Final Comprehensive Report: FC 95

Exhibit
2617
State of Minnesota v. 3M Co.,
Court File No. 27-CV-10-28862

STUDY SUMMARY FOR WORK PERFORMED DURING 1977-1979

TEST SUBSTANCE

Identity: Perfluorooctanesulfonate; may also be referred to as PFOS or FC-95. (1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt, CAS # 2795-39-3)

Remarks field: The test substance is a white powder of uncharacterized purity.

The attached is an overview created in 1979 for studies completed from 1977 to 1979. Robust summaries have already been submitted for many of these studies. Others have not been summarized due to the fact new studies exist that supercede these or they are being repeated.

STUDIES

Water solubility; biodegradation; soil sorption; octanol/water partition coefficient; Static Acute Toxicity to Bluegill Sunfish (*Lepomis macrochirus*); Static Acute Toxicity to Rainbow Trout (*Salmo gairdneri*); Static Acute Toxicity to Fathead Minnow (*Pimephales promelas*); Static Acute Toxicity to *Daphnia magna*; Chronic Flow Through Study on Fathead Minnow (*Pimephales promelas*)

DATA QUALITY

Reliability: These studies have been assigned Klimisch rankings = 2. They satisfied criteria for quality testing at the time performed, but have some deficiencies. In many cases actual concentrations were not measured. The value was determined by indirect measurement (e.g., solubility) or using nominal concentrations (e.g., aquatic toxicity). In some cases, the analytical methodology itself was questionable. Additionally, these studies lack sufficient characterization of the test substance purity.

OTHER

Submitter: 3M Company, Environmental Laboratory, P.O. Box 33331, St. Paul, Minnesota, 55133

Last changed: 5/3/00

MICHIGAN STATE UNIVERSITY

DEPARTMENT OF CROP AND SOIL SCIENCES
PLANT & SOIL SCIENCES BUILDING

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May 19, 1993

Dr. Robert D. Howell
3M Company
3M Center, Bldg. 2-3E-09
St. Paul, MN 55144-1000

Dear Dr. Howell:

Enclosed are my review comments regarding the nine 3M Technicial Reports, recommendations for improving the quality of the individual studies, and some recommendations for future research. Please review this information and let me know if I can be of any further assistance.

I do have interest in submitting a research proposal to 3M in accordance with the recommendations for future research. Perhaps we could discuss this further. I enthusiastically support your efforts to obtain information on the environmental fate and behavior of the 3M products.

My consulting fee for the work performed to date is $3,200.00 (three and one half days for review of materials and preparation of reports plus one half day consultation with Dr. Howell at MSU, at $800.00 per day).

Sincerely,

Stephen A. Boyd, Ph.D.
Professor

Review of Technical Report Summary
Final Comprehensive Report FC 95

An octanol-water partition coefficient of 10 would predict a supercooled liquid solubility of 250 g/L using the equation:

$$\log K_{ow} = -0.862 \log S_w + 0.710$$

Conversely if the water solubility of the solid is 286 mg/L, then the supercooled liquid solubility could be ~ 2860 mg/L. Using the above equation, this predicts a K_{ow} value of about 500. The predicted values are quite different than the measured values, and the measured K_{ow} and S_w values seem inconsistent, i.e., if the measured K_{ow} is correct, I would expect a higher water solubility, and if the measured solubility is correct I would expect a higher K_{ow}. The values look suspicious.

FC 95 is described as an anionic surfactant. If so, does it form micelles and exhibit a well defined critical micelle concentration similar to SDS for example. If so, then I'm not certain talking about water solubilities is appropriate. Rather behavior above and below the CMC should be examined.

Table 2 presents soil sorption data which is virtually meaningless. The percent sorbed is going to vary depending on the experimental variables of amount of soil, type of soil, volume of water, concentration of FC 95. You need to measure the entire soil sorption isotherm and obtain a sorption coefficient. This should be done on several soils. Again, if FC 95 is a conventional micelle forming surfactant I would expect different soil sorption behavior above and below the CMC. I would not expect linear isotherms.

