate of Fluorochemicals" study*.

Nearly all Commercial Chemicals Division liquid and low molecular weight fluorochemical products have been subjected to environmental screening studies. In most cases, these studies determined 1) the concentrations of fluorochemicals which cause acute lethality to fish (96-hr. LC_{50}); 2) laboratory BOD/COD tests determined the portion of the product that microorganisms can degrade readily; and 3) for sewered fluorochemical products, microbial bioassays determined the levels which inhibit waste treatment microorganisms.

In the Part I study, more extensive laboratory studies were done to further evaluate the environmental effects of selected fluorochemicals (1,2,3). Data from this study are summarized in Table 1, and the main body of this present report references and discusses these data in greater detail as background information for the Fate of Fluorochemicals Study Part II.

The major general findings of the Fate of Fluorochemicals Program Part I and other field and laboratory studies on fluorochemicals performed over the last three years are:

1. Fluorochemicals have some common characteristics. The most environmentally significant is their greater resistance, compared to their hydrogen or other halogen analogs, to degradation through chemical, biochemical, and photochemical mechanisms. Some of this stability appears to extend to the nonfluorinated portions of fluorochemical molecules. This stability is due to the inherent strength of the

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* The Environmental Laboratory conducted the Fate of Fluorochemicals Study Part I from 1976 through 1979. Four fluorochemical products (EAI 80021, LR 5625, cc 795-23, and LR 3844-4) were examined in some detail and several 3M technical reports were written. The present proposal references many of these earlier technical studies. The Environmental Laboratory wrote comprehensive reports on three of the four chemical products (1,2,3). Analytical difficulties--which now have been solved (4,5)--stymied the work on cc 795-23.

carbon-fluorine bond and is probably enhanced by the hydrophobicity of the perfluorinated portions of 3M fluorochemicals. This hydrophobicity would be expected to repel water from the fluorochemical molecules so that hydrolysis and degradation by enzymes is minimized.

2. Most 3M fluorochemicals exhibit low orders of toxicity to aquatic organisms in both acute and subchronic tests. Some fluorochemical surfactants, however, have been found to be exceptions. EAI 80021, for example, was moderately toxic to fathead minnows in critical life-stage studies(6). It should be noted, however, that a majority of commonly used nonfluorinated surfactants are also moderately toxic in acute aquatic tests (7).

3. The fluorochemical alcohol, LR 3844-4, has very low water solubility, a high octanol-water partition coefficient, and tends to concentrate in the lipid portions of fish(8,9).

4. Regression analysis of experimental soil sorption coefficients and water solubilities of four 3M fluorochemicals shows that these two parameters correlate well with the same regression equation derived for nonfluorinated organics(10). This suggests that some of the classic structure-activity relationships for physical properties also may be applicable to fluorochemicals.

5. Preliminary field studies at Decatur demonstrated that the soil environmental compartment receives the highest concentration of fluorochemicals from the application of wastewater treatment sludge. A laboratory analysis showed sludge to contain 730 ppm of organic fluorine(11,12). In comparison, fluorochemicals entering the Tennessee River in wastewater effluent were present at 10.9 ppm organic fluorine, but the volume of the effluent is 200 times that of the sludge (13).

B. Remaining Environmental Concerns

Major environmental questions which were not addressed during the Fate of Fluorochemicals Study Part I or which have surfaced since 1979, include:

1. What are the environmental fate and effects of fluorochemical polymers?

2. What is the applicability of SAR (Structure Activity Relationship) estimation techniques to fluorochemicals?

TABLE 1

DATA ON FLUOROCHEMICALS INCLUDED IN FATE OF FLUOROCHEMICALS STUDY PART I

PRODUCT	EAI 80021	LR 5625	LR 3844-4	cc 795-23
STRUCTURE	$C_8F_{17}SO_3^-K^+$	$C_7F_{15}CO_2^-NH_4^+$	$C_8F_{17}SO_2N(Et)C_2H_4OH$	$[C_8F_{17}SO_2N(Et)C_2H_4O]_2PO_2^-NH_4^+$
MW	538	431	571	1221
PHYSICAL PROPERTIES (Room Temp)				
Aqueous solub., mg/l:	1080	$>5\times10^5$	0.05, 0.16	—
Octanol-Water Part., log K_{ow}:			6-7	—
Vapor Press.:	—	Unknown (a)	Unknown (a)	—
Soil Adsorp., K_{oc}:	45	17	1500	—
Soil TLC:	Inconclusive	Inconclusive	No mobility	—
DEGRADATION				
Chemical Hydrolysis: detected	—	—	Hydr. to EAI 80021 in alcoholic KOH ($T_{1/2}$=77 hrs.)	No reaction at pH 3-12.3 and 45°C for 24 hrs.
Photochemical, in solution:	None (b)	None (b)	None (b)	
adsorbed to soil:			Inconclusive results	—
Biological, Shake flask:	None (2 1/2 month)	None (2 1/2 month)	None (3-month) (c)	Inconclusive
Warburg:	None-3 hrs.		Probably none	
SCAS (d):	—	—	None (7-day)	—
BOD_{20}:	None	None		Probably none (e)
EFFECTS				
Fish, 96-Hr. LC_{50}, mg/l, Fathead:	38	766	>0.1 (f)	>3600 mg/l
Bluegill:	68	569	—	—
Trout:	11	—	—	—
30-Day Subchronic MTC (g), mg/l, Fathead egg-fry	1.9	>100	>.0013	—
Bioconcentration,	Residue detected qualitatively in fish placed in Decatur effluent.	—	In lab studies fish accumulated 200-600 times aqueous conc. Fish placed in Decatur effluent accumulated 7 ppm.	—
Daphnia 48-Hr. LC_{50}, mg/l:	50	632	>0.1 (d)	—
Algal 14-day EC_{50}, mg/l, cell weight:	146	73	>0.1 (d)	—
cell count:	95	43	—	—
Microbial, mg/l:	No inhibition of activated sludge respiration rate at 4000 mg/l	No inhibition of act. sludge respiration rate at 1000 mg/l	No effect on wastewater treatment at 0.1 mg/l (d)	No effect on wastewater treatment at 1200 mg/l

Footnote:

(a) Steam distills.
(b) Study done in DI water at >300 nm
(c) Slight O_2 uptake was observed but no degradation products found.
(d) SCAS - Semicontinuous Activated Sludge.
(e) Masked by degradation of isopropanol.
(f) The limit of compounds solubility.
(g) MTC - Minimum Threshold Concentration

3. What is the fate of fluorochemicals in soil systems?

4. What are the chronic effects on biota from exposure to realistic environmental concentrations?

This proposal explores areas where further study is needed and outlines a three-year systematic testing program to address these issues within a modest budget. These further studies are needed so that 3M can continue to ensure the long-term environmental safety of its fluorochemical-containing products.

The refractory nature (i.e., persistence) of fluorochemicals identifies them as potential candidates for environmental regulations, including further testing requirements under laws such as the Toxic Substances Control Act, the European Communities' Sixth Amendment, or Japan's Chemical Control Law.

C. Timing

The study will be conducted over a three-year period, with field studies requiring the greatest amount of elapsed time. Specific items are given priority ratings from I to III indicating importance and the order in which the program will progress.

D. Costs

The total cost of the study over the three-year period is estimated to be three to four man years (approx. $300,000). For a summary listing of projected costs by test type and priority, see Table 14 in the summary section (V). Table 15, also in the summary, is a schedule by quarter of proposed work and costs.

II. FLUOROCHEMICAL RISK ASSESSMENT

This section introduces the reader to the processes used in assessing the environmental risk of chemicals in general and 3M fluorochemicals in particular.

The evaluation of the environmental impact of a chemical starts with basic questions on what a chemical will do in the environment. These basic questions lead to more specific questions about the chemical's environmental impact based on our understanding of the properties and ecological interactions of this chemical and chemicals in general.

The most important basic question is: Will a chemical harm any life? This question leads to two others: What concentration of a chemical causes harm; and to what concentration will various plants and animals be exposed in the environment? Laboratory tests (bioassays) can be performed to determine what levels cause harm to selected species, but in order to answer how much exposure will occur, many additional questions must be answered. How much will be produced? How much will be disposed and how? Is the chemical sorbed by sediment? Do animals or plants bioconcentrate the chemical? Does the chemical partition mainly into air, water, or soil? Does the chemical degrade readily? and so on. The answers to these questions sometimes lead to yet other questions that can be answered experimentally. For instance, one may know that a chemical degrades in the environment but not know the major routes of degradation. Does it photodegrade? Is it chemically oxidized? Can it biodegrade, or can it hydrolyze? There are laboratory tests to evaluate the probability of each of these possibilities.

A full list of possible questions is quite long, but the length can be shortened in two ways. First, testing is done in an orderly progression so that the results of the first tests performed indicate which tests are not appropriate in the next round of tests (i.e., tier or sequential testing schemes). As properties of a chemical are elucidated, we can see that certain other tests are inappropriate. For instance, if we find that a chemical will rapidly and completely degrade, there is likely no need to perform bioaccumulation tests.

The second way of thinning a list of chemical questions or tests is by using "structure activity relationships" (SAR). This is a technique scientists use to say that chemical, physical, and biological properties depend, in a predictable way, upon the molecular structure. If we understand these relationships, we can predict relevant properties from the structure. This science is being used more and more frequently by both industry and regulatory bodies in environmental risk analysis.

Structure activity relationships are derived from empirical observations or theoretical concepts. Equations written to describe these observations or theories are then used to predict properties of untested chemicals falling within the structural limits of the system. Additional chemicals are then tested to validate and refine the relationships.

Tests and observations used in environmental studies range from simple laboratory measurements to field tests and observations. Field studies are a real-world luxury for environmental scientists, but in the case of fluorochemicals, an important opportunity exists to back up laboratory tests and predictions with field observations on a unique class of proprietary chemicals. The combination of field and laboratory measurements gives a much more convincing appraisal of what the environmental impact really is--or is not.

Importantly, prudent testing of new chemicals as they evolve can help minimize, but never entirely eliminate, future testing of structurally related chemicals. Careful planning can yield a proper and complete testing program that will answer basic questions about the chemical of immediate concern and build a basis to make predictions about the behavior of similar chemicals produced in the future.

In the case of fluorochemicals, structural considerations and test results to date give rise to concern for environmental safety. For example:

- Fluorochemicals are halogenated organics and for this reason may be linked in the minds of regulators with chlorinated and brominated compounds that have caused problems in the past (e.g., PCB, PBB, DDT, etc.).
- Fluorochemicals are even more resistant to degradation than chlorinated and brominated chemicals.

These concerns give rise to legitimate questions about the persistence, accumulation potential, and ecotoxicity of fluorochemicals in the environment.

These questions and concerns should be answered for at least two reasons. First, where there is "smoke" (structural and stability similarities with known hazardous chemicals) there eventually will be a high level of concern from regulators and the public. 3M needs to have sound answers at hand with which we can respond to these concerns, questions, and possibly inaccurate accusations.

Second, the properties of fluorocarbons appear to be unique. They often do not act as other halocarbons do. In other words, the current structure activity relationships may or may not apply. In fact, it appears that 3M fluorochemicals pose very little problem compared with other halocarbons, and are environmentally "sound." But since these observations are contrary to many predictions, the hard data needed to support such a contention must be of the highest quality and more extensive than normal. Proper testing can strengthen the contention that our products are environmentally sound, or it can enable us to identify problems as soon as possible. Showing that our products are environmentally sound could have a beneficial marketing effect, and finding problems early can help 3M avoid potentially costly environmental problems and adverse publicity.

The potential application to new products or manufacturing process of reliable property values and relationships should not be overlooked as a by-product of this type of characterization program.

III. COMMON CONCERNS WITH 3M FLUOROCHEMICALS

This section deals with concerns that apply to all 3M fluorochemicals. It is divided into 3 parts: A. Structure-Activity Relationships. Presents use of SAR and proposes the development of further capabilities with fluorochemicals; B. Field studies. This subsection describes the minimal field data now available on 3M fluorochemicals and proposes further study at and surrounding the Decatur plant site; and C. Incineration. Gives existing information and questions concerning the incineration of 3M fluorochemicals.

A. Structure Activity Relationships

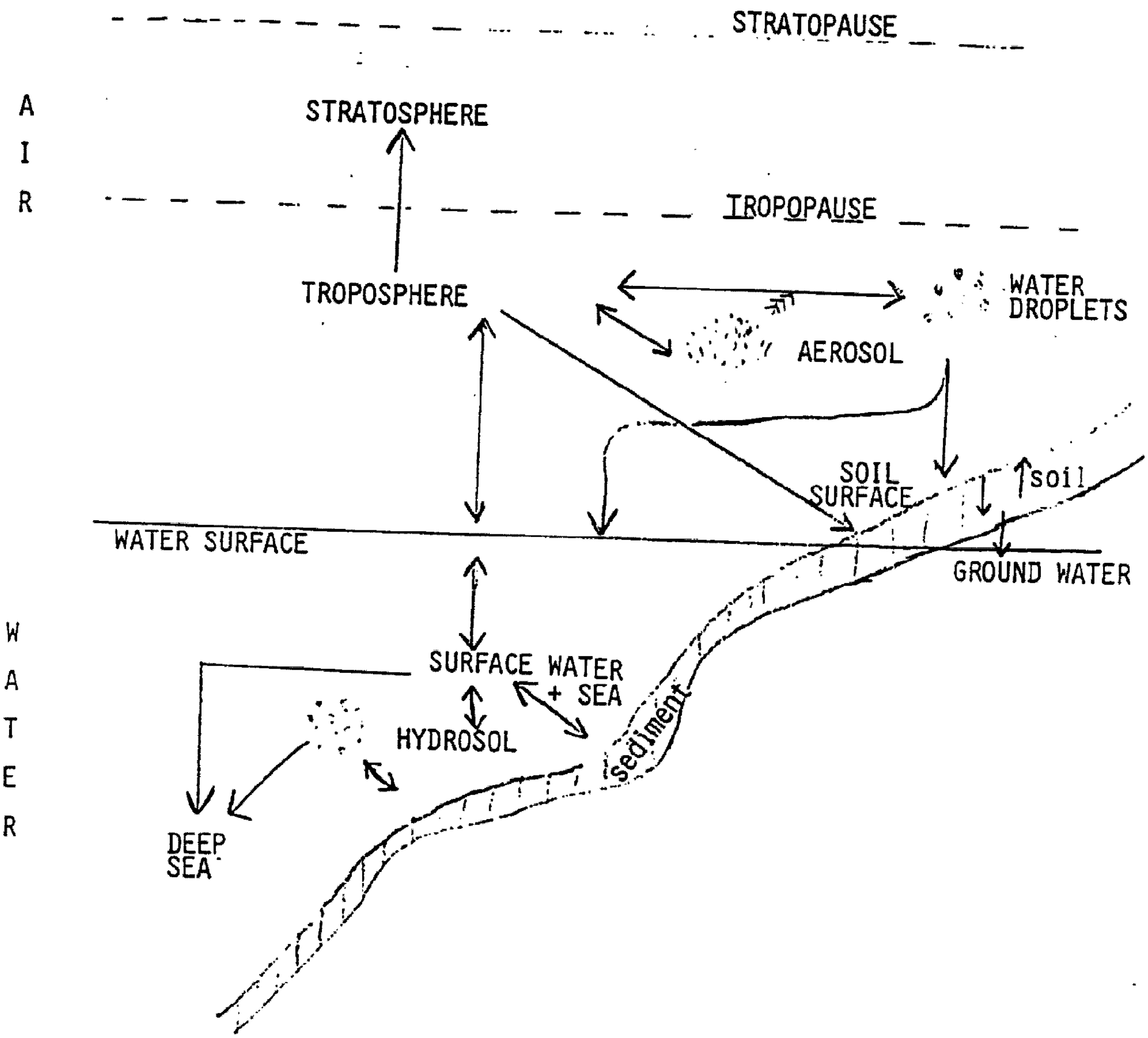
1. Background

State-of-the-art environmental risk assessment procedures use models to predict the mobility of chemicals and their concentrations in various environmental compartments. Most of these models are mathematical simulations of representative environmental systems and scenarios which require inputs of physical, chemical, and biochemical properties, which include aqueous solubility, octanol-water partition coefficient, vapor pressure, soil organic matter adsorption coefficient, and chemical, biochemical, and photolytic degradation rates. Figure 1 illustrates the types of movement between environmental compartments which are frequently modeled in risk assessment procedures.

In the absence of laboratory data, these chemodynamic properties can be estimated by structure activity relationships (SAR). While SAR provides a quick and economical method of estimating the chemical properties needed for environmental modeling, the applicability of existing SAR methods to the 3M line of fluorochemicals has not been validated. The current literature does not have sufficient information to defend using existing SAR approaches with perfluorinated chemicals, so SAR applications to 3M fluorochemicals are suspect.

The U.S. EPA is actively engaged in developing SAR estimation-mathematical modeling for the purpose of predicting the environmental behavior of chemicals. The extent of EPA commitment to SAR was clearly illustrated in a letter from the EPA's Assistant Administrator for Pesticides and Toxic Substances to the Department of State. In this letter, he states that physicochemical information is more readily and more accurately developed by existing Office of Toxic

Fig. 1. Important pathways of an organic chemical in the environment



Substances QSAR (Quantitative Structure Activity Relationship) methodologies than by the MPD (Minimum Premarket Data Base) measurements prescribed by the EEC 6th Amendment [14]. Additional information on the importance of SAR to the U.S. EPA can be found in Appendix IV.

Since EPA can be expected to be concerned eventually with the risk and hazard of fluorochemicals, they are likely to apply data generated by these SAR methods to mathematical models to predict the environmental fate and effects of 3M (and other) fluorochemicals. Since the applicability of this approach to fluorochemicals is not validated, development of sufficient scientific knowledge is necessary to identify the true risks and to refute any inaccurate risk assessment which could affect 3M fluorochemicals.

The development of SAR predictive capabilities for fluorochemicals should also have utility to 3M in areas other than environmental, e.g., the design of perfluorinated structures with unique properties required for processing, product formulation, or new product development.

2. Objective

The objective of this proposed work will be to determine the applicability of SAR methods to 3M fluorochemicals, and, if necessary, obtain new data for SAR development. In this respect, two stages of structure activity analysis are of primary interest:

1) The use of equations interrelating properties; and
2) The estimation of physical properties from molecular structure.

SAR studies on fluorochemicals are complicated by the remarkable differences in physical-chemical properties between the fluorochemicals and other organic chemicals. The simplest method for aqueous solubility measurement[15,16] uses HPLC quantitation, which will not be effective for the fluorochemicals, since most 3M fluorochemicals have no strong chromophores for UV detection. Alternative analytical methods, such as GC or total fluorine analysis, will require an extraction step. A more important potential problem involves the expected difficulty in getting pure samples of fluorochemicals.

The two-phase proposal has been designed to most rapidly and efficiently examine SAR application to fluorochemicals. The phases are:

<u>Phase I</u>: Evaluate existing, empirically derived SAR application to fluorochemicals.

<u>Phase II</u>: Derive new SAR for fluorochemicals

3. <u>Phase I</u>

Phase I will permit us to test the validity of applying existing SAR to 3M fluorochemicals without requiring method development or getting pure fluorochemical samples.

SAR procedures are most commonly derived as empirical relationships, which are applied to estimating properties of unknown substances. Extrapolation of an SAR to a new series of substances remains highly suspect until it can be validated. Such validation can be achieved by empirical methods, which requires physical property measurement by theoretical arguments or by a combination of the two.

This first phase will test application of the well-known SAR between octanol/water partition coefficient, K_{OW}, and aqueous solubility, S_w, for non-electrolyte solutes[10,15,16,17,18,19]. This relationship is given by Equation 1a for pure liquids and by Equation 1b as a general expression for pure crystalline solids as well as liquids.

$$\log K_{OW} = A \log S_w + C \qquad \text{1a}$$
$$\log K_{OW} = A \log S_w + B\,(mp-25) + C \qquad \text{1b}$$

In these equations, mp is the melting point in °C of a crystalline solid or 25 for a liquid, and A, B, and C are constants derived from linear regression analysis.

