SOIL ADSORPTION

TEST SUBSTANCE

Identity: N-methylperfluorooctane sulfonamidoethanol; may also be referred to as N-MeFOSE Alcohol, FC-790, or FM-3925. (1-Octanesulfonamide, N-methyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-, CAS # 24448-09-7)

Remarks: Material is an off-white, waxy solid. Sample purity and lot number were not recorded.

METHOD

Method: Adsorption-desorption studies developed using procedures described by Davidson, 1976 and Hamaker, 1975.
GLP (Y/N): No
Year (study performed): 1979
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 used was an aliquot from the 24-hour sample taken during the water solubility study on N-MeFOSE Alcohol. This solution was prepared by the Vieth method and gave a concentration of 2.16 mg/L. 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, 2.2% organic carbon, with pH 6.5 and cation exchange capacity of 15.3 meq./100 g. Standard solutions of N-MeFOSE alcohol were prepared in deionized water at concentrations of 2.16 mg/L, 1.21 mg/L, 0.691 mg/L, 0.389 mg/L, 0.216 mg/L, and 0.022 mg/L. Forty ml of each solution was shaken with 5 gram samples of the soil in a 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 30 minutes, and each supernatant solution was decanted off into glass sample vials.

Supernatant solutions were analyzed by extracting with ethyl acetate and running GC.

RESULTS

K: 77
K_{oc}: 3,500*

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

* The study report had calculated using the formula: K_{oc} = 100 K/% organic carbon.

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. Study is using an inaccurate solubility value and the purity of the test substance is not sufficiently characterized. The analytical methodology was not validated, therefore there is no way to evaluate the accuracy of the reported analytical results. It was noted in the report that a high percentage of FM 3925 was adsorbed onto the glass used in the experiment. No attempt was made to correct for this loss of test substance in the calculations of sorption to soil. The Vieth Method of perparing a saturated solution would disproportionately dissolve the more soluble components of N-MeFOSE alcohol which is not a pure material. The study was not performed in duplicate, and the soil was not analyzed to verify the amount remaining. Additionally, the following are summarized comments made by Professor Stephen Boyd, Michigan State University:

Use of oven dried soils not recommended. Should be air-dried and characterized for moisture content.

Use of deionized water for desorption experiments is not recommended as it causes the soil to disperse. Use dilute $CaCl_2$.

Ethyl acetate extraction not validated.

Did not establish that the sorption isotherm is linear.

There is no evidence for electrostatic forces being involved in soil binding of FM 3925.

REFERENCES

3M Technical Report "Adsorption of FM-3925 on Soil." S.K. Welsh and C.H. Schrandt, Project 9970612631 Fate of Fluorochemicals, Report No. 013, March 22, 1979.

Review of Technical Report Summary. Adsoprtion of FM 3925 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-3925 on Soil. S.K. Welsh and C.H. Schrandt, Project 9970612631 Fate of Fluorochemicals, Report No. 13, Mar. 22, 1979" made by Professor Stephen A. Boyd, Michigan State University, dated May 19, 1993.

Review of Technical Report Summary
Adsorption of FM 3925 on Soil

Materials and Methods

I would not recommend oven drying soils. Use air dried soils and do a separate moisture determination (oven drying) to get the moisture content.

Solubility was determined earlier as 2.3 ppm.

Desorption experiments should probably use dilute $CaCl_2$ solutions instead of deionized water which will cause the soil to disperse.

The extraction procedure described utilizing ethyl acetate needs validation. The percent recoveries of FM 3925 from standard solutions should be reported.

The sorption isotherm only extends to an equilibrium concentration of about 0.22 ppm which is 10 times lower than the water solubility (S_w) of FM 3925. The isotherm needs to be extended to 0.5 S_w or greater, i.e., equilibrium aqueous concentrations approaching S_w. This is the only way to establish the linearity of the isotherm. I'm again not certain of the meaning of the desorption experiments. I would not draw any major conclusions regarding mobility from those data.

