
Adsorption of FC 95 and FC 143 on Soil (Note: the 3M
Env. Lab summary is titled: Summary of the Soil
Adsorption study of the Potassium Salt of
Perfluorooctanesulfonic acid, 7/22/98)

SOIL ADSORPTION

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. This testing is being repeated per current procedures and best available practices.

METHOD

Method: Adsorption-Desorption study using the approach recommended by the U.S. EPA for pesticide registration

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

Stock and test solution preparation: Test solutions were made by diluting a stock solution of ¹⁴C-labeled Perfluorooctanesulfonate. The type of solvent used to make the stock solution is not noted, nor is the activity of the radio-labeled test substance.

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 gms. Standard solutions of the ¹⁴C-labeled compound were prepared in D.I. water at concentrations of 282 mg/L, 158 mg/L, 90 mg/L, 51 mg/L, and 28 mg/L. Twenty-five ml of each solution was shaken with duplicate 5 gram samples of the soil in a 50 ml polypropylene centrifuge tubes for 24 hours on a wrist shaker at room temperature (16-19°C).

Desorption extraction were performed with D.I. water after the adsorption phase of the experiment. The samples from the adsorption and desorption experiments were centrifuged individually at 5000 rpm for 10 minutes, after which, three aliquots of each supernatant solution were prepared for scintillation counting. From the raw counting data, compound concentrations were calculated for all of the supernatant solutions.

RESULTS

K: 0.99 (N=1)
K_{oc}: 66*

Remarks field: The linear shape of the adsorption isotherms indicated that perfluorooctanesulfonate adsorption on soil would be independent of concentration.

* The study report had calculated a soil / organic carbon partitioning coefficient of 45. After review, it was determined that the value should have been 66 based on the formula ($K_{oc} = K' \times 100 / 1.5(\% \text{ organic carbon})$); $K' = (x/m)/C_e$).

CONCLUSIONS

The study substance is expected to exhibit high mobility in the kind of soil tested and would move with the groundwater.

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

DATA QUALITY

Reliability: Klimisch ranking 2. This study lacks detail on the stock solution and the purity of the radio-labeled test substance. Additionally, some calculations have questionable reliability.

REFERENCES

3M Technical Report "Adsorption of FC 95 and FC 143 on Soil." S.K. Welsh, Project 9970612633 Fate of Fluorochemicals, Report No. 1, Feb. 27, 1978

OTHER

Last changed: 5/2/00

SUMMARY OF THE SOIL ADSORPTION STUDY OF THE POTASSIUM SALT OF PERFLUOROOCTANESULFONIC ACID

Introduction

Soil adsorption-desorption studies were conducted to indicate the mobility of potassium perfluorooctanesulfonate in a sandy loam soil. The approach used was that recommended by the U.S. Environmental Protection Agency for pesticide registration.

Materials and Methods

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./100gms. Standard solutions of the ^{14}C -labeled compound were prepared in D.I. water at concentrations of 282 mg/l, 158 mg/l, 90 mg/l, 51 mg/l, and 28 mg/l. Twenty-five ml of each solution was shaken with duplicate 5 gram samples of the soil in a 50 ml polypropylene centrifuge tubes for 24 hours on a wrist shaker at room temperature (16-19 °C).

Desorption extractions were performed with D.I. water after the adsorption phase of the experiment. The samples from the adsorption and desorption experiments were centrifuged individually at 5000 rpm for 10 minutes, after which, three aliquots of each supernatant solution were prepared for scintillation counting. From the raw counting data, compound concentrations were calculated for all of the supernatant solutions.

Results and Discussion

The linear shape of the adsorption isotherms indicated that potassium perfluorooctanesulfonate adsorption on soil would be independent of concentration. A soil adsorption coefficient (K) of 0.99 indicated that this compound would be mobile in this kind of soil and would move with the groundwater.

A soil organic carbon partitioning coefficient (K_{oc}) was calculated in this report to be 45. However, after closer examination the K_{oc} value should be 66 ($K_{oc} = 100 * K / (1.5\% \text{ organic carbon})$). Again, this value indicates high mobility in this kind of soil.

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 Technical 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
Adsorption of FC 95 and FC 143 in Soil

Material and Methods

Should give recoveries of compounds in blank (no-soil) experiments. States that polypropylene sorbs less than glass on polyethylene, but doesn't give a numerical value.

The large headspace (25 ml in a 50 tube) is undesirable; any losses of the ^{14}C -label, e.g., from volatilization or sticking to the tube, will inflate the sorption coefficient since the method calculates the amount sorbed by difference between the initial and final equilibrium solution concentrations. Also the 24 hour mixing period seems arbitrary. Were experiments done for different periods of time to establish that equilibrium was reached within 24 hours?