These equations were empirically developed using linear regression analysis on K_{OW} and S_w data. The data base from which the equations were derived did not include any good analogs of 3M fluorochemicals. Subsequent publications[15,16,17,20,21] have demonstrated a thermodynamic basis for this SAR, in which Equation 1 is explained by the activity coefficients for the solutes in octanol (γo) and water (γw). For this description, we have selected the Mackay treatment[20], Equations 2 and 3, in which γo and γw are expressed on a molar basis.

$$K_{OW} = 0.115 \frac{\gamma_w}{\gamma_o} \quad (2$$

$$S_w = 55.5 \frac{(f/fR)}{w} \quad (3$$

In these equations, f/f_R is the fugacity ratio for the pure solute to the liquid reference state (f/f_R = 1 for liquids). The fugacity of crytalline solids is less than 1. Its f/f_R ratio can be estimated by means of its melting point. Combining Equations 2 and 3 yields Equation 4 for pure liquid solutes.

$$\log K_{OW} = -\log S_w - \log \gamma_o + \log M_O \quad (4$$

The Mo in this equation is the molarity of octanol in itself (6.36 moles/liter).

If γ_o remains constant, then a log K_{OW} vs. log S_w correlation, as given by Equation 1a, will have a slope, A, equal to -1, which empirical regression analysis on nonfluorochemicals confirms. The melting point term in Equation 1b accounts for the difference in fugacities of the solute as a solid and as a liquid (the defined reference state). Any series of solutes where γ_o varies will not yield the linear regression expressions of Equation 1. since 3M fluorochemicals are not miscible with octanol, nonideal behavior and a wide variation in their octanol activity coefficients, γ_o, can be expected. <u>These arguments ultimately predict that the existing SAR defined by Equation 1 will not apply to 3M fluorochemicals</u>.

Amidon and Williams offered Equation 4a as a general relationship for relating aqueous solubility to octanol/water partition coefficient (22). They derived this equation from thermodynamic relationships for the following sequence: solid melted to supercooled liquid; supercooled liquid dissolved to yield an octanol solution; solute partitioned from octanol solution into aqueous solution. This equation uses the solubility parameter, δ, for the organic solute as a means of estimating its activity in octanol. Since this equation might be valid for nonionic fluorochemicals, it should be tested.

$$\log K_{OW} = -\log S_w - 7.3\text{x}10^{-4} \Delta S_F\,(mp-25) - 7.3\text{x}10^{-4}\,(V_2\,(10.3-\delta)^2 + 0.8 \quad (4a$$

In this equation, ΔS_F is the entropy of fusion, V_2 is the molar volume and δ is the Hildebrand solubility parameter for the substitute.

To avoid the need for pure fluorochemical isomers and methods development that are prerequisite to the direct study of the relationship between K_{OW} and S_W for fluorochemicals, an alternative approach is proposed. This approach will examine aromatic hydrocarbon partitioning between water and fluorochemical solvents by means of Equation 5, which can be derived by the Mackay approach(20,21).

$$\log K_{FW} = -\log (f/f_R)S_w - \log \gamma_F + \log M_F \qquad (5$$

Here, K_{FW} is the fluorochemical solvent-water partition coefficient, γ_F is the solute activity coefficient in the fluorochemical solvent, and M_F is the molarity of the fluorochemical solvent in itself. A nonlinear relationship for K_{FW} vs. S_w regression would be evidence that γ_F for aromatic hydrocarbons would not be constant. If γ_F varies for a series of hydrocarbon solutes, then γ_o for a perfluorochemical series analogous to the fluorochemical solvent is expected to also vary. This would support the concept that Equation 1 will not be valid for 3M fluorochemicals(23).

Two procedures for K_{FW} measurement are being considered. They are the standard shake flask method or preferably the new column generator technique developed by the National Bureau of Standards (15,16,17). The fluorochemical solvents selected should provide a reasonable estimate of the behavior of 3M fluorochemical types ranging from fluorochemical inert liquids to fluorochemical alcohols. We have selected as the preliminary candidate solvents: 1) perfluorooctane; 2) 1,1,2,2-tetrahydroperfluorooctanol from DuPont ($C_6F_{13}C_2H_4OH$); and 3) N-Et FOSE alcohol (LR 3844-4), which is a solid. This series of fluorochemicals, however, does not cover fluorochemicals which ionize in water, such as EAI 80021. Either measurement technique (shake flask or generator column) could be applied to the liquid fluorochemicals, but the solid, LR 3844-4, would require the generator column approach. We will select aromatic hydrocarbons from Table 2. This table comes from the National Bureau of Standards studies of octanol-water partitioning and aqueous solubility. We expect to choose about 10 solutes, based upon statistical needs.

TABLE 2*

AQUEOUS SOLUBILITIES AND OCTANOL/WATER PARTITION COEFFICIENTS OF ORGANIC COMPOUNDS

Aromatic Hydrocarbons

Solute	Aqueous Concentration: This Study (M)	Aqueous Concentration: Literature Value (M)	log $\gamma_s^{w(i)}$	log $K_{o/w}$: This Study[j]	log $K_{o/w}$: Literature
Toluene	6.28×10^{-3}	5.80×10^{-3} [c]	3.17	2.65[a]	2.69[f]
Ethylbenzene	1.76×10^{-3} [a]	1.52×10^{-3} [c]	3.66	3.13[a]	3.15[f]
o-Xylene	2.08×10^{-3}	1.61×10^{-3} [c]	3.60	3.13[a]	3.12[f]
m-Xylene	1.51×10^{-3} [a]	1.38×10^{-3} [c]	3.73	3.20[a]	3.20[f]
p-Xylene	2.02×10^{-3} [a,b]	1.47×10^{-3} [c]	3.60	3.18[a,b]	3.15[f]
n-Propylbenzene	4.34×10^{-4} [a,b]	4.99×10^{-4} [f]	4.22	3.69[a,b]	3.68[f]
n-Butylbenzene	1.03×10^{-4} [a,b]	8.79×10^{-5} [c]	4.79	4.28[a,b]	4.26[f]
n-Pentylbenzene	2.59×10^{-5} [a]	---	5.35	4.90[a]	---
n-Hexylbenzene	6.27×10^{-6} [a]	---	5.92	5.52[a]	---
1,2,3-Trimethyl benzene	5.45×10^{-4} [a]	4.01×10^{-4} [c]	4.13	3.55[a]	---
1-Ethyl-2-methylbenzene	6.21×10^{-4} [a]	---	4.07	3.53[a]	---
Chlorobenzene	2.62×10^{-3} [a]	2.84×10^{-3} [e]	3.56	2.98[a]	2.84[f]
Bromobenzene	2.62×10^{-3} [e]	4.41×10^{-3} [e]	3.56	2.98[a]	2.99[f]
Iodobenzene	9.84×10^{-4} [a]	---	3.96	3.28[a]	3.25[f]
o-Fluorobenzyl chloride	2.88×10^{-3} [a]	---	3.47	2.67[a]	---
m-Fluorobenzyl chloride	2.86×10^{-3} [a]	---	3.46	2.77[a]	---
m-Cresol	2.59×10^{-2} [a]	---	2.52	1.96[a]	---
Nitrobenzene	3.11×10^{-2} [a]	---	2.50	1.85[a]	---

* Indicates that the literature data are calculated values according to Hansch et al., 1968.
(a) HPLC method of analysis.
(b) GC method of analysis.
(c) Sutton and Calder, 1975.
(d) McAuliffe, 1966.
(e) Hansch et al., 1968.
(f) Hansch and Leo, 1979.
(g) MacKay et al., 1980.
(h) Reddick and Burger, 1955.
(i) Average standard deviation of log γ_s^w measurements is 0.04.
(j) Average standard deviation of log $K_{o/w}$ measurements is 0.04.

*From National Bureau of Standards (15).

TABLE 2 (Continued) -17-

AQUEOUS SOLUBILITIES, AND OCTANOL/WATER PARTITION COEFFICIENTS, OF ORGANIC COMPOUNDS

Miscellaneous Aromatic Compounds

Solute	Aqueous Concentration This Study (M)	Aqueous Concentration Literature (M)	log γ_s^w [i]	Log $K_{o/w}$ This Study [j]	Log $K_{o/w}$ Literature
n-Heptylbenzene	2.54×10^{-6} [a]	---	6.28	---	---
n-Octylbenzene	3.48×10^{-7} [a]	---	7.11	---	---
Hexamethylbenzene	1.45×10^{-6} [a]	---	---	4.61 [a]	---
1,2,3,5-Tetramethyl-benzene	---	---	---	4.04 [a]	---
Naphthalene	2.39×10^{-4} [a]	2.36×10^{-4} [g]	---	3.35 [a]	3.37 [f]
1-Methylnaphthalene	2.23×10^{-4} [a]	2.11×10^{-4} [g]	---	---	---
1-Ethylnaphthalene	7.41×10^{-5} [a]	6.40×10^{-5} [g]	---	---	---
1-Fluoronaphthalene	3.53×10^{-4} [a]	---	---	---	---
1-Chloronaphthalene	1.07×10^{-4} [a]	---	---	---	---
1-Bromonaphthalene	6.72×10^{-5} [a]	---	---	---	---
p-Fluorobenzyl chloride	---	---	---	2.73 [a]	---
o-Dichlorobenzene	---	---	---	3.38 [a]	3.38 [f]
m-Dichlorobenzene	---	---	---	3.48 [a]	3.38 [f]
p-Dichlorobenzene	---	---	---	3.37 [a]	3.38 [f]
1,2,3-Trichlorobenzene	---	---	---	4.04 [a]	---
1,2,4-Trimethylbenzene	---	---	---	3.63 [a]	---
1,2,3,4-Tetramethyl benzene	---	---	---	3.98 [a]	---
Phenol	0.813 [a]	---	---	1.45 [a]	---
2,5-Dimethylphenol	6.61×10^{-2} [a]	---	---	2.35 [a]	---
2,4-Dimethylphenol	6.40×10^{-2} [a]	---	---	2.34 [a]	---
2,6-Dimethylphenol	7.90×10^{-2} [a]	---	---	2.31 [a]	---
2,3,6-Trimethyl phenol	1.16×10^{-2} [a]	---	---	2.67 [a]	---
2,4,6-Trimethyl phenol	---	---	---	2.73 [a]	---
o-Cresol	2.52×10^{-2} [a]	---	---	1.96 [a]	---

[*] Indicates that the literature data are calculated values according to Hansch *et al.*, 1968.
[a] HPLC method of analysis.
[b] GC method of analysis.
[c] Sutton and Calder, 1975.
[d] McAuliffe, 1966.
[e] Hansch *et al.*, 1968.
[f] Hansch and Leo, 1979.
[g] MacKay *et al.*, 1980.
[h] Reddick and Burger, 1955.
[i] Average standard deviation of log γ_s^w measurements is 0.05.
[j] Average standard deviation of log $K_{o/w}$ measurements is 0.04.

The following table summarizes the anticipated scheduling and manpower for the work proposed in Phase I:

Function	Man-hours
Setup time	50-80
Analytical method development	50-70
System testing and range finding	50-70
Partition measurements using approximately ten solutes for each solvent:	
1) Perfluorooctane	125-200
2) 1,1,2,2-tetrahydro-perfluorooctanol	100-150
3) LR 3844-4	70-100
Total Phase I	445-670

4. Phase II

As described above, SAR refers to both molecular substituent factor analysis for estimating physical-chemical properties (24,25,26,27) and correlation equations which relate two or more physical-chemical properties (18,19,21,28-37). Both approaches will require a data base of laboratory measurements to which standard regression analyses are applied to yield the SAR.

The objectives of this phase will depend upon the observations in Phase I and a literature review. It is anticipated that the SAR development will include estimating perfluorochemical fragment substituent constants for one or more key physical-chemical properties, such as K_{OW}, S_W, and vapor pressure, and making interproperty correlations, such as K_{OW} vs. S_W or soil organic matter sorption coefficient, K_{OC} vs. S_W.

The study will gather available data in the literature and from within 3M on the aqueous solubility, vapor pressure, octanol-water partition coefficient, and soil-water partition coefficient of fluorochemicals. When necessary, laboratory measurements will be made to fill in the gaps. It is anticipated that such measurements will be more accurate than in previous studies since attempts will be made to use test chemicals which exist as single isomers rather than products which are mixtures of structural and molecular weight isomers.

Correlations will then be made between measured fluorochemical properties, comparing them with those published in the literature for other types of organic compounds. Examples of relevant published correlations are those of vapor pressure and water solubility by Amidon and Anik (28); of aqueous solubility and partition coefficient by Banerjee et al (21); and of partition coefficient and biosorption partition coefficient developed by Steen and Karickoff(37).

If correlations between the physical chemical and chemodynamic properties of fluorochemicals are strong, the developed estimation approach will be applied to existing literature data and to actual 3M fluorochemicals. Attempts will also be made to derive substituent constants for important 3M fluorochemical groups such as C_8F_{17}-. Values of properties estimated by this approach will be compared with measured properties for validation.

The following is an estimated work load for Phase II. It anticpates the derivation of C_8F_{17}, CF_3 and CF_2 fragment constants for the Hansch and Leo approach to K_{OW} estimation and the derivation of correlation equations between K_{OW} vs. S_W and K_{OC} vs. K_{OW} or S_W.

Function	Man-hours
Substituent constants, K_{OW}	
Literature review	35-50
Property measurement	300-400
Statistical analysis	20-25
Correlation equations	
Literature review	5-10
Property measurements	250-350
Statistical analysis	20-25
K_{OC} vs. K_{OW} or S_W	
Method development for K_{OC} measurement	200-300
K_{OC} measurements	250-350
Statistical analysis	20-25
Total Phase 2	1100-1535

B. Field Studies

1. Background

The purpose of field studies is to determine what happens to chemicals in the real world. The results often confirm, but sometimes refute, laboratory predictions, and they often uncover unpredictable phenomena. In other words, field studies determine where in the environment chemicals accumulate, how they move in the environment, and whether or not they cause any adverse effects.

In evaluating the fate and effects of substances, a field study is extremely valuable but rarely practical. Such studies are frequently too costly to be justified for low volume chemicals. Release may be too widespread to allow for easy monitoring, or in the case of new chemicals, sufficient field release to allow detection may not have occurred.

The uncontrolled nature of field studies also presents potential problems. Unrelated natural or man caused factors may complicate data interpretation. For example, toxic discharges from nearby industrial or agricultural activities may mask the effects of the chemicals of interest.

For the fluorochemicals, though, a field study is possible since there has been known production and limited environmental release for years at a few facilities. By designing the proper studies, one can use these sites to evaluate the real-world fate and effects of fluorochemicals. This, in turn, will allow evaluation of the validity and the utility of predictions based only on laboratory observations. Such comparisons will also enable the Environmental Laboratory to make better estimates of the fate and effects of similar substances in the future with much less data and hence for less cost.

Table 3 summarizes results of past field studies on fluorochemical residues at the Decatur plant (11,12). The distribution of organic and inorganic fluorine was measured in the plant's wastewater treatment sludge and effluent, as well as in the soil where sludge had been applied. Some fluorochemical components were identified. Because these were only preliminary quantitative evaluations, it cannot yet be concluded that high fluorochemical concentrations have not accumulated near the plant site.

TABLE 3

FLUORIDE MEASUREMENTS AT THE DECATUR PLANT

	Measured Fluorine		
	Total	Inorganic	Organic
Sludge		223	730[a]
Effluent		23.7	10.9[b],0.096
Soil (Sludge Treated)	300[c]	440[c]	
Decatur Soil (untreated)	24.4	8.9	

a Major volatile fluorochemical was LR 3844-4. LR 5625 and $C_8F_{17}SO_2NHEt$ were also identified.

b Identified LR 5625.

c Apparent analytical error (CRL Anal. #6937).

Fish placed in the Decatur effluent bioconcentrated those fluorochemicals with low water solubility (38). Residue concentrations in the fish were measured at 10 ppm for the FOSE amide ($C_8F_{17}SO_2NHEt$) and 7 ppm* for LR 3844-4 ($C_8F_{17}SO_2NEtC_2H_4OH$). Neither LR 2929 nor LR 5625 was detected. EAI 80021 was detected but not quantified.

This greater bioaccumulation of low water soluble fluorochemicals agrees with SAR relationships between bioaccumulation and water solubility or octanol-water partition coefficient derived for nonfluorinated organic chemicals (24,39).

*For perspective, FDA allows PCB concentrations up to 2 ppm in edible portions of fish.

2. Field Study at Decatur Plant

A field study is recommended to measure distribution, biological uptake, and effects of fluorochemicals near the Decatur plant. In this study, we want to determine: 1) if fluorochemicals are long lived as predicted; 2) if they concentrate near the point of entry or are diluted throughout the environment; 3) if they concentrate in one compartment of the environment such as air, water, soil, sediment or biota; 4) if they cause any ecological effects.

Fluorochemicals have been produced at the Decatur plant for about thirty years. Since then, they have been entering the environment through landfilling of tars and other by-products, through water discharges, both before and after the installation of a modern wastewater treatment facility, through vapor discharges from manufacturing processes and wastewater aeration basins, and more recently through the field incorporation of wastewater sludge containing fluorochemicals.

Analytical capabilities will be tested and evaluated prior to study initiation. While there is concern about all fluorochemicals produced at Decatur, we plan to monitor only three (perfluorooctanoic acid, perfluorooctyl sulfonate, and LR 3844-4). Specific analyses, however, will only be made after first determining the need by looking at the levels of total organic fluorine. This preliminary screening for total organic fluorine will eliminate an unnecessarily large number of costly specific fluorochemical analyses. We can obtain estimations on how these chemicals and other fluorinated chemicals move and act in the environment by looking at just organic fluorine.

A comparison of the difference between the total organic fluorine concentration and the concentration of the three specific monitored chemicals would indicate whether other fluorinated chemicals may be important as environmental contaminants, and thus whether they should also be identified. Other fluorochemicals found in significant quantities in Decatur soil, sludge, biota, wastewater, and receiving water by methods such as capillary GLC may also be identified and quantitatively determined in the study.

The analytical techniques selected must have adequate specificity for 3M fluorochemicals to ensure accurate identification in order to avoid false alarms. Analytical work, done to determine if Tennessee River fish bioconcentrated 3M fluorochemicals, has clearly illustrated the potential for incorrect results with nonspecific analytical techniques(40,41). In this study, preliminary GLC analysis with electron capture detection separated three peaks from fish extracts that moved identically to those of three 3M fluorochemical controls (40). Had analysis stopped here, it would have appeared that 3M fluorochemicals were bioconcentrating into fish from ambient concentrations. However, confirmational analytical work using microwave sustained helium plasma detection showed that the peaks from the fish tissue extracts were not due to fluorochemicals (41).

Before sampling, conceptual modeling will be conducted in an attempt to predict the field study findings. These predictions will be based on old and new laboratory data, available discharge records, and maps of the site. When possible, widely used environmental models such as the EPA's EXAMS System will also be applied. This exercise will help to ensure a meaningful interpreation of the field study results and will immediately draw attention to unexpected results. It will also help in evaluating the applicability of existing models, which are based mostly on hydrocarbon data, in predicting the environmental behavior of fluorochemicals.

The following is a list of proposed sampling sites and procedures. These procedures and sites may be adjusted as other information on the properties of the chemicals and nature of the sampling sites become available. At the time of sampling, complete details of the sampling sites, including pictures, will be recorded.

a) Sludge

A series of grab sludge samples will be taken to compare with other samples previously taken. Sludge should be sampled when it is being pumped from storage to be applied to fields. The results will be used to estimate quantities and variability of fluorochemicals entering the soil environment through sludge incorporation. (7 samples, 96 hrs.)

b) Effluent

Effluent will be collected at the outflow of the biological treatment system before mixing with cooling water. Concentrations entering the reservoir will also be calculated based on relative flow rates and the assumption that no fluorochemicals are present in cooling water. One 5-liter sample will be taken during each of four different weeks so that the variation in the effluent characteristics can be evaluated. Single controls will also be taken from two waste treatment systems not treating fluoro-chemicals. The results of the anlysis will give an estimation of the quantities of fluorochemicals entering the lake. The values will be compared with those from sediment and biota. (6 samples, 84 hrs.)

c) Soil

Soil from the fields where sludge has been incorporated will be collected in accordance with accepted methods (42) and analyzed for total organic fluorine and, if this is found in high quantities, for the three fluorochemicals specified above. Approximately ten samples will be collected from the fields in different locations. Sampling depth will be between the surface and 12".