There is absolutely no evidence for electrostatic forces being involved in soil binding of FM 3925. This is pure conjecture and almost certainly wrong. The only electrostatic mechanism would be to protonate the N of FM 3925 to create a cationic species that could interact with negatively charged sites in soil clays and soil organic matter. The pKa of FM 3925 would indicate the likelihood of that. The linear isotherms (if they are in fact linear) suggest solute partitioning not adsorption by electrostatic forces. Solute partitioning involves dissolution of FM 3925 in amorphous soil organic matter. The magnitude of the sorption coefficient (K_{oc}) depends on the relative solubility of FM 3925 in soil organic matter and water. The K_{oc} values reported for FM 3925 is 3500 (100 K/% organic carbon = 100 x 330/2.2). The K value reported was 77 so it should be: K_{oc} = 100 x 77/2.2 = 3500. This may be a reasonable value although it would be easier to evaluate if the K_{ow} was known. Gareen and Karickhoff (1990, Pesticides in the Soil Environment, Chapter 4, Sorption Estimates for Modeling, Soil Science Society of America, Madison, WI) give the empirical equation:

$$\text{Log } K_{oc} = -0.68 \log S\ (\mu g/ml) \times 4.273$$

which using the solubility of 2.3 yields a predicted K_{oc} of about 10,000 so its at least close. Equations like this using solubilities of solids that haven't been corrected for melting point, i.e., converted to supercooled liquid solubilities, give pretty rough estimates. I think you could get a better estimate if you knew K_{ow}.

Recommendations

1. Measure the octanol water partition coefficient, relate measured S to K_{ow} via Chiou's equation:

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

remembering S_w of a solid should be converted to supercooled liquid solubility if the melting point is much over 100°C.

2. Extend range of equilibrium aqueous concentrations to approach S_w in the sorption isotherm experiments. Test other soils to evaluate

3. Determine the pKa of FM 3925 to evaluate likelihood of electrostatic interactions.

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TECHNICAL REPORT SUMMARY

Date: 3/22/79

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: 9970612631
Report Title: Adsorption of FM-3925 on Soil	Report Number: 013
To: A. N. Welter	
Author(s): Stephen K. Welsh & C. H. Schrandt	Employee Number(s): 073583, 113152
Notebook Reference: #51050	No. of Pages Including Coversheet: 11

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
Fluorochemical

CURRENT OBJECTIVE:

To obtain an indication of FM-3925 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-3925 in a sandy loam soil, adsorption/desorption experiments similar to those of Davidson, 1976, and of Hamaker, 1975, were conducted. FM-3925 was judged to be immobile based on an adsorption coefficient of 77; less than 15% desorption with three desorption extractions; and water solubility of only 2.16 mg/l.

006547

Information Liaison Initials: SKW

CONCLUSIONS

The adsorption coefficient for FM-3925 was 77. Considering the adsorption coefficient, desorption characteristics, and water solubility, FM-3925 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-3925 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 USEPA in pesticide registration requirements.

MATERIALS AND METHODS

Duplicate 5-g samples of oven-dried (103° C.) Brill sandy loam soil (57% sand, 36% silt, and 7% clay, with 2.5% organic matter, 2.2% organic carbon, with pH 6.5 and CEC of 15.3 meg/100 g) were shaken with 40 ml of solution in 50 ml glass centrifuge tubes for 24 hours on a wrist-action shaker at room temperature (16-19° C.). Glass tubes were used because it was believed, based on prior experience, that glass would adsorb less FM-3925 than polypropylene or polyethylene tubes.

Solutions were made by diluting a stock solution of the chemical. The stock solution was the 24-hour sample from the second Vieth study of water solubility (46269-53 and 48277-8). Concentrations of FM-3925 were 2.16 mg/l, 1.21 mg/l, 0.691 mg/l, 0.389 mg/l, 0.216 mg/l, and 0.022 mg/l (100%, 56%, 32%, 18%, 10%, and 1% of stock).

After shaking the initial solutions, as well as the three desorption extractions with deionized water, the samples were centrifuged at 3000 rpm for 30 minutes, and each supernatant solution was decanted off into glass sample vials.

After removing the 40 ml of initial solution for analysis, 40 ml of DI water was put into the tubes for the first desorption extraction. Similarly, the second and third desorption extractions were conducted.

