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TECHNICAL REPORT SUMMARY

Date: 2/27/78

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Project: Fate of Fluorochemicals	Project Number: 9970612633
Report Title: Adsorption of FC 95 and FC 143 on soil	Report Number: 1
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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 FC 95 and FC 143 mobility in 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.

As a part of the Fate of Fluorochemicals Project, an indication of mobility of FC 95 and FC 143 in sandy loam soil was desired. Adsorption-desorption experiments (after Davidson, 1976, and Hamaker, 1975) along with water solubility data can provide such information. The adsorption coeffients for FC 95 and FC 143 were determined to be 0.99 and 0.38, respectively. For FC 95 adsorption and desorption could be described by a single valued function while for FC 143, they could not. Based on these data, both compounds would be judged mobile in the sandy loam soil used in this study.

Information Liaison Initials: SKW

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CONCLUSIONS

Adsorption coefficient for FC 95 and FC 143 were 0.99 and 0.38, respectively. For FC 95, adsorption and desorption could be described by a single valued function while for FC 143, they could not. Considering adsorption coefficients, desorption characteristics and water solubilities, both compounds would be judged mobile in the sandy loam soil used in this study.

INTRODUCTION

As a part of the Fate of Fluorochemicals Project, an indication of mobility of FC 95 and FC 143 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. EPA in pesticide registration requirements.

MATERIALS AND METHODS

Duplicate 5-g samples of air-dried Brill sandy loam soil (57% sand, 36% silt, 7% clay, 2.5% organic matter, 1.5% organic carbon, with pH 6.5 and C.E.C. of 15.3 meq./100g) were shaken with 25 ml of solution in 50 ml. polypropylene centrifuge tubes for 24 hours on a wrist action shaker at room temp. (16-19^{o}C). Polypropylene tubes were used because they were found in separate experiments (3M Tech Notebook #470673, C. H. Schrandt) to absorb less FC 95 and FC 143 than glass or polyethylene tubes.

Solutions were made by diluting a stock solution of each chemical. Concentrations of ^{14}C-labeled FC 95 were 282 mg/l., 158 mg/l., 90 mg/l., 51 mg/l., 28 mg/l., (100%, 56%, 32%, 18%, 10%, 1% of stock). Concentrations of ^{14}C-labeled FC 143 were 523 mg/l., 293 mg/l., 167 mg/l., 94 mg/l., 52 mg/l., and 5.2 mg/l.

After shaking the initial solutions as well as the three desorption extractions with deionized water, the samples were centrifuged at 5000 rpm for 10 min., and three aliquots of each supernatant solution were taken for scintillation counting.

After the adsorption step, 22.5 ml of solution were recovered. Therefore, it was assumed that 2.5 ml of liquid remained with the soil in each step and this amount was accounted for in the desorption calculations (see Results and Discussion section).

In the FC 95 experiment, the supernatant liquid was simply drained off at each step and the next 25 ml of liquid were put into the tubes. In the FC 143 experiment, the supernatant liquid remaining after the draining step was absorbed with a cotton swab before putting the next 25 ml of liquid into the tubes.

The procedures for the FC 95 and FC 143 experiments were recorded in 3M Technical Notebook #40673, p. 49 and p. 51, respectively.

From the raw counting data, disintegrations per minute (DPM) and FC 95 and FC 143 concentrations were calculated for all of the supernatant solutions.

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

RESULTS AND DISCUSSION

FC 95

Adsorption data for FC 95 are presented in TABLE I and FIGURE 1. Comparing the regression equation of the adsorption isotherm (FIGURE 1) $x/m = -0.29 + 0.99C$ with the Freundlich equation $x/m = KC^{1/N}$, it could be seen that the adsorption coefficient, K, equaled 0.99 and the exponent, N, equaled one. The linear shape of the adsorption isotherms (N=1) indicated

that FC 95 adsorption on soil would be independent of concentration. The low adsorption coefficient (K=0.99) indicated that FC 95 would be mobile, i.e., it would move readily with the ground water through this sandy loam soil.

TABLE I

FC 95 ADSORPTION DATA

A	B	C
Initial FC 95 Conc., mg/l	Equil. Conc., C, mg/l.	% Removed By Soil $\left(\frac{A-B}{A} \times 100\right)$
282.2	233.9	17.1
158.0	134.2	15.1
90.0	76.9	14.6
51.0	42.0	17.8
28.0	22.1	21.1
2.8	2.0	27.0

D	E	F
Total FC 95 In Initial Sol'n (A x 0.025 liters)	Total FC 95 in Sol'n at Equil., mg (B x 0.025 liters)	FC 95 Adsorbed on Soil, x/m, µg/g $\left((D-E) \times \frac{10^3 \text{ µg/mg}}{5 \text{ g Soil}}\right)$
7.0500	5.84750	240.8
3.9500	3.35500	119.0
2.2500	1.92250	65.7
1.2750	1.05000	45.3
0.7000	0.55250	29.5
0.0700	0.05000	3.8

Desorption data for FC 95 are shown in TABLE II and FIGURE 2. For comparison, desorption isotherms for the pesticide fluometuron are given in FIGURE 3.