In addition to these samples, approximately six soil samples from the ditches that collect runoff water from the field will be taken at points outside the sludge application area.

Two controls will be taken from a location with the same soil type at least 10 miles from the manufacturing facility. The exact locations of the sampling sites will be set after review of the sludge incorporate rates in the fields and the runoff patterns of the fields.

The results from the analysis of these samples will be used to estimate how much of the applied fluorochemical stays in the soil at the site and how much of the fluorinated sludge is washed from the field, possibly to the adjacent reservoir. (18 samples, 252 hrs.)

d) Field Vegetation

Six crop samples will be collected at harvest time from fields receiving sludge and two from control fields.

These samples will first be analyzed for total organic fluorine. Then if there are high levels, the crops will be analyzed for LR 5625, EAI 80021, and LR 3844-4, and a rat feeding study using the crop will be initiated. The purpose of the feeding study will be to determine the uptake kinetics of the fluorocarbons from the crop. The details of the feeding study will be set if or when it is appropriate. (8 samples, 108 hrs not including possible feeding studies)

e) Fallout

One important possible mode of entry of the fluorochemicals into the environment is through air emissions from plant manufacturing processes or volatilization due to aeration of the waste treatment system. Chemicals entering the environment through the air are usually either diluted into the air and therefore carried off or they precipitate out, usually locally. When there is such fallout, the concentration is usually greatest closest to the source and falls off with distance from the source.

Thus, we propose sampling the soil close to the plant and at increasing distances from the plant. Two sampling vectors would be set up. The first would follow the predominant downwind trajectory and the other upwind. Four soil core samples would be collected along each vector at intervals of 100M, 200M, 400M, and 800M. Two control samples will be taken several miles from the plant. The location is yet to be determined. Samples will not be taken from those points where sampling vectors intersect waste disposal sites or the river (10 samples, 144 hrs).

f) Sediment

Previous studies have shown that several of the fluorochemicals bind to soil and thus would be expected to also bind to aquatic sediments. For this reason there is a need to look at aquatic sediment to see how much fluorochemical does bind. Chemicals that bind to sediment and are in water tend to fractionate into the sediment very rapidly, and are usually found in higher concentrations where effluent waters enter a lake or pond. The concentration decreases with distance away from the entry point.(1) For this reason, we propose to sample sediment at the effluent entry point and at the middle and mouth of the cove into which the discharge flows. Since the flow of the effluent after entering the reservoir can vary, additional sampling will follow three vectors:

one up the shore line: one down the shore line, and one perpendicular to the shore line. Sampling depth will be determined on-site and will depend on the bottom topography along each vector. Control samples will also be taken from points on the river well above and below the plant site. Only the top 1-2 centimeters of sediment would be sampled. The sampling method has not been determined yet, but it could be either done by diving and scraping the top 1-2 centimers or by using a Vanbean sampler with a removable top to obtain the top 1-2 centimeters. (9 samples, 132 hrs.)

g) Biota

There will be two types of biotic sampling. First, to estimate possible effects and second, to determine if biota accumulate fluorochemicals. The sampling points will be the same as for the sediment samples for the same reason and so that the concentrations in the sediment can be directly compared with the concentration in the biota. If there is an effect on biota, then either species diversity or populations will likely decrease with increasing concentration of the chemical causing the effect. The clam, Corbicula, will be sampled in order to determine the concentration of fluorochemicals in biota.[43] (18 samples, 204 hrs.)

h) Water Column

The concentration of fluorochemicals in the water column will be measured at each of the sites where the biota and sediment are sampled in order to directly compare the concentration of fluorochemicals in the water versus the sediment and the biota. The parts of the water column that will be sampled will depend on the mixing pattern of the water, the flow of the effluent, and topography of sampling sites. One possibility is to sample water close to the bottom, at the middle of the water column, and close to the surface. (12 samples, 168 hrs.)

3. Priority

This field work is needed for three reasons: 1) very little data now exists on the actual environmental concentration and impact of fluorochemicals; 2) the study will assist in clarifying those physical, chemical, and biochemical properties of fluorochemicals that are most important in determining their environmental fate; 3) it will provide the necessary data for validation or correction of our present estimated environmental concentrations from our modeling studies.

The primary objective of the field study, however, is to determine if unanticipated or unreasonably high fluorochemical concentration exists in any site near the Decatur manufacturing plant and to extend such information to predictions at other manufacturing and use sites.

The phases of this study are given the following priority:

Phase 1 (confirm analytical capabilities) - Priority I - 150 hours
Phase 2 (modeling to predict findings) - Priority I - 20 hours
Phase 3 (field samples and sample analysis) - Priority III - 1200 hours

C. Incineration

1. Background

Incomplete combustion of fluorochemicals can lead to the formation of acutely toxic by-products such as carbonyl fluoride and perfluoroisobutylene in addition to the HF normally formed.

Incineration studies conducted by EE&PC at a pilot scale incineration facility looked for possible toxic by-products (such as CF_2O, OF_2, perfluoroolefins or NF_3) from cc 788-19 (100 ml) combustion (with 5 gallons #2 fuel oil) at 2185°F. None of these components were detected at 1 and 5 ppm in condensable and volatile components, respectively. However, literature sources describing other fluorochemical combustion studies have observed some of these toxic components (44).

2. Approval and Decision Points

A test burn of fluorochemicals at the Decatur incinerator is recommended. The Decatur incinerator has been selected for this study because it is more likely to allow the formation of incomplete combustion products than the more sophisticated Chemolite incinerator. Thus, if the Decatur incinerator does not produce significant levels of toxic by-products, we would assume that the similar Cordova or more modern Chemolite incinerators are at least as effective in destroying fluorochemicals without producing toxic by-products.

Samples of the material to be incinerated will be analyzed for HF and Total Organic Fluorine. Suggested stack gas analytical parameters include HF, CF_2O (carbonyl fluoride), perfluoroisobutylene, total organic carbon (TOC), total organic fluoride, and CO.

Analytical capabilities and sample handling, stability, and preservation requirements will be evaluated prior to the test. As some of these possible by-products are quite reactive, sample handling difficulties are anticipated and could cause cancellation or changes to portions of this proposal.

3. Priority

The study is a confirmatory test planned to tell us if the Decatur incinerator does or does not emit unreasonable amounts or concentrations of hazardous degradation products.

A Priority III is assigned to this proposal.

IV. ENVIRONMENTAL PROPERTIES OF FLUOROCHEMICAL CLASSES

This section reviews our present knowledge of the following classes of 3M fluorochemicals: A. Inert Liquids; B. Low MW Acids and Their Salts; C. Surfactants; D. Phosphates; E. Alcohols; F. Acrylates; G. Urethanes; H. FLUOREL® and Kel-F® Polymers; and I. Catalysts.

The section on each fluorochemical class is further divided into a "Background" section and a "Recommended Testing" section. The Background sections outline our present understanding of the environmentally significant aspects of the fluorochemical class' physical properties, degradability, and effects. The "Recommended Testing" section proposes additional work and gives decision points and expected test output. Each study is given a priority rating of I, II, or III in which the numbers indicate both the need and the order in which the proposed studies should be done.

The proposed physical properties measurements will broaden profiles on individual fluorochemicals which are representative of these important fluorochemical classes. These data will be used both to model their environmental fate and as a data base for SAR development.

Degradations studies will determine which, if any, of the possible environmental degradation mechanisms (chemical, biochemical or photochemical) are important in the environmental fate of the fluorochemical classes.

Effects testing will determine the concentration of fluorochemicals that could adversely affect ecological systems.

These three types of data, when used in combination with modeling and field data, will yield a good indication of the likelihood of adverse environmental effects from these 3M fluorochemical classes.

A. Inert Liquids

1. Background

a) Physical Properties

Commercial Chemicals Division Technical brochure Y-ITPB-1(21.3)JR summarizes the physical properties of Fluorinert Electronic Liquids. These data indicate that all FLUORINERT liquids have sufficient volatility to enable them to eventually evaporate and disperse into the atmosphere.

Calculations based on models developed by Cupitt (45) show that, once in the atmosphere, the FLUORINERT liquids are not likely to be removed by dissolving in rain water or by adsorbing to and settling with particulates. In any case, because of their high volatility, any of these inert fluorochemicals removed from the atmosphere by these processes will likely eventually reevaporate to the atmosphere.

Some unanswered questions do exist concerning the physical properties of the inert fluorochemicals. For example, how strongly do they adsorb to soil? Soil sorption data allows us to predict mobility and determine if they, like some chlorinated solvents, are likely to move from spill and land disposal sites and contaminate groundwater sources. The Environmental Laboratory should be able to evaluate this possibility after development of structure activity relationships (SAR) capabilities. The low toxicity of FLUORINERT® Liquids, discussed below, makes this potential problem noncritical, but even if completely innocuous, the presence of man-made chemicals in groundwater is a sensitive and high profile subject.

b) Degradation

Fluorochemical inert liquids are very stable, resisting degradation under both extreme chemical and physical conditions. In addition, these liquids show no susceptibility to biodegradation in BOD and other biodegradation tests.

Their stability suggests that they will persist in the atmosphere for very long times. This hypothesis is substantiated by analytical findings of Dietz and co-workers (46,47,48). They found that perfluoromethylcyclohexane and perfluorodimethylcyclohexane have remained in the atmosphere near the concentration expected from their total worldwide production. The great majority of these two perfluorochemicals were released to the atmosphere in the 1940's at Oak Ridge, and eighty percent, or possibly all, of this fluorochemical is still in the atmosphere.

Due to the transparency of perfluoroparaffins and amines above 280 nm (49,50,51,52), the FLUORINERT products are not expected to degrade in the troposphere or lower stratosphere. Nitrogen-containing FLUORINERT products, which have the longest wavelength UV absorption, may photodegrade in the mid-stratosphere, but other FLUORINERT chemicals will probably only photodegrade in the upper stratosphere and above.

Unlike other organic materials, degradation of inert liquids through reaction with OH radical is also unlikely to provide a significant sink for perfluorocarbons (53). Reactions with $O(^1D)$ (which occurs primarily in the stratosphere) may have some significance (53).

The lifetime of these products is probably determined by the extremely long time required for molecules to diffuse into the upper regions of the atmosphere where photolysis, photooxidation or significant reaction with singlet oxygen can occur (54). Estimated atmospheric lifetimes of perfluorocarbons due to these reactions are on the order of hundreds of years (53).

Preliminary literature findings on chlorofluoromethanes and ethanes suggest that FLUORINERTS, unlike chlorofluorocarbons, are unlikely candidates to photodegrade after adsorbing to sand in spite of the strength of SiF bonds (55). The literature shows that increasing the number of fluorines in a chlorofluorocarbon greatly decreases its rate of photodegradation when adsorbed to sand (39,55). Thus, one would expect that these completely fluorinated compounds would degrade even more slowly than chlorofluoromethanes. In addition, these experiments have shown no detectable C-F bond breakage.

Kanno has reported on the sensitized photodegradation of Freon 12 with very high concentrations of nitrogen oxides in air. This study, which used a xenon lamp, shows the formation of HF indicating breakage of the C-F bond (56). Similar sensitized photodegradation could possibly occur with the FLUORINERTS but would likely be at an extremely slow rate.

c) Effects

As a class, FLUORINERT liquids show little toxicity. A summary of the environmental effects data on this class of compounds is shown in Table 4. No significant toxicity has been found. All of the thirteen FLUORINERT liquid products which have been subjected to acute fish bioassays have had 96-hr. LC_{50} values greater than 1,000 mg/l and are classified as insignificant hazard*.

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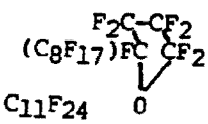
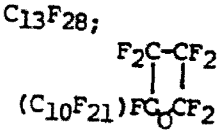
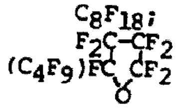
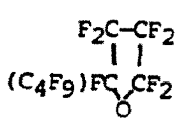
*Appendix 1 gives a scale rating aquatic toxicity data from highly toxic to insignificant hazard.

In addition, one FLUORINERT liquid (cc 742-7) was found to be nontoxic to Daphnia (LC_{50} >1500 mg/l), and four were found not to adversely affect activated sludge microorganisms.

TABLE 4

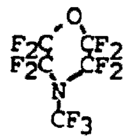
SUMMARY OF ENVIRONMENTAL EFFECTS OF FLUORINERT® LIQUIDS

Product	Typical Boiling Range (°C)	Major Components	96-Hr. LC_{50}[a,b] (mg/l)	Other Data and Lab Request or Reference
LR 5120	138-189	$(C_4F_9)_3N$	>1,000 >5,000	5120 2455
LR 4894[c]	139-185	 $C_{11}F_{24}$	1,686 1,893	4894
LR 3844-1	165-185	$(C_4F_9)_3N$	>5,000	Did not support fungal growth[d]. 2455
LR 2465-1	139-180	$C_{12}F_{24}$ (cyclic, 8 isomers)	>1,500 >5,000	Retarded activated sludge O_2 depletion rate[e]. (57), 2465 No adverse effect on lab scale treatment system[f] (57).
LR 7981	207-225	$(C_5F_{11})_3N$	>1,000	7981
~~LR 6589~~[g] L 4308	203-221	$C_{13}F_{28}$; 	>1,000[h]	No effect on activated sludge O_2 depletion rate EAI 79215, 79213, 6589
LR 6589	244-262	$(C_6F_{13})_3N$	>1,000	6589
LR 7842	50-60	C_6F_{14}	>1,000	7842
LR 2455-3	99-107	C_8F_{18}; 	>5,000	Did not support fungal growth[d]. 2455
cc 742-7	90-107	C_8F_{18}; 	>5,000 >1,000	>1,500 mg/l, 48-Hr. LC_{50} Daphnia. 2455

3MA10065500

3M_MN00000055

(Table 4 continued)

Product	Typical Boiling Range(°C)	Major Components	96-Hr. LC_{50}[a,b] mg/l	Other Data and Lab Request or Reference
cc 788-19	50-60		>5,000	Retarded activated slu O_2 depletion rate[e]. No adverse effect on lab scale treatment system[f]. 2455, 5713(5
LR 4913	90-107	Cyclic C_8F_{16}	>1000[h]	4913
cc 809-21	75-90	C_7F_{16}	>1,000	No effect on activated sludge O_2 depletion rat 6262

Footnotes:

(a) All 96-hr. LC_{50} tests were on Fathead minnows (Pimephales promelas) unless indicated.

(b) All 96-hr. LC_{50} values are for nonmiscible mixtures.

(c) L-4380 is a possible LR 5120 component. It is a mixture of various isomers of perfluoro-octyl tetrahydrofuran.

(d) ASTM G-21-70 growth rating was 1 indicating sparse and scattered growth. The analyst felt this growth was due to a mass of spores in the inoculum and not to growth on product

(e) Activated sludge mixed liquor with a dissolved oxygen concentration of 7 mg/l had a slightly longer oxygen depletion time than the control.
This was probably not due to toxicity but to the fact that perfluorinated organic liquids dissolve large quantities of oxygen which they can transfer to the aqueous phase. Thus, since more O_2 was present, a longer time was needed for its utilization.

(f) LR 2465-1 and cc 788-19, even at unreasonably high concentrations (13 g/l nonmiscible mixtures), had no adverse effect on lab scale semicontinuous activated sludge systems operated for 11 days.

(g) L-4308 is a possible LR 7981 component.

(h) Bluegill sunfish (Lepomis macrochirus).

The low toxicity of FLUORINERT® liquids, indicates that this group of chemicals presents an insignificant risk of causing adverse environmental effects to aquatic organisms. The low aquatic exposure resulting from their low water solubility and high volatility further reduces the risk.

2. Recommended Testing

No laboratory studies on FLUORINERT® Liquids are recommended at this time. However, an ongoing literature study has been established. This study is enabling the Environmental Laboratory to continually increase its understanding of the fate and effects of these chemicals.

B. Low MW Acids and Their Salts

1. Background

a) Physical Properties

Commercial Chemicals Division products in this class consist of two fluorochemical acids (cc 8110-9 and cc 805-1) and some of their salts. In the unneutralized form, the fluorochemical acids are very strongly acidic and corrosive, making them hazardous materials. However, except in the case of large spills or discharges, they would be neutralized in the environment.

Calculated Henry's Law constants for these products suggest that they will ultimately migrate to and disperse in the aquatic environment[58]. Unlike the inert fluorochemical liquids, the atmosphere will not be a significant sink. The high water solubility of these products also makes them unlikely to bioconcentrate in living systems or to bond strongly to soil or sediments.

b) Degradation

cc 805-1 showed no biochemical oxygen demand (BOD) in a 20-day test and no dichromate chemical oxygen demand (COD) (LR 5695). Similar results would be expected for cc 8110-9. The lack of a chemical oxygen demand suggests extreme resistance to chemical degradation in the environment.

c) Effects

Environmental screening data on the neutralized products shows them to have very little toxicity (insignificant hazard) (see Table 5 and Appendix I). Neutralized cc 805-1 caused no acute lethality or other toxic effects to fish in 96 hrs. at 2000 mg/l. At this same concentration, cc 8110-9 caused minimum lethality: only two of 60 fish died.

Table 5 also shows that the neutralized acids have no significant acute toxicity to activated sludge microorganisms at concentrations much higher than would normally occur in a waste treatment system.

The low toxicity of these chemicals, the fact that they are likely to dilute in the aquatic environment and not concentrate in either living or nonliving systems, and their low production volumes makes the probability of significant adverse effects from this group of chemicals remote. Nevertheless, some concern exists about the apparent extreme resistance of these products to degradation.

2. Recommended Testing

No further environmental testing is recommended on these products at this time.

TABLE 5

TOXICITY OF NaOH NEUTRALIZED FLUOROCHEMICAL ACIDS AND OTHER SALTS OF THESE ACIDS

Product	Formula	96-Hr. LC_{50} (mg/l)(a)	Microbial Inhibition Concentration(b) (mg/l)	Lab Reques No.
cc 8110-9	C_3F_7COOH	-	-	-
Neutralized	C_3F_7COONa	>2000	>1000	7364
cc 805-1	CF_3SO_3H			
Neutralized	CF_3SO_3Na	>2000	>1000	5696
cc 786-6	CF_3SO_3Li	>1000(c)	-	4388
cc 791-17	$[CF_3SO_3^-][H_2N(C_2H_5)_2]^+$	>1000	-	4740

(a) Bioassays used Fathead minnows (Pimephales promelas) unless indicated.

(b) Concentration causing an immediate reduction of activated sludge oxygen uptake rate.

(c) Bluegill sunfish (Lepomis macrochirus).

C. Surfactants

1. Background

a) Physical Properties

Water Solubility - LR 5625 ($C_7F_{15}COONH_4$) and EAI 80021 ($C_8F_{17}SO_3K$) were studied as representative FC surfactants in the Fate of Fluorochemicals Program Part I [2,3]. From an environmental perspective, both products have high water solubility. Since this study, EAI 80021 solubility has been more accurately measured, and determined to be about 1,080 mg/l [59]. This solubility measurement was subsequently confirmed by the analysis of a water saturated sample of EAI 80021 sent to Dohrmann during the Environmental Laboratory's evaluation of their TOC equipment [60].

LR 5625 is very soluble. Its actual solubility limit was not determined. Solubility work on this compound was terminated after a sample was found to totally dissolve in a volume of water of equal weight [61]. Solubility data on other 3M fluorochemical surfactants are given in Table 6.

These high water solubilities suggest that EAI 80021, LR 5625, and other 3M fluorochemical surfactants will dilute in aquatic environments with little partitioning from the water phase into sediment, lipid tissues, or suspended organic matter. These data also indicate that these fluorochemicals are likely to remain in the aqueous phase during wastewater treatment and not to concentrate into wastewater sludge.