The samples, now in glass sample vials, were analyzed by first adding 5 ml of Burdick and Jackson distilled in glass ethyl acetate to each vial, mixing on a Genie Vortex Mixer at maximum speed for 30 seconds, and centrifuging at 2500 rpm for 10 minutes. The ethyl acetate layer (about 1 ml) was then drawn off with a transfer pipet to a clean vial, and then two more extractions were conducted with 2 ml of ethyl acetate each followed by mixing and centrifuging as above, and the ethyl acetate layers from each successive extraction were combined in the same clean vial. Then, 15 ml of ethyl acetate was added, and the extracts were evaporated to near dryness under nitrogen and then transferred to 4-ml concentrator tubes and brought up to 1 ml with ethyl acetate. After transferring to automatic sampler vials, gas chromatograms were run on duplicate 5-µl injections of the extracts. GC equipment and conditions included:

Column - 6' x 1/8" O.D. stainless steel, 10% Carbowax 20M on 60/80 mesh Chromasorb W-AW; Chromatograph-HP 5713, Ni 63 Detector; Conditions - Inject Port 200° C., Detector 300° C., Flow 35 cc/min. Ar/CH_4 95/5, Oven temp. 175° for 16 min., then up to 230° C. at 32°/min. for 4 min.

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-3925 are given in TABLE I. The amount of FM-3925 removed from solution by the soil (Column C) was 83-90% of the initial amount at the various 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-3925 per gram soil are shown in Column F. The regression equation of the adsorption isotherm shown in FIGURE 1 was x/m = -1.7 + 77C, so that the adsorption coefficient, K, was 77. The linear shape of the adsorption isotherm indicated that FM-3925 adsorption on soil would be independent of concentration in solution. The high percentage adsorbed and the relatively high adsorption coefficient indicated that FM-3925 would be immobile in this sandy loam soil.

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 15% was removed by the three desorption extractions with water (TABLE II, Column I). This small amount of desorption is also shown by the fairly horizontal slopes of the desorption isotherms compared with the slope of the adsorption isotherm. This very small amount of desorption was another indication of the immobility of FM-3925.

The large amount adsorbed and the small amount desorbed suggests strong binding of FM-3925 to soil particles by intermolecular interactions involving electrostatic forces.

The adsorption coefficient based on soil organic carbon, K_{OC}, for FM-3925 would be 3,500 (100 K/% organic carbon = 100x330/2.2). Compared with K_{OC} values for a selected group of pesticides and other fluorochemicals (TABLE III), 3,500 is quite high and is another indication of low mobility of FM-3925.

These adsorption and desorption data, along with the low water solubility of FM-3925 (2.16 mg/l), provide good evidence that FM-3925 would have very low mobility in the sandy loam soil used in this study.

In a "control" using the full-strength stock solution and no soil, it was found that 53% of the FM-3925 was removed from solution (100 x (2.16-1.007)/2.16), being adsorbed on the glass tubes (TABLE IV). Of the amount adsorbed, 20% (100 x (46.1-37.1)/46.1) was subsequently desorbed in three desorption extractions with DI water (the desorption isotherm is shown in FIGURE 2).

This control experiment indicated that a considerable portion of the FM-3925 removed from solution (TABLE I, Column C) was being adsorbed on the glass rather than on the soil. In order to correct for this in the calculations, it would be necessary to conduct such controls at each of the initial concentrations. While such a correction would make it truly a "soil adsorption" experiment, it probably wouldn't change the conclusions. The % removed "by soil" would be lower, and the amounts on the soil (TABLE I, Column F) would be lower moving the adsorption isotherm down, but the adsorption coefficient (the slope of the isotherm) may not change. Likewise, the desorption isotherms may be shifted down without changing the desorption coefficients. Also, since there is no carbon in the glass, the adsorption coefficient based on organic carbon content of the soil, K_{oc}, should remain the same.

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, USEPA, 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 Experiments," in Chemicals, Human Health and the Environment, A Collection of Dow Scientific Papers, Vol. 1, Dow Chemical USA, Midland, MI 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., NY.