A K_{oc} value of 45 is reported based on data from another report (reference 3). To evaluate the appropriateness of this value, it should be obtained on several different soils and be relatively constant, or be consistent with K_{oc} values predicted from empirical relationships such as:

$$\log K_{oc} = 0.904 \log K_{ow} - 0.539$$

(Chiou et al. Environ. Sci. Technol. 17:227-231)

Using the K_{ow} value of 10, the predicted K_{oc} value is about 2 which is much lower than the measured value of 45. Again, this points to the inconsistencies of the measured K_{ow}, S_w and K_{oc} values reported. The K_{ow} and/or S_w values measured are also being used to predict bioconcentration factors using empirical relationships like the one above. This is a reasonable approach <u>if</u> the K_{ow} or S_w values are accurate. As mentioned above K_{ow} and S_w reported seem to be inconsistent, so I don't have a lot of confidence in using them to predict other things like BCF.

Recommendation

1. Need an accurate determination of water solubility and octanol-water partition coefficient (See methodology of Chiou and Schmedding, 1980 - given in previous report.)

2. Determine the CMC of FC 95, and recognize that its behavior above and below the CMC will be different.

3. Obtain soil sorption isotherms on several soils and calculate K_{oc} values from these.

4. Check for consistency between S_w, K_{ow} and K_{oc} values.

3M

Form 6747-11 A

TECHNICAL REPORT SUMMARY

Date: 3/15/79

TO: TECHNICAL COMMUNICATIONS CENTER – 201-2CN

(Important – If report is printed on both sides of paper, send two copies to TCC.)

Division: Environmental Laboratory (EE & PC)	Dept. Number: 0535
Project: Fate of Fluorochemicals	Project Number: 9970612643
Report Title: Final Comprehensive Report: FC 95	Report Number: 011
To: R. A. Prokop	
Author(s): A. N. Welter	Employee Number(s): 09362
Notebook Reference:	No. of Pages Including Coversheet: 12

SECURITY ▶ ☐ Open (Company Confidential) ☒ Closed (Special Authorization)

3M CHEMICAL REGISTRY ▶ New Chemicals Reported ☐ Yes ☒ No

KEYWORDS: (Select terms from 3M Thesaurus. Suggest other applicable terms.)

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

D. L. Bacon
R. L. Bohon
V. Pothapragada

CURRENT OBJECTIVE:

Final Report: Encompasses all work performed during the period 1977 - 1979.

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.

Information Liaison Initials: C.F.U.

Introduction

The rationale for performing environmental effects studies on fluorochemicals has been discussed previously[1].

The subject fluorochemical of this report is FC 95 (an anionic surfactant) which has a potential for widespread distribution in the environment as this material is used by the chrome plating, and etching industries, both domestically and internationally. FC 95 chemically is the potassium salt of perfluorooctane sulfonic acid.

$$C_8\ F_{17}\ SO_3K$$

FC 95

This material is an off-white powder, having a molecular weight of 538 and the chemical structure shown above.

This report consolidates all available information in the areas of aquatic toxicity, soil sorption studies, degradation, water solubility and partition coefficients and defines the probable environmental risk of FC 95.

Methods

Water solubility, biodegradation and soil sorption studies have been the subject of technical reports[1-3]. These specific experimental methodologys have been defined in these reports and should be consulted for specific details.

A) Aquatic Testing

The testing protocols utilized for this study were modeled after that described by USEPA (1975)[4].

B) Acclimation Procedure

The bluegill sunfish *(Lepomis macrochirus)*[a], rainbow trout *(Salmo gairdneri)*, and fathead minnows *(Pimephales promelas)*[b] used in this study were obtained from private hatcheries. Stock fish were held in fiberglass holding tanks filled with carbon-filtered well water maintained at 14-15°C. A daily photoperiod of 16 hours light and 8 hours dark, with a 30-minute transition period, was maintained throughout the acclimation and testing period. The fish were fed Tetra-Min[c] daily, food being withheld 48 hours prior to and throughout the test period. Fish were so acclimated for 14 days prior to testing.

