SOIL ADSORPTION

TEST SUBSTANCE

Identity: N-ethylperfluorooctane sulfonamidoethanol; may also be referred to as N-EtFOSE Alcohol or FM-3422. (1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-, CAS # 1691-99-2)

Remarks: Material is an off-white, waxy solid of uncharacterized purity.

METHOD

Method: Adsorption-desorption studies developed using procedures described by Davidson, 1976 and Hamaker, 1975.
GLP (Y/N): No
Year (study performed): 1978
Statistical methods: Statistical analysis and plotting of the data was done with the MINITAB package of the 3M TRAC computer service.
Temperature: 16-19°C during the 24-hours of wrist-action shaker exposure.
Stock and test solution preparation: The stock solution was made by putting a few milligrams N-EtFOSE alcohol in D.I. water and stirring with a magnetic stirrer for several days.The supernatant was poured into a graduated cylinder to settle for 4 days and then 50 ml portions were drawn off and centrifuged. The test solutions were made by diluting aliquots of the stock solution.
Remarks field: The Brill sandy loam soil was characterized as having 57% sand, 36% silt, 7% clay, 2.5% organic matter, 1.5% organic carbon, with pH 6.5 and cation exchange capacity of 15.3 meq./100 g. Standard solutions were prepared in deionized water at concentrations of 0.49 mg/L, 0.27 mg/L, and 0.16 mg/L. Forty-five ml of each solution was shaken with 5 gram samples of the soil in 50 ml glass centrifuge tubes for 24 hours in duplicate on a wrist shaker at room temperature (16-19°C).

Desorption extractions were performed with deionized water after the adsorption phase of the experiment. The samples from the adsorption and desorption experiments were centrifuged individually at 3000 rpm for 10 minutes, and 40 ml of each supernatant solution were extracted with ethyl acetate for analysis by GC. The remaining supernatant was drained off and 45 ml of D.I. water were put into the tubes.

RESULTS

K: 392*
K_{oc}: 26,147*

Remarks field: The linear shape of the adsorption isotherm indicated that N-EtFOSE alcohol adsorption on soil would be independent of concentration in solution.

* The study report had indicated a K of 330. This is the coefficient of C in the regression equation, not the adsorption coefficient value. A K_{oc} value was calculated using the formula: K_{oc} = 100 K/% organic carbon. However, the calculation used an organic carbon content of 2.2% while the report indicates the organic carbon to be 1.5%. This is a discrepancy. If the 1.5% value is used along with the corrected K value, the $\mathbf{K_{oc}}$ becomes 26,147.

CONCLUSIONS

The study substance is expected to exhibit low mobility in the kind of soil tested.

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

DATA QUALITY

Reliability: Klimisch ranking 3. The purity of the test substance is unknown. Testing was not performed in duplicate. There was no analysis of the soil to verify amount remaining. Additionally, comments made by Professor Stephen Boyd, Michigan State University are summarized below and included with the report. They also indicate the unreliable nature of this study.

The batch method does not compensate for losses due to volatilization, sorption to the container, degradation, or other mechanisms.

The concentrations used in the study were significantly above the solubility limit of the test substance, indicating there was crystalline N-EtFOSE alcohol in the stock solution.

The number of data points and range of test substance concentrations are too small to definitively determine soil sorption.

Test parameters were not sufficient to establish the isotherm linearity.

REFERENCES

3M Technical Report "Adsorption of FM-3422 on Soil." Stephen K. Welsh, Project 9970612631, Fate of Fluorochemicals, Report No. 009, September 1, 1978.

Review of Technical Report Summary. Adsoprtion of FM 3422 on Soil. Professor Stephen A. Boyd, Michigan State University, May 19, 1993.

OTHER

Last changed: 5/17/00

Attached are comments on the 3M Technical Report "Adsorption of FM-3422 on Soil. Stephen K. Welsh, Project 9970612631 Fate of Fluorochemicals, Report No. 9, Sept. 1, 1978" made by Professor Stephen A. Boyd, Michigan State University, dated May 19, 1993.