TABLE I

FM-3925 ADSORPTION DATA

A Initial FM 3925 Conc., mg/l	B Equil. Conc., C, mg/l	C % Removed by Soil & Glass Tubes $\frac{A-B}{A} \times 100$
2.160 (100%)	0.2135 ± 0.0516	90
1.210 (56%)	0.1455 ± 0.0106	88
0.691 (32%)	0.0940 ± 0.0156	86
0.389 (18%)	0.0490 ± 0.0042	87
0.216 (10%)	0.0370 ± 0.0028	83
0.022 (1%)	*	

D Total FM 3925 In Initial Sol'n, mg (A x 0.04 liters)	E Total FM 3925 In Sol'n at Equil., mg (B x 0.04 liters)	F FM 3925 Adsorbed on Soil, x/m, µg/g (D-E 10/5g)
0.0864	0.00854	15.57
0.0484	0.00582	8.52
0.0276	0.00376	4.78
0.0156	0.00196	2.72
0.0086	0.00148	1.43

*All samples at the 1% initial concentration were below the detectable limit, and these were not included in the calculations.

TABLE II

FM-3925 DESORPTION ISOTHERM DATA

A Equil. Conc. in Solution, C, mg/l (Table 1, Column B)	B Equil. Conc. in First Desorption mg/l	C Equil. Conc. in Second Desorption mg/l
0.2135 ± 0.0516	0.1160 ± 0.0057	0.0605 ± 0.0021
0.1455 ± 0.0106	0.0585 ± 0.0035	0.0410 *
0.0940 ± 0.0156	0.0310 ± 0.0057	0.0130 ± 0.0028
0.0490 ± 0.0042	0.0165 ± 0.0007	0.0100 *
0.0370 ± 0.0028	0.0050 ± 0.0057	0.0010 ± 0.0

D Equil. Conc. in Third Desorption mg/l	E Amount Adsorbed on Soil, x/m µg/g (Table 1, Column F)	F Amount on Soil After First Desorption, µg/g
0.0525 ± 0.0134	15.57	14.64
0.0260 *	8.52	8.05
0.0080 ± 0.0099	4.78	4.53
0.0080 ± 0.0	2.72	2.59
0.0035 ± 0.0035	1.43	1.39

G Amount on Soil After Second Desorption, µg/g	H Amount on Soil After Third Desorption, µg/g	I Percent Desorbed $\frac{(E-H)}{E}$ 100
14.16	13.74	12
7.72	7.52	12
4.43	4.36	9
2.51	2.44	10
1.38	1.35	5

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
	(FM 3925 - - - - - - - - - - -	3,500)
	Chloroxuron	4,986
	(FM 3422 - - - - - - - - - - -	15,000)
	Paraquat	20,000
(immobile)	DDT	243,000