For clarity FC 95 desorption isotherms are not drawn in FIGURE 2. However, all of the data points lie very close to the adsorption isotherms indicating that adsorption and desorption could be described by a single-valued function with desorption coefficients, K', equaling the adsorption coefficient, K.

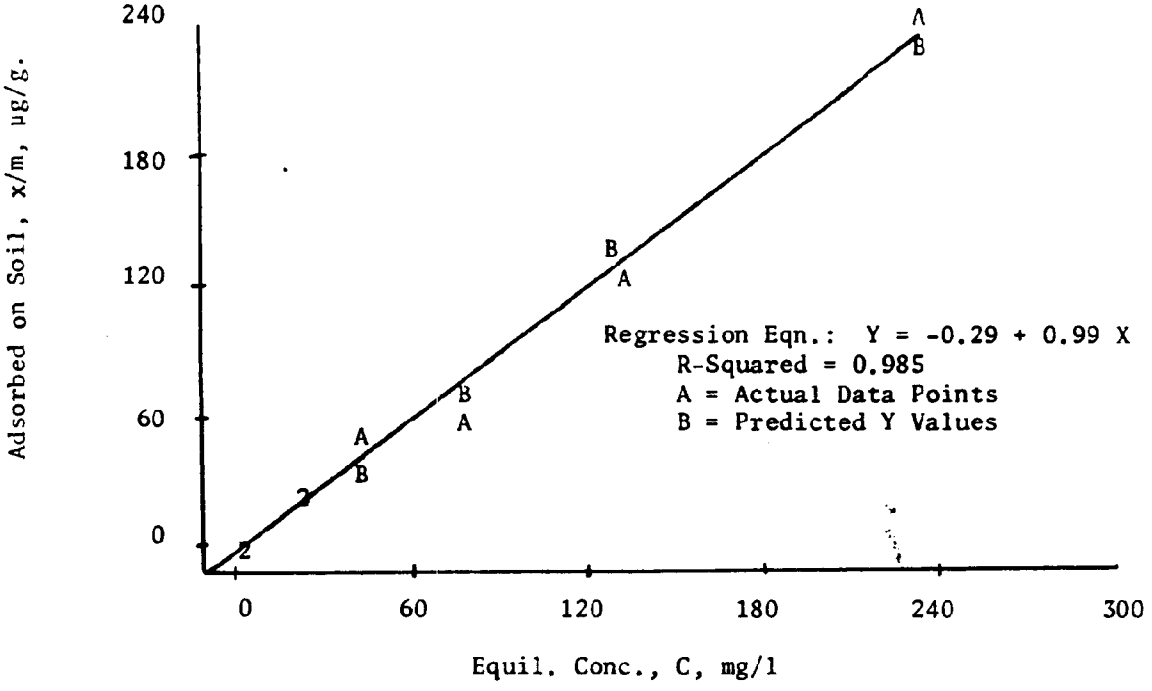

FIGURE 1

FC 95 Adsorption Isotherm

This, along with the observation that approximately all of the adsorbed FC 95 was subsequently desorbed (TABLE II, Column H) indicated that binding forces were weak and would be another indication of high mobility of FC 95.

Material balance data for FC 95 are presented in TABLE III and these data indicate that all of the chemical was accounted for throughout the experiment.

TABLE II

FC 95 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.	D Equil. Conc. in Third Desorption mg/l.
233.900	52.7000	14.9000	5.20000
134.200	30.3000	9.0000	2.80000
76.900	18.3000	5.3000	1.80000
42.000	9.6000	2.9000	1.00000
22.100	5.3000	1.7000	0.60000
2.000	0.6000	0.2000	0.10000

E Amount Adsorbed on Soil, x/m µg/g (Column F, TABLE I)	F Amount on Soil After First Desorption, µg/g	G Amount on Soil After Second Desorption, µg/g	H Amount on Soil After Third Desorption, µg/g
240.800	67.6000	12.0000	-9.1500
119.000	19.4500	-14.9000	-25.8000
65.700	3.3000	-16.7000	-23.9500
45.300	13.2000	2.0500	-2.0000
29.500	11.4000	4.7000	2.2500
3.800	1.7000	0.9000	0.4500

*Columns F, G, and H were calculated in the same way as Column F, TABLE I with correction for the amount of FC 95 in the 2.5 ml of solution remaining from the previous step in each case (See Materials and Methods Section.)