TABLE 6

SOLUBILITY AND OCTANOL/WATER PARTITION COEFFICIENTS OF FLUOROCHEMICAL SURFACTANT PRODUCTS

	Water Solubility at Room Temp.	Reference
cc 8011-23	>250 g/l	(62,63)
LR 2456-1	(a)	
EAI 80021	1 g/l	(59,60)
cc 802-23	10 g/l	(64)
cc 795-7	>500 g/l	(65)
cc 805-10(hydroxy foamer)	(a)	
LR 2318-2	(a)	
LR 2929	200 g/l (gel)	(66)
cc 773-588	50 g/l (gel)	(66)
LR 5625	>500 g/l	(61)
LR 2337-1	300 g/l (gel)	(66)
cc 7711-18	1 g/l	(67)
cc 777-3	1 g/l (b)	(68)

Footnotes:

(a) Solubility is unknown but probably high (>1%) because it is sold at 25% solids in a water-organic solvent solution.

(b) Cloudy solution.

<u>Octanol/Water Partition Coefficient</u> - An octanol/water partition coefficient (K_{OW}), or more accurately, an octanol/water distribution coefficient, is available for only one fluorochemical surfactant, cc 8011-23 (K_{OW}=0.65). Since cc 8011-23 is an ionic material and thus does not exist as the same solute species in the two immiscible solvents*, this is not a true partition coefficient. Quantitative SAR methods have not been fully developed for ionic species (24).

The applicability of this distribution ratio value for cc 8011-23 to existing regression equations correlating physical-chemical and chemodynamic properties is questionable. Nevertheless, the regression equation of Banerjee et al (21), which correlates K_{OW} with water solubility (S), appears to make a reasonable prediction. Using the midpoint of the melting range as the melting point (69), this equation predicts the solubility of cc 8011-23 to be 250 g/l.

*cc 8011-23 will exist in the dissociated state in the aqueous phase and primarily in the associated state in n-octanol.

Soil Adsorption Coefficients - Soil organic matter adsorption coefficients, K_{OC}, of 17 for LR 5625 and 45 for EAI 80021 (70) indicate very high mobility in soil. This is congruent with their high water solubility. A regression analysis based on data for EAI 80021, LR 5625, LR 3844-4, and LR 4197-2 showed the following relationship between solubility (S) and soil organic matter adsorption coefficient (K_{OC}):

$$\log K_{OC} = 3.58 - 0.513 (\log S).$$

This regression equation is nearly identical to the correlation reported by Kenaga and Goring (10) for 106 organic compounds:

$$\log K_{OC} = 3.64 - 0.55 (\log S).$$

This preliminary correlation again supports the prospect that some currently described structure relationships may be applicable to fluorochemical surfactants and alcohols.

Developing soil thin-layer chromatography (TLC) plates with water is another method of measuring the affinity of chemicals for soil. Procedures have been proposed by the USEPA to measure mobility in soil by this method (71), and preliminary measurements by a very similar method have been made on EAI 80021 and LR 5625 (72). Unfortunately, the amount of EAI 80021 spotted was too small to allow visualization. LR 5625, however, showed low mobility. This finding seems to contradict both the soil adsorption coefficient measurements given above and the predictions of low soil sorption based on the high water solubility of 3M fluorochemical surfactants. These adsorption (K_{OC}) and TLC measurements were conducted in two different soil types, but while edaphic factors* can cause

- -

*The following are edaphic factors which can affect chemical mobility in soil (73):

1) Complexation with organics
    a) Cation exchange with organics
    b) Organic anion fixation
    c) Nonpolar organic reactions
2) Adsorption by mineral species (e.g., clay)
3) Chemical oxidation-reduction effects
4) Precipitation reactions and pH effects
5) Ion exchange reactions
    a) With layered silicates
    b) With hydroxy oxides of Fe and Mn
    c) With organic matter
    d) With lime materials (agricultural or natural)

differences in chemical mobility, differences of this magnitude are unlikely with these fluorochemical surfactants. Clarification of these data is needed.

Biosorption - A biosorption study has been conducted on cc 8011-23, the diethanolamine salt of perfluoroethylcyclohexyl sulfonic acid (74). The fluorochemical portion of this material was found not to bind strongly to activated sludge. The results of this study indicate that the fluorochemical portion of cc 8011-23 is likely to remain in the aqueous phase during passage through a wastewater treatment system. The behavior of this water soluble fluorochemical is thus similar to that predicted for EAI 80021 and LR 5625, and because of its similarity to EAI 80021 (the perfluorinated portion is also a saturated, C_8 sulfonic acid), the finding adds credence to this prediction.

Studies with rats done by Riker have shown that perfluorooctane sulfonate is very difficult to recover quantitatively from tissues and feces even when extracted by a series of nonpolar to polar organic solvents. Perfluorooctane sulfonate in the blood was also found to be essentially completely bound to soluble proteins (75). These two findings suggest that perfluorooctane sulfonate may bind strongly to nonsoluble proteinaceous materials, both in animal tissues and in soils or sediments of the aquatic or terrestrial environment. These findings and the predictions based on them are contrary to the prediction of the Environmental Laboratory based on water solubility measurements.

Vapor Pressure - No actual vapor pressure measurements were made on EAI 80021, LR 5625, or any other 3M fluorochemicals in the Fate of Fluorochemical Study Part I. The parameter can be very useful, however, in predicting the rate of movement and distribution of a chemical between the atmosphere and terrestrial and aquatic environments (45), e.g., vapor pressure approximates the rate of volatilization from aqueous solution or from the adsorbed state on soil (76).

LR 5625 can be sublimed completely and recovered unchanged (by IR) at 178°C and atmospheric pressure (77). Most LP 5625 probably enters the environment through volatilization from its use in PTFE manufacture. On the other hand, our experience in handling EAI 80021 and trying to analyze it by TOC and CLC indicates that its vapor pressure is probably quite low. These data indicate the need for quantitative measurement of vapor pressure and volatilization from aqueous systems that will enable predictions of environmental distribution.

b) Degradation

One 3M fluorochemical surfactant, LR 5625, is a perfluorocarboxylic salt. Several of these surfactants, like FAI 80021, are perfluorosulfonic acid salts, and the remainder, such as LR 2929 and the hydroxy foamer, are organic-amide derivatives of fluorochemical sulfonic acids. Degradability assessments on this latter group must separately consider the perfluorinated and nonfluorinated portions.

Biodegradation - Neither FAI 80021 nor LR 5625 degraded in 2 1/2-month shake flask biodegradation studies using inocula from three separate treatment systems [78]. Two of these inocula were from systems treating 3M fluorochemical wastes, and thus more likely than nonacclimated inocula to have microorganisms capable of growing on these fluorochemicals. This was the most rigorous laboratory biodegradation test ever done on these fluorochemical surfactants. Other biodegradation tests, including a 3-hr. Warburg study on FAI 80021 [79] and BOD_{20} tests on both FAI 80021 and LR 5625 (LR #3844), also showed no degradation. No testing has been done under anaerobic conditions.

These data are adequate to demonstrate that biodegradation of FAI 80021 and LR 5625 cannot be depended on to occur in an aquatic environment. This resistance to degradation is consistent with their perfluorinated structured. However, to more substantially rule out the possibility of biotransformation and the concomitant formation of daughter products of unknown toxicity, tests more rigorously favoring biodegradation should be performed.

Table 7 shows biodegradation data on other fluorochemical surfactant products. The products in this table do not contain biodegradable solvents which tend to mask the biodegradability of the fluorochemical surfactants in nonspecific tests, such as BOD.

These data show that fluorochemical surfactants with no nonfluorinated organic portions, e.g., cc 802-23, EAI 80021, and LR 5625, have essentially no biochemical oxygen demand. Those with ionically bonded organics, i.e., cc 8011-23 and cc 795-7, have BOD's close to that which would be -

TABLE 7

BIODEGRADATION DATA ON NONSOLVENT-CONTAINING FLUOROCHEMICAL SURFACTANTS

Product[a]	Test Results	Reference or Lab Request
cc 8011-23	BOD_{20} 0.28 g/g[b]	6260
cc 802-23	BOD_{20} <3800 mg/kg BOD_{20} Nil	3844 1231
cc 795-7	BOD_{20} 82,000 mg/kg[c]	4895
LR 2929	7-Hr. Warburg BOD=70% of $ThOD_{NH_3}$[d] of the organic portion.	(79)
cc 7711-27	BOD_{20} Nil	1870
cc 7711-18	BOD_{20} = 0.107 g/g[e]	4197
cc 777-3	BOD_{20} = 0.17 g/g[f]	4951
LR 5062 (MCL Emulsifier)	BOD_{20} 9600 mg/l	5062
cc 805-10S (Hydroxy Foamer)	BOD_{20} <9300 mg/kg	8139

(a) Structures for these products are in Table 9.

(b) The BOD_{20} of cc 8011-23 is approximately 90% of the theoretical oxygen demand of the diethanolamine portion of this chemial.

(c) cc 795-7 is a 25% aqueous solution of a diethanolamine salt. The fluorochemial portion of this salt is the same as that of EAI 80021.

(d) $ThOD_{NH_3}$ is the theoretical oxygen demand assuming no oxidation of the nitrogen. This ThOD also assumes no degradation of the perfluorinated portion of the molecule.

(e) BOD_{20} = 10% of COD

(f) BOD_{20} = 25% of COD

expected from their organic portion (diethanolamine) alone. Fluorochemical surfactants with covalently bonded organic portions gave mixed results. Those with quaternary ammonium organic portions, i.e., MCL, hydroxy foamer, and cc 7711-27, had no BOD. This is not unexpected since even nonfluorinated quaternary ammonium surfactants are frequently difficult to biodegrade. Those surfactants with polyethylene glycol components, i.e., cc 7711-18 and cc 777-3, had BOD_{20} values equal to 10-20% of their COD's. This indicates some partial degradation of the nonfluorinated organic portions of cc 7711-18 and cc 777-3 since the observed BOD is greater than would be expected from organic by-products. One of these, cc 7711-18, did not biodegrade at all in the first 7 days. Slight biodegradation was seen at 10 days with the rate increasing at the 14-day observation and continuing at 20 days with no indication of plateauing.

These data suggest that longer biodegradation test periods, using acclimated organisms, might lead to more complete degradation of the nonfluorinated portion of polyethylene glycol adduct fluorochemical surfactants.

LR 2929 has the highest BOD_{20}/COD (77%) of those surfactants with covalently bound organics, but it was tested by a somewhat more rigorous biodegradation test method (79). Attempts to confirm this biodegradability have been made with cc 8011-10 (LR 6300), a product containing the LR 2929 surfactant, but samples from this study are still awaiting analysis in the Commercial Chemicals Division Laboratory.

Photodegradation - Both EAI 80021 and LR 5625 have been tested for photodegradation in aqueous solutions using an artificial light source (wavelength >300 nm) (80,81). No photodegradation was observed. These photodegradation studies did not contain sensitizing agents. No photodegradation studies have been done on surfactants with covalently bonded nonfluorinated portions or when adsorbed onto solid surfaces such as sand or silica gel.

c) Bioconcentration

No bioconcentration studies have been done on fluorochemical surfactants in the Environmental Laboratory. Studies in Riker have shown that male rats excrete prefluorooctane sulfonate and perfluorooctanoate very slowly (75). Perfluorooctane sulfonate is strongly protein bound which prevents excretion through the kidney. Perfluorooctanoate is less strongly protein bound (approx. 97.5%), but the small fraction of free material that filters through the glomerulus seems to be actively readsorbed by male rat kidneys. Researchers at DuPont have made similar findings on hamsters (75). Female rats can excrete perfluorooctanoate, but both male and female people appear to behave more like male rats and only very slowly clear their bodies of this material.

d) Effects

Table 8 summarizes the current set of bioassay data on EAI 80021 and LR 5625. EAI 80021 was about a factor of ten more toxic to fish and daphnia than LR 5625. On the other hand, LR 5625 retarded algae growth by approximately twice as much as EAI 80021. Based on the NIOSH aquatic toxicity scale (see Appendix I), EAI 80021 would be considered to have slight to moderate toxicity to fish, while LR 5625 would be classified as practically nontoxic to fish and slightly toxic to algae.

Environmental screening tests have also been run on other surfactant products (Table 9). In some of these products, e.g., LR 2456-1 and cc 805-10, the fluorochemical surfactants are sold in solvent systems containing water and isopropanol or butyl Carbitol®. Bioassays were run on these products as sold. Since these solvents have very little toxicity to fish, it is assumed that all the toxicity observed was due to the fluorochemical and not the solvents. Synergistic or antagonistic effects, however, are possible. Based on our limited experience, antagonism, which would make the surfactants appear somewhat less toxic, is more likely.

TABLE 8

AQUATIC BIOASSAY DATA ON LP 5625 AND EAI 80021

Species	Parameter	Concentration mg/l EAI 80021	LR 5625	Lab Request or Reference
Fathead	96-Hr. LC_{50}	32,29,38	766	1429,2340,5625,(c)
Bluegill	96-Hr. LC_{50}	68	569	(d),3844
Trout	96-Hr. LC_{50}	11	—	(e)
Daphnia	48-Hr. LC_{50}	50	632	
Fathead	30-Day Egg-Fry	1.9(a)	100(b)	(82,83)
Green algae	Cell weight 14-Day EC_{50}	146	73	(84,85)
Green algae	Cell count 14-Day EC_{50}	95	43	(84,85)

(a) Color and behavioral changes observed at 1.0 mg/l while egg-fry survivability was decreased at 1.9 mg/l.

(b) No effect noted during this study at doses up to and including 100 mg/l.

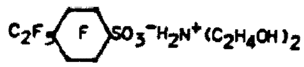
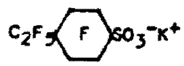
(c) Environmental Laboratory Aquatic Toxicity Worksheet on EAI 80021 Lot 583, Fathead minnow, started 8/22/77.

(d) M. T. Elnabarawy, Environmental Laboratory Aquatic Toxicity Data Sheet on EAI 80021 Lot 583, Bluegill sunfish, started 5/23/78.

(e) M. T. Elnabarawy, Environmental Laboratory Aquatic Toxicity Data Sheet on EAI 80021, Lot 583, Rainbow trout, started 2/21/78.

TABLE 9

FISH 96-HR. LC_{50} DATA FOR FLUOROCHEMICAL SURFACTANTS

Product	Chemical Structure	Fathead minnow 96-Hr. LC_{50} (mg/l)	Lab Request Number
cc 8011-23		43	6260
LR 2456-1	$C_8F_{17}SO_3^-NH_4^+$	20-25[a]	2318,2456
cc 802-23		155,200	3844,2563
cc 795-7	$C_8F_{17}SO_3^-H_2N^+(CH_2CH_2OH)_2$	8[b]	(86)
cc 805-10 (Hydroxy Foamer)	$C_6F_{13}SO_2N(CH_2CH(OH)CH_2SO_3^-)-C_3H_6N^+(CH_3)_2C_2H_4OH$	20-25[a]	5720,4950
LR 2318-2	$C_{10}F_{21}SO_3^-NH_4^+$	4[a]	2318,2456
cc 816-27	$C_8F_{17}SO_2N(C_2H_5)CH_2COO^-K^+$	430[c]	7009
LR 2929	$C_8F_{17}SO_2N(C_2H_5)CH_2COO^-K^+$	34,30[c]	2254,2340
cc 8011-10	$C_8F_{17}SO_2N(C_2H_5)CH_2COO^-K^+$	260[c]	6300
cc 7711-27	$C_8F_{17}SO_2NHC_3H_6N^+(CH_3)_3I^-$	20,31	2340,1955
cc 7711-18	$C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_{14}OH$	285[b]	4197
cc 777-3	>90% $C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_{7.2}CH_3$ <10% $C_8F_{17}SO_2NH(CH_2CH_3)$	208	4951
LR 5062	$C_8F_{17}SO_2NHC_3H_6N^+(CH_3)_3Cl^-$	30	5408

Footnotes:

(a) LC_{50} values reported are those calculated for the surfactant solids. This calculation assumes neither synergism nor antagonism from solvent systems.

(b) Blugill sunfish.

(c) This fluorochemical was tested both as a 100% solids material (LR 2929) and as water-isopropanol and water-butyl Cellosolve-ethanol solutions (cc 816-27, cc 8011-10). The solvent appears to have an antagonistic effect on toxicity, but it's also possible that differences in by-product concentration could have caused the observed toxicity differences.

Other environmental effects data on fluorochemical surfactants are shown in Table 10. These tests showed that the surfactants have little or no immediate toxicity to activated sludge at concentrations much greater than those normally expected to reach a wastewater treatment system.

While most sludge toxicity tests were run for 5-10 minutes, the test with EAI 80021 showed no inhibition even when exposure of the sludge to the fluorochemical was continued for four hrs. The data does not show whether fluorochemical surfactants have a delayed or chronic effect on sludge, i.e., by inhibiting growth or causing population shifts, but due to their low acute toxicity, this seems unlikely.

One unusual result was that cc 7711-18 is more than two orders of magnitude more toxic to Daphnia than to fish. Large differences between Daphnia and fish toxicity were not seen with cc 8011-23, EAI 80021, nor LR 5625.

cc 7711-18 is the only fluorochemical surfactant which has undergone testing to determine its chronic effects on Daphnia [87] and its acute effects on vascular plants. While the product showed chronic toxic effects at very low concentration exposures, 0.1 mg/l, to daphnids, it was found not to be very toxic to vascular plants. It had no effect on germination, root growth, or hypocotyl growth of soybeans, ryegrass, or corn at concentrations ranging from 1000-1800 mg/l.

Fish bioassays on cc 816-27, LR 2929, and cc 8011-10, which all contain the same fluorochemical surfactant, suggest that solvents found in cc 816-27 and cc 8011-10 may have a significant antagonistic effect on the toxicity of this fluorochemical. Acute fish bioassays on an LR 2929 sample both in the presence and absence of isopropanol would clarify if the great differences in toxicity observed (Table 9) were due to antagonistic effects or differences in toxicity of different lots of this surfactant.

Testing is currently underway (LR #8442) on L-6778, LR 2929-1, a product similar to cc 816-27, that may partially answer this question. As an addendum to the routine screening, the Environmental Laboratory is also looking at the toxicity of this product after evaporating off the solvent. The need for further testing will depend on the results of this testing.

Fish 96-hr. LC_{50} on LR 2929 with and without solvent - Priority III

Since most fluorochemical surfactants find their way into aquatic environments, 28-day Daphnia bioassays similar to that done on cc 7711-18 (87), and 14-day multigeneration algal bioassays similar to those done on LR 5625 and EAI 80021 are recommended for all of the major flouorochemical surfactants.

Toxicity tests on those organisms, which represent 2 major components of the aquatic community, plants and invertebrates, will give a broader perspective of the toxic potential of fluorochemical surfactants to the aquatic environment. This broader perspective is needed because the minimal daphnid and algal test data presently available has shown that toxicity to these organisms cannot be predicted reliably from fish bioassay data. For example, cc 7711-18 is practically nontoxic to fish but moderately to highly toxic to daphnids, and EAI 80021 when compared with LR 5625 is more toxic to fish but less toxic to algae.

These tests should be done on the neat fluorochemicals to avoid synergistic effects from solvents in which they are sold. Chronic Daphnia studies will be done only on products with LC_{50} values less than 100 mg/l or which show a delayed onset of toxicity in preliminary acute bioassays on this organism.

b) Degradation

Biodegradation - cc 777-3 and cc 7711-18 have both given indications of partial biodegradation in a 20-day BOD test, suggesting possible degradation of the Carbowax portion of these molecules. Studies on cc 777-3 under more rigorous conditions are recommended to substantiate these partial degradation findings and to identify degradation products.

The recommended test approach involves using preacclimated microorganisms as inocula for a 28-day BOD (92). If biodegradation tests are positive, an attempt will be made to identify major degradation products. This testing is important to substantiate the previous inconclusive findings of partial microbial degradation of 3M fluorochemicals with covalently bonded nonfluorinated moieties and to determine if perfluorooctane sulfonic acid (the EAI 80021 fluorochemical) is the major degradation product. Analytical methods could involve techniques such as methylation and capillary GC or TLC of radiolabeled cc 777-3 degradation products. The ^{14}C label should be on the perfluorinated portion of the cc 777-3 molecule.

28-Day BOD:
    cc 777-3 - Priority I
    Degradation Product Identification - Priority II

No degradation has been observed in BOD tests on the hydroxy foamer, cc 805-10S, or on any other quaternary ammonium fluorochemical surfactant. Since the hydroxy foamer is an important component of "LIGHT WATER" products and is also finding a significant use in copper mining, rigorous biodegradation tests such as the SCAS* test or soil respirometric tests are recommended. This testing would be greatly facilitated by the use of radiolabeled hydroxy foamer with the radiocarbon tag placed on the hydrocarbon portion of the molecule.

