Internal Correspondence

cc: J. T. Ling - 21-2W-07 (Memo only)
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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

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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.

Exhibit
1284
State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

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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"

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# FATE OF FLUOROCHEMICALS - PHASE II

Prepared by:

Environmental Laboratory (EE & PC)

E. A. Reiner, Editor

May 20, 1983

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## 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.

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TABLE OF CONTENTS

"3M CONFIDENTIAL"

## TABLES AND FIGURES

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# FATE OF FLUOROCHEMICALS - PHASE II

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.

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# 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.

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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 I

DATA ON FLUOROCHEMICALS INCLUDED IN FATE OF FLUOROCHEMICALS STUDY PART I

CONFIDENTIAL

| 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): | — | — | | — |
| $BOD_{20}$: | None | None | None (7-day) | 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

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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.

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## 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.

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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.

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## 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