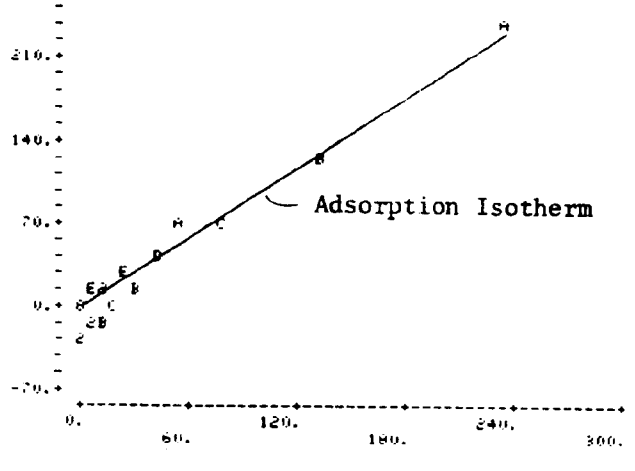

FIGURE 2

FC 95 DESORPTION DATA POINTS AND ADSORPTION ISOTHERM

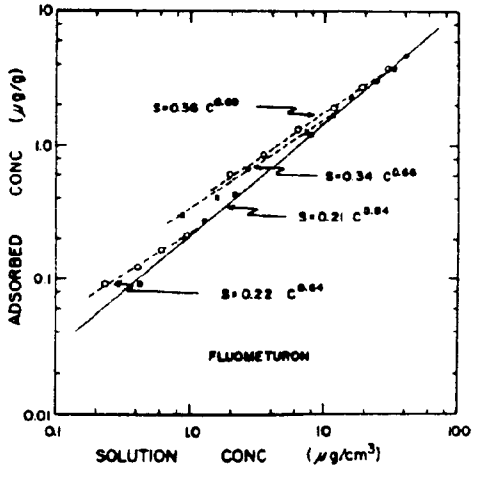

FIGURE 3

ADSORPTION AND DESORPTION ISOTHERMS FOR FLUOMETURON ON COBB SAND. SOLID AND BROKEN LINES ARE BEST FIT FOR ADSORPTION AND DESORPTION, RESPECTIVELY. (From Davidson, et al. 1975)

TABLE III

FC 95 Material Balance*

A Total Initial FC 95 in Solution, mg. (Column D, TABLE I)	B FC 95 in Solution at Equil., mg. (Column E, TABLE I)	C FC 95 on soil at Equil., mg. (A - B)
7.05000	5.84750	1.20250
3.95000	3.35500	0.59500
2.25000	1.99250	0.32750
1.27500	1.0500	0.2250
0.7000	0.55250	0.14750
0.0700	0.05000	0.02000

D Amount Removed by First Desorption, mg.	E Amount Removed by Second Desorption, mg.	F Amount Removed by Third Desorption, mg.
0.864500	0.278000	0.105750
0.497750	0.171750	0.054500
0.311000	0.100000	0.036250
0.159000	0.055750	0.020250
0.090500	0.033500	0.012250
0.011500	0.004000	0.002250

G Total Amount Desorbed by Three Desorptions, mg (D+E+F)	H Amount Remaining on Soil After 3 Desorptions, mg. (C - G)	I Amount Desorbed as Percent of Amount Adsorbed (G/C x 100)
1.2483	-0.45750	103.805
0.7240	-0.12900	121.681
0.4473	-0.11975	136.565
0.2350	-0.01000	104.444
0.1363	0.11250	92.373
0.0178	0.002250	88.750

*Columns D, E, and F were obtained by first calculating the amount (mg) of FC-95 in 27.5 ml (25 ml added plus 2.5 ml remaining from previous step) of solution in each respective step and then subtracting the amount (mg) in the 2.5 ml of solution remaining from the previous step.