If results indicate significant degradation, an attempt will be made to identify degradation products.

Soil Respirometry or SCAS:
    Hydroxy foamer - Priority II
    Degradation product identification - Priority III

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*Semicontinuous activated sludge

While the structure of EAI 80021 and LR 5625 suggests they will have extreme resistance to biodegradation, testing to date is only sufficiently rigorous to show that their degradation cannot be depended upon to occur in an aquatic environment. More rigorous aerobic biodegradation tests are recommended to further substantiate the expected complete resistance of EAI 80021 and LR 5625 to biodegradation. Conditions rigorously favoring biodegradation will be used such as mixing the products with garden soil and compost further inoculated with sludge that has been acclimated to these chemicals. Such studies could be extended up to 1 year depending on results, and would be periodically primed with fresh decaying materials. Analytical methods will involve testing for fluoride release using the fluoride electrode, measurement of $^{14}CO_2$, absorbed in base, or searching for other degradation products of radiolabeled fluorochemicals by TLC autoradiography.

Rigorous (soil) aerobic biodegradation:
EAI 80021 - Priority II
LR 5625 - Priority II

Rigorous anaerobic biodegradation tests involving long-term (i.e., weeks-months) burial of LR 5625 as a representative perfluorinated surfactant in water-saturated soil are also recommended. Analytical methods will be the same as for the rigorous aerobic tests.

Rigorous anaerobic biodegradation:
LR 5625 - Priority III

Photodegradation - Since no photochemical degradation of a 3M fluorochemical surfactant has yet been demonstrated in aqueous solution[71,72], exploratory photodegradation studies are suggested to test possible activation by surfaces such as silica sand or "sensitizing agents" like the organic components of natural water.

Candidate fluorochemical surfactants, preferably radiotagged, will be both coated onto sand or silica gel and also dissolved in water containing sensitizing agents. Both the coated silica and aqueous samples will then be irradiated in Vycor tubes by sunlight for 3, 6, and 12-month periods. After irradiation, the samples will be extracted, analyzed for initial fluorocarbon and/or daughter products by TLC autoradiograph, or GLC following methylation, and for fluoride release using the fluoride electrode.

TABLE 10

OTHER ENVIRONMENTAL EFFECTS DATA[a] ON FLUOROCHEMICAL SURFACTANTS

Product	Immediate Inhibition of Activated Sludge	48-Hr. LC_{50} Daphnia magna	Other Effects	Lab Request No. or Reference
cc 8011-23	None at 250 mg/l	18 mg/l		6260S 6457S
EAI 80021	None at 4000 mg/l[b]			(79)
cc 802-23	None at 100 mg/l			5428
cc 795-7	Node at 250 mg/l			4895
cc 805-10[c]	None at 150 mg/l			4950S
cc 816-27	None at 500 mg/l			7009
LR 2929			No inhibition of microbial activity at low mg/l[d]	2174
cc 8011-10	None at 500 mg/l			6003
cc 7711-27			No inhibition of microbial activity at low mg/l[d]	2174
cc 7711-18		1.5 mg/l 1.0 mg/l	No effect on soybean, rye, and corn growth and germination at 1800 mg/l[e]	4197 (87)
cc 777-3	None at 1000 mg/l		0.15 mg/l caused reduced survivability, number of broods, and brood size in 28-day daphnid life cycle study. Later generations were less sensitive.	5951
LR 5062[e]	30% inhibition at 1000 mg/l None at 100 mg/l			5062

Footnotes:

(a) All values based on surfactant solids.
(b) Exposure to EAI 80021 continued for 4 hrs. as opposed to 5 to 10 min. sludge exposures in other tests.
(c) Hydroxy foamer.
(d) Measured by TTC (2,3,5-Triphenyltetrazolium chloride) test for dehydrogenase activity re: "Dehydrogenase Enzyme as a Parameter of Activated Sludge Activities," Ford, et al. Proceedings of the 21st Industrial Waste Conference, Purdue, May 3, 4, and 5, 1966.
(e) The no effect level for soybean root length was 1000 mg/l.
(f) MCL emulsifier.

2. Recommended Testing

"... ITIAL"

a) Physical Chemical

Solubility - Water solubility data on 3M fluorochemical surfactants is adequate for use in estimating the environmental mobility of these compounds. Further water solubility measurements on 3M fluorochemical surfactants are not specifically recommended, but some may be included as part of efforts to develop structure activity relationships for fluorochemicals.

Partition Coefficients - Octanol/water partition coefficient measurements on fluorochemical surfactants EAI 80021 and LR 5625 are recommended. True "partition coefficients" can't be made on these ionic materials, but octanol/water distribution coefficients can be measured. The usefulness of such distribution coefficients in predicting chemodynamic properties from octanol/water partition coefficients is now uncertain, but these measurements will be helpful in determining their utility in this area. EAI 80021 and LR 5625 are appropriate choices for this testing since they represent the range of fluorochemical surfactant solubility: EAI 80021 is one of the least soluble FC surfactants, and likely to have one of the highest octanol/water distribution coefficients among this class of fluorochemicals, while LR 5625 has one of the highest solubilities.

Distribution coefficients will be measured, if possible, by standard procedures such as those approved by the OECD (88) and the USEPA (89). The separated phases will be analyzed for total organic fluorine, for the specific fluorochemical by capillary GLC following methylation, or by using radiolabeled materials. Standard samples prepared in water-saturated octanol and octanol-saturated water will be used as controls.

These distribution coefficient measurements are given the following priority:

EAI 80021 - Priority I
LR 5625 - Priority I

Soil TLC - Since preliminary soil TLC tests on LR 5625 and EAI 80021 gave ambiguous results, we recommend repeating these tests. The standard USEPA soil TLC procedure will be followed (71). The procedure requires a ^{14}C-labeled substrate and produces a standard TLC R_f value that characterizes the mobility of the fluorochemical in soil systems.

Soil TLC testing of fluorochemical surfactants is given the following priority.

EAI 80021 - Priority II
LR 5625 - Priority II

Bioadsorption - As LR 5625 and EAI 80021 have been found to bind to protein in rats, it seems probably that they would also bind to the microbial proteins in activated sludge. It is recommended that Bioadsorption Studies be run using the Environmental Labratory protocol (74) and radiolabeled materials. Such studies would be useful in determining whether these compounds would be most likely to pass through a wastewater treatment system in the aqueous phase or bind strongly and be disposed of with activated sludge.

Biosorption testing of fluorochemical surfactants.

LR 5625 - Priority III
EAI 80021 - Priority III

Vapor Pressure - Vapor pressure measurements are necessary to estimate the volatilization of fluorochemicals and to make quantitative predictions of environmental distribution. Measurements will be made following standard USEPA (90) or OECD procedures (91) and will most probably be performed by Analytical and Properties Research at CRL.

EAI 80021 - Priority III
LR 5625 - Priority II

Greater priority is given to work on LR 5625 since this material will typically enter the atmosphere through its use in PTFE manufacture. It is also a higher volume product.

LR 5625 and EAI 80021 Photodegradation:
On silica - Priority III
Sensitized - Priority III

Hydroxy foamer* photodegradation:
Sensitized - Priority III

c) Bioconcentration

Because an active mode of concentrating perfluorooctanoic acid exists in rats (75), it seems possible that fish or other organisms could actively concentrate this or other fluorochemical surfactants from the environment. Laboratory studies should be done to prove or disprove this possibility. Whole body fish bioconcentration studies using EPA-approved techniques (93) and radiolabeled materials are recommended.

Fish bioconcentration studies on fluorochemical surfactants.

Perfluorooctanoate (LR 5625) - Priority I
Perfluoroctane sulfonic acid (EAI 80021) - Priority I

d) Effects

Aquatic bioassays are proposed to complete the aquatic toxicity profiles of several selected fluorochemical surfactants. These bioassays will employ standard Environmental Laboratory procedures (87,94,95).

Environmental screening tests have been done on the hydroxy foamer in two mixtures, cc 796-3 and cc 805-10 (LR Nos. 4950 and 5720). Assuming that all of the toxicity of these mixtures is due to the FC solids, the hydroxy foamer has a 96-hr. LC_{50} for Fathead minnow of 20-25 mg/l. Tests on the surfactant alone to confirm this toxicity level are desirable.

Fish - 96-hr. LC_{50} on Solvent-free Hydroxy Foamer - Priority III

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* Photodegradation tests on hydroxy foamer are recommended only if it does not biodegrade under rigorous conditions.

14-Day Algae Bioassays on the neat fluorochemicals contained in:

LR 2929	Priority II
cc 805-10	Priority II
cc 773-58	Priority II
cc 777-3	Priority II

28-Day Daphnia Bioassay on the neat fluorochemicals contained in:

LR 5625	Priority II
LR 2929	Priority II
cc 805-10	Priority II
cc 773-58	Priority II
cc 777-3	Priority II

D. Phosphates

1. Background

The Environmental Laboratory has generated data on cc 795-23, which is one of the highest volume products in the FC product line. It is a mixture containing mostly the ammonium salt of the di-phosphate ester of the ethyl FOSE alcohol, LR 3844-4 but also containing some of the mono- and tri-phosphate ester salts.

a) Physical Properties

The Environmental Lab has generated no physical-chemical data on the fluorochemical component of cc 795-23.

b) Degradation

Hydrolysis - The results of a hydrolysis study on cc 795-23 (NB 46269 p. 22, 24) show that incubation at 45°C for 24 hours at pH 3, 6, 9, 10, 12, and 12.3 did not increase the LR 3844-4 concentration above that initially present as an unreacted chemical precursor of cc 795-23. This work is significant because it suggests that rapid chemical hydrolysis of cc 795-23 to LR 3844-4 is unlikely in the environment.

Biodegradation - Biodegradation testing on cc 795-23 involved both biochemical oxygen demand (BOD) tests (96, LR #3488) and inconclusive shake flask tests from the Fate of Fluorochemicals Study Part I.

The BOD test results lead to the conclusion that the cc 795-23 fluorochemical component is not easily biodegraded. The 20-day BOD of cc 795-23 is only about half of the chemical oxygen demand (LR 3844). Since isopropanol, which makes up 40% of the organics, should have been nearly completely degraded in this test, very little, if any, degradation could have occurred to the remaining 60%, which is the fluorochemical component.

The shake flask biodegradation studies are inconclusive because no analytical technique for cc 795-23 was available at the time. A nonspecific analytical technique (TOC) also did not work because material precipitated from solution, possibly due to calcium in the culture medium.

c) Effects

The available data demonstrate three environmental effects properties of cc 795-23: 1) it has minimal acute toxicity to aquatic organisms (96-hr. LC_{50} Fathead minnow (Pimephales promelas) >3600 mg/l) (96, LR 1204, LR 2191, LR 2256); 2) it does not significantly affect waste treatment system operation at <1200 mg/l (96), and 3) it does not retard the biodegradability of treated cardboard (97).

2. Recommended Testing

a) Physical Properties

To enable the evaluation of cc 795-23 environmental mobility, measurement of water solubility, partition coefficient, soil sorption, soil TLC, and vapor pressure of cc 795-23 fluorochemical components* are recommended. Of these, solubility and partition are most important since they can most easily be used to predict other chemodynamic properties.

Water Solubility - The Environmental Laboratory will measure fluorochemical solubility in water using current recommended methodology (98). Analysis of the saturated water samples could involve GLC of the methylated samples, allowing determination of the relative solubility of the mono- and di- esters. Alternatively, or for confirmation purposes, radiolabeled cc 795-23 could be used.

Water Solubility of cc 795-23 - Priority I

Octanol/Water Partition Coefficient - K_{OW} will be measured by standard procedures (88,89). The analytical procedures will be the same as those described above for measuring cc 795-23 water solubility.

Distribution Coefficient of cc 795-23 - Priority I

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*"fluorochemical components" refers to the mono-, di-, and tri-phosphate ester salts of ethyl FOSE alcohol.

Soil/Organic Matter Adsorption Coefficient (K_{oc}) Soil sorption measurements are proposed to aid in evaluating the mobility of cc 795-23 in the soil environment. For example, these data will aid in predicting the rate and extent of leaching from landfills to groundwater. This work will follow standard procedures (98,99,100). The analytical methods will be the same as used for water solubility and K_{ow}, but because of possible interferences caused by soil, the need for radiolabeled material is greater.

K_{oc} of cc 795-23 - Priority III

Soil TLC - This procedure will confirm K_{oc} measurements. USEPA recommended procedures will again be followed (71). These EPA procedures require radiolabeled materials.

Soil TLC of cc 795-23 - Priority III

Vapor Pressure - Vapor pressure measurement for cc 795-23 is proposed to complete its physical property profile. This measurement is necessary to estimate the extent and rate of its movement into the atmosphere (101). Analytical and Properties Research at CRL is probably the most appropriate laboratory for this testing.

Vapor Pressure of cc 795-23 - Priority III

b) Degradation

Degradation studies on cc 795-23 will allow estimation of its persistence in the environment and identification of degradation products.

Proposed biodegradation studies, as a first stage, will simply involve looking for an increased concentration of LR 3844-4, the most likely degradation product, by GLC as was done in the above described cc 795-23 hydrolysis experiment. In this case, extraction with ethyl ether or dioxane will be necessary to insure complete extraction of LR 3844-4 which we have found binds strongly to biological sludge and soil.

If studies give an indication of cc 795-23 biodegradation, further work will be done involving specific analysis for cc 795-23 components and other possible degradation products such as EAI 80021. As described above, these specific analytical methods will consist of gas-liquid chromatography of methylated extracts, or, if possible, thin-layer chromatography of radiolabeled cc 795-23.

All proposed testing will be done under conditions rigorously favoring biodegradation. cc 795-23 will be incubated for extended periods in a mixture of compost and soil.

Rigorous Soil Biodegradation Tests on cc 795-23 - Priority III

c) Effects

A 28-day Daphnia bioassay (87) and a 14-day algae test (84) are needed to complete the environmental effects profile on this important fluorochemical. Procedures and decision points will be the same as those recommended for fluorochemical surfactants.

cc 795-23:

14-day Algae Bioassay - Priority II
28-day Daphnia Bioassay - Priority II

E. Alcohols

1. Background

a) Usage

Only a few relatively small-volume products, cc 815-11, cc 783-1 and cc 796-10, contain the free fluorochemical alcohols as other than an uncompletely reacted raw material. Thus, the importance of the alcohols (LR 3844-4 and LR 4197-2) from an environmental assessment perspective is mainly a concern with wastes from manufacture and the possible release of these alcohols from the degradation of other products such as the fluorochemical acrylates and the phosphates (cc 795-23) in which the alcohols are chemically bound.

b) Physical Properties

Water Solubility - Water solubility measurements have been made on LR 3844-4 (102,103) and LR 4197-2 (104) by the Veith technique (105). This process saturates water by recirculating it through a column of sand or glass beads coated with a low solubility material. Unfortunately, the technique preferentially leaches the more soluble components of impure materials from the column.

This defect of the procedure can be significant with this class of products since both alcohols are actually mixtures of several isomers which likely have different solubilities but were undifferentiated by the analytical method used. This lack of purity makes it impossible to accurately and reproducibly measure solubility and partition coefficient by any standard method, but the Veith technique is particularly deficient in this respect. For example, the two solubility values given for LR 4197-2 (2.3 mg/l and 0.82 mg/l) resulted from two sequential recirculations through the same coated column. From these data, it appears that the more soluble components came off in the first washings. Thus, the 0.82 mg/l value probably more closely represents the solubility of the major LR 4197-2 component.

The lack of chemical purity may also be the cause of variability in LR 3844-4 solubility measurements. Early, apparently repeatable results showed an LR 3844-4 water solubility of 0.05 mg/l (102), but our latest set of measurements consistently showed a value of about 0.16 mg/l (103).

Octanol/Water Partition Coefficient - The partition coefficient for the ethyl FOSE alcohol is also not accurately known, but the ratio of the product's water solubility and octanol solubility (106) indicates that the partition coefficient is high (possibly between 10^6 and 10^7). On the other hand, using the average measured solubility of LR 3844-4, 0.1 mg/l (0.18 µM), the regression equation of Chiou et al (19) predicts an octanol/water partition coefficient for LR 3844-4 of 3×10^5. The distribution coefficient of LR 4197-2 has been measured by the standard Environmental Laboratory procedure and was determined to be 5.7×10^4 (107).

These water solubility and partition coefficient data suggest that the two fluorochemical alcohols would tend to partition from water into sediments, lipid tissues of aquatic organisms, and suspended organic matter, such as activated sludge.

Soil Sorption - LR 4197-2 and LR 3844-4 were found to have soil organic carbon adsorption coefficients, K_{OC}, of 3,500 and 15,000 (108,109), respectively, which indicates very low mobility in soil and is in agreement with the low water solubilities of these compounds. Preliminary soil TLC measurements were also made on LR 3844-4 (72). In this test, the LR 3844-4 remained at the origin, which is consistent with its K_{OC} and water solubiltiy data. Together, the water solubility, soil sorption, and soil TLC measurements indicate that LR 3844-4 will have very low mobility in the soil environment.

Vapor Pressure - From nonquantitative observations, the volatility of LR 3844-4 was found to be substantial (102,106). LR 3844-4 steam distills or coevaporates appreciably with water. These observations suggest that LR 3844-4 has a significant vapor pressure. Due to its structural similarity, LR 4197-2 likely behaves in a similar manner.

c) Degradation

Chemical Degradation - Lab tests have shown that LR 3844-4, when treated with 5% KOH in absolute ethanol at 50-53°C, hydrolyzes to form EAI 80021 with a half-life of 77 hours (106). These results, however, cannot be extrapolated to estimate environmentally relevant alkaline hydrolysis rates in water. Alkoxides formed in alcohol are much stronger bases than hydroxyls in water. This stronger activity can cause reactions to take place in alcohol that may not occur in water.

Our present understanding is that LR 3844-4 would not hydrolyze at a significant rate in the environment since sulfonamides are stable in water at normal pH, only hydrolyzing in strong acid or caustic solutions (110).

Photodegradation - Photolysis studies by the Agrichemical Group on LR 3844-4 in DI water have given negative results (111). In addition, the Environmental Laboratory has done two photodegradation studies on LR 4197-2. The first involved exposing a saturated aqueous solution of LR 4197-2 for 30 days to a 40 W fluorescent black light (112). The second involved exposing supersaturated aqueous solutions of LR 4197-2 to natural sunlight for 7 months both in the presence and absence of acetophenone, a photochemical "sensitizing" agent (113). Neither study showed any significant photodegradation. Aquatic photolysis doesn't appear likely to cause significant degradation of these compounds.

A photolysis study on LR 3844-4 adsorbed to soil (114) has given slight positive, yet inconclusive, results. In this study, adsorption to silica could have lowered energy requirements for photodegradation.

Biodegradation - No biodegradation of either LR 3844-4 or LR 4197-2 has been substantiated by analytical means in any of several biodegradation tests conducted in the Environmental Lab. The tests conducted on LR 3844-4 include a Warburg (79), a 10-day semicontinuous activated sludge (115), and a 6-month shake flask study which used inocula from a number of sources, including soil and sludge that had been exposed to fluorochemicals (115). These studies show that rapid aerobic, microbial conversion of LR 3844-4 to other products is unlikely.

In contrast, perfluorooctane sulfonic acid (EAI 80021) has been identified in rat and monkey serum following 30 and 90-day LR 3844-4 feeding studies (116). Its concentration was 300-750 times greater than that of residual LR 3844-4, suggesting that it is a major metabolite of LR 3844-4 in mammalian systems. Due to the great diversity of catabolic capabilities in microorganisms, this finding increases the probability that microbial systems may eventually be found that are also capable of this conversion. It also suggests that biotransformation could occur in other organisms, such as fish or food crops grown on soil in which fluorochemical-containing wastewater sludge has been incorporated.

d) Bioconcentration

It has been demonstrated that fish will bioconcentrate LR 3844-4 in their tissues, with whole fish values ranging from 200-600 times the concentration of this material in the water [8,9]. These bioconcentration factors (BCF) values were independent of species. BCF data of similar orders of magnitude were found for both bluegill sunfish or channel catfish. Muscle samples had a BCF value of approximately 200, whereas relatively more fatty tissues bioconcentrated LR 3844-4 to a much greater degree, e.g., BCF = 1000 in brain tissue. This finding that LR 3844-4 tends to concentrate in lipophilic material qualitatively agrees with predictions of the regression equation developed by Neely [117] relating octanol/water partition coefficient (K_{OW}) to BCF. Quantitatively the equation predicts whole fish BCF's about one order of magnitude higher than that observed.