Details on the stock solution are lacking. What solvent was used and what is the specific activity and radiochemical purity of the ^{14}C -FC 95.

The idea of using a cotton swab after the draining step is unusual. Hopefully this didn't remove soil as well as water. The ~20% or less decrease in solute concentration due to this isn't as high as I'd like to see it. A 50% or greater decrease would be better.

This section generally lacks detail that would normally be required for.

Results and Discussion

The linearity of the isotherm has been shown over the concentration range used. To demonstrate that the entire isotherm is linear, the linearity must extend to equilibrium concentrations that approach the water solubility of the compound. Do you know of FC95 or FC143? If not, how were the initial solution concentrations selected?

The sorption coefficient (K) of FC 95 appears to be about 1 as indicated. The organic matter normalized sorption coefficient ($K_{\text{om}} = K/f_{\text{om}}$) is $K_{\text{om}} = 1/0.025 = 40$, or $\log K_{\text{om}} = 1.6$. This is a soil sorption coefficient intermediate between benzene and toluene. It would be good to examine some additional soils to confirm this K_{om} value. Generally, the K_{om} values converge within a factor of 2 to 3 for different soils. This would increase the accuracy of the one measured value.

I've spot checked the soil concentrations of FC-95 for both the sorption and desorption experiments and I get essentially the same values. The calculations look good.

The K values for FC 143 is lower than FC 95 indicating that it probably has a lower water solubility. The hysteresis in the desorption isotherm is surprising, and has been observed for many organic compounds. The sorption isotherm is linear indicating a single sorptive process. The conclusion regarding "three different binding mechanisms ... with stronger binding at higher concentrations and the converse at lower concentrations" is very speculative based on the single experiment. If one examines column I "Amount Desorbed as a Percent of Amount Adsorbed" the values range from

*This was
included
in the report*

26 to 212 percent, so it's pretty inconclusive. There is a fairly good discussion of hysteresis in J. Environ. Qual. 12:325-330 by Koskinen and Cheng who observed this phenomena for the weak acid pesticide 2,4,5-T. The causes of hysteresis are varied and complicated and may include microbial degradation of the compound during desorption, and changes in the physical and/or chemical properties of the soil-solution system. For example, desorption using distilled water (as is the case here) could result in soil dispersion so that a clear supernatant solution could not be obtained. This can cause quenching of radioactivity in solution and other problems leading to error.

The "material balance" as presented in the report is a little misleading. To obtain a material balance you should measure the amount of ^{14}C -activity in soil at the end of the experiment, and add it to the measured solution concentrations.

General Comments. The K_{oc} values calculated here use an organic carbon content of 2.2% whereas the value stated in the Materials and Methods is 1.5%? ✓

The water solubilities are cited as 300 mg/L for FC 95 and $> 20\text{g/L}$ for FC 143. Surely the latter value is wrong. If the solubilities are truly that different, then the sorptive properties should be vastly different, which they are not. If FC143 has a solubility of $> 20,000\text{ mg/L}$, then I would expect no sorption. This value must be erroneous.

Recommendations:

1. Obtaining K , K_{oc} values on additional soils. Determine if K_{oc} is relatively constant.
2. Obtain a true mass balance by measuring ^{14}C -activity in soil and solution phase.
3. Interpret desorption data more cautiously.
4. Get correct value of water solubility of FC 143.

TECHNICAL REPORT SUMMARY

Date
2/27/78

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

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

Division	EE & PC
Project	Fate of Fluorochemicals
Report Title	Adsorption of FC 95 and FC 143 on soil
To	D. L. Bacon
Author(s)	Stephen K. Welsh SKW
Notebook Reference	#40673, #47704

SECURITY	☐ Open (Company Confidential)	☐ Closed (Special Authorization)	3M CHEMICAL REGISTRY
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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.

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 coefficients 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.

$K_{oc} =$

$(100)(K) =$ Report is in error

$70 OC$

$(100)(0.99) = 66$

1.5 For FC-95

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°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 ¹⁴C-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 ¹⁴C-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 ($\frac{A-B}{A} \times 100$)
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 ($A \times 0.025$ liters)	Total FC 95 in Sol'n at Equil., mg ($B \times 0.025$ liters)	FC 95 Adsorbed on Soil, x/m, $\mu\text{g/g}$ ($\frac{(D-E) \times 10^3 \mu\text{g/mg}}{5 \text{ g Soil}}$)
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 .

