3M

TECHNICAL REPORT SUMMARY

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EE & PC-Div.
Fluorochemical
(Analytical)
(Aquatic)
(Degradation)
(Soil)
(Toxicity
(Bioconcentration)

CURRENT OBJECTIVE:

Final Report: Encompasses all work performed during the period 1975-1978.

REPORT ABSTRACT: (200-250 words) This abstract information is distributed by the Technical Communications Center to alert 3M'ers to Company R&D. It is Company confidential material.

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Information Division Interests

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Trial Exhibit 13

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Exhibit 2563
State of Minnesota v. 3M Co.,
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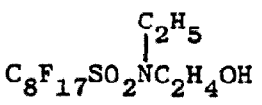
INTRODUCTION

Fluorochemicals, per se, are unique materials manufactured by the Commercial Chemicals Division. There has been a general lack of knowledge relative to the environmental impact of these chemicals; therefore, a research proposal outlining studies designed to evaluate these effects was submitted to this division (1). This proposal detailed studies which would provide basic information in the areas of physicochemical characteristics, soil adsorption, aquatic toxicity, biodegradability, and bioaccumulation.

The rationale for performing the studies outlined above was as follows: 1) Physicochemical characteristics - Chemical reactivity studies would provide an insight into whether or not chemical degradation is an important mechanism occurring at conditions simulating "real world" situations. Water solubility - Compounds of relatively low solubility would tend to be adsorbed at equilibrium concentrations as opposed to those considered to be highly soluble which would not adsorb readily. Use of solubility data may also be predictive of the bioconcentration potential of a chemical. Partition coefficient - These data provide information relative to the following properties of chemicals: physical adsorption on solids, biomagnification, and lipophilic storage. These data, when used in conjunction with water solubility data, would provide a dual check on the projected bioconcentration tendency of a chemical. 2) Soil adsorption - These studies are performed to provide answers relative to the movement of test chemicals in a terrestrial ecosystem, and to further estimate the ability of the terrestrial ecosystem to act as an environmental "sink" for these chemicals. 3) Aquatic toxicity - An assumption has been made that the test chemical will eventually appear in the aquatic ecosystem. The question arises as to whether or not acute (short-term) or chronic (long-term) toxic effects are associated with exposure to fluorochemicals. 4) Biodegradability - Do microorganisms exist which are capable of utilizing the fluorochemical structure as a food source? This question is of paramount importance since an affirmative answer would indicate that these molecules can be completely biodegraded. If these materials are not biodegradable, what is their fate in the environment? Can by-products and/or intermediates be identified? 5) Bioconcentration These studies enable one to determine the effect of sublethal exposures of a chemical on aquatic organisms. In addition, further concentration of a chemical within the food chain can occur as a result of chemical uptake. Human food sources can be similarly affected by bioconcentration of a chemical with a resultant effect on human health. Using these derived data in concert with usage patterns and per annum production figures, extrapolations relative to primary and secondary receptors, estimated environmental sink, and estimated environmental concentrations were made.

The subject fluorochemical of this report is FM 3422, which has a potential for widespread distribution in the environment because of its incorporation into most SCOTCHGARD and SCOTCHBAN products. FM 3422 chemical is n-ethyl-n-(hydroxyethyl) perfluorooctane sulfonamide and has the following abbreviated name: N-ethyl fose. This material is a white solid following sublimation at 60°/ <1 mm Hg, having a molecular weight of 571, and the following chemical structure:



FM 3422

This report consolidates all available information in the aforementioned area of investigation and defines the probable environmental risk of FM 3422.

METHODS

The results of these investigations have been the subject of several technical reports (2-4,7,9-12), and interoffice memos (5,8). The experimental methodology has been defined in these attached reports, and they should be consulted for specific details.

RESULTS

Table 1 lists in synopsized form data obtained during the physico-chemical characterization of FM 3422. This material is slightly water soluble, 0.05 ppm at 15° C., highly lipid soluble at this temperature, having a partition coefficient of 6.6×10^6 (2,3,5). These data are highly suggestive that FM 3422 will bioconcentrate in aquatic organisms (see Table 3). The chemical degradation test was performed using 20% alcoholic KOH. Over a 24-hour period, 92.3% of the starting material, FM 3422, was hydrolyzed. Although no attempts were made to quantitate the loss of FM 3422 by evaporation, it was observed that virtually complete loss of the starting material had occurred (Table 1) (6).