FC 143

Data for FC 143 are presented in TABLE IV and TABLE V and in FIGURE 4. The adsorption isotherm indicated FC 143 mobility similar to that of FC 95 with K=0.38 and N=1. Regression analyses were not performed on the desorption isotherms, however, the graphed data (FIGURE 4) indicated that adsorption and desorption could not be described by a single-valued function. That is, the K' and N' values for desorption would not be the same as K and N for adsorption. Subjective evaluation would indicate that the desorption coefficients K', would be much smaller than the adsorption coefficient, K, at solution concentrations greater than about 25 mg/l, since the slope of the adsorption isotherm was much greater than the slopes of the desorption isotherms in this range. At solution concentrations less than 25 mg/l., the desorption coefficients would appear to be much greater than the adsorption coefficient. From this it would appear that two or three different binding mechanisms were involved with stronger binding occuring at the higher concentrations and the converse at lower concentrations. While this may indicate a tendency for FC 143 to be immobile at high concentrations, it would be quite mobile in any situations involving low concentrations.

Material balance data for FC 143 are presented in TABLE VI. While the two concentrations resulting in 212%and 201% desorption (last column in TABLE VI) were erratic, in general, the data indicated that all of the FC 143 was accounted for throughout the experiment.

TABLE IV

FC 143 Adsorption Data

A Initial FC 143 Conc., mg/l.	B Equil. Conc., C, mg/l.	C % Removed By Soil $\left(\frac{A - B}{A} \times 100\right)$
522.5	485.8	7.0
292.6	279.1	4.6
167.2	160.3	4.1
94.1	92.2	2.0
52.3	49.9	4.5
5.2	5.1	1.9

D Total FC 143 in Initial Sol'n, mg (A x 0.025 liters)	E Total FC 143 in Sol'n at Equil., mg (B x 0.025 liters)	F FC 143 Adsorbed on Soil, x/m, µg/g $\left(\frac{(D-E) \times 10^3 \text{ µg/mg}}{5 \text{ g Soil}}\right)$
13.0625	12.1450	183.5
7.3150	6.9775	67.5
4.1800	4.0075	34.5
2.3525	2.3050	9.5
1.3075	1.2475	12.0
0.1300	0.1275	0.5

TABLE V

FC 143 Desorption Isotherm Data*

A	B	C	D
Equil. Conc. in Solution, C, mg/l (Column B, Table IV)	Equil. Conc. in first Desorption Solution, mg/l.	Equil. Conc. in Second Desorption Solution, mg/l.	Equil. Conc. in Third Desorption solution, mg/l.
485.800	47.6000	6.80000	3.50000
279.100	28.8000	4.80000	2.90000
160.300	17.2000	3.40000	2.00000
92.200	10.7000	2.00000	0.50000
49.900	6.1000	0.80000	0.20000
5.100	0.6000	0.10000	0.01000

E	F	G	H
Amount Adsorbed on Soil, x/m, µg/g (Column F, TABLE IV)	Amount on Soil After First Desorption µg/g	Amount on Soil After Second Desorption µg/g	Amount on Soil After Third Desorption µg/g
183.500	164.600	151.000	135.150
67.500	50.850	38.650	25.100
34.500	20.050	9.950	0.650
9.500	-3.250	-8.900	-10.650
12.000	3.400	2.050	1.350
0.500	-0.250	-0.500	-0.505

*Columns F, G, and H were calculated in the same way as Column F, TABLE IV with correction for the amount of FC 143 in the 2.5 ml of solution remaining from the previous step in each case (See Materials and Methods Section).