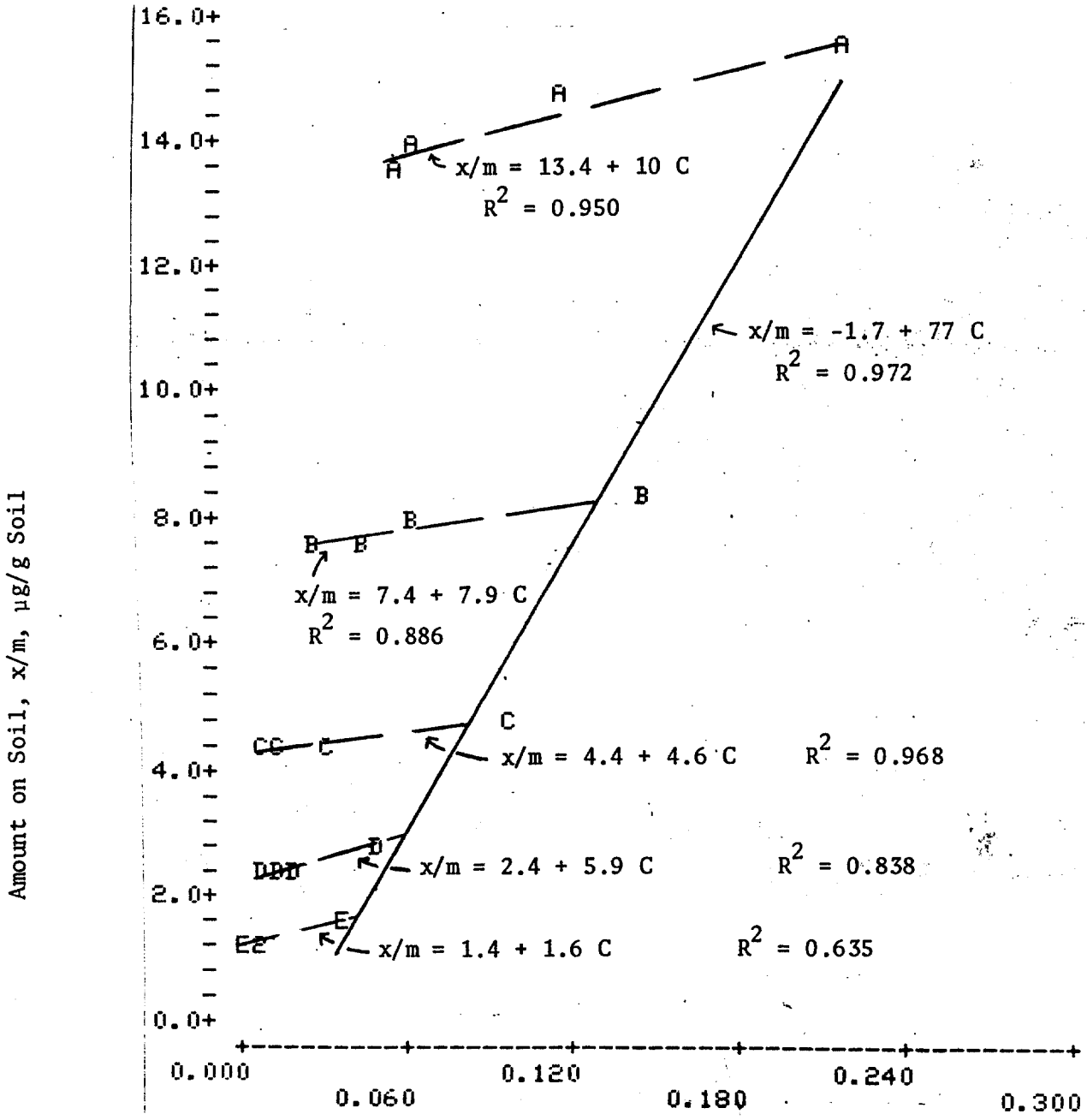

FIGURE 1

FM-3925 ADSORPTION AND DESORPTION ISOTHERMS

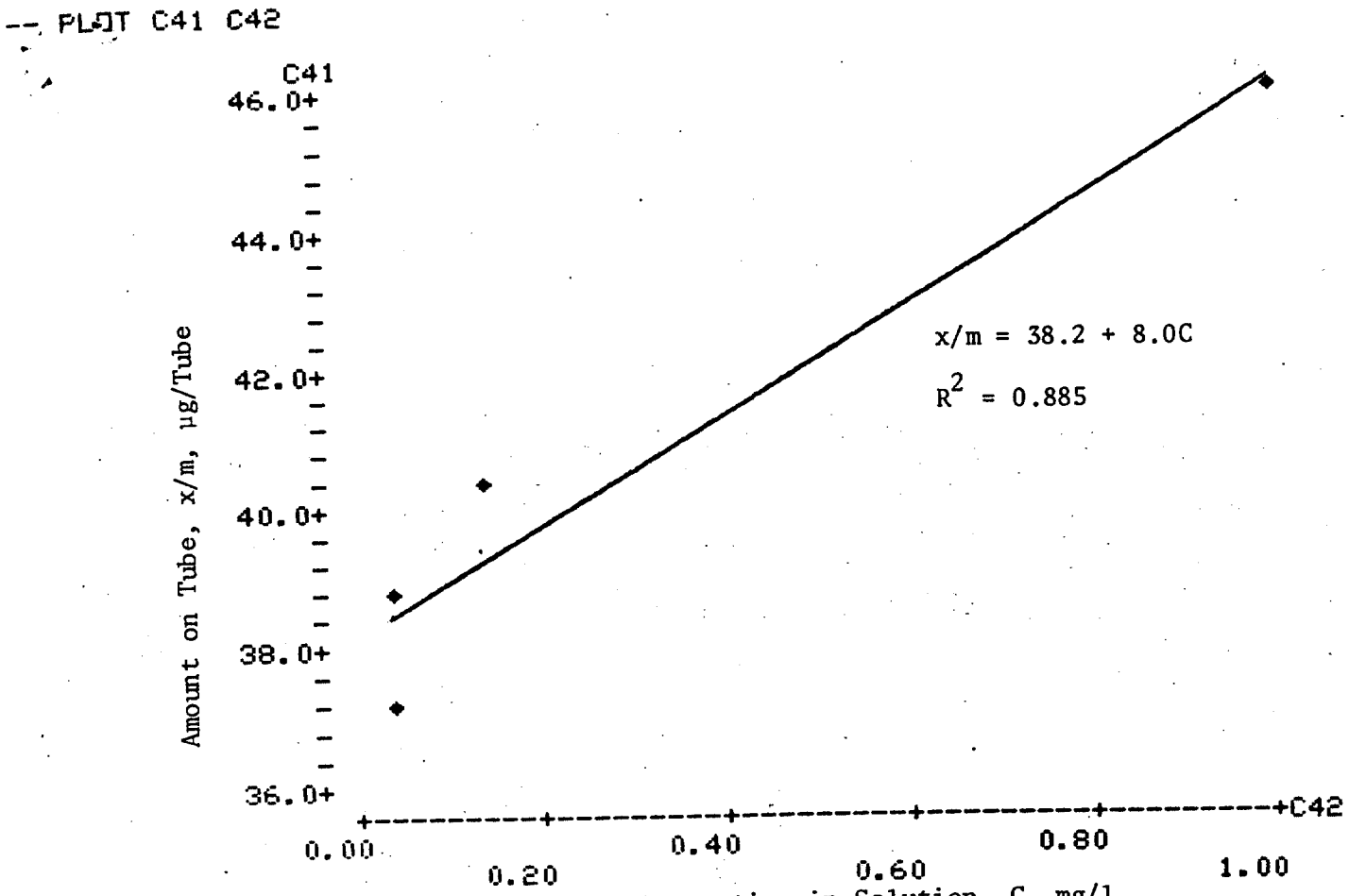

FIGURE 2

FM-3925 DESORPTION FROM GLASS TUBE

TABLE IV

FM-3925 DESORPTION FROM GLASS TUBE DATA

	Equilibrium Conc. in Solution, C, mg/l	Amount Remaining on Tube, x/m, µg/Tube
Initial	1.007	46.1
First Desorption	0.141	40.5
Second Desorption	0.043	38.8
Third Desorption	0.042	27.1

APPENDIX I

RAW FM-3925 SOIL ADSORPTION DATA
(µg/l)

Initial FM-3422 Conc., µg/l

2160 (100%)
1210 (56%)
691 (32%)
389 (18%)
216 (10%
21.6 (1%)

Equil. Conc., C, µg/l
A & B are Duplicate Samples,
Duplicate Injections into GC

A	B
176,177	250
136,140	154,151
104,105	85,80
52,52	46,45
39,38	35,34
<5	<5

Equil. Conc. in First Desorption
A & B are Duplicate Samples,
Duplicate Injections into GC

A	B
120,119	112,112
56,56	62,59
28,25	35,35
16,16	16,17