Acute short-term (96-hour) static bioassays were performed on FC95 Lot 583. Carbon-filtered well water of known composition

a. Dale Fattig Fish Farm, Brady, Nebraska
b. Dennis Fender Fish Hatchery, Baltic, Ohio
c. Tetra-Min - a commercial fish food of known composition

was used as the diluent. All glass aquaria (35 x 20 x 20 cm), containing 16.1 of diluent or diluent plus toxicant comprised a study chamber. Fathead minnows *(Pimephales promelas)*, bluegill sunfish *(Lepomis macrochirus)*, and rainbow trout *(Salmo gairdneri)*, uniform in size and weight, were tested at each chemical concentration of each test material. Test fish were randomly assigned to various test chambers within 30 minutes following toxicant addition. Test temperatures for the fathead minnow and bluegill sunfish were maintained at 18°C range 17-19, while the rainbow trout tests were conducted at 14°C. Mortality, temperature, dissolved oxygen level, and pH of all test solutions were measured at 24-hour intervals or until total mortality had occurred. General observations relative to behavioral changes were similarly recorded when appropriate. Organisms used in this study were considered to be generally healthy and free of disease.

Instrumentation used included a temperature compensating Orion pH meter, ASTM thermometers ±1°C. for temperature monitoring, and a Yellow Springs Dissolved Oxygen meter.

All aquatic studies were replicated. LC_{50} values with 95% confidence limits were calculated using the USEPA (Duluth) Probit computer program on the 3M TRAC System.

C) Aquatic Invertebrates - 48 hour Static LC_{50}

Daphnia magna, 20 organisms per test, were exposed to FC 95, lot 583 at varying concentrations for 48 hours. First instars were counted and placed in carbon filtered well water, with chemical added and solubilized prior to the addition of the *Daphnia magna*.

Test concentrations were 42, 56, 75, 100 and 135 mg/l.

LC_{50} values with 95% confidence limits were calculated using the USEPA (Duluth) Probit computer program on the 3M Trac System.

The test protocol utilized for this study was modeled after that described by USEPA (1975)[4].

Results

Table 1 lists water solubility and partition coefficient data obtained using radio-labelled FC-95. This material is water soluble, 286 ppm[1], slightly lipid soluble having a partition coefficient of 7-10[5]. Based on these data it can be concluded that FC 95 would not bioconcentrate to an appreciable extent in the environment. Chiou et al[6] have described an emperical relationship between water solubility of a chemical and its bioconcentration factor. In this system the ascribed error is considered to be one order of magnitude. When applying the data generated for FC 95 to this proposed relationship this chemical would be projected to possess a bioconcentration factor of approximately 200.

TABLE 1 - Physicochemical Characterization of FC-95

Parameter	Test	Results
Solubility	Veith Method	286 ppm
Partition Coefficient	n-octanol/water	7-10

FC-95 was found to be completely resistant to biodegradation under the test conditions employed[2]. This 2 1/2 - month shake culture biodegradation study utilized microbial test cultures derived from activated sludge inocula obtained from the waste treatment systems of Chemolite, Decatur, and the Twin Cities Metro plants. During the period of this study, a strain of microbes which could degrade FC-95 did not develop, hence this material would be expected to persist in the environment for extended periods of time unaltered by microbial catabolism.

In working with fluorochemicals, it has been suggested that if these materials do degrade either chemically or biologically that one degradation product would be FC-95. We have never observed the formation of FC-95 by either of these routes; therefore, the environmental levels of FC-95 are not anticipated to increase as a result of the exogenous production of this material.

Soil sorption studies have shown that approximately 18.8% (range 14.6-27.0) of the FC 95 is adsorbed to the Brill sandy loam soil used in these studies (Table 2)(3). Complete desorption of the FC 95 which had been adsorbed to soil was accomplished within three (3) desorption trials (Table 2). Mobility of FC 95 was calculated utilizing the scheme devised by Hamaker[7] 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, FC 95 had a K_{oc} value of 45, being considerably more mobile than Paraquat, K_{oc} 20,000 and slightly less mobile when compared to Chloramben, K_{oc} 12.8. These data indicate that those forces which bind FC 95 to soil are weak, hence the complete desorption of material adsorbed to the soil and secondarily the fact that this material is highly mobile.(3).

Results of the acute static aquatic tests are tabulated (Table 3). Based on aquatic toxicity criteria established by NIOSH FC 95 would be considered slightly toxic to the vertebrates and invertebrate utilized in this test[8]. It is noted that the invertebrate data correlate well with those data obtained when testing both warm water species. This observation has been made repeatedly, therefore, one may consider *Daphnia magna* data as a valid predictor of chemically induced toxicity to warm water vertebrate species (9,10). A statistical analysis will be utilized to validate this concept.