Review of Technical Report Summary
Adsorption of FM-3422 on Soil

This report describes a batch sorption/desorption isotherm experiment for FM 3422 on a single sandy loam soil. FM 3422 has a reported solubility in water of 0.05 mg/L (50 ppb). This is considerably lower than FC-95 or FC-143. FM 3422 is a non-ionic compound whereas FC 95 and FC 143 are both anionic. It would be very helpful to have accurate water solubilities and octanol-water partition coefficients for these compounds. The latter would be more useful in predicting K_{om} values using empirical relationships between K_{om} and K_{ow} that have been reported in the literature. Water solubilities of solids are more difficult to use for predicting K_{om} because they should be converted first to the corresponding supercooled liquid solubilities. A favorable comparison of measured K_{om} to K_{om} predicted from K_{ow} using published empirical relationships would strengthen my confidence in these values. One problem with the batch method used is that any loss (e.g., by volatilization, sorption to the container, degradation) is counted as soil sorption which results in higher apparent K values.

Material and Methods

The concentrations of FM 3422 prepared in distilled water are given as .49 mg/L, 0.27 mg/L and 0.16 mg/L. However in the abstract the water solubility is reported as 0.05 mg/L. We have a discrepancy here of a factor of 10? Either the 0.05 mg/L solubility is wrong or there was crystalline FM 3422 in the stock solution. The number of data points (three) and the range of concentrations are both too small. The range of concentrations evaluated should be at least an order of magnitude, with at least five or six initial concentrations. Also, the isotherm should be extended to a solute concentration that approaches its water solubility; this is the only way to establish the linearity of the isotherm.

Results and Discussion

The three concentrations tested, and the narrow range of concentrations isn't sufficient to establish isotherm linearity.

The conclusion that binding of FM 3422 to soil involves electrostatic forces is not justified. In fact, the data do not indicate electrostatic interactions. This mechanism would almost certainly give non-linear isotherms. High sorption coefficients can be obtained without invoking some mechanism based on strong (e.g., electrostatic) molecular interaction. My opinion is that FM 3422 partitions into soil organic matter in the same sense that it would partition into a bulk organic solvent phase such as octanol. The magnitude of the sorption coefficient is a ratio of the solubility in the soil organic matter phase to the solubility in water, analogous to an octanol-water partition coefficient. The magnitude of the sorption coefficient is determined largely by the water solubility of the solute. The water solubility of FM 3422 is apparently quite low, hence the sorption coefficient is high. DDT is a good example of a compound with low water solubility (5.5 ppb) resulting in a high sorption coefficient. Certainly DDT does not sorb by an electrostatic mechanism.

The partition mechanism does manifest linear isotherms.

As far as an electrostatic interaction, this would require protonation of the nitrogen. It would be useful to know the pKa of the compound; then the likelihood of electrostatic interactions with soil organic matter or soil clays could be evaluated.

Again the K_{oc} calculation uses an organic carbon content of 2.2%. The value given in the materials and methods is 1.5%, so there is a discrepancy here. The K_{oc} calculation is appropriate for nonionic compounds that partition into soil organic matter. For compounds that sorb by electrostatic interactions, the K_{oc} value is not applicable. In that case the degree of sorption would probably be related more directly to the cation exchange capacity of the soil. The K_{oc} value does appear to be quite high, and if correct, would indicate low mobility.

Recommendations

1. Get an accurate water solubility (S_w) and K_{ow} values for FM 3422.

2. Measure the pKa of FM 3422 if this is not known.

3. Measure additional soil sorption isotherms using a wider range of solute (FM 3422) concentrations which should approach the water solubility of the compound. That is, in your isotherm there should be a data point where $C = S_w$ or $0.5\ S_w$.

3M

Form 6747 11 A

TECHNICAL REPORT SUMMARY

Date: 9/1/78

TO: TECHNICAL COMMUNICATIONS CENTER – 201-2CN

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

Division: Environmental Engineering & Pollution Control	Dept. Number: 0535
Project: Fate of Fluorochemicals	Project Number: 9970612631
Report Title: Adsorption of FM-3422 on Soil	Report Number: 009
To: A. N. Welter	
Author(s): Stephen K. Welsh	Employee Number(s): 73583
Notebook Reference: #40673	No. of Pages Including Coversheet: 8

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
Soil
Adsorption
Mobility

CURRENT OBJECTIVE:

To obtain an indication of FM-3422 mobility in a sandy loam soil.

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.

To obtain an indication of mobility of FM-3422 in a sandy loam soil, adsorption/desorption experiments similar to those of Davidson, 1976 and of Hamaker, 1975 were conducted. FM-3422 was judged to be immobile based on an adsorption coefficient of 330; less than 5% desorption with two desorption extractions; and water solubility of only 0.05 mg/l.