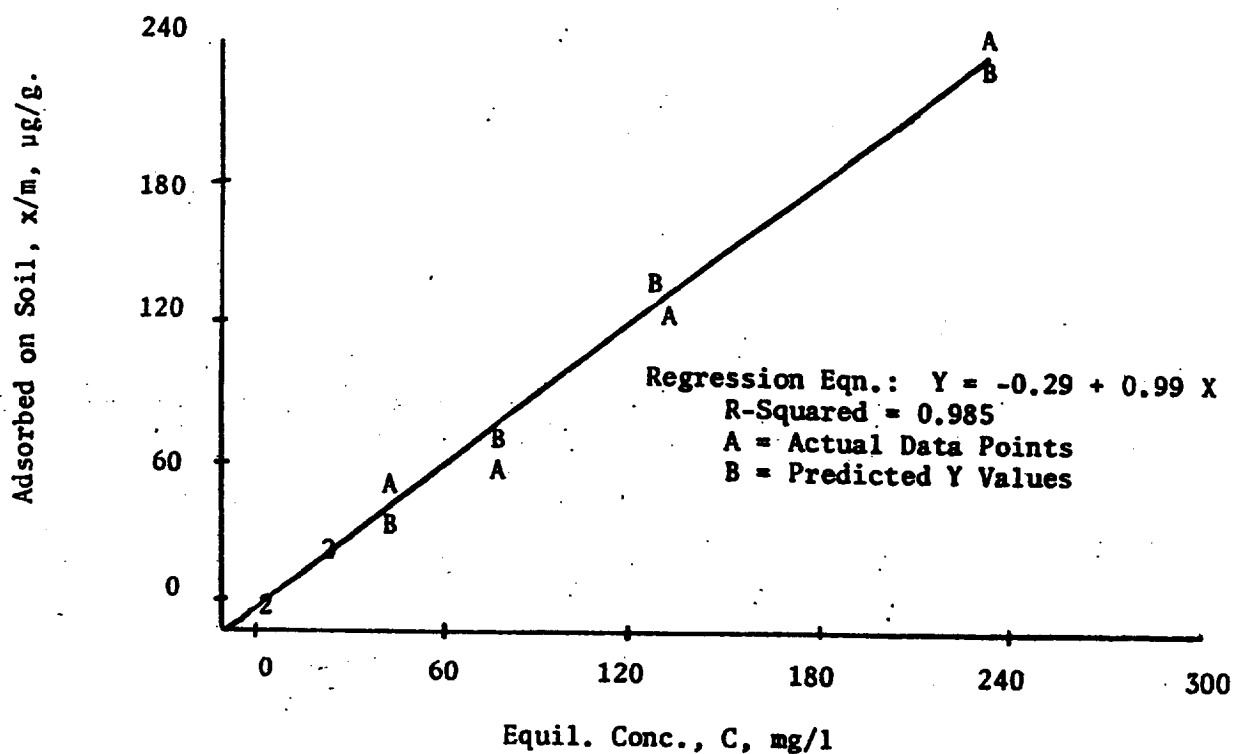


FIGURE 1

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	B	C	D
Equil. Conc. in Solution, C, mg/l.	Equil. Conc. in First Desorption mg/l.	Equil. Conc. in Second Desorption mg/l.	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	F	G	H
Amount Adsorbed on Soil, x/m $\mu\text{g/g}$ (Column F, TABLE I)	Amount on Soil After First Desorption, $\mu\text{g/g}$	Amount on Soil After Second Desorption, $\mu\text{g/g}$	Amount on Soil After Third Desorption, $\mu\text{g/g}$
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.)