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 ^{14}C FC 95 at sublethal levels on hatchability, survival, weight and length changes (Table 4). It is generally accepted that the immature or young of a species are quite sensitive indicators of chemically induced toxicity. In the parameters under investigation the percent survival was statistically reduced (P.05) at a FC 95 concentration of 1.9 mg/l. The remaining test parameters were unaffected by this chemical. The mechanism responsible for the increased mortality observed at the highest test concentration can not accurately be determined based on these studies, although it is to be noted that hatchability was not affected at this dose level.

In the contracting laboratory's report, the observation was made that the fish in the 1.9 mg/l tank were exhibiting stress behavior; erratic swimming, darkened coloration. A similar observation was made of a few fish in the 1.0 mg/l tank suggesting that the toxic action of FC 95 is cumulative.

Based on the results of the histopathological examination, a 30-day exposure to 1.9 mg/l ^{14}C FC 95 did not contribute to abnormal histopathology (Table 5).

TABLE 2 - Soil Sorption Test on FC 95

Parameter	Test	Solution	Results
Soil Sorption	Adsorption	Water	18.8%
	Desorption	Water	100% of amount adsorbed
	K_{oc}		45

TABLE 3 FC 95: 96 Hour Acute Static Testing

Test Organism	96h LC_{50} mg/l	Limits lower mg/l	Upper mg/l
Fathead Minnow	37.6 51	28.4 46	50.2 56
Bluegill Sunfish	68	62	74
Rainbow Trout	11	8.6	12.5
B. Invertebrate 48 Hour Static Test			
Daphnia Magna	50 49.2	42.8 38.7	56 56.6

TABLE 4 Percentage Hatch, Percentage Survival, Mean Total Length and Average Wet Weight of Fathead Minnow Fry (*Pimephales promelas*) during Exposure to Varying Concentrations of ^{14}C FC 95[a,b]

			30 Days Post Hatch	
Concentration mg/l	Hatch %	Survival %	Total Length mm	Wet Weight mg
1.9	95	42[c]	20.5	72
1.0	96.5	86	20	62.5
0.45	96.5	90	20.5	66
0.28	95.5	94	21	64
0.12	97.5	95	20	63
Control	98	93	20	61.5
Solvent Control	89	100	21	64.5

[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]Significantly reduced at P = 0.05

TABLE 5 Histopathological Examination of Fathead Minnow (*Pimephales promelas*) exposed 30 day to 1.9 mg/l ^{14}C FC 95[a,b]

Test Material	Number of Observations	Histopathological Findings
Control	10	9/10 fatty liver change 1/10 bacterial gill disease 9/10 tissue autolysis
^{14}CFC 95	10	8/10 fatty liver change 2/10 normal

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

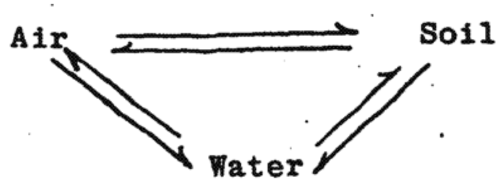
[b]Summary table submitted to Environmental Laboratory, 3M, St. Paul, as part of final report.

Both groups of organisms exhibited fatty liver changes, control, 9/10, and dosed organisms 8/10. Evidence of tissue autolysis in the control group is indicative of a delay in histological preparation of tissues following death of the organism.