Information Liaison Initials: SEW

CONCLUSIONS

The adsorption coefficient for FM 3422 was 330. Considering the adsorption coefficient, desorption characteristics, and water solubility, FM 3422 would be judged immobile in the sandy loam soil used in this study.

INTRODUCTION

As a part of the Fate of Fluorochemicals Project, an indication of mobility of FM 3422 in sandy loam soil was desired. Adsorption-desorption experiments (after Davidson, 1976 and Hamaker, 1975) along with water solubility data can provide this indication of mobility. This approach is used by the U.S.E.P.A. in pesticide registration requirements.

MATERIALS AND METHODS

Duplicate 5-g samples of air-dried Brill sandy loam soil (57% and, 36% salt, 7% clay, 2.5% organic matter, 1.5% organic carbon, with pH 6.5 and C.E.C. of 15.3 meg/100g) were shaken with 45 ml of solution in 50 ml glass centrifuge tubes for 24 hours on a wrist action shaker at room temp. (16-19^{o}C). Glass tubes were used because they were found in separate experiments to adsorb less FM-3422 than polypropylene or polyethylene tubes.

Solutions were made by diluting a stock solution of the chemical. The stock solution was made by putting a few milligrams FM 3422 in D.I. water on 1/25/78 and stirring with magnetic stirrer for several days. On 2/6/78 the supernatant was poured into a graduated cylinder to settle

until 2/10/78 when 50 ml portions were drawn off and centrifuged in glass tubes at 3000 rpm for 10 min. The centrifuged solution was put in a glass jar for storage. Concentrations of FM 3422 were 0.49 mg/l., 0.27 mg/l., and 0.16 mg/l (100%, 56%, 32% of stock).

After shaking the initial solutions as well as the two desorption extractions with deionized water, the samples were centrifuged at 3000 rpm for 10 min. and 40 ml of each supernatant solution were extracted with ethyl accetate (See APPENDIX I for procedure) for analysis by GC.

After removing the 40 ml for extraction, the remaining supernatant liquid was drained off and 45 ml of D.I. water were put into the tubes.

Statistical analysis and plotting of the data was done with the MINITAB package of the 3M TRAC computer service.

RESULTS AND DISCUSSION

Adsorption data for FM 3422 are given in TABLE I. The amount of FM 3422 removed from solution by the soil (Column C) was 98% at all three starting (initial) concentrations.

Equilibrium concentrations in solution(C) in mg/l. are shown in Column B and amounts adsorbed on the soil(x/m) in µg FM 3422 per gram soil are shown in Column F. The regression equation of the adsorption isotherm shown in FIGURE 1 was $x/m = 0.33 + 330C$, so that the adsorption coefficient, K, was 330. The linear shape of the adsorption isotherm indicated that FM 3422 adsorption on soil would be independent of concentration in solution. The high percentage adsorbed and the relatively high adsorption coefficient indicated that FM 3422 would be immobile in this sandy loam soil.

TABLE I

FM-3422 Adsorption Data

A Initial FM-3422 Conc., mg/l.	B Equil. Conc., C, mg/l.	C % Removed by Soil $\frac{A-B}{A} \times 100$
0.49 (100%)	0.0120 ± 0.002	98
0.27 (56%)	0.0063 ± 0.005	98
0.16 (32%)	0.0032 ± 0.0005	98

D Total FM-3422 In Initial Sol'n, mg (A x 0.045 liters)	E Total FM-3422 In Sol'n at Equil., mg (B x 0.045 liters)	F FM-3422 Adsorbed on Soil, x/m, µg/g $(D-E\ 10^3/5g)$
0.022	0.00054	4.30
0.012	0.00028	2.37
0.007	0.00014	1.41