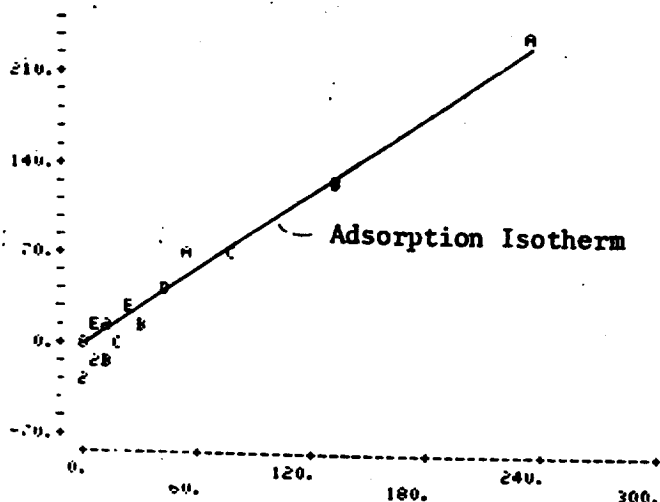


FIGURE 2

FC 95 DESORPTION DATA POINTS
AND ADSORPTION ISOTHERM

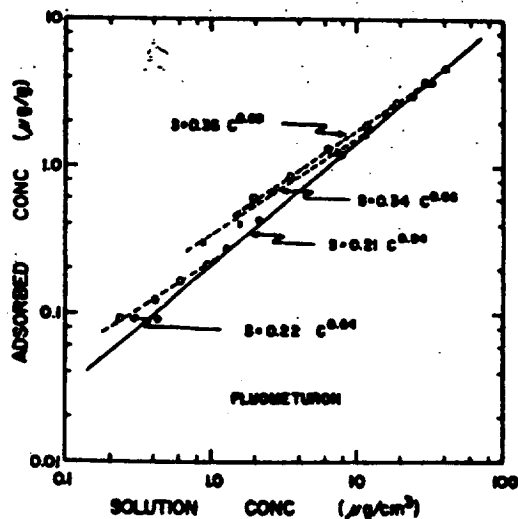


FIGURE 3

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

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 Desorp- tions, 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 occurring 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	B	C
Initial FC 143 Conc., mg/l.	Equil. Conc., C, mg/l.	% Removed By Soil ($\frac{A - B}{A} \times 100$)
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	E	F
Total FC 143 in Initial Sol'n, mg (A x 0.025 liters)	Total FC 143 in Sol'n at Equil., mg (B x 0.025 liters)	FC 143 Adsorbed on Soil, x/m, $\mu\text{g/g}$ (D-E) X $10^3 \frac{\mu\text{g/mg}}{5 \text{ g Soil}}$
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	Equil. Conc. in first Desorp- tion Solution, mg/l.	Equil. Conc. in Second Desorp- tion Solution, mg/l.	Equil. Conc. in Third Desorption solution, mg/l.
(Column B, Table IV)			
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	Amount on Soil After First Desorp- tion μg/g	Amount on Soil After Second Desorp- tion μg/g	Amount on Soil After Third Desorp- tion μg/g
(Column F, TABLE IV)			
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).