FM 3422 was found to be "completely resistant" to biodegradation under the test conditions employed (4). The use of enriched cultures, semicontinuous activated sludge, or shake flask die-away studies with sequential adaptive transfers did not develop a strain of microbes which could biodegrade FM 3422 (4). This chemical would be expected to persist in an aerobic microbial environment. During the course of these studies, it was observed that FM 3422 possessed a strong affinity for organic solids, a fact which may well account for the results obtained in our soil sorption studies (1,9).

TABLE 1

PHYSICOCHEMICAL CHARACTERIZATION OF FM 3422

Parameter	Test	Results
Chemical Degradation	Alkaline Hydrolysis[1]	At 24 hours, 7.7% of original amount remained. 20% alcoholic KOH
Solubility	Veith Method[1]	0.05 ppm, range 0.04-0.06 ppm at 15° C.
Partition Coefficient	n-octanol/water[2]	6.6×10^6 at 15° C
Volatility	Evaporation from water[3]	Virtually complete loss. No effort made to quantitate.

[1]Mendel, A. Technical Report "Analytical Methodology on FM 3422," November 15, 1977.

[2]Memo: Greg Vraspir to Dale Bacon. "Gas Chromatographic Analysis of FM 3422." March 26, 1976.

[3]Mendel, A. to A. N. Welter: Personal communication.

Soil sorption studies have shown that approximately 98% of the FM 3422 is adsorbed to the Brill sandy loam soil used in these studies (Table 2) (9). Utilizing information obtained during the biodegradation tests, it is quite plausible that the high level of FM 3422 adsorbed to soil is a reflection, in part, of the affinity this material possesses for organic solids. Minimal desorption of FM 3422 from soil as a water solution was obtained, <5% (Table 2). A priori one would assume that this material would be relatively immobile. Hamaker (13) has devised a scheme whereby adsorption coefficients are converted to a constant, K_{OC}, which reflects the organic content of the soil. Hamaker has shown that the relative mobility of a group of pesticides could be determined in this fashion and that a relative ranking, moving from highly mobile to immobile materials would result. In applying this test, FM 3422 had a K_{OC} value of 15,000, being slightly more mobile than Paraquot, K_{OC} 20,000, and significantly less mobile when compared to Prometryne, K_{OC} 513 or Chloramben, K_{OC} 12.8.

TABLE 2

SOIL SORPTION TESTS ON FM 3422

Parameter	Test	Solution	Results
Soil Sorption	Adsorption[1]	Water	98% Adsorbed
	Desorption[1]	Water	<5% Desorbed
	K_{OC}[2]		15,000

[1]Welsh, S. K. "Technical Report in preparation: "Adsorp ..on of FM 3422 on Soil."

[2]Hamaker, J. W. "Interpretation of Soil Leaching Experiments" in Chemicals, Human Health and the Environment, A Collection of Dow Scientific Papers, Vol. 1, Dow Chemical USA, Midland, Michigan 48640.

FM 3422 is not acutely toxic to the fathead minnow *(Pimephales promelas)* at its water solubility level.

All bioconcentration studies were conducted using FM 3422 coated glass beads as the medium for transferring FM 3422 to the aquatic environment (Table 3). In the two species tested, equivalent values for the bioconcentration propensity of FM 3422 were obtained. When analyzing pooled organs (n=2) for FM 3422, the following facts emerge: the skin, skeleton, liver, and gills bioconcentrate FM 3422 at a level quite similar to the whole organism. The gall bladder bioconcentrated FM 3422 to a greater extent than did any other organ (Table 3). As this is a storage organ for bile, and the bile becomes more concentrated by virtue of the loss of liquids, it is reasonable to expect that the level of FM 3422 would be elevated. The bile salts themselves may be the transport mechanism for FM 3422, this material being expelled into the gastrointestinal tract by the gall bladder. The brain, comprised principally of lipid material, would be expected to bioconcentrate FM 3422 based on partition coefficient data. No side effects were exhibited by the test organisms during the duration of this study. The slightly elevated level of FM 3422, observed in the kidney samples, may indicate that the renal system is an excretory route for FM 3422 or its by-products or that FM 3422 is retained by the lipid segments of the kidney. The gastro-intestinal tract may similarly serve as an organ of excretion for FM 3422 and/or the elevated value may, as with the kidney, be indicative of FM 3422 uptake by the lipid fraction of this organ. A third possibility is that this value reflects the increase generated by the bile within the G.I. tract.