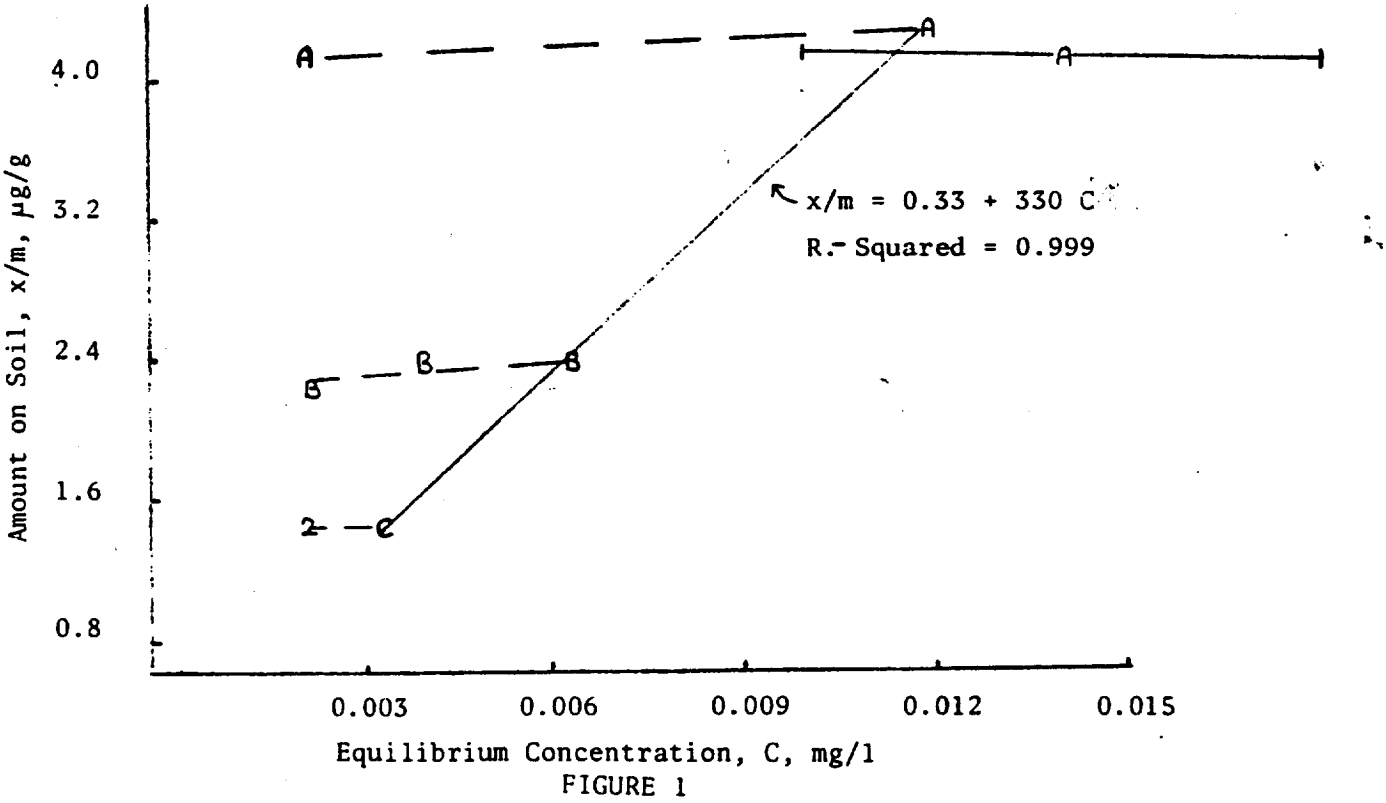

FIGURE 1

FM 3422 Adsorption and Desorption Isotherms

Solid line is adsorption isotherm, broken lines are desorption isotherms. A's are data for highest initial concentration, B's for middle initial concentration, C's for lowest initial concentration. Standard deviation for the "A" value furthest right is shown to indicate that this value may be acceptable.

Desorption data are given in TABLE II and the desorption isotherms are shown in FIGURE 1. Of the amounts initially adsorbed on the soil, less than 5% was removed by the two desorption extractions with water (TABLE II, Column G). This small amount of desorption is also shown by the almost horizontal slopes of the desorption isotherms. This very small amount of desorption was another indication of the immobility of FM 3422.

TABLE II

FM 3422 DESORPTION ISOTHERM DATA

A Equil. Conc. in Solution, C, mg/l.	B Equil. Conc. in First Desorption mg/l.	C Equil. Conc. in Second Desorption mg/l
0.0120 ± 0.002	0.014 ± 0.004	0.002 ± 0
0.0063 ± 0.005	0.004 ± 0.001	0.002 ± 0
0.0032 ± 0.0005	0.002 ± 0	0.002 ± 0

D Amount Adsorbed on Soil, x/m µg/g	E Amount on Soil After First Desorption, µg/g	F Amount on Soil After Second Desorption, µg/g	G Percent Desorbed $\frac{(D-F)}{D}$ 100
4.302	4.176	4.158	3.3
2.373	2.337	2.319	2.3
1.411	1.393	1.375	2.6

The large amount adsorbed and the small amount desorbed suggests strong binding of FM 3422 to soil particles by intermolecular interactions involving electrostatic forces.