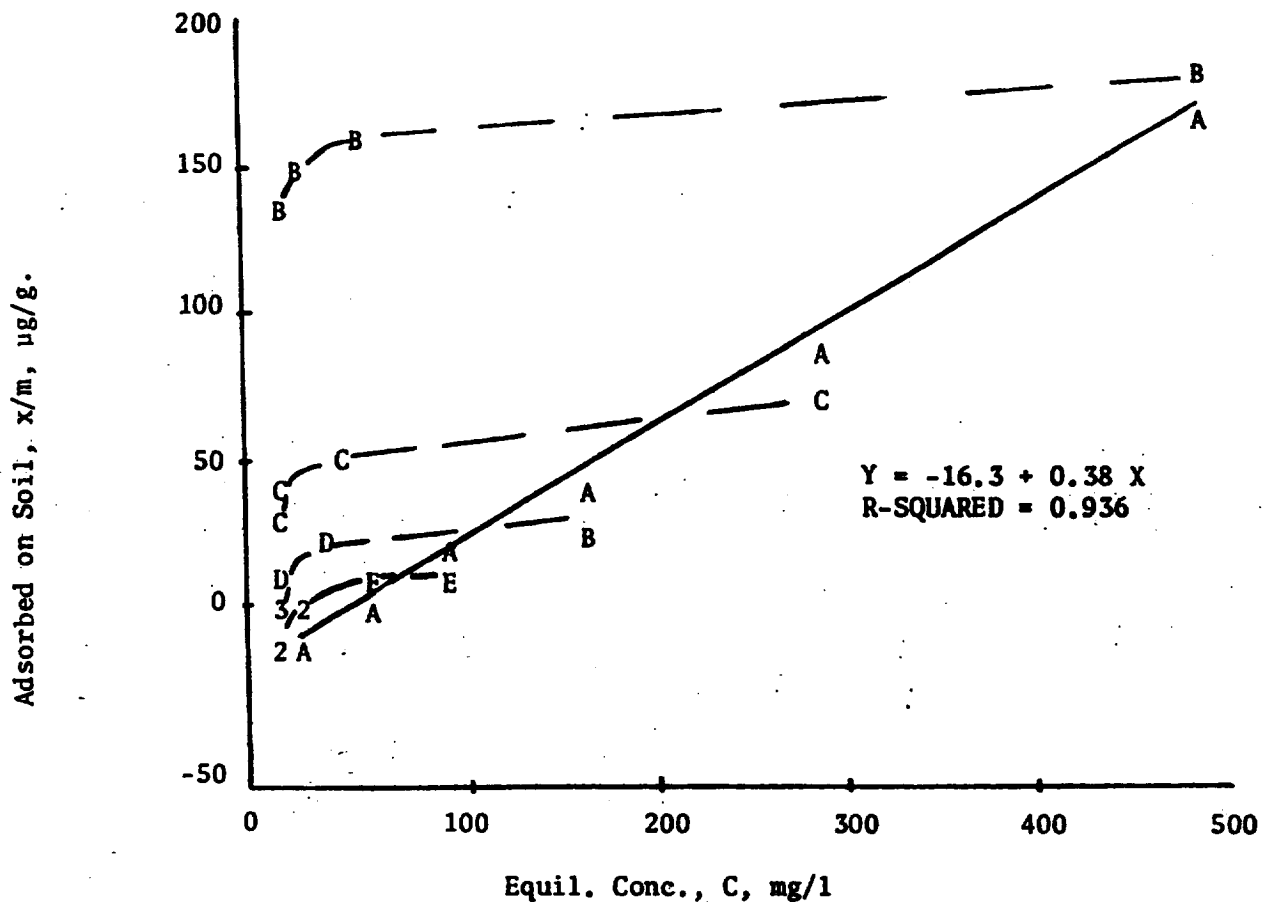


FIGURE 4

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 $K_{oc} = 100 K / (\% \text{ organic carbon})$ 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 De- sorbed by Three Desorptions, mg (D+E+F)	Amount Remaining on Soil After 3 Desorp- tions, mg. (C - G)	Amount Desorbed as percent of Amount Ad- sorbed (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

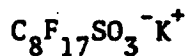
*Columns D, E, and F were obtained by first calculating the amount (mg) of FC 143 in 27.5 ml (25 ml added plus 2.5 ml remaining from previous step) of solution in each respective step and then subtracting the amount (mg) in the 2.5 ml of solution remaining from the previous step.

TABLE VII

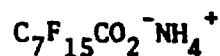
Comparison of Adsorption Coefficients
for a Selected Group of Pesticides
(Hamaker and Thompson, 1972)

	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
	Chloroprotham	245
	Prometone	300
	Ametryn	380
	Diuron	485
	Prometryne	513
	Chloroxuron	4,986
(immobile)	Paraquat	20,000
	DDT	243,000

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:



FC 95



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
- R² - 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

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. 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.
- 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, Mich. 48640

Attached are comments on the 3M Technical Report "Adsorption of FC 95 and FC 143 on Soil. S.K. Welsh, Project 9970612633 Fate of Fluorochemicals, Report No. 1, Feb. 27, 1978" made by Professor Stephen A. Boyd, Michigan State University, dated May 19, 1993.

Review of Technical Report Summary Adsorption of FC 95 and FC 143 in Soil

Material and Methods

Should give recoveries of compounds in blank (no-soil) experiments. States that polypropylene sorbs less than glass on polyethylene, but doesn't give a numerical value.

The large headspace (25 ml in a 50 tube) is undesirable; any losses of the ^{14}C -label, e.g., from volatilization or sticking to the tube, will inflate the sorption coefficient since the method calculates the amount sorbed by difference between the initial and final equilibrium solution concentrations. Also the 24 hour mixing period seems arbitrary. Were experiments done for different periods of time to establish that equilibrium was reached within 24 hours?

Details on the stock solution are lacking. What solvent was used and what is the specific activity and radiochemical purity of the ^{14}C -FC 95.

The idea of using a cotton swab after the draining step is unusual. Hopefully this didn't remove soil as well as water. The ~20% or less decrease in solute concentration due to sorption isn't as high as I'd like to see it. A 50% or greater decrease would be better.

This section generally lacks detail that would normally be required for publication.

Results and Discussion

The linearity of the isotherm has been shown over the concentration range used. However, to demonstrate that the entire isotherm is linear, the linearity must extend to equilibrium solution concentrations that approach the water solubility of the compound. Do you know the solubility of FC95 or FC143? If not, how were the initial solution concentrations selected?

The sorption coefficient (K) of FC 95 appears to be about 1 as indicated. The organic matter normalized sorption coefficient ($K_{\text{om}} = K/f_{\text{om}}$) is $K_{\text{om}} = 1/0.025 = 40$, or $\log K_{\text{om}} = 1.6$. This is a soil sorption coefficient intermediate between benzene and toluene. It would be worthwhile to examine some additional soils to confirm this K_{om} value. Generally, the K_{om} values should converge within a factor of 2 to 3 for different soils. This would increase my confidence in the accuracy of the one measured value.

I've spot checked the soil concentrations of FC-95 for both the sorption and desorption experiments and I get essentially the same values. The calculations look good.

The K values for FC 143 is lower than FC 95 indicating that it probably has a higher water solubility. The hysteresis in the desorption isotherm is surprising, and has been over-interpreted. The sorption isotherm is linear indicating a single sorptive process. The conclusion regarding "three different binding mechanisms ... with stronger binding at higher concentrations and the converse at lower concentrations" is very speculative based on the single experiment. If one examines column I "Amount Desorbed as a Percent of Amount Adsorbed" the values range from

26 to 212 percent, so it's pretty inconclusive. There is a fairly good discussion of hysteresis in J. Environ. Qual. 12:325-330 by Koskinen and Cheng who observed this phenomena for the weak acid pesticide 2,4,5-T. The causes of hysteresis are varied and complicated and may include microbial degradation of the compound during desorption, and changes in the physical and/or chemical properties of the soil-solution system. For example, desorption using distilled water (as is the case here) could result in soil dispersion so that a clear supernatant solution could not be obtained. This can cause quenching of radioactivity in solution and other problems leading to error.