Egg-fry studies were contracted to EG & G Bionomics Laboratory, and their results comprise Tables 4 and 5. These studies were undertaken to assess the effect of FM 3422 at sublethal levels on hatchability, survival, weight, and length changes (Table 4). It is generally accepted that the immature or young are quite sensitive indicators of chemically induced toxicity. In the parameters under investigation (percent hatch, percent survival, length and weight), no statistically significant differences occurred over the range of FM 3422 concentrations tested when comparing treated vs. control groups (Table 4).

Based on the results of the histopathological examination, a 30-day exposure to a nominal concentration of 12.5 µg/l FM 3422 did not contribute to abnormal histopathology (Table 5). Both the test group and control organisms indicated the presence of gill hyperplasia, although more prevalent in the control group (Table 5).

TABLE 3

BIOCONCENTRATION OF FM 3422 IN FRESHWATER FISH

Species or Organ	Test Duration	Whole Body Burden FM 3422 FM 3422 in H_2O	Organ Burden FM 3422 FM 3422, H_2O
Bluegill[1]	14	300	
Channel Catfish[1]	14	200	
Channel Catfish[2]	7	400 575	
Brain[2,3]	7		1340
Gills	7		540
Liver	7		470
Gall Bladder	7		26550
Gastrointestinal Tract	7		1060
Kidney	7		710
Muscle	7		280
Skeleton	7		500
Skin	7		530

[1]Welter, A. N. Technical Report: Aquatic Fate of a Fluorochemical, FM 3422, October 14, 1977.

[2]Welter, A. N. Technical Report: Bioconcentration and Clearance Studies of FM 3422, August 16, 1978.

[3]All values obtained following analysis of pooled sample (n=2).

TABLE 4

RESULTS OF CONTINUOUS AQUEOUS EXPOSURE TO FM 3422 ON HATCHABILITY OF EGGS AND GROWTH AND SURVIVAL OF FRY OF FATHEAD MINNOW *(PIMEPHALES PROMELAS)* [a,b]

Concentration µg/l[c]	% Hatch	% Survival	Fry, Mean Values Length mm	Weight mg
12.5 (14)	89.5	98	21	65
6.9 (11)	92.5	90	22	69.5
2.3 (16)	90	96	20.5	63.5
0.95 (12)	96	92.5	21	64.5
0.72 (16)	91	92	21	67.5
	92.5	87	21	70
	92.5	86	20	65

[a]Work performed by EG & G Bionomics Laboratory, Inc.

[b]Summary table submitted to Environmental Laboratory, 3M, St. Paul, as part of final report.

[c]Mean values, n values in parentheses. Reference 48838-4,5, June 8, 12, 1978.

TABLE 5

RESULTS OF HISTOPATHOLOGICAL EXAMINATION
OF FRY OF FATHEAD MINNOW *(PIMEPHALES PROMELAS)*
EXPOSED TO 12.5 µg/l OF FM 3422[a]

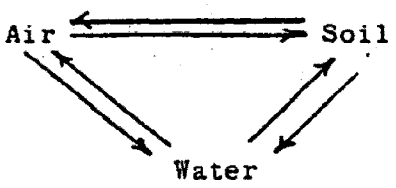
Test Material	Number of Observations	Histopathological Findings
FM 3422	10	9/10 Normal 1/10 Gill Hyperplasia
Control	10	3/10 Normal 6/10 Liver Fatty Change 3/10 Gill Hyperplasia (Epithelium) I