Fish cleared accumulated LR 3844-4 upon return to clean water. Experiments with both channel catfish and bluegill sunfish showed clearance to be about 95% complete in 14 days [8]. A second study, using only channel catfish, showed 70% whole body clearance in five days [9]. Muscle, the major edible component of fish, cleared 50% of the LR 3844-4 in the same five-day period.

A major question remains about this bioconcentration work since a review of the raw data (NB #41947, p. 21, 23, 24, 25, 41, and NB #46269, p. 35) shows that no tests were done to demonstrate that the solvents used (octanol and ethyl acetate) would quantitatively extract LR 3844-4 from fish tissue. Work on microorganisms suggests that some binding to cellular material is irreversible [115].

e) Effects

Bioassay data on the fluorochemical alcohols, which include acute fish and daphnia studies on both LR 3844-4 and LR 4197-2, and algal studies on LR 3844-4, indicate a lack of toxicity of these compounds at or near their solubility limits, ca, 0.1 and 1 mg/l, respectively (Table 11). Egg-fry studies on LR 3844-4 indicated no toxicity at 2 ug/l or approximately 1/3 water saturation. This was the highest concentration used in this study. This lack of toxicity has also been indirectly substantiated by other tests. For example, a semicontinuous activated sludge system operated for 10 days with 500 mg/l·

of emulsified LR 3844-4 and produced no apparent toxicity to the sludge microorganisms (115). In bioconcentration studies on bluegill sunfish and channel catfish (8,9), LR 3844-4 showed no toxic effect despite the fact that the fish concentrated LR 3844-4 to whole body concentrations of up to approximtely 300 mg/kg (9).

TABLE 11

BIOASSAY DATA ON LR 3844-4 AND LR 4197-2

Test	LR 3844-4	LR 4197-2	References
48-Hr. LC_{50} Daphnia magna	exceeds water solubility	(1350 mg/l)[c]	(1,118)
96-Hr. LC_{50} Bluegill sunfish	exceeds water solubility	exceeds water solubility >100 mg/l)[c]	(1,118)
30-day egg-fry[a] exposure	MTC[b] >20 ug/l		(119)
Algae[d] 14-day EC_{50} cell count	>1,800 mg/l[c]		(120)

Footnotes:

(a) Fry were Fathead minnow (Pimephales promelas).
(b) MTC - Minimum Threshold Concentration (20 ug/l was the highest concentration used).
(c) This concentration is greatly above maximum water solubility.
(d) The green algae used in these studies was Selenastrum capricornutum.

2. Recommended Testing

a) Physical Properties

Water Solubility and K_{OW} - More accurate measurements of LR 3844-4 water solubility, LR 3844-4 octanol/water partition coefficient (K_{OC}), and LR 4197-2 water solubility are needed for structure activity work. These measurements preferably should be made on individually isolated isomers. Work will be done using EPA-approved protocols and, if available, radiolabeled fluorochemicals to simplify analysis and cut analytical costs.

Water Solubility:

LR 3844-4 - Priority III
LR 4197-2 - Priority III

Distribution coefficient (K_{OW}):

LR 3844-4 - Priority I

Soil Sorption - Soil Thin-Layer Chromatography (TLC), using the U.S. EPA protocol (79), is recommended to substantiate the prediction that fluorochemical alcohols have low soil mobility. Adsorption data obtained using this procedure may show differences among various fluorochemical alcohol isomers. These studies will aid in determining the rate and extent of movement of these alcohols in soil environments such as landfills and sludge incorporative sites. Soil TLC measurements on LR 3844-4 are of lower priority since this type of work has already been done, although prior to the availability of a standard procedure. Soil TLC requires radiolabeled materials.

Soil TLC:

LR 4197-2 - Priority II
LR 3844-4 - Priority III

Vapor Pressure - Since preliminary laboratory observations indicate that LR 3844-4 readily volatilizes from water, quantitative measurements of vapor pressure and aqueous volatility are needed to model the movement of this compound and LR 4197-2 between various environmental compartments and the atmosphere. Measurements may be most efficiently performed by Analytical and Properties Research, CRL.

Vapor pressure and volatilization measurements are proposed for:

LP 3844-4 - Priority I
LR 4197-2 - Priority II

b) Degradation

Chemical Degradation - Chemical hydrolysis of LR 3844-4 has only been measured in the presence of alcoholic KOH. These findings cannot be extrapolated to estimate environmental half-lives. Therefore, tests more directly applicable to the environment are needed.

Testing under high temperatures (up to 60°C) and pH's (up to pH 11) may be necessary to observe hydrolysis within a reasonable time frame. Knowledge of the hydrolysis rate of LR 3844-4 is important because it is likely to be the most significant mode of environmental degradation for this chemical. To date, neither microbial nor photodegradation tests have shown them to be important. If hydrolysis is observed, attempts will be made to extrapolate findings to predict half-lives under normal environmental conditions and to identify hydrolysis products.

This testing can give only an upper limit to half-life since other mechanisms of hydrolysis may play a more dominant role at neutral pH. For example, mechanisms such as hydrolysis by H_2O alone or general acid-base hydrolysis catalyzed by metals or other materials in the environment would not be speeded up by increasing the pH. Radiolabeled material will facilitate this testing.

Proposed hydrolysis tests:

LR 3844-4 - Priority III
LR 4197-2 - Priority III

<u>Photolysis</u> - A previous study has given an indication that some photodegradation of LR 3844-4 may occur when adsorbed to soil. Testing to measure the photolysis of LR 3844-4 adsorbed to silica sand or silica gel is recommended to confirm this finding.

Testing will involve placing a thin coating of LR 3844-4 on silica sand or preferably silica gel from a solvent, spreading a thin layer of the coated substrate on the bottom of an airtight Vycor® container, and exposing to sunlight for up to one year. The container used will be transparent to sunlight down to 290 nm to permit the maximum environmental degradation rate.

Photolysis of LR 3844-4 on Silica Gel or Sand - Priority III

Biodegradation - Hydrolysis, photolysis, and biodegradation studies under moderately rigorous conditions have not shown degradation of environmental significance in previous testing. A need exists to run aerobic microbial biodegradation studies under the most rigorous conditions conceivable at moderate cost. Such studies would allow us to determine whether measurable biolysis might be occurring in the environment, but was undetectable under the milder laboratory conditions of previous tests.

The proposed biodegradation study will modify standard soil burial methods by simultaneously composting organic material with the soil. This approach, which increases microbial activity in the soil, has been found to greatly increase the degradation rate of organic compounds very resistant to degradation(121).

This study would be greatly facilitated by the use of radiotagged LR 4197-2 and LR 3844-4. This would allow detection of ^{14}C-EAI 80021 or other degradation products by TLC if the label were on the perfluorinated portion. If the label were on the hydrocarbon portion of the fluorochemical alcohol, $^{14}CO_2$ evolution would be measured, and if results indicated significant degradation, the program would be expanded to identify degradation products.

Proposed rigorous soil aerobic biodegradation testing:

LR 3844-4 - Priority I
LR 4197-2 - Priority II

No study of LR 3844-4 biodegradation under anaerobic condition has been done. Rigorous anaerobic tests are also recommended such as mixing ^{14}C-LR 3844-4 in river sediments or water-saturated soil supplemented with digester sludge and adequate nutrients. Such testing would provide optimal conditions for anaerobic degradation. It is relevant to the fluorochemical alcohols since water solubility, octanol/water partition coefficient, and soil sorption data all suggest that the alcohols are likely to accumulate in sediments or soil. This testing would preferably be done with the ^{14}C label on the perfluorinated portion of LR 3844-4.

Proposed Anaerobic Testing:

LR 3844-4 - Priority II

Biotransformation - The metabolism of LR 3844-4 by fish has not been investigated in our previous studies. Indications have appeared in the internal 3M literature (122,123) that this process is operative in mammalian systems. It is, therefore, recommended that similar studies be done on fish and plants. Fish studies could be performed alone or in conjunction with other long-term studies such as fish chronic tests.

Accumulation in plants is of significance since food crops are grown in areas in which LR 3844-4-containing sludge is applied. A preliminary study of accumulation of FC's, including the methyl and ethyl FOSE alcohols, into crops grown at Decatur is now underway. Samples are awaiting analysis in the Commercial Chemicals Division Analytical Laboratory (124). Proposed laboratory studies will examine roots and aboveground portions of corn and soybeans grown to maturity. Again, radiolabeled LR 3844-4 should be used in future studies and plant tissue assayed for parent and degradation compounds.

Information from this study will be used to estimate environmental risk of sludge soil incorporation practices. It will allow determination of whether vegetation grown at these sites could uptake, accumulate, and pass fluorochemicals into the human food chain. Abnormalities in plant growth and development will also be checked. The study will follow proposed standard procedures for vegetation uptake measurement (125).

Proposed fish biotransformation studies:

LR 3844-4 - Priority III

Proposed plant uptake and biotransformation studies:

LR 3844-4 - Priority II

c) Bioconcentration

Fish bioconcentration data are suspect because, as indicated above, no checks were done to show quantitative extraction of LR 3844-4 from fish tissue. It is recommended that such checks be done at this time. Testing would involve adding LR 3844-4 to fish tissue homogenized in water, mixing for 1 hr. and 8 hrs. This would be followed by extracting with ethyl acetate and n-octanol, the solvents used in the fish bioconcentration studies, as well as ethyl ether, a solvent which unlike the other two solvents extracted LR 3844-4 quantitatively from microorganisms. Analysis will be by GLC with electron capture detection or by the use of radiolabeled material.

Confirmation of fish bioconcentration study extraction procedure:

LR 3844-4 - Priority I

d) Effects

We recommend expanding the bioassay data on LR 3844-4 with a 28-day daphnia bioassay. This data will allow a more complete evaluation of the environmental safety of the important fluorochemical alcohols. This testing is needed to determine if this apparently long-lived environmental contaminant causes any long-term toxic effects. Tests on daphnids, a representative of the invertebrates, are particularly useful since they are generally more sensitive to toxicants than fish and algae. These tests are also much less costly than other chronic studies. Daphnia magna life cycle studies are completed in 28 days as opposed to nine months for fish.

28-Day Daphnia Bioassay LR 3844-4 - Priority II

F. Acrylates

1. Background

a) Chemical Characteristics

The 3M fluorochemical acrylate products are all formulated products. They contain components such as solvents and emulsifying agents, in addition to fluorochemical-containing acrylate polymers.

The acrylate polymers are made from fluorochemical acrylate and common hydrocarbon acrylate monomers. MeFOSEA ($C_8F_{17}SO_2N(CH_3)$ C_2H_5-O-C(O)CH:CH_2) is the most important fluorochemical monomer(126).

There are two types of acrylate fluorochemical polymers: emulsion and solution polymers. The emulsion polymers (those polymerized as emulsions in water) have molecular weights (MW) ranging from 200,000 to greater than a million. The solution polymers (those polymerized in organic solvents) have molecular weights ranging from 20,000 to 200,000. The MW ranges are estimates since there are really little hard data on MW (126).

These acrylate products may also contain some unreacted fluorochemical alcohol (approx. 1%), and this low level contaminant may be the most environmentally significant aspect of these products. Low molecular weight components are of more environmental concern than polymers because they are likely to be more mobile, having higher solubility and vapor pressure, and they are more likely to pass through or into biological membranes, possibly causing toxic effects. Thus, because of their high MW and their inertness, the acrylate polymers, per se, are not likely to cause significant adverse effects.

b) Physical Properties

The Environmental Lab has generated no physical properties data on acrylate polymers. Based on their chemical structure, these products are likely to have low water solubility, and based on their MW, they are expected to have negligible volatility and little mobility in a soil environment.

c) Degradation

The only significant question with acrylate polymers is whether they will break down under environmental conditions to release more environmentally significant low MW FC components. As a general rule, FC acrylates are more stable (they depolymerize less readily) than their hydrocarbon analogs (126).

Chemical Degradation - Due to their known chemical stability, it seems unlikely that the acrylate products would undergo rapid chemical degradation in lab tests simulating normal environmental conditions. The products, however, are known to degrade in strong base (pH 11-12) but are not easily acid hydrolyzed (126). This suggests that the acrylates will undergo some slow basic hydrolysis in the environment.

Photodegradation - The acrylates (e.g., MeFOSEA/BA) do not discolor when exposed to light (126) which suggests resistance to photodegradation, but some such degradation is possible on sunlight exposed fabrics. Both waterborne and solid manufacturing wastes containing fluorochemical acrylates are not likely to be exposed for long period to solar radiation since the high MW of these polymers suggests that they will not volatilize and that they will move into sediments or be buried in soils where little solar exposure is possible.

Biodegradation - The likelihood of rapid biodegradation is low. Evaluation of biodegradation tests done by the Environmental Laboratory, however, is complicated by the presence of biodegradable surfactants and solvents in the tested acrylate products. In all cases, though, the extent of biodegradation can be explained as being solely due to the nonacrylate components. The lack of ready biodegradation is substantiated by the fact that hydrocarbon acrylates are generally not biodegradable (127,128), and FC acrylates are likely to be even more resistant.

d) Effects

Environmental effects tests have been done on a large number of acrylate products. Some of these data are summarized in Table 12. This table groups products containing the same acrylate polymer together. It gives the weight percentages of the specified acrylate polymers in the nonaqueous component of each product. As these data are for formulated products, they do not directly represent the toxicity of the fluorochemical acrylate polymers. In fact, the solvents and surfactants in these products are the major cause of product toxicity. The data only allow one to set minimum LC_{50} values for the fluorochemical acrylate polymers.

Only one acrylate product family (cc 805-14) has an aquatic LC_{50} value low enough to be classified as moderately toxic (see Appendix I). This causes little concern since these products are unlikely to reach the aquatic environment in significant concentrations. cc 805-14 is now being assessed (LR 8185) and an attempt will be made to determine the likely cause of this toxicity.

Tests to determine the acute toxic effects to activated sludge have also been done on a number of fluorochemical-acrylate products. In all cases, the products were found not to inhibit sludge respiration rates at product concentrations likely to reach waste treatment systems.

Only one fluorochemical acrylate monomer N-BuFOSEA, is sold alone as a product. This material, sold as cc 813-26 and cc 8111-16, is practically nontoxic. Its acute 96-Hr. LC_{50} fathead minnow is 235 mg/l.

TABLE 12

TOXICITY OF ACRYLATE PRODUCTS TO AQUATIC ORGANISMS[a]

Product	% this Polymer in Nonaqueous Components	96-Hr. LC_{50} of Acrylate Assuming it caused all the Toxicity (mg/1)[b]	96-Hr. LC_{50} of Total Product (mg/1)	Lab Request No. or (Referenc
Products Containing the Emulsion Polymer: 95/5 MeFOSEA/BA				
LR 2485-2	19	40 125	400 1250	2485 1204
cc 815-1	33	20 51[c] 38[d] 43[e]	131 339[c] 249[d] 284[e]	(129)
cc 8110-92	42	34 34[c] 22[d] 34[e]	180 179[c] 118[e] 180[d]	(130)
cc 805-15	27	25	170	(131)
cc 805-17	12	33	689	6814
cc 806-6	55	46	233	5785
cc 805-24	38	78	527	(132)
cc 8010-32	47	66	575	6363
cc 811-17	54	71	440	6671
cc 766-29	20	12[c] 26[d]	132[c] 283[d]	4068
Products containing the emulsion polymer: 49/29/16/6 MeFOSEA/Vinylidine chloride/ODMA/N methylol acrylamide				
cc 7811-1	59	>295	>1000	4625
Products containing the emulsion polymer: Chloroprene/EtFOSEA				
LR 2563-3	50	167 487	600 1750	2563 1204

TABLE 12 (continued)

Product	% this Polymer in Nonaqueous Components	96-Hr. LC_{50} of Acrylate Assuming it caused all the Toxicity (mg/l)[b]	96-Hr. LC_{50} of Total Product (mg/l)	Lab Request No. or (Reference
Products containing the solution polymer: 50/50 MeFOSEA/C.W. 4000 DMA				
cc 824-32	67	>600 1132 1695	>2000 3762 5630	8021 (133) 1204
cc 813-17	9	9.5	286	6888
Products containing the solution polymer: 70/20/10 MeFOSEA/Polymeg - 2000 DMA/Butyl Acrylate				
cc 805-15	27	25	170	(131)
cc 805-16	77	>300	>1000	
cc 805-16	77	28	96[f]	5884
cc 782-43	48	130	328	4200
Products containing: 35/35/20/10 MeFOSBA/MeFOSEA/Polmeg -2000 DMA/BA				
cc 803-15	36	>360	>1000	5546
Products containing: 70/30 MeFOSEA/CW 750A				
LP 2256-3	100	1800	9000	2256
Products containing: 50/50 EtFOSEMA/ODMA				
cc 794-2	50	45[d]	180[d]	(134)
Products containing: 65/35 N-MeFOSEMA/ODMA				
cc 8011-235	10		140	2485
cc 8012-41	10	>100[g]	184	7820
Products containing: 75/25 MeFOSEA/Alfol 1620A				
cc 782-14	80	95[d] 38[e]	238[d] 94[e]	4197
Products containing MeFOSEA/Alfol-1620A				
LP 2543-4	95	479 400	1200 1000	2456 2256

3M [illegible]

TABLE 12 (continued)

Product	% this Polymer in Nonaqueous Components	96-Hr. LC_{50} of Acrylate Assuming it caused all the Toxicity (mg/l)[b]	96-Hr. LC_{50} of Total Product (mg/l)	Lab Request No. or (Referenc
Products containing 70/15/5/10 MeFOSEA/Alfol 6120A/IOA/CW 750A				
cc 805-14	35	3.5	21	8185
Products containing 50/50 chloroprene/EtFOSEMA				
LR 2563-3	50	167 487 362	600 1750 1300	2563 1204 2485
Products containing 56.7/28.3/15 MeFOSEA/(EtFOSE/TDI/HOPMA)/BA				
cc 775-27	93	179	480	5508
Products containing 25/25/50 MeFOSEA/(EtFOSE/TDI/HOEMA)/Alfol 1620A				
cc 8111-4	40	>800	>2000	7461
N Bu FOSEA Monomer				
cc 813-26	100	235	235	6813

Footnotes:

a Organism is Fathead minnow, unless noted.
b Assuming no synergistic or antagonistic effects, this represents a minimum 96-Hr. LC_{50} for the polymer. The actual LC_{50} for the acrylate, however, is likely to be much higher.
c Rainbow trout (Salmo gairdneri)
d Bluegill sunfish (Lepomis macrochirus)
e Daphnia magna 48-Hr. LC_{50}
f The emulsifers Tween 80 and Span 80 which make up 1.5% of the product were replaced by Siponic L-4. This small change made the product 10 times as toxic.
g Toxicity measured after solvent evaporation

2. Recommended Testing

a) Physical Properties

No physical properties tests are recommended on fluorochemical acrylate polymers.

b) Degradation

Chemical Degradation - Measurements of the alkaline hydrolysis rate of two representative acrylates are recommended. These data will enable us to estimate upper limits on the hydrolysis rates of these products at environmental pH's. The acrylates recommended for this testing are 95/5 MeFOSEA/BA and 50/50 MeFOSEA/C.W. 4000 DMA. MeFOSEA/BA is a high molecular weight emulsion polymer used in LR 2485-2, cc 811-17, and several other products. It is likely to be one of the most resistant to hydrolysis. MeFOSEA/CW 4000 DMA is a much lower MW solution polymer used in cc 8011-24A, cc 798-21, and other products. The Carbowax® portion of the product may increase the affinity of this product to water, possibly increasing its susceptibility to hydrolysis. This is expected to be one of the most readily hydrolyzed of the fluorochemical acrylate polymers.