The "material balance" as presented in the report is a little misleading. To obtain a material balance you should measure the amount of ^{14}C -activity in soil at the end of the experiment, and add it to the measured solution concentrations.

General Comments. The K_{oc} values calculated here use an organic carbon content of 2.2% whereas the value stated in the Materials and Methods is 1.5%?

The water solubilities are cited as 300 mg/L for FC 95 and $> 20\text{g/L}$ for FC 143. Surely the latter value is wrong. If the solubilities are truly that different, then the sorptive properties should be vastly different, which they are not. If FC143 has a solubility of $>20,000\text{ mg/L}$, then I would expect no sorption. This value must be erroneous.

Recommendations:

1. Obtaining K , K_{oc} values on additional soils. Determine if K_{oc} is relatively constant.
2. Obtain a true mass balance by measuring ^{14}C -activity in soil and solution phase.
3. Interpret desorption data more cautiously.
4. Get correct value of water solubility of FC 143.

TECHNICAL REPORT SUMMARY

Date
2/27/78

TO: TECHNICAL COMMUNICATIONS CENTER - 201-2CN

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

Division EE & PC		Dept. Number 0222
Project Fate of Fluorochemicals		Project Number 9970612633
Report Title Adsorption of FC 95 and FC 143 on soil		Report Number 1
To D. H. BAACON		
Author(s) Stephen K. Welsh SKW		Employee Number(s) 73583
Notebook Reference #40673, #47704		No. of Pages Including Coversheet 14
SECURITY ☐ Open (Company Confidential)	☐ Closed (Special Authorization)	3M CHEMICAL REGISTRY ☐ 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.

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 coefficients 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.

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°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 ¹⁴C-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 ¹⁴C-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 ($\frac{A-B}{A} \times 100$)
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, $\mu\text{g/g}$ ($\frac{D-E}{5 \text{ g Soil}} \times 10^5 \frac{\mu\text{g}}{\text{mg}}$)
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 .