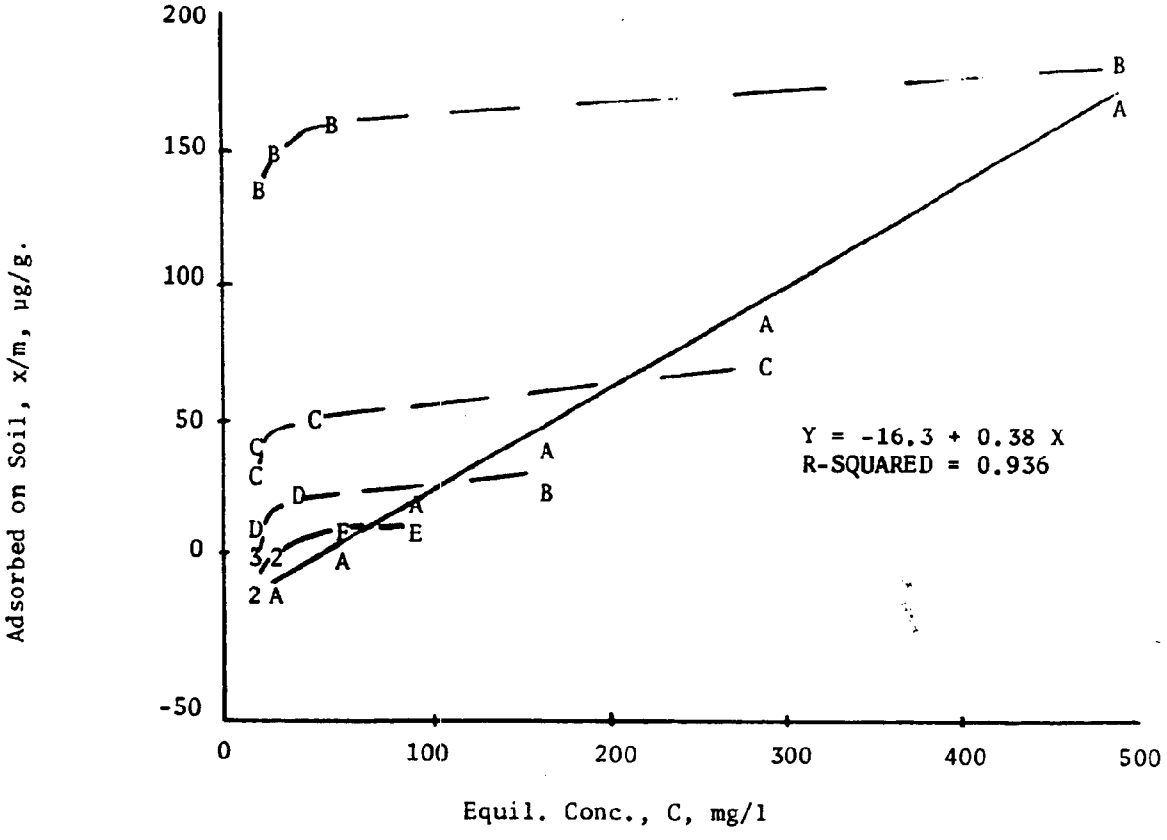

FIGURE 4

FC 143 ADSORPTION AND DESORPTION ISOTHERMS

Solid line is best fit adsorption isotherm. Dotted lines are estimated desorption isotherms. A's are adsorption isotherm data points. B, C, D, E, and F are desorption data points for the respective concentrations.

GENERAL COMMENTS

The FC 95 and FC 143 adsorption coefficients from these experiments may be converted to the analogous constants based on soil organic carbon content, K_{oc}, with the equation K_{oc} = 100 K/(% organic carbon) giving a K_{oc} of 45 for FC 95 and 17 for FC 143 (2.2% organic carbon for this soil). Comparing these values to those in TABLE VII, it can be seen that FC 95 and FC 143 are at the low end of the spectrum, again indicating high mobility of these compounds.

TABLE VI

FC 143 MATERIAL BALANCE*

A	B	C
Total FC 143 Initially in Solution mg. (Column D, Table IV)	FC 143 in Solution at Equil., mg. (Column E, TABLE IV)	FC 143 on Soil at Equil., mg. (A - B)
13.0625	12.1450	0.9175
7.3150	6.9775	0.3375
4.1800	4.0075	0.1725
2.3525	2.3050	0.0475
1.3075	1.2475	0.0600
0.1300	0.1275	0.0025

D	E	F
Amount Removed by First Desorption, mg.	Amount Removed by Second Desorption, mg.	Amount Removed by Third Desorption, mg.
0.09450	0.06800	0.079250
0.08325	0.06100	0.066750
0.07225	0.05050	0.046500
0.06375	0.02825	0.008750
0.04300	0.00675	0.003500
0.00375	0.00125	0.000025

G	H	I
Total Amount Desorbed by Three Desorptions, mg (D+E+F)	Amount Remaining on Soil After 3 Desorptions, mg. (C - G)	Amount Desorbed as percent of Amount Adsorbed (G/C x 100)
0.2418	0.676750	26.349
0.2120	0.125500	62.815
0.1693	0.003250	98.116
0.1008	-0.053250	212.105
0.0535	0.006750	88.750
0.0050	-0.002525	201.000

*Columns D, E, and F were obtained by first calculating the amount (mg) of FC 143 in 27.5 ml (25 ml added plus 2.5 ml remaining from previous step) of solution in each respective step and then subtracting the amount (mg) in the 2.5 ml of solution remaining from the previous step.

TABLE VII

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
	Paraquat	20,000
(immobile)	DDT	243,000

FM3922

15,000

The small amounts adsorbed and ease of desorption is consistent with the relatively high water solubility of FC 95 (300 mg/l) and FC 143 (> 20 g/l.) and with the chemical nature of the molecules - organic salts which ionize in aqueous solution:

$C_8F_{17}SO_3^-K^+$ FC 95

$C_7F_{15}CO_2^-NH_4^+$ FC 143

Terms

DPM - Disintegrations per minute

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' - Desorption coefficient

N - Exponential term in Freundlich Equation

N' - Exponential term for desorption equation

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

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