Laboratory procedures will be modeled after standard methods (e.g., 135).. Products containing the emulsified fluorochemical acrylate polymer will be hydrolyzed first within environmentally relevant pH (4-9) and temperature (20°-45°C) ranges. Low molecular weight fluorochemical hydrolysis products will be searched for using thin-layer chromatography, if ^{14}C-tagged fluorochemical acrylates are available, or gas liquid chromatography, otherwise. If no low molecular weight fluorochemicals are detected in the pH 4-9 range, hydrolysis rate will be determined at high pH and extrapolations made to estimate hydrolysis rates under normal environmental conditions.

Hydrolysis of fluorochemical acrylates:

cc 8011-24A - Priority II
LR 2485-2 - Priority III

<u>Photochemical Degradation</u> - The susceptibility of the same two fluorochemical acrylates to photolysis should be simply checked by coating the products on silica gel, coating this on the inside of a sealed high silica glass container (Vycor®), and exposing to sunlight for one year. Following such exposure, the product could be compared with dark controls, using analytical methods described above, for the amount of extractable low MW fluorochemical.

Fluorochemical acrylates are used as a soil resistant coating for carpeting and textiles. In this use, some of the acrylates will be exposed to sunlight, and it is possible that the textile dyes might act as photochemical "sensitizer" for the fluorochemical degradation, capable of absorbing and transferring solar energy to the acrylate polymers. For this reason, it is also proposed that dyed textile fibers coated with the candidate fluoroactylates be sealed in Vycor® containers, exposed to sunlight, and analyzed for low MW fluorochemicals as described above.

Photolysis of fluorochemical acrylates:

A. On silica gel
   cc 8011-24A - Priority III
   LR 2485-2 - Priority III
B. On dyed textile fibers
   cc 8011-24A - Priority III
   LR 2485-2 - Priority III

<u>Biodegradation</u> - Rigorous biodegradation tests are recommended to see if depolymerization of the fluorochemical acrylates will occur. Testing will be similar to that recommended for LR 3844-4 involving burial with composting organic material in garden soil and analyzed for the release of low MW fluorochemical degradation products. Such tests should be run for at least one year. The use of radiolabeled acrylates would greatly improve the sensitivity of such tests and would allow monitoring of degradation by capturing radiolabeled CO_2 or by isolating radiolabeled fluorochemical degradation products. Radiolabeling could be achieved by incorporating either radiolabeled HC or FC acrylate monomers into the polymers.

Preliminary tests will be done to determine if low MW fluorochemical species that are possible degradation products can be retreived from the soil system. These preliminary tests will also be used to determine whether loss of fluorochemical monomers from the soil system through volatilization is likely.

Rigorous soil biodegradation tests on fluorochemical acrylates:

cc 8011-24A - Priority III
LR 2485-2 - Priority III

c) Effects

Acute fish bioassays are needed on the acrylate polymers alone, separated from the solvents and surfactants which keep them in emulsion or solution. Such separation could probably be made by dialysis. This method would probably remove monomers and low MW oligomers as well. Such bioassays on the dialyzed material would be useful in supporting the existing evidence that the fluorochemical acrylate polymers themselves are nontoxic.

Acute fish bioassays of dialyzed:

cc 8011-24A - Priority II
LR 2485-2 - Priority II

G. Urethanes

1. Background

a) Composition

Unlike the acrylates, the fluorochemical urethanes are not polymeric materials, but are trimers, tetramers, or other small oligomers of fluorochemical alcohols, diisocyanates and sometimes hydrocarbon alcohols. Their molecular weights are in the range of one to two thousand.

b) Physical Properties

The Environmental Laboratory has no physical properties data on the fluorochemical urethanes. These materials have low water solubility, but their solubility in lipid materials is unknown [126]. Based on their MW, they are expected to have low volatility.

c) Degradation

The fluorochemical urethanes are more stable than their hydrocarbon analogs, but they are less stable than the fluorochemical acrylates. These materials are more likely than the acrylates to degrade through hydrolsis; photolysis, or biochemical mechanisms, releasing low MW fluorochemical monomers to the environment.

d) Effects

Environmental effects data on these products are shown in Table 13. Like the acrylates, the fluorochemical urethanes are sold in mixtures with other materials, including solvents, surfactants, and polymers that can mask the toxicity of the urethane. The table shows, however, that some of these products have high concentrations of fluorochemical urethane and little toxicity. These data indicate that at least two of the three urethanes are at worst practically nontoxic assuming no antagonistic effects on toxicity from other product components.

2. Recommended Testing

a) Physical Properties

The possibility of bioconcentration of urethane products should be further investigated. One possibility is that their molecular size may limit their capacity to bioconcentrate. Further literature study is needed on the effects of molecular size or molecular weight on the bioconcentration potential of fluorochemicals.

Most SAR methods predict bioconcentration from octanol/water partition coefficient. It is recommended that the octanol/water partition coefficient of the EtFOSE/TDI urethane be determined as a representative of this group of fluorochemicals. The most appropriate method of making this measurement appears to be the use of reverse-phase high-pressure liquid chromatograph (136). This method will prevent possible interference from other components of the product mixture. The TDI component of the molecule should facilitate UV detection.

n-Octanol/water partition coefficient of:

2 EtFOSE/TDI - Priority III

3M [illegible]

TABLE 13

AQUATIC TOXICITY DATA ON URETHANE-CONTAINING PRODUCTS[a]

Product	Wt. % Urethane in Product	96-Hr. LC_{50} (mg/l)	Lab Request Number or (Reference)
Products containing EtFOSE/MDI			
cc 8110-92	10.5	180 179[c] 118[d] 180[e]	(130)
cc 806-6	10.5	233	5785
cc 8010-30	6.2	575	6363
cc 803-15	4	>1000	5546
cc 811-17	9	440	6671
cc 811-18	20 (98% of solids)	>2000 mg/l	6672
Products containing EtFOSE/TDI			
cc 803-3	15	102	5493
cc 782-5	15	56	4369
cc 795-19	14	65	5055
Products containing 2 EtFOSE/ODA[b]/PAPI			
LR 2485-2	10	400 1250	2485 1204
cc 815-1	15	131 339[c] 249[d] 284[e]	(129)
cc 8110-93B cc 8110-96B	30 30	1148 1306	5511 5983
cc 812-35	5	689	6814
cc 805-24	15	527	(132)

Footnotes:

a All data on Fathead minnows unless otherwise noted.
b ODA = Stearyl alcohol.
c Rainbow trout.
d Bluegill sunfish.
e _Daphnia magna_, 48-Hr. LC_{50}

3MA10065547

3M_MN00000102

b) Degradation

Tests similar to those for the acrylates are recommended to check susceptibility of the urethane products to biodegradation, photodegradation, and chemical hydrolysis. As with the acrylates, hydrolysis tests will be run on the product as sold. Photodegradation tests will be done on the product residue left on silica gel and on dyed textile fabrics. Biodegradation tests will be done on the product residue in soil.

It is recommended that testing be done on cc 811-18. This product contains 20% solids, and 98% of their solids are EtFOSE/MDI. The remaining 2% is MCL emulsifier, a 3M fluorochemical surfactant. The presence of this surfactant could cause some confusion in interpreting results if only very low levels of degradation occur. The use of radiolabeled urethanes would simplify analytical work and prevent such confusion.

Degradation tests on fluorochemical urethane cc 811-18 (EtFOSE/MDI):

Hydrolysis - Priority II
Rigorous soil biodegradation - Priority III
Photodegradation on silica gel - Priority III
Photodegradation on dyed fabric - Priority III

c) Effects

Although no bioassays have been done on the fluorochemical urethane alone, bioassays on the formulated products can allow a determination of the worst case or lowest possible toxicity due to the urethane. Such predictions assume that all the toxicity of the product is due to the fluorochemical, and also assume no toxicity or antagonistic effects from other product components. Using this technique, present environmental data shows that EtFOSE/MDI and EtFOSE/ODA/PAPI urethanes have little toxicity. But similar data on EtFOSE/TDI urethanes allow us only to say that its 96-hr. fish $LC_{50} \geq 15$ mg/l (LR #5493). Its LC_{50} is probably much higher (less toxic) than this. To complete the data base, bioassays are needed on products with high levels of this urethane. cc 7512-25 is one possible product for use in such testing since it contains 20% EtFOSE/TDI as its only fluorochemical component. A sample of the urethane alone would be even better to demonstrate its probable lack of significant toxicity.

96-Hr. Fish LC_{50}:

EtFOSE/TDI - Priority II

H. FLUOREL® and KEL-F® Polymers

1. Background

These products are high MW polymers made from one or more of the following monomers: vinylidene fluoride, hexafluoropropane, and chloro-or bromo-trifluor-ethylene Some also have curative systems. After being fully cured, these polymers are nontoxic, insoluble, nonvolatile, and extremely inert.

FLUOREL®-FLUOREL® Brand fluoroelastomer cc 8010-11A has been found to leach small amounts of fluoride (0.43 mg/g) and small amounts of COD (0.74 mg/g) (Lab request 3270). A later study under different conditions leached 0.26 mg of COD per gram of cc 8010-11A [137]. The leachate from cc 8010-11A was found to be toxic to fish and daphnids [137,138], but after curing at 350°F for 15 minutes, no toxic material leached [138].

Toxicity was also not found after longer curing periods. cc 8010-11B, an identical FLUOREL® fluoroelastomer, except that it does not contain a curative system, leached only .01 mg of COD/g, and the leachate was not toxic to fish or daphnids [138]. These results indicate that the curative system, and not residual fluorochemical monomers or the fluorochemical polymers themselves, are the cause of the toxicity from uncured FLUOREL® fluoroelastomers.

Kel-F® - No environmental testing has been done on the Kel-F® polymers.

2. Recommended Testing

No environmental testing is recommended for the FLUOREL® and Kel-F® polymers.

I. Catalysts

1. Background

3M makes two hexafluorophosphate salts which are used as catalysts for the curing of epoxy resins. At this time, these are used in low volume products (cc 792-8 and cc 794-6) and their prospect for significantly increased volume do not seem great.

2. Recommended Testing

No recommendations to include these products in the Part II Fate of Fluorochemicals program are made at this time.

V. SUMMARY

A summary of proposed testing with priority ranking and cost are given in Table 14. Table 15 predicts costs per quarter over the proposed three-year study period. In these tables, priorities range from I for very important to III for less critical. Table 1 in the introduction gives a summary of results from the Fate of Fluorochemicals program, Part I. Summaries of environmental data on the various classes of 3M fluorochemicals are found in other tables throughout the report.

The testing recommended in this report is intended to fill gaps in the present understanding of the environmental fate and effects of 3M Fluorochemicals. Environmental profiles developed from these studies will enable the Environmental Laboratory to give recommendations for product modifications or use and disposal instructions that will minimize possible environmental effects. These profiles will also enable rapid and accurate response to the environmental concerns of government agencies and 3M customers.

An example of a regulatory problem caused by lack of data on fluorochemicals has, in fact, recently surfaced. The USEPA has proposed a rule exempting certain classes of polymers from PMN requirements. Fluorine-containing polymers, however, are not included in this exemption. While 3M fluorochemical polymers are probably as environmentally safe as the polymers included in the exemption, we lack environmental data to substantiate this viewpoint and hence cannot press the agency for modification of the regulation.

Previous testing has allowed the formation of a basic understanding of the environmental properties of 3M fluorochemicals, but only limited information is available on their volatility, solubility, their movement in soil and their long-term stability. In some cases, environmental toxicity information is also less complete than desirable.

Fluorochemical products are suspect because of the extreme stability of their perfluorinated portions. Knowledge of their environmental properties is, therefore, very important in order to minimize the chances of finding, in the future, that 3M fluorochemicals are causing environmental problems that are impossible or extremely costly to undo.

TABLE 14

SUMMARY OF RECOMMENDED STUDIES ON FLUOROCHEMICALS

Test or Measurement	Product Category	Product(a)	Priority of Work	Testing Time Requirements (Hrs)	Cost (
SAR(b)	All 3M fluorochemicals				
1) Application of existing SAR to Fluorochemicals			I	650	29,25
2) Derive new SAR for fluorochemicals			II	1,300	58,50
Field Studies	All 3M fluorochemicals				
1) Confirm analytical			I	150	6,75
2) Predictive modeling			I	20	90
3) Field Sampling and analysis			II	1,200	54,00
Incineration	All 3M fluorochemicals		III	200	9,00

Footnotes:

(a) Chemistry of Products is shown in Appendix II
(b) SAR = Structure Activity Relationships
(c) Hydroxy Foamer

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Table 14 (continued)

Test or Measurement	Product Category	Product(a)	Priority of Work	Testing Time Requirements (Hrs)	Cost (:
Physical Properties					
1) Water Solubility	Phosphates	cc 795-23	I	35	1,57:
	Alcohols	LR 3844-4	III	50	2,25(
		LR 4197-2	III	50	2,25(
2) n-Octanol-Water distribution coefficient					
a) Shaking	Surfactants	EAI 80021	I	25	1,12:
		LR 5625	I	25	1,12:
	Phosphates	cc 795-23	I	40	1,80(
	Alcohols	LR 3844-4	I	25	1,12:
b) HPLC	Urethane	2 EtFOSE/TDI	III	25	1,125
3) Soil Sorption					
a) K_{OC}	Phosphates	cc 795-23	III	90	4,050
b) TLC	Surfactants	EAI 80021	II	15	675
		LR 5625	II	15	675
	Phosphates	cc 795-23	III	15	675
	Alcohols	LR 3844-4	III	15	675
		LR 4197-2	II	15	675
4) Vapor Pressure	Surfactants	EAI 80021	III	15	675
		LR 5625	III	15	675
	Phosphates	cc 795-23	III	15	675
	Alcohols	LR 3844-4	I	15	675
		LR 4197-2	II	15	675
5) Bioadsorption	Surfactants	EAI 80021	III	15	675
		LR 5625	III	15	675
Degradation					
1) Alkaline Hydrolysis	Alcohols	LR 3844-4	III	40	1,800
		LR 4197-2	III	40	1,800
	Acrylates	cc 8011-24A	II	60	2,700
		LR 2485-2	III	60	2,700
	Urethane	cc 811-18	II	60	2,700

Table 14 (continued)

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Test or Measurement	Product Category	Product[a]	Priority of Work	Testing Time Requirements (Hrs)	Cost ($
2) Photolysis					
a) on Silica	Surfactants	EAI 80021	III	100	4,500
		LR 5625	III	100	4,500
	alcohols	LR 3844-4	III	100	4,500
	Acrylates	cc 8011-24A	III	100	4,500
		LR 2484-2	III	100	4,500
	Urethanes	cc 811-18	III	100	4,500
b) on dyed fabrics	Acrylates	cc 8011-24A	III	100	4,500
		LR 2485-2	III	100	4,500
		cc 811-18	III	100	4,500
	Urethanes				
c) sensitized in water	Surfactants	EAI 80021	III	100	4,500
		LR 5625	III	100	4,500
		cc 805-10S[c]	III	100	4,500
3) Biodegradation					
a) Acclimated Seed BOD_{28}	Surfactants	cc 777-3	I	20	900
		Daughter Products I.D.	II	25	1,125
b) Soil Respirometry	Surfactants	cc 805-10S[c]	II	20	900
		Prod. I.D.	III	25	1,125
c) Rigorous Aerobic	Surfactants	EAI 80021	II	45	2,025
		LR 5625	II	45	2,025
	Phosphates	cc 795-23	III	45	2,025
	Alcohols	LR 3844-4	II	45	2,025
		LR 4197-2	II	45	2,025
	Acrylates	cc 8011-24A	III	45	2,025
		LR 2485-2	III	45	2,025
	Urethanes	cc 811-18	III	45	2,025
D) Rigorous Anaerobic	Surfactants	LR 5625	III	45	2,025
	Alcohols	LR 3844-4	II	45	2,025
4) Biotransformation					
a) Plants	Alcohol	LR 3844-4	II	50	2,250
b) Fish	Alcohol	LR 3844-4	III	25	1,125
Bioconcentration					
a) Fish	Surfactants	EAI 80021	I	55	2,475
		LR 5625	I	55	2,475
b) Confirm extraction method	Alcohol	LR 3844-4	I	25	1,125
Effects					
1) 96-Hr. Fish Tox.	Surfactants	cc 805-10S[c]	III	10	450
		LR 2929 (with & without solvent)	III	20	900

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Table 14 (continued)

Test or Measurement	Product Category	Product(a)	Priority of Work	Testing Time Requirements (Hrs)	Cost (
	Acrylate	Dialyzed cc 8011-24A	II	25	1,12
		Dialyzed LR 2485-2	II	25	1,12
	Urethane	EtFOSE/TDI	II	10	45(
2) 14-Day Algae	Surfactants	LR 2929	II	35	1,57
		cc 773-58	II	35	1,57
		cc 777-3	II	35	1,57
		cc 805-10S[c]	II	35	1,57
	Phosphates	cc 795-23	II	35	1,57
3) 28-Day Daphnia	Surfactants	LR 5625	II	50	2,25(
		LR 2929	II	50	2,25(
		cc 773-58 solids	II	50	2,25(
		cc 777-3	II	50	2,250
		cc 805-10S	II	50	2,250
	Phosphates	cc 795-23	II	50	2,250
	Alcohol	LR 3844-4	II	50	2,250
Total Priority I				1,140	51,300
Total Priority II				2,285	102,825
Total Priority III				3,465	155,925
Total Project				6,890	310,050

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TABLE 15

SCHEDULE OF PROPOSED WORK

This table prioritizes work and schedules it by quarter following program approval. The schedule assumes a 1-1 1/2 man rate of expenditure and availability of the radiolabeled materials listed in Appendix III.