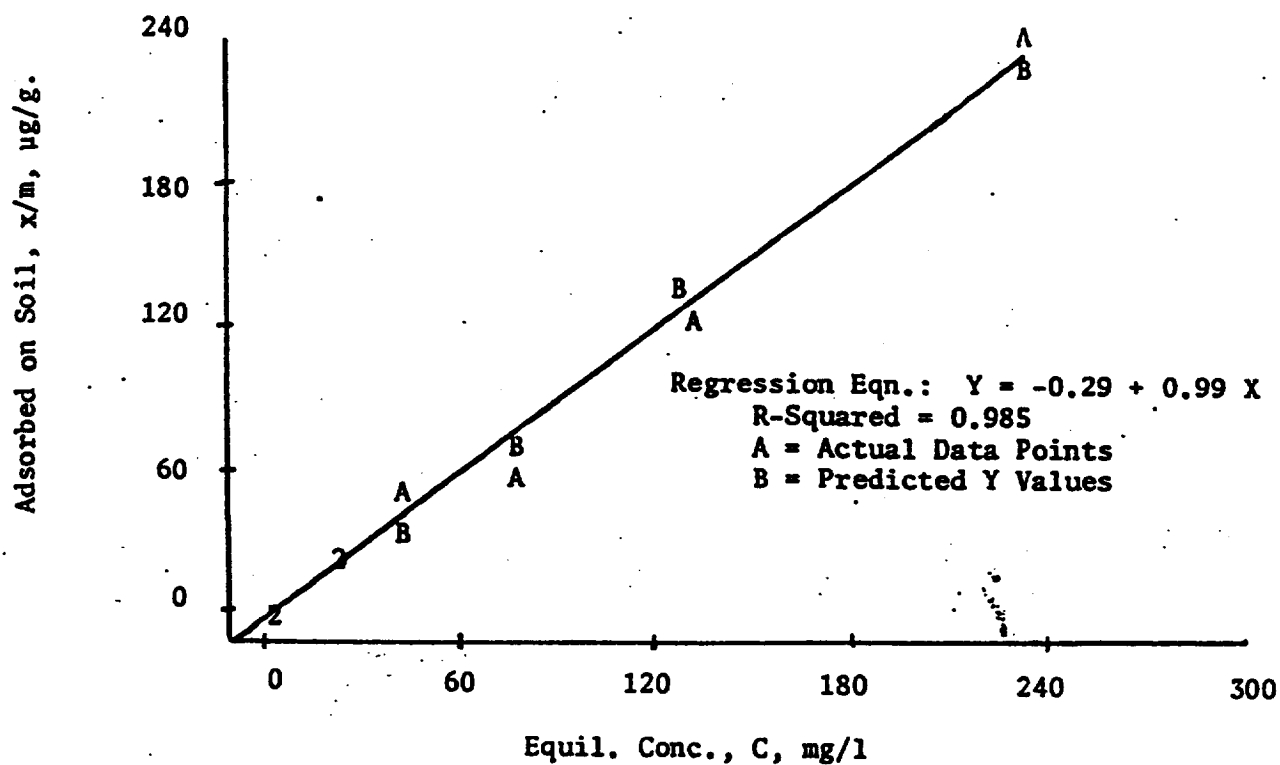


FIGURE 1

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	B	C	D
Equil. Conc. in Solution, C, mg/l.	Equil. Conc. in First Desorption mg/l.	Equil. Conc. in Second Desorption mg/l.	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	F	G	H
Amount Adsorbed on Soil, x/m $\mu\text{g/g}$ (Column F, TABLE I)	Amount on Soil After First Desorption, $\mu\text{g/g}$	Amount on Soil After Second Desorption, $\mu\text{g/g}$	Amount on Soil After Third Desorption, $\mu\text{g/g}$
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.)

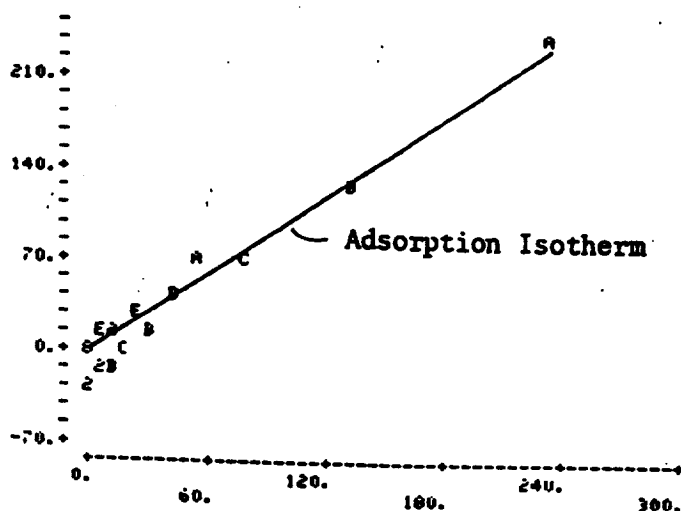


FIGURE 2

FC 95 DESORPTION DATA POINTS
AND ADSORPTION ISOTHERM

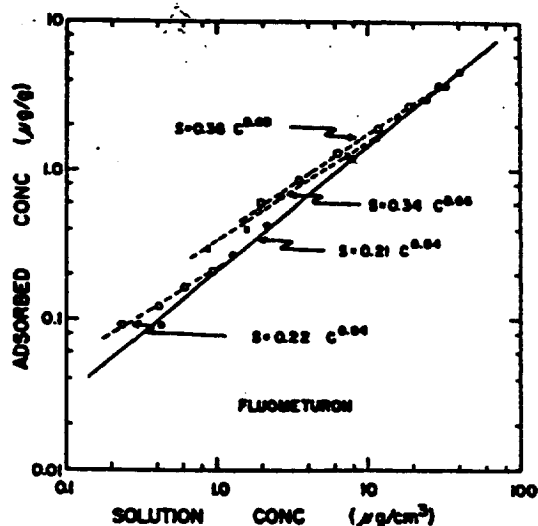


FIGURE 3

ADSORPTION AND DESORPTION ISOTHERMS FOR
FLUOMETURON ON COBB SAND. SOLID AND BROKEN
LINES ARE FOR ADSORPTION AND

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 Desorp- tions, 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 occurring 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	B	C
Initial FC 143 Conc., mg/l.	Equil. Conc., C, mg/l.	% Removed By Soil ($\frac{A - B}{A} \times 100$)
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	E	F
Total FC 143 in Initial Sol'n, mg (A x 0.025 liters)	Total FC 143 in Sol'n at Equil., mg (B x 0.025 liters)	FC 143 Adsorbed on Soil, x/m, $\mu\text{g/g}$ (D-E) X $10^3 \frac{\mu\text{g/mg}}{5 \text{ g Soil}}$
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	Equil. Conc. in first Desorp- tion Solution, mg/l.	Equil. Conc. in Second Desorp- tion Solution, mg/l.	Equil. Conc. in Third Desorption solution, mg/l.
(Column B, Table IV)			
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	Amount on Soil After First Desorp- tion μg/g	Amount on Soil After Second Desorp- tion μg/g	Amount on Soil After Third Desorp- tion μg/g
(Column F, TABLE IV)			
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).