<5,<5	9,9
<5	<5

Equil. Conc. in Second Desorption
A & B are Duplicate Samples,
Duplicate Injections into GC

A	B
59,59	62,62
42,40	-
11	15
10,9	-
<5	<5,<5
<5	<5

Equil. Conc. in Third Desorption
A & B are Duplicate Samples,
Duplicate Injections into GC

A	B
60,63	44,42
26,26	-
<5,<5	15,15
8,8	8,8
6,6	<5,<5
<5	<5

Control

Control

	A	B
Initial	815,872	1140,1200
1st	185,191	96,94
2nd	86,84	<5,<5
3rd	82	<5,<5

APPENDIX II

AVERAGES OF DUPLICATE INJECTIONS
FROM APPENDIX I
(µg/l)

Equil. Conc. µg/l	
A	B
177	250
138	153
105	83
52	46
39	35

First Desorption	
A	B
120	112
56	61
27	35
16	17
<5	9

Second Desorption	
A	B
59	62
41	-
11	15
10	-
<5	<5

Third Desorption	
A	B
62	43
26	-
<5	15
8	8
6	<5

Control

	A	B	Mean ± S.D.
Initial	844 µg/l	1170 µg/l	1007 ± 231
First Desorption	188	95	141.5 ± 65.8
Second Desorption	85	<5	43 ± 59.4
Third Desorption	82	<5	41.5 ± 57.3