The adsorption coefficient based on soil organic carbon, K_{oc}, for FM 3422 would be 15,000 (100 K/% organic carbon = 100x330/2.2). Compared with Koc values for a selected group of pesticides and other fluorochemicals (Table III), 15,000 is quite high and is another indication of low mobility of FM 3422.

TABLE III

Comparison of Adsorption Coefficients for a Selected Group of Pesticides (Hamaker and Thompson, 1972)

	Chemical	K_{oc}
(mobile)	Chloramben	12.8
	(FC-143 - - - - - - - - - -	17)
	2,4-D	32
	(FC-95 - - - - - - - - - -	45)
	Propham	51
	Bromacil	71
	Monuron	83
	Simazine	135
	Propazine	152
	Dichlobenil	164
	Atrazine	172
	Chloropropham	245
	Prometone	300
	Ametryn	380
	Diuron	485
	Prometryne	513
	Chloroxuron	4,986
	(FM-3422	15,000)
	Paraquat	20,000
(immobile)	DDT	243,000

These adsorption and desorption data along with the low water solubility of FM 3422 (0.05 mg/l.) provide good evidence that FM-3422 would have very low mobility in the sandy loam soil used in this study.

Terms

C - Concentration of chemical in solution at equilibrium

x/m - Concentration of chemical adsorbed on soil at equilibrium

R^2 - Coefficient of determination

K - Adsorption coefficient

K_{oc} - Adsorption coefficient based on soil organic carbon content

References

Davidson, J. M., et. al., 1975, Use of Soil Parameters for Describing Pesticide Movement Through Soils, U. S. EPA, EPA-660/2-75-009.

Davidson, J. M., 1976, "Vertical Movement and Distribution of Organics in Soils," Presented at Symposium on Nonbiological Transport and Transformation of Pollutants on Land and Water, at National Bureau of Standards, Gaithersburg, MD., May 11-13, 1976.

Hamaker, J. W., 1975, "Interpretation of Soil Leaching Experiements," in Chemicals, Human Health and the Environment, A Collection of Dow Scientific Papers, Vol. 1, Dow Chemical USA, Midland, Mich. 48640

Hamaker, J. W. and J. M. Thompson, 1972. "Adsorption" in Organic Chemicals in the Soil Environment. C. A. I. Goring and J. W. Hamaker (eds.). Marcel Dekker, Inc., N. Y.

APPENDIX I

FM-3422 Analytical Procedure

Reference: N.B. #46269-50 - Results obtained from this method.

The 40 ml H_2O samples that were submitted by S. K. Welsh on 2/2/78 were analyzed in the following manner.

The 40 ml H_2O sample was placed in a 125 ml sep. funnel, fitted with teflon stopcock. 10 ml of saturated NaCl H_2O was added by pipet. 7 ml of ethyl acetate* added by pipet to sample in sep. funnel. The funnel was inverted 50 times and the phase allowed to separate. The top EtAc phase was drawn off with a transfer pipet and placed in a dry 10 ml volumetric flask. Note: Of the 7 ml EtAc added, 3 ml is recovered due to 10% EtAc solubility in H_2O. Also, if emulsion is a problem the foamy layer of EtAc water can be placed in a glass contrifuge tube and spun at 5000 rpm for 10 min. to break emulsion. The EtAc is then transferred to the volumetric flask. The extraction is carried out a second and third time, as above, using 3 ml EtAc each time. All EtAc extracts combined in 10 ml volumetric flask which is then diluted to the line with EtAc.

5 microliter injections of the samples were made into E.C.G.C. with the following conditions. Standard FM-3422 solutions in EtAc are injected for comparison.

Inst: Hewlett-Packard Model 5713 equipped with Ni 63 electron capture detector.
Column: 6' x 1/8" O.D. S.S. 10% CW-20M on 60/80 Mesh Chromosorb W-AW
Oven Temp - 180°C Isothermal
Inj. Port Temp - 200°C
Det. Temp. - 300°C
Flow 40 C.C./min - Argon: Methane 95:5

*Analytical Reagent - Mallinckrodt (R) - Ethyl Acetate

G. A. Vraspir