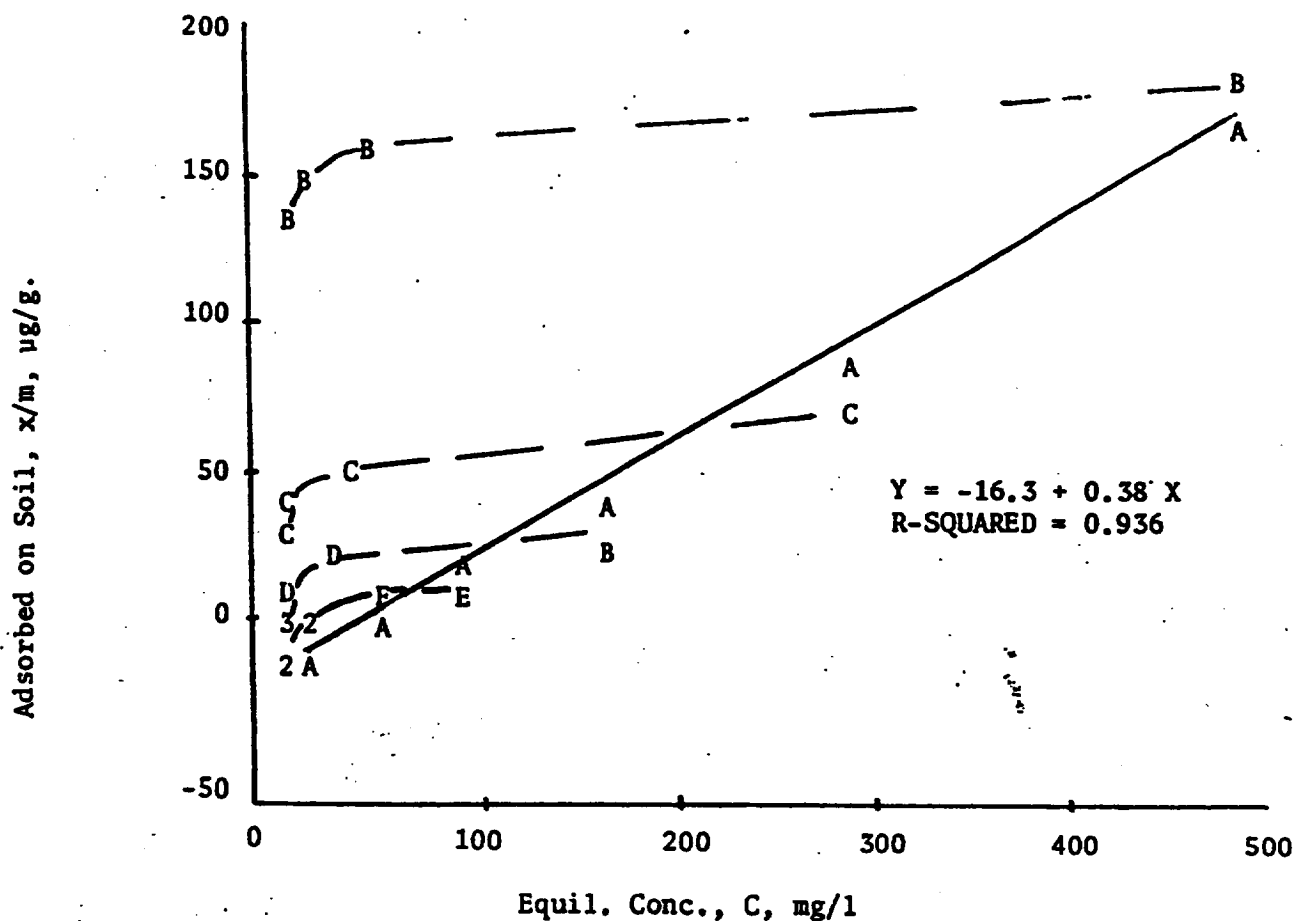


FIGURE 4

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 $K_{oc} = 100 K / (\% \text{ organic carbon})$ 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 De- sorbed by Three Desorptions, mg (D+E+F)	Amount Remaining on Soil After 3 Desorp- tions, mg. (C - G)	Amount Desorbed as percent of Amount Ad- sorbed (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

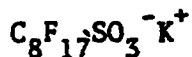
*Columns D, E, and F were obtained by first calculating the amount (mg) of FC 143 in 27.5 ml (25 ml added plus 2.5 ml remaining from previous step) of solution in each respective step and then subtracting the amount (mg) in the 2.5 ml of solution remaining from the previous step.

13
TABLE VII

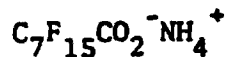
Comparison of Adsorption Coefficients
for a Selected Group of Pesticides
(Hamaker and Thompson, 1972)

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	FH 3722	15,000
	Paraquat	20,000		
	DDT	243,000		
(immobile)				

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:



FC 95



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

References

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- 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.
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- 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, Mich. 48640