[a]Work performed under contract to EG & G Bionomics Laboratory

DISCUSSION

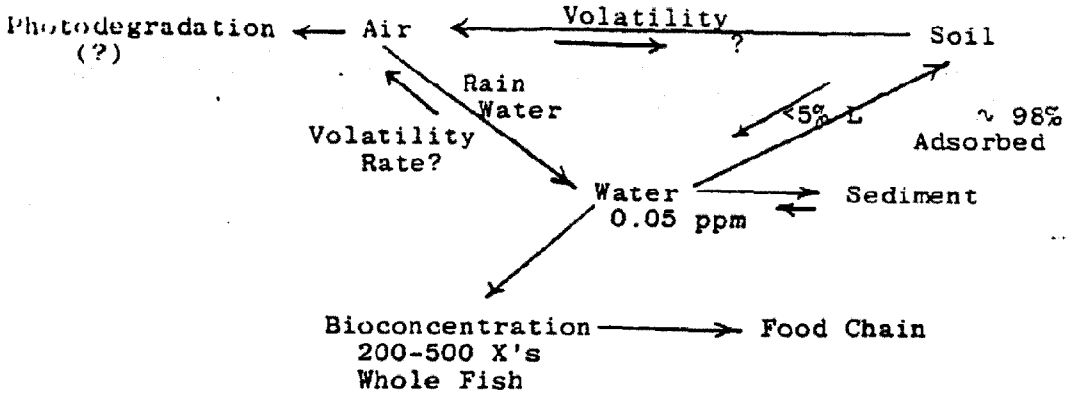
The primary purpose of this report is to provide a single source for all environmental data generated relating to FM 3422 and to provide an analysis of potential environmental risk.

The environment may be considered to be a closed system which can be depicted as follows:



It, therefore, follows that a chemical entering this system may either establish an equilibrium within this cycle or break the cycle.

In the specific case at hand, we can represent the impact of FM 3422 in the following manner:



Based on this representation, FM 3422, which enters the environment primarily via the waterways and secondarily by means of the terrestrial ecosystem and atmosphere, is removed from the environment when adsorbed to the soil and sediment. It, therefore, appears that the environmental sinks for FM 3422 are the sediment/sludge and soil. Intermediate receptors for FM 3422, based on available experimental evidence, are aquatic organisms. It is in regard to this latter effect that a possible deleterious action of FM 3422 may be found.

It has been established that FM 3422 does bioconcentrate in aquatic organisms as indicated by elevated organ and whole body burdens. The aquatic species used for these tests are utilized as a human food source, hence in the long-term human health effects may be correlated with the presence of FM 3422 in the aquatic ecosystem.

This fact appears of minimal importance when considered in relation to the estimated environmental sink for FM 3422. We have shown experimentally that this material is bound to soil and sediment. In fact, in the soil desorption studies, Brill sandy loam, <5% of FM 3422 was desorbed. The observation during biodegradation studies that FM 3422 was bound to organic solids lends further credence to the concept that soil and sediment are the environmental sinks for this compound. With the minimal amounts being desorbed less FM 3422 would, therefore, be available in the aquatic ecosystem, hence less material available for bioconcentration by organisms in the human food chain.

We can estimate the environmental concentration of FM 3422, thereby providing estimated values for incorporation into our projected environmental scheme.

We have made several assumptions which are basic to the simplistic model used in our calculations:

1) Total production is at Chemolite and is discharged.

2) No FM 3422 is removed by the treatment facility.

3) All effluent discharged to the Mississippi River.

4) FM 3422 is discharged uniformly.

5) River flow and all other parameters are constant, hence not subject to seasonal and/or climatic conditions.

The formulae used in these projections include:

1) $\text{MG/min.} = \frac{(\text{River Flow CFM})(\text{Conversion gal/ft}^3)(\text{Time min.})}{\text{Production per annum}}$

2) MG/min. x 1440 = MG/Day

3) Lbs/day = (mg/l x wt. lbs. H_2O per gal)(MG/Day)

Mississippi River flow at Hastings, MN, based on a 10-year low flow record, is 10,000 CFS.