Discussion

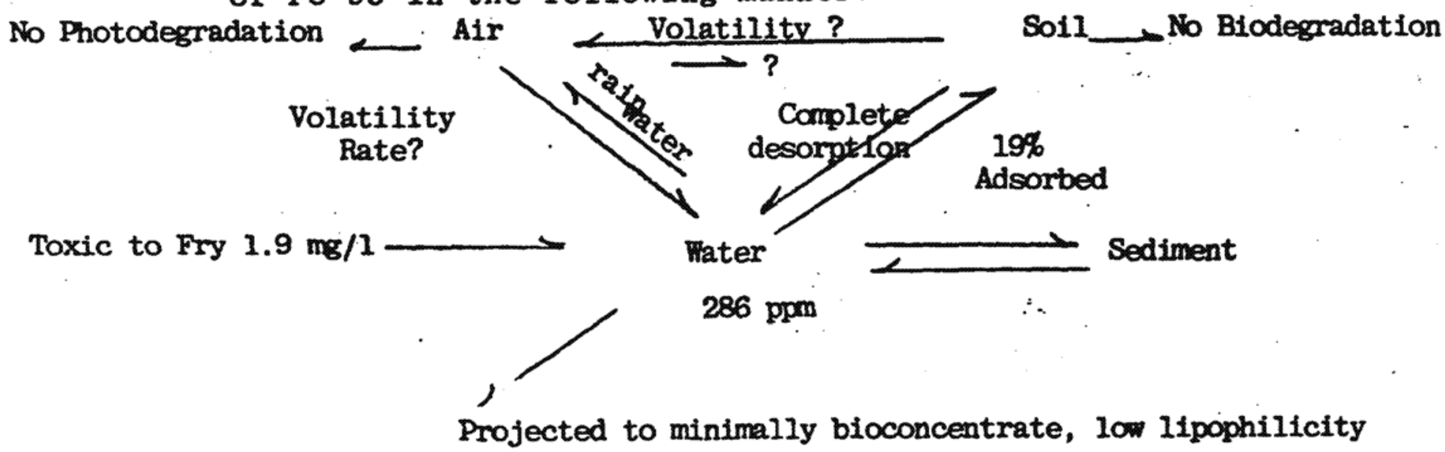
The primary purpose of this report is to provide a single source for all environmental data generated relating to FC 95 and to provide an analysis of potential environmental risk.

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



It, therefore, follows that chemicals entering this system may establish an equilibrium, remain within a single environment, or impact on all phases of the depicted cycle.

In the specific case at hand we can represent the impact of FC 95 in the following manner:



As schematically represented above FC 95 enters the environment primarily by means of the waterways and secondarily <u>via</u> the terrestrial ecosystem and atmosphere. FC 95 does not adsorb permanently to either soil and/or sediment. Complete desorption of FC 95 from soil did occur in the laboratory model[3]. It is unknown whether or not this material volatilizes, a fact which assumes importance in light of the finding that FC 95 does not undergo photolysis.[11] Based on the foregoing it appears that waterways are the environmental sink for FC 95 and aquatic organisms are the intermediate receptors. It is in the aquatic area that a possible deleterious action of FC 95 may be found.

X As noted above, reduced survival rates of fathead minnow fry were recorded at FC 95 concentrations of 1.9 ppm. The no effect level of FC 95 may be assumed to be approximately 0.19 ppm. These data may serve in a predictive fashion, hence the above noted levels of FC 95 may impact on a human food source by significantly reducing the survival rates of these organisms.

It is to be emphasized that the environmental concentration of FC 95 more accurately describes the degree of risk associated with this chemical.

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

1) Total production is at Chemolite and it is discharged in its entirety.

2) No FC 95 is removed by the treatment facility.

3) All effluent is discharged to the Mississippi River.

4) FC 95 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) $\text{MG/min} = \dfrac{(\text{River Flow, CFM})(\text{Conversion, gal/ft}^3)(\text{Time, min})}{\text{Production, per annum}}$

2) MG/min X 1440 = MG/Day

3) Lbs/day = (mg/1 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 FC 95 in the Mississippi River below Chemolite was calculated. During the period 1973-1978, the EEC for FC 95 was calculated to be 5 ng/l at Hastings, MN, while the EEC projected for the period 1978-1983 is projected at 7 ng/l. Since the water compartment is the environmental sink for FC 95 it is determined that at the present and projected levels of production, FC 95 will not present an unreasonable environmental risk.

Conclusions

Under the test conditions employed in characterizing the physicochemical and environmental properties of FC 95 it has been determined that this material:

1) is water soluble, 286 ppm
2) has an n-octanol/water partition coefficient of ~10
3) is resistant to microbial degradation
4) is highly mobile in Brill sandy loam soil
5) In a contracted study, survival rate of the fathead minnow fry was reduced to a statistically significant extent when the exposure concentration was 1.9 mg/l FC 95. No other parameters were adversely affected nor was abnormal histopathology observed at this dose level.
6) would have an estimated environmental concentration of approximately 7 ng/l under conditions, wherein all FC 95 were manufactured at Chemolite and would be discharged uniformly into the Mississippi River.
7) may not be a metabolite as a result of chemical or biological degradation, hence no increase in environmental levels of FC 95.
8) FC 95, under the test conditions described will not present an unreasonable environmental risk.

Bibliography

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