Year 1, Quarter 1

Priority	Category	Description	Time in hrs.
I	SAR	- Begin study on applicability of existing SAR methods	150
I	Field	- Confirm analytical capabilities for TOF, EAI 80021, LR 5625, and LR 3844-4 in spiked soil, sediment, sludge, tissue and water samples.	150
I		- Predictive modeling for proposed field study.	20
I	Physical Properties	- Water solubility of cc 795-23	35
I		- n-octanol/water distribution coefficient of EAI 80021, LR 5625, cc 795-23, and LR 3844-4.	115
I		- vapor pressure of LR 3844-4	15
I	Biodegradation	- Acclimated seed BOD or Shake flask study on cc 777-3 (save products)	20
I	Bioconcentration	- Determine if extraction procedures used in past LR 3844-4 fish bioconcentration studies were quantitative	25
		Time quarter 1 -	530 hrs.
		Cost quarter 1 -	$23,850

Year 1, Quarter 2

Priority	Category	Description	Time in hrs.
I	SAR	- Continue study on existing SAR applicability.	125
II	Field	- Begin field sampling and analysis.	300
II	Biodegradation	- Identify biodegradation products of cc 777-3	25
I	Bioconcentration	- Fish bioconcentration studies on EAI 80021 and LR 5625	110
		Time quarter 2 -	560 hrs.
		Cost quarter 2 -	$25,200

Year 1, Quarter 3

I	SAR	- Continue study on existing SAR applicability.	125
II	Field	- Continue field sampling and analysis.	300
II	Biodegradation	- Rigorous aerobic on EAI 80021, LR 5625, LR 3844-4, & LR 4197-2.	180
		Time quarter 3 -	605 hrs.
		Cost quarter 3 -	$27,225

Year 1, Quarter 4

I	SAR	- Continue SAR applicability	125
II	Field	- Continue field sampling and analysis	300
II, III	Physical Properties	- Soil TLC of EAI 80021, LR 5625, cc 795-23, LR 3844-4, and LR 4197-2	75
II	Effects	- 14-day algae LR 2929, cc 773-58 Solids, and cc 777-3	105
		- 96-hr. LC_{50} fish on dialyzed acrylate polyers cc 8011-24A, and LR 2485-2	50
		Time quarter 4 -	655 hrs.
		Cost quarter 4 -	$29,475

Year 2, Quarter 1

Priority	Category	Description	Time in hrs.
I	SAR	- Finish SAR applicability	125
II	Field	- Finish field sampling and analysis	300
II, III	Physical Properties	- Vapor pressure of EAI 80021, LR 5625, cc 795-23, & LR 4197-2	60
II	Effects	- 14-day algae cc 805-10S and cc 795-23	70
		- 28-day Daphnia LR 5625 and LR 2929	100
		Time quarter 5 -	655 hrs.
		Cost quarter 5 -	$29,475

Year 2, Quarter 2

Priority	Category	Description	Time in hrs.
III	SAR	- Start to derive new SAR for fluorochemicals	300
II, III	Degradation	- Alkaline hydrolysis of representative acrylates and urethanes	180
II		- Biotransformation of LR 3844-4 in plants	50
II	Effects	- 28-day Daphnia on cc 773-58 solids, cc 777-3, & cc 805-10S	150
		Time quarter 6 -	680 hrs.
		Cost quarter 6 -	$30,600

Year 2, Quarter 3

Priority	Category	Description	Time in hrs.
III	SAR	- Continue new SAR for fluorochemicals	250
III	Physical Properties	- Water solubility of fluorochemical alcohols LR 3844-4 and LR 4197-2	100
II, III	Biodegradation	- Soil respirometry on hydroxy foamer with product identification	45

Priority	Category	Description	Time in hrs.
II, III		- Rigorous anaerobic biodegradation of LR 5625, LR 3844-4	90
III		- Biotransformation of LR 3844-4 in fish	25
II	Effects	- 28-day Daphnia cc 795-23 and LR 3844-4	100
		Time quarter 7 -	610 hrs.
		Cost quarter 7 -	$27,450

Year 2, Quarter 4

Priority	Category	Description	Time in hrs.
III	SAR	- Continue new SAR for fluorochemicals	250
III	Incineration	- Look for toxic fluorochemical by-products in Decatur Incinerator emissions	200
III	Bioadsorption	- Determine adsorption of surfactants EAI 80021 and LR 5625 to activated sludge	30
	Degradation	- Sensitized photolysis of surfactants in water on LR 5625 and cc 805-10S	200
		Time quarter 8 -	680 hrs.
		Cost quarter 8 -	$30,600

Year 3, Quarter 1

Priority	Category	Description	Time in hrs.
III	SAR	- Continue new SAR for fluorochemicals	250
III	Physical Properties	- Octanol/water distribution coefficient of urethane by HPLC	25
III	Degradation	- Sensitized photodegradation surfactant EAI 80021	100
		- Photodegradation of alcohol, LP 3844-4, and urethane, cc 811-18, on silica	200
III	Effects	- 96-hr. fish tox on cc 805-10S LP 2929 solids, & EtFOSE/TDI	40
		Time quarter 9 -	615 hrs.
		Cost quarter 9 -	$27,675

Year 3, Quarter 2

Priority	Category	Description	Time in hrs.
III	SAR	- Complete new SAR for fluoro-chemicals	250
III	Physical Properties	- Measure K_{oc} for cc 795-23	90
III	Degradation	- Photolysis of acrylates cc 8011-24A and LR 2485-2 on silica	200
III		- Rigorous aerobic biodegradation of phosphate cc 795-23 and urethane cc 811-18	90
		Time quarter 10 -	630 hrs.
		Cost quarter 10 -	$28,350

Year 3, Quarter 3

Priority	Category	Description	Time in hrs.
III	Degradation	- Alkaline hydrolysis of alcohols LR 3844-4 & LR 4197-2	80
		- Photolysis on silica of surfactants EAI 80021 and LR 5625	200
		- Photolysis of acrylates and urethanes on dyed fabrics	300
		- Rigorous aerobic biodegradation of acrylates cc 8011-24A and LR 2485-2	90
		Time quarter 11 -	670 hrs.
		Cost quarter 11 -	$30,150

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APPENDIX I

AQUATIC TOXICITY RANKING SYSTEM

NIOSH adopted the following toxicity scale to aid in interpreting aquatic toxicity data listed in the Registry of Toxic Effects of Chemical Substances:

Description	LC_{50} Concentration
Insignificant hazard	>1,000 mg/l
Practically nontoxic	100-1,000 mg/l
Slightly toxic	10-100 mg/l
Moderately toxic	1-10 mg/l
Highly toxic	<1 mg/l

This scale, which was developed based on published data from studies on adult and juvenile aquatic organisms, provides a basis on which acute aquatic toxicity data can be put in some perspective. In using this scale, one should be aware that many other factors, in addition to acute aquatic toxicity, contribute to determining the impact of a chemical on an aquatic environment. Important among these other factors are solubility, volatility, environmental entry concentration, bioconcentration potential, persistence, and the size and mixing rate of the receiving aquatic environment.

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APPENDIX II

This Appendix is a cross-reference between report code numbers and product chemical composition. The alphanumeric codes used in the report are primarily those assigned b Commercial Chemicals Division to keep track of work requests to the Environmental Laboratory. These numbers begin with "cc". Although many products have more than one cc number because more than one request for work on the product has been made to the Environmental Lab, only one cc number was selected. Thus each product has only one cc number in this report. In those cases where a cc number could not be found, Envir. Assess. Inq. (EAI) numbers or Lab Request (LR) numbers were used.

KEY TO CHEMICAL PRODUCTS DISCUSSED IN REPORT

This table includes those products which are discussed within the text of the report. It does not include all products which only appear in tables.

Product Number	Class	Chemical Name (3M Synonym)	Chemical Formulation
cc 742-7	Inert liquid	Perfluorinated alkanes and cyclic ethers boiling range 90-107°C	e.g., (C_8F_{18}) $(C_4F_9)C_4F_7$-O (ring)
cc 7512-25	Urethane	20% 2-EtFOSE/TDI 12.5% alumina Dispal .75 sulfamic acid 66.75 solvents and water	
cc 773-53	Surfactant	See cc 7711-27	
cc 777-3	Surfactant	See cc 777-4A&B	
cc 777-4A&B	Surfactant	>90%	$C_8F_{17}SO_2NH(Et)(CH_2CH_2O)_{7.2}CH_3$
		<10%	$C_8F_{17}SO_2NH(Et)$
cc 777-4B	—	N-ethyl-1-perfluoro-octane sulfonamid (FOSE amide)	$C_8F_{17}SO_2\overset{H}{N}\text{-}C_2H_5$
cc 7711-18	Surfactant	(N-EtFOSE alcohol-ethylene oxide adduct)	$C_8F_{17}SO_2N(C_2H_5)(CH_2CH_2O)_{14}CH$
cc 7711-27	Surfactant	3(((perfluorooctyl) sulfonyl) amino)-N,N,N-trimethyl-1-propanaminium iodide	$[C_8F_{17}SO_2\overset{H}{N}C_3H_6H(CH_3)_3]^+I^-$

Product Number	Class	Chemical Name (3M Synonym)	Chemical Formulation
cc 783-1	Alcohol	(90 - 100%N-MeFOSE alcohol + 0 - 10%N-EtFOSE Alcohol)	See LR 4197-2 See LR 3844-4
cc 783-38	Acrylate	17% 70/15/5/10 MeFOSEA/ Alfol-1620A/IOA/CW 750A 11% other acrylate polymer 52% water 20% solvent	
cc 788-19	Inert liquid	N-perfluoromethyl perfluoromorpholine	$C_5F_{11}NO$
cc 792-8	Catalyst	50% $Ø_3S^+PF_6^-$ 50% dimethoxyethyl phthalate	
cc 794-6	Catalyst	45% $Ø_3I^+PF_6^-$ 45% dimethylphthalate 10% ERL-4221 epoxy resin	
cc 795-7	Surfactant	Perfluorooctanesulfonic acid, diethanolamine salt	$C_8F_{17}SO_3^- H_2N^+(CH_2CH_2OH)_2$
cc 795-23	Phosphate	33% solids: N,N'-(phosphinicobis (oxy-2,1-ethanediyl)) bis(N-ethyl perfluoro-1-octane sulfonamide) (ammonium salt of diphosphate ester of N ethyl FOSE alcohol) Note some mono and tri-esters are also present +49% water, 18% alcohol.	$[C_8F_{17}SO_2N(C_2H_5)CH_2CH_2O]_2$ $PO(ONH_4)$
cc 796-3	Surfactant	15.1% hydroxy foamer 3.2% butyl carbitol 81.7% water	See cc 805-10
cc 796-10	Alcohol	(MeFOSE alcohol)	See LR 4197-2
cc 798-21	Acrylate	12.5% MeFOSE/Epi/Adipic acid, 1.5% MeFOSEA/C.W. 400 DMA, 28% MMA/EMA; 3% emulsifiers; 54 % water, and 1% max. ethyl acetate	
cc 802-23	Surfactant	Perfluoroethyl cyclohexyl sulfonic acid, potassium salt	C_2F_5 (F) $SO_3^-K^+$
cc 805-1	Low MW Acid	Trifluoromethane sulfonic acid (Triflate)	CF_3SO_3H

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Product Number	Class	Chemical Name (3M Synonym)	Chemical Formulation
cc 805-10	Surfactant	Product containing 25% FC Hydroxy Foamer, 25% solvent and 50% H_2O	C_2H_4OH $C_6F_{13}SO_2N-C_3H_6N^+(CH_3)_2$ $CH_2CHCH_2SO_3^-$ OH
cc 805-10S	Surfactant	100% FC Hydroxy Foamer solids	See cc 805-10
cc 8010-11A	FLUOREL® Polymer	96% fluoroelastomer 1% dichlorodiphenyl sulfone 2% bisphenol AF 0.5% triphenyl benzyl phosphonium chloride 0.45% tetramethylene sulfone 0.05% sodium methylate	78% mole % CH_2CF_2 and 22 mole % C_3F_6
cc 8010-11B	FLUOREL® Polymer	100% fluoroelastomer	76/24 CF_2CH_2/CF_3CFCF_2
cc 8011-10	Surfactant	See LR 2929	
cc 8011-23	Surfactant	Perfluoroethyl cyclohexyl sulfonic acid, diethanolamine salt	C_2F_5(F)$SO_3^-H_2N^+(C_2H_4OH)_2$
cc 8011-24A	Acrylate	30% 50/50 copolymer of N-MeFOSEA/Carbowax 4000 55% water 8% solvent 7% Carbowax 4000	
cc 811-17	Acrylate/urethane	25% 65/35 mixture of emulsified 95/5 MeFOSEA/BA and EtFOSE/MDI 5% Ethylene glycol 70% water 1% max. ethyl acetate	
cc 811-18	Urethane	20%: 98% EtFOSE/MDI 2% MCL emulsifier 80%: water Trace: ethyl acetate	
cc 813-26	Acrylate	2-Propenoic acid-4-(((heptadecafluoro-octyl) sulfonyl)methyl-amino)-butyl ester (N-butyl FOSE acrylate)	$C_8F_{17}SO_2N(C_3H_7)C_2H_4O$ $C(O)CHCH_2$

Product Number	Class	Chemical Name (3M Synonym)	Chemical Formulation
cc 815-11	Alcohol	(Wide range N-Et alcohol)	See LR 3844-4
cc 816-27	Surfactant	See LR 2929	
cc 8110-9	Low MW Acid	Perfluorobutyric acid	C_3F_7COOH
cc 8111-16	Acrylate	See cc 813-26	
EAI 80021	Surfactant	Perfluorooctanesulfonic acid, potassium salt	$C_8F_{17}SO_3K$
LR 2456-1	Surfactant	Perfluorooctane sulfonic Ammonium salt	$C_8F_{17}SO_3^-NH_4^+$
LR 2485-2	Acrylate	A polymer of 95% MeFOSEA = and 5% butyl acrylate = Emulsifier is 5% Ethoquad 18/25 based on solids	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OC(O)CHCH_2$; $CH_3(CH_2)_3OC(O)CHCH_2$
LR 2929	Surfactant	N-ethyl-n-[(perfluorooctyl) sulfonyl] glycine, potassium salt	$C_8F_{17}SO_2N(C_2H_5)CH_2COOK$
LR 2929-1			See LR 2929
LR 3844-4	Alcohol	N-ethyl-N(2-hydroxy ethyl)-1-perfluorooctanesulfonamide (N-ethyl FOSE alcohol)	$C_8F_{17}SO_2N(C_2H_5)C_2H_4OH$
LR 4197-2	Alcohol	N-ethyl-N(hydroxymethyl)-1-perfluorooctane sulfonamide (N-methyl FOSE alcohol)	$C_8F_{17}SO_2N(CH_3)C_2H_4OH$
LR 5062	Surfactant	3-(((heptadecafluorooctyl) sulfonyl) amino) -N,N,N-trimethyl-1-propanamium chloride (MCL emulsifier)	$C_8F_{17}SO_2NHC_3H_6N^+(CH_3)_3CL$
LR 5625	Surfactant	Perfluorooctanoic acid, ammonium salt	$C_7F_{15}COO^-NH_4^+$

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APPENDIX III

NEEDS FOR ^{14}C-RADIOLABELED FLUOROCHEMICALS

Report Section	Test	Priority	Placement of ^{14}C Label	Importance of Having Label (a)
IV.C.2.a.	Distribution coef. of EAI 80021 and LR 5625	I	anywhere	Low
IV.C.2.a.	Soil TLC of EAI 80021 and LR 5625	II	anywhere	Necessary
IV.C.2.a.	Bioadsorption of EAI 80021 and LR 5625	III	anywhere	High
IV.C.2.b.	Acclimated seed BOD of cc 777-3	II	on perfluorinated portion	Moderate
IV.C.2.b.	Soil respirometry on Hydroxy Foamer, cc 805-10S	II	on Hydrocarbon portion	High
IV.C.2.b.	Aerobic soil biodegradation tests on LR 5625, EAI 80021	II	anywhere	High
IV.C.2.b.	Anaerobic soil biodegradation tests on LR 5625	III	anywhere	High
IV.C.2.b.	Photodegradation of LR 5625, EAI 80021, cc 805-10S	III	on perfluorinated portion	Moderate
IV.C.2.c.	Bioconcentration of EAI 80021 and LR 5625	I	anywhere	High
IV.D.2.a.	Water solubility of cc 795-23	I	anywhere	Low
IV.D.2.a.	Octanol/water partition coefficient of cc 795-23	I	anywhere	Low
IV.D.2.a.	Soil adsorption of cc 795-23	III	anywhere	Moderate
IV.D.2.a.	Soil TLC of cc 795-23	III	anywhere	Necessary
IV.D.2.b.	Aerobic soil biodegradation of cc 795-23	III	on perfluorinated portion	High
IV.E.2.a.	Water Solubility of LR 3844-4 and LR 4197-2	III	anywhere	Low
IV.E.2.a.	Octanol/water partition coef. of LR 3844-4	I	anywhere	Low
IV.E.2.a	Soil TLC of LR 3844-4	III	anywhere	Necessary
IV.E.2.a	Soil TLC of LR 4197-2	II	anywhere	Necessary

Report Section	Test	Priority	Placement of ^{14}C Label	Importance of Having Label[a]
IV.E.2.b.	Alkaline hydrolysis of LR 3844-4 and LR 4197-2	III I	on perfluorinated portion	Moderate
IV.E.2.b.	Photolysis of LR 3844-4 on sand	III	on perfluorinated portion	Moderate
IV.E.2.b.	Soil biodegradation of LR 3844-4 and LR 4197-2	I for LR 3844-4 II for LR 4197-2	preferably on perfluorinated portion	High
IV.E.2.b.	Anaerobic soil biodegradation of LR 3844-4	II	on perfluorinated portion	High
IV.E.2.b.	Biotransformation in fish and plants of LR 3844-4	III-fish II-plants	on perfluorinated portion	Moderate
IV.E.2.c	Extractability of LR 3844-4 from fish tissue	I	anywhere	Moderate
IV.F.2.b.	Hydrolysis of cc 8011-24A and LR 2485-2	II II	preferably on MeFOSEA monomer	Moderate
IV.F.2.b.	Photolysis of cc 8011-24A and LR 2485-2	III	preferably on MeFOSEA monomer	Moderate
IV.F.2.b.	Soil biodegradation of cc 8011-24A and LR2485-2	III	preferably on MeFOSE monomer	High
IV.G.2.b.	Hydrolysis of EtFOSE/MDI (cc 811-18)	II	on EtFOSE monomer	Moderate
IV.G.2.b.	Rigorous soil biodegradation of EtFOSE/MDI	III	on EtFOSE monomer	High
IV.G.2.b.	Photolysis of EtFOSE/MDI	III	on EtFOSE monomer	Moderate

Footnotes:

(a) Terms in this column are defined as followed:

Low = radiolabeled material is preferred but testing could readily be done without it;
Moderate = The use of radiolabeled material would greatly facilitate testing;
High = Testing would be difficult, possibly impossible, without radiolabeled materials;
Necessary = Testing could not be done without radiolabeled material.

Appendix IV

This artical from the BNA Chemical Regulation Reporter shows the importance that Structure-Activity relationships will take in future U.S. EPA Chemical Assessment.

Research

EVALUATION OF BIOLOGICAL PESTICIDES, STRUCTURE-ACTIVITY RELATIONSHIPS PLANNED

New research on "key" environmental issues, including the role of structure-analysis in evaluating chemical hazards and the effects of biological pesticides on non-target organisms, is planned during 1983, according to a draft of the Environmental Protection Agency's 1983 research outlook.

Discussed Nov. 29 at a Science Advisory Board meeting, the draft said structure-activity relationships (SAR) currently used to assess chemicals are based upon limited data and often are speculative. "Often the SAR information is essentially the product of prevailing but unverified toxicological opinion," the report said. EPA currently uses structure-activity assessments in its evaluation of chemicals submitted for premanufacture review.

New research by the agency's Office of Research and Development would seek to "make decisions based on SAR more independent than they are now and of greater use in assuring that toxic chemicals and pesticides are adequately regulated," the report said.

The outlook paper's sections on toxics and pesticides said research also is planned on:

- Key methods of meeting the agency's monitoring, data collection, and data analysis requirements under the Toxic Substances Control Act;
- The most important environmental parameters that should be used in the physical and biological mathematical models that the agency uses to predict exposure, hazard effects, and risks;
- The primary environmental endpoint responses for toxic substances and pesticides;
- New tests needed to assess chemical hazards and evaluate risk;
- Use of field information to verify models used to predict pesticide exposure;
- Improvements needed on mathematical models of pesticide transport, fate, and exposure; and
- Registration criteria and environmental measurements needed to register biological pesticides.

Structure-Activity Relationships

The agency plans research into development of reliable structure-activity analyses because the SAR is "an attractive and potentially useful method which, if valid, can produce rapid, timely, inexpensive, scientifically acceptable data for evaluating the biological effects of chemicals and pesticides and for better assessing the risks," the draft report said.

Specifically, the agency would develop a data base of existing information and correlations and would seek data on the causal relationship between molecular structure and chemical, physical, and biological behavior.

By 1985, the agency hopes to produce models for evaluating environmental fate and toxicity of several chemical classes in a variety of media. By 1986, a working system is expected to be completed using molecular structure descriptions and combinations to predict genetic and carcinogenic activity in humans, according to the draft.

Biological Control Agents

Environmental research to evaluate the effects of biological control agents on non-target organisms also will begin in 1983, the agency said. Initially, EPA plans to develop hazard evaluation protocols to determine effects from microbial agents and for some biochemicals in estuarine, freshwater, and terrestrial ecosystems.

The organisms, both biochemical and microbial pest control agents, are registered for use under the Federal Insecticide, Fungicide, and Rodenticide Act. "These microorganisms are known to attack targeted pests, but their transport, persistence, and fate in the environment and their effects on non-target species are not clearly understood," the report said.

Specific research planned by the agency includes:

- Determining the scope of the biological control agents' effects in terrestrial environment, 1983;
- Testing protocols for estimating hazards to non-target terrestrial species, 1984;
- Testing with non-target freshwater organisms under field conditions, 1985; and
- Studying exposure of aquatic animals to insect viruses, 1984.

Research Milestones

EPA also set a variety of research milestones for the next five years. These include the development of methodologies for several short-term tests, such as identifying the effects of toxicants upon the nervous system. A short-term methodology for identifying the teratogenic potential of chemicals

also will be sought in an effort "to support or eliminate the need for extensive animal tests," the draft said.

The agency also aims to develop methods "capable of evaluating the responses of entire systems, systemic disease processes, and specific target organisms to acute, sub-chronic, and chronic toxicant insult," according to the report.