The total 5-year production figures were provided by D. R. Ricker, Commercial Chemicals Division. In utilizing these figures, an estimated environmental concentration of FM 3422 in the Mississippi River below Chemolite was calculated. During the period 1973-1978, the EEC for FM 3422 was calculated to be 28 µg/l at Hastings, MN, while the EEC projected for the period 1978-1983 is projected at 37.5 µg/l. Based on these figures, one can estimate the environmental distribution of FM 3422 utilizing the percent of material adsorbed to Brill sandy loam as indicative of the amount which would be extracted from the Mississippi River (Table 6). It is to be understood that a further assumption has been made for the purposes of this calculation and that is that we are dealing with Brill sandy loam soil exclusively. The amount of FM 3422 projected to be found in the soil-sediment system, the environmental sink for FM 3422, for the period 1978-83 is 36.7 µg/g, whereas the water compartment will contain but 0.8 µg/l.

Utilizing these calculations and experimentally derived environmental properties and attendant rationale, it can be determined that FM 3422, at the present levels of production, will not present an unreasonable environmental risk.

TABLE 6

DISTRIBUTION OF FM 3422
ESTIMATED AT 5-YEAR INCREMENTS

Years	Total µg/l	Water µg/l	Soil-Sediment µg/g
1973-78	28	.6	27.4
1978-83	37.5	.8	36.7

CONCLUSIONS

Under the test conditions employed in characterizing FM 3422, it has been determined that this material

1) is slightly water soluble, 0.05 ppm;
2) has an n-octanol/water partition coefficient of 6.6×10^6;
3) is volatile. No effort was made to quantitate FM 3422 loss *via* evaporation;
4) is resistant to aerobic microbial attack and that binding to organic solids does occur;
5) is relatively immobile in Brill sandy loam soil. Experimentally, 98% of FM 3422 was adsorbed to this soil type while <5% could be desorbed. In determining the K_{OC} values for this soil type, a value of 15,000 was obtained which is indicative of a relatively immobile material;
6) In a contracted study, a 30-day chronic exposure of fathead minnow egg and fry to varying concentrations of FM 3422 did not show statistical differences in precent hatchability, percent survival, changes in weight and length when comparing treated versus untreated organisms;
7) will bioconcentrate in lipid-containing organs; brain and gastrointestinal tract, to a greater extend when compared to the muscle fillet of the channel catfish, 1000 *vs.* 200 respectively;
8) would have an estimated environmental concentration of approximately 37.5 ppb under conditions, wherein all FM 3422 were made at Chemolite and was discharged uniformly into the Mississippi River;
9) based on the foregoing, it is concluded that under the test conditions of these experiments that FM 3422 will not present an unreasonable environmental risk.

REFERENCES

(1) Bacon, D. L. and R. L. Bohon: "A Proposal to Study the Fate of Fluorochemicals in the Environment," April 4, 1975.

(2) Mendel, A. Technical Report - Analytical Methodology on FM 3422, November 15, 1977.

(3) Mendel, A. Memo: Additions to Technical Report dated November 15, 1977. December 27, 1977.

(4) Reiner, E. A. Technical Report - Biodegradation Studies of Fluorocarbons II, January 9, 1978.

(5) Vraspir, Greg. Interoffice memo to Dale Bacon: Gas Chromatographic Analysis of FM 3422. March 26, 1976.

(6) Mendel, A. to A. N. Welter, Personal Communication.

(7) Mendel, A. Technical Report in preparation.

(8) Welsh, S. K. Interoffice Memo to Dale Bacon: FC Project Soil Adsorption, September 22, 1977.

(9) Welsh, S. K. Technical Report in preparation: Adsorption of FM 3422 on Soil.

(10) Elnabarawy, M. T. Technical Report: Bioconcentration of FM 3422 in Bluegill Sunfish and in Channel Catfish, May 17, 1977.

(11) Welter, A. N. Technical Report: Aquatic Fate of a Fluorochemical, FM 3422. October 14, 1977.

(12) Welter, A. N. Technical Report: Bioconcentration and Clearance Studies of FM 3422. August 16, 1978.

(13) Hamaker, J. W. "Interpretation of Soil Leaching Experiments" in Chemicals, Human Health and the Environment, A Collection of Dow Scientific Papers, Vol. 1, Dow Chemical USA, Midland, Michigan 48640.

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