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To: D. L. Bacon	
Author(s): Arthur Mendel	Employee Number(s): 043939
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CURRENT OBJECTIVE:

Progress Report

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.

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INTRODUCTION

This report describes supporting analytical work not detailed in reports on bioassay, die-away, soil absorption-desorption, solubility, and the like on various fluorochemicals.

DISCUSSION AND RESULTS

The loss of FM 3422 on rotary evaporation of its water solutions was noted previously (1) , and only ten percent of FM 3422 was recovered; see the experimental section of this report for details. In another experiment, a water solution of FM 3422 was allowed to evaporate under ambient conditions with essentially complete loss of FM 3422. Interestingly, similar losses of PCB's in water due to volatilization were reported (2). Note that the solubility of PCB's in water is very similar to that of FM 3422 (around 1 ppm or less). In the case of PCB's, volatilization was minimized by working in a cool environment and covering samples with a layer of hexane.

The distribution coefficient for FM 3422 was reported earlier (3), wherein the solubility of FM 3422 in water was not completely defined but based on experimental work, thought to be less than 0.05 ppm. This value was based on water solutions filtered through various size membranes and examining the aqueous filtrate with a light beam (Tyndall effect). It is known that membrane filters contain impurities which may interfere by removing a substrate in water or otherwise contaminating the water (4,5). The solubility of FM 3422 in water using the Veith technique (6) was calculated to be 0.05 ppm, and the distribution coefficient for FM 3422 is thus $330{,}000_6$ppm (in n-octanol) divided by 0.05 ppm (in water) or $P = 6.6 \times 10^6$.

N-alkyl-substituted perfluorooctanesulfonamides have been shown to undergo alkaline and acidic hydrolysis; however, the reaction takes days (7). A pilot study on the basic ethanolysis of FM 3422 also confirmed that this substrate is not rapidly degraded (46269-45) and that the salt of perfluorooctanesulfonic acid was formed (infrared and TLC studies). Accordingly, a kinetic study was conducted on FM 3422 using 10% potassium hydroxide in absolute ethanol (to ensure complete solution). The reaction rate obeyed first order kinetics with a rate constant $K = 9 \times 10^{-3}$ hr^{-1} and a half life of seventy-seven hours.

In earlier studies (8), glass containers were shown to be satisfactory for the quantitative recovery of FM 3422 from water in the parts per million (ppm) or less concentration range. In the current work, similar aqueous solutions of FC-95 could be kept in polypropylene, but not in polyethylene, polycarbonate, or glass. Aqueous solutions of FC-143 could be kept in polypropylene; polyethylene and glass were less suitable. These studies were done with radioactive compounds (see experimental).

Based on studies to date, it appears that compounds such as FC-95 and FC-143, which have highly ionizable groups adhere to glass (which may be considered to have an ionic surface) but not to plastic (hydrocarbon or nonionic surface). For quantitative recoveries then, such compounds should be stored in plastic containers. On the other hand, nonpolar compounds, such as FM 3422, adhere (dissolve?) to plastic but not to glass, and the latter would be the container of choice. Another rationale involves the distribution coefficient. Samples which have a high distribution coefficient (i.e., are very lipophilic) would prefer to adhere (dissolve?) to plastic compared to glass (so use glass containers), while samples which have a low distribution coefficient (i.e., are very hydrophilic) would prefer to adhere to glass compared to plastic (so use plastic containers).

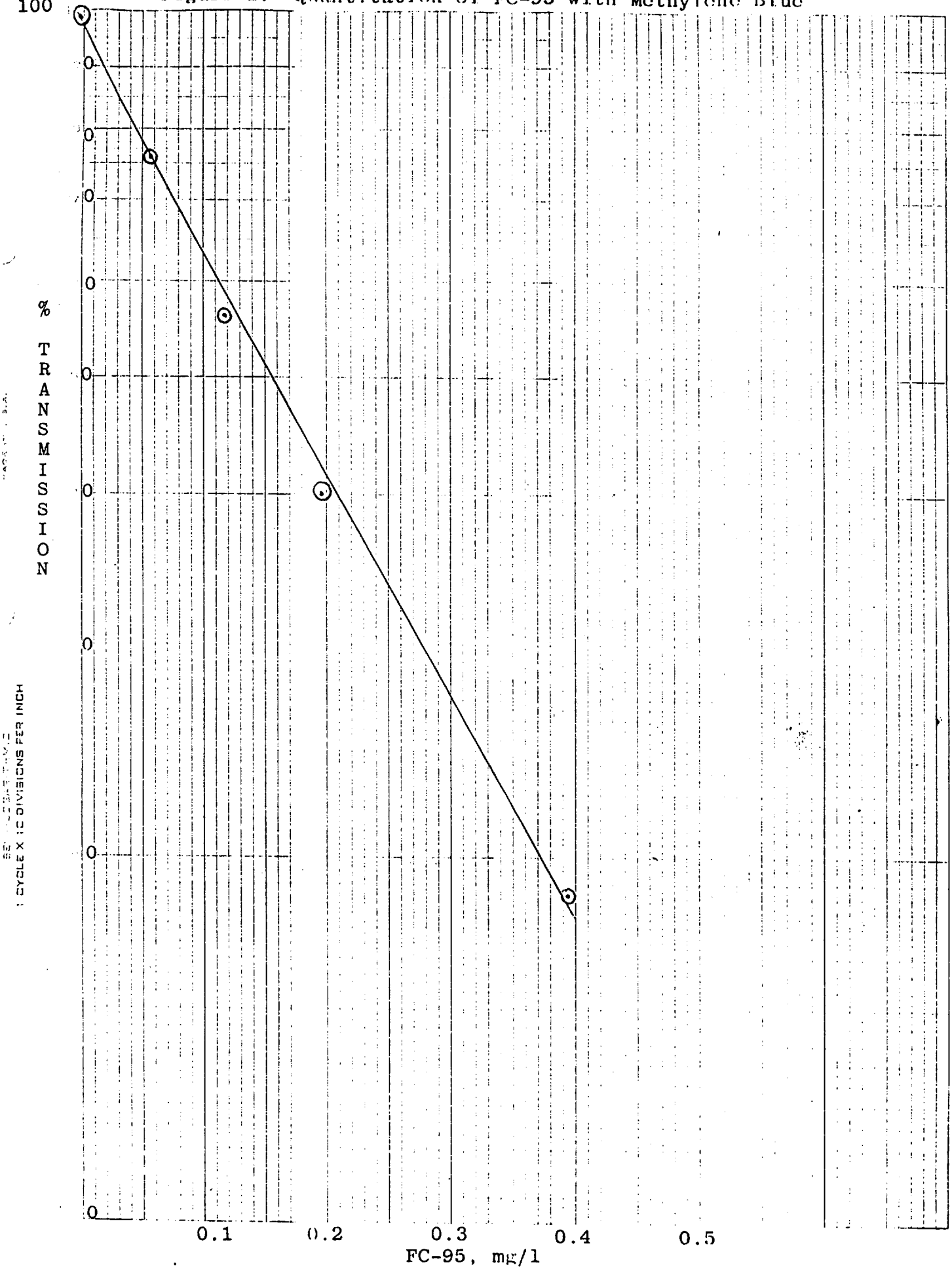
The use of the proper aquaria (glass or plastic) and the most suitable containers for shipping water samples and fish back to the Environmental Laboratory for further analyses was made known to Bionomics Laboratory personnel before they conducted critical life stage studies on FC-95, FC-143, and FM 3422. Aluminum foil-lined caps, used to seal bottles containing aqueous solutions of FM 3422, were also examined before use for possible contaminants that might interfere with subsequent GC analyses; no interferences were observed.

Since a simple, rapid method for quantitation of FC-95 is still not available, the methylene blue procedure for methylene blue active substances (MBAS, (10)) was used to quantitate FC-95. A linear range from 0.4 to 0.06 ppm was noted on semilog paper (Figure 1). Of course, MBAS, such as linear alkyl sulfonates (detergents), if present, will give a positive interference.

TLC and GC were also performed on die-away experiments with radio-labeled FC-95 and FC-143. Die-away samples were spotted directly on E. Merck silica gel TLC plates which were then developed and visualized by autoradiography. A comparison with controls showed no new compounds were formed respectively. Samples including controls were methylated and gas chromatographed to see if any new volatile materials were generated but none were observed in either case. GC of the samples prior to methylation also indicated that no new compounds were formed in each case.

Chiou and co-workers (9) published an article which described an empirical equation relating experimental n-octanol/water distribution coefficients to aqueous solubilities of many organic materials. Their correlation, which covered more than eight orders of magnitude in solubility (from 10^{-3} to 10^{4} ppm) and six orders of magnitude in distribution coefficient (from 10 to 10^{7}), may allow an assessment of distribution coefficient from solubility with a predicted error of less than one order of magnitude. Furthermore, these workers observed a correlation between the bioconcentration factors in

Figure 1. Quantitation of FC-95 with Methylene Blue



rainbow trout and the aqueous solubilities for some stable organic compounds. It was of interest to apply their empirical equations to solubility, bioconcentration factor, and distribution coefficient data obtained in the Environmental Laboratory on FM 3422, FC-95, and FC-143. Results are summarized in Figures 2 and 3 (11).

Soil thin-layer chromatography (soil TLC) of pesticides appears to offer a simple, yet reliable, method of evaluating relative mobility in soils, even though a universal "standard" soil has not been designated. The advantages of soil TLC include rapidity, reproducibility, and low equipment costs.

In the current study, a soil-coated TLC plate was spotted with radiolabeled FM 3422, FC-95, and FC-143, and the ascending water-developed plate was visualized by autoradiography. Results show that none of the samples appear to migrate (R_f=0). Soil TLC in the descending development mode will be done to simulate the leaching of materials through soil.

To date, no evidence has been noted for the biodegradation of FM 3422. It was thought that electrochemical oxidation (voltammetry) might be successful. If so, the potential required would be an indication of the ease or difficulty of oxidation of this alcohol to the aldehyde and/or acid. Furthermore, it was hoped that voltammetry (i.e., oxidation potential) might be a good general physical-chemical predictor of the biodegradation of a candidate. In this work, FM 3422 in acetonitrile was not oxidized by electrochemical procedures using a platinum electrode. Under the same conditions, n-butanol was not oxidized either (CRL Req. B34247). It appears that this method is probably not a good index for the "oxidation potential" of a candidate organic.

Figure 2
Relationship of Partition Coefficients to Water Solubility
of Organic Compounds

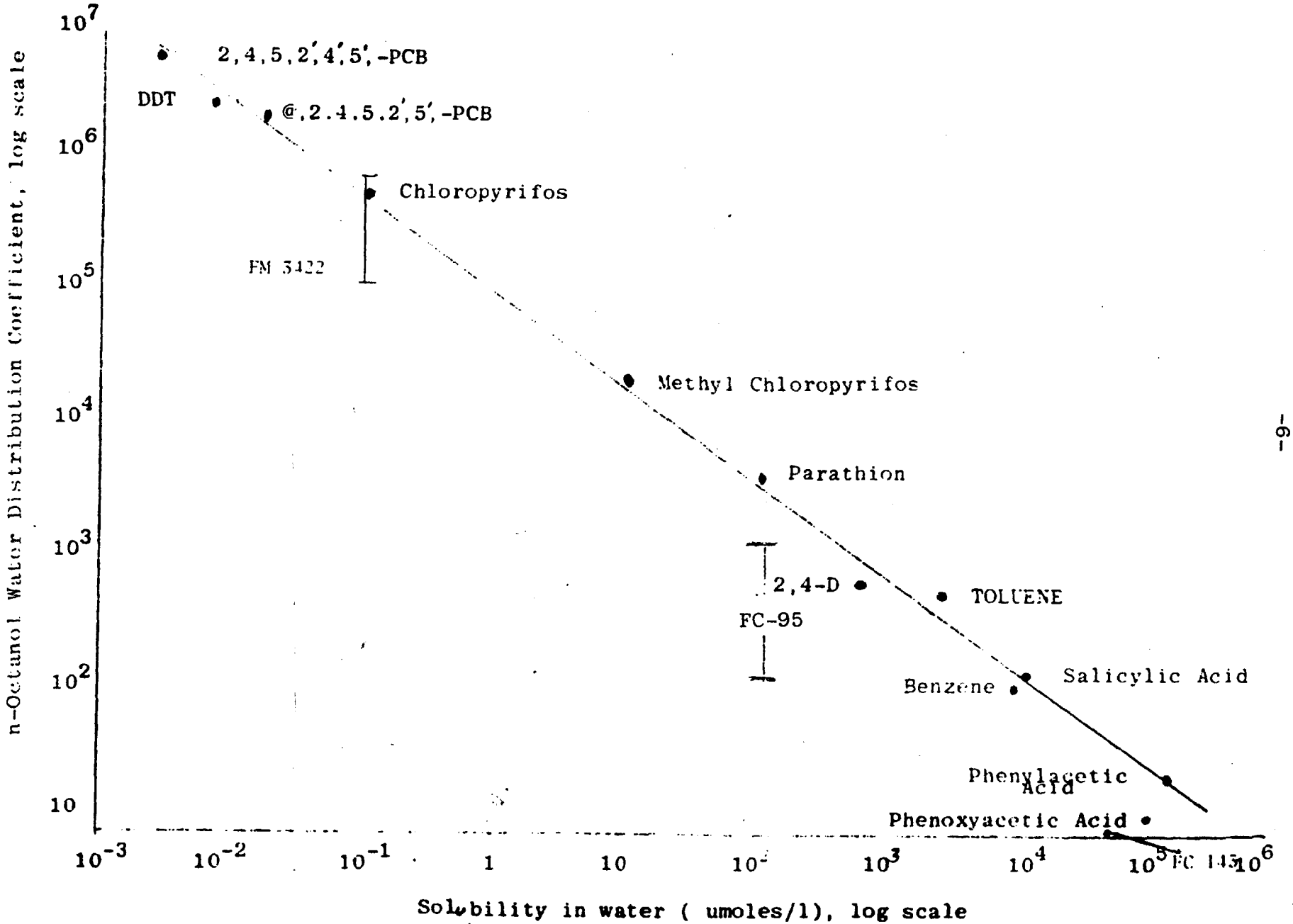
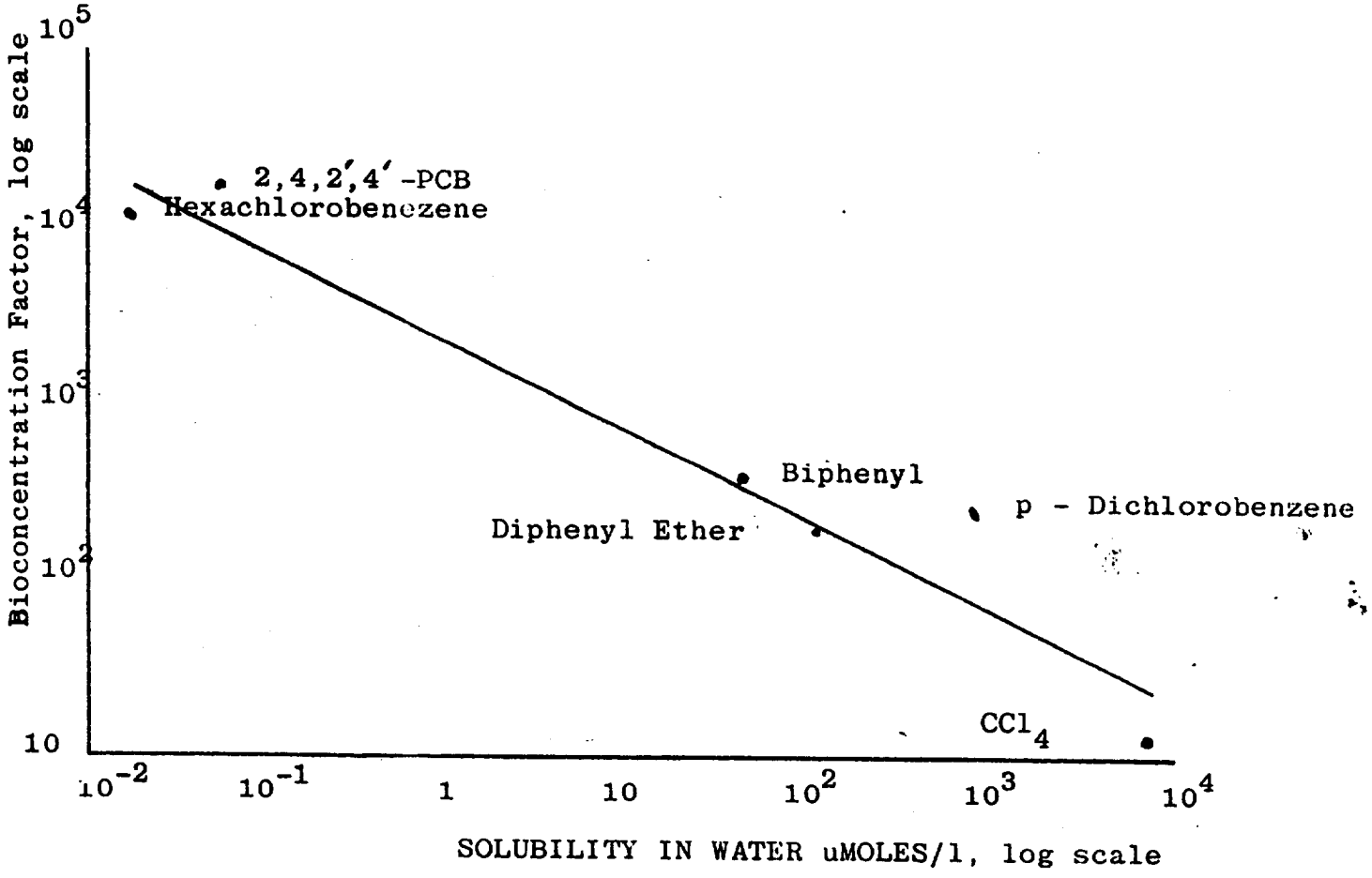


Figure 3

Relationship of Bioconcentration Factor
to Water Solubility of Organic Compounds



EXPERIMENTAL

Volatility Studies on FM 3422

A. Rotary Evaporation under Reduced Pressure (41947-38,-39,-40)

Water, saturated with FM 3422 conducted in aquaria (see 42669-17), was used for samples, and a 5 ppm reference of FM 3422 in methanol was also prepared. GC analyses indicated the water thus saturated had a 5 ppm concentration of FM 3422 (note that this is high, based on the Veith technique used later. This high value may be due to supersaturation and/or micelle formation because these liquids had a large Tyndall effect, and the solutions were not filtered). A 25-ml water sample above was concentrated on a rotary evaporator under water aspirator pressure. The residue was taken up in octanol and gas chromatographed. Results showed that only 0.5 ppm of FM 3422 remained. A replicate experiment indicated that only 0.6 ppm of FM 3422 remained. Thus about ninety percent of this alcohol was lost due to volatilization.

B. Evaporation under Ambient Conditions (44191-43, -44; 46269-32)

A saturated aqueous solution of FM 3422 prepared and determined by the Veith technique (6; see 44191-43 and references therein) was shown to have a concentration of 0.05 ppm. For the evaporation study, 100 ml (vol. pipet) of this solution was transferred to a beaker and its contents allowed to evaporate (ca. 1.5 weeks). The beaker was rinsed with 2 ml (vol. pipet) of methanol, and an aliquot was gas chromatographed. Results indicated that 0.007 ppm of FM 3422 remained.

Reaction of FM 3422 with Alcoholic Potassium Hydroxide (48277-29, -31, -39; 46269-4, -5):

An alcoholic potassium hydroxide solution was prepared in a 500-ml round-bottomed flask (containing two joints, one a ℔ 24/40 female and the other a ℔ 10/30 female for aliquot withdrawal, and containing a teflon-coated magnetic stirrer bar, and an air-cooled condenser topped with an Ascarite^{R} protection tube) by dissolving 11.6 g of 86.2% potassium hydroxide (10 g if 100% KOH) in 200 ml of absolute alcohol. This solution was then maintained at 50-53^{o} by an external oil bath for the duration of the experiment (504 hours).

One milliliter aliquots were withdrawn from this solution with a volumetric pipet through the normally closed ℔ 10/30 entry port. This aliquot was quantitatively transferred to a 25-ml volumetric flask containing about 10 ml of absolute alcohol, one drop of phenolphthalein solution and three drops of concentrated nitric acid. The purpose was to stop any further reaction and to neutralize the base which proved to adversely affect the gas chromatographic

column used subsequently. The volumetric flask was diluted to the mark with absolute alcohol, and an aliquot of this solution was subjected to gas chromatographic analysis on the Hewlett-Packard Model 5813 gas chromatograph using electron capture detection.

To the above alcoholic KOH solution was added 40 mg of sublimed FM 3422, and immediately thereafter (solution of the FM 3422 required about 1 minute) a 1-ml aliquot was withdrawn and designated as time zero. Aliquots were removed and analyzed at times indicated in Table 1 and illustrated in Figure 4. A first-order reaction rate is shown by the following kinetic treatment (12):

$$\ln(a-x) = -kt + \ln a \qquad \text{or}$$

$$\ln_{10}(a-x) = \frac{-k\ t}{2.303} + \ln_{10} a$$

Since for any experiment, a is a constant, the above is an equation for a straight line. When plotting ln(a-x) versus t, $\ln_{10} a$ will be the y intercept (found to be 2.2) with the slope equal to $-k/2.303$) and found to be -0.004.

Table 1
Alkaline Alcoholysis of FM 3422

t (hrs.)	C (ppm)*	$\ln_{10} C$
0	169	2.22
1	178	2.25
4	176	2.24
7	165	2.22
24	135	2.13
48	111	2.04
72	88	1.94
96	73	1.86
168	44.4	1.65
216	27.5	1.44
264	20.3	1.31
336	7.3	0.86
384	0.6	0.78
432	1.2	0.04
504	**	

* This number represents the average of two replicates done in duplicate.
** Poor electronic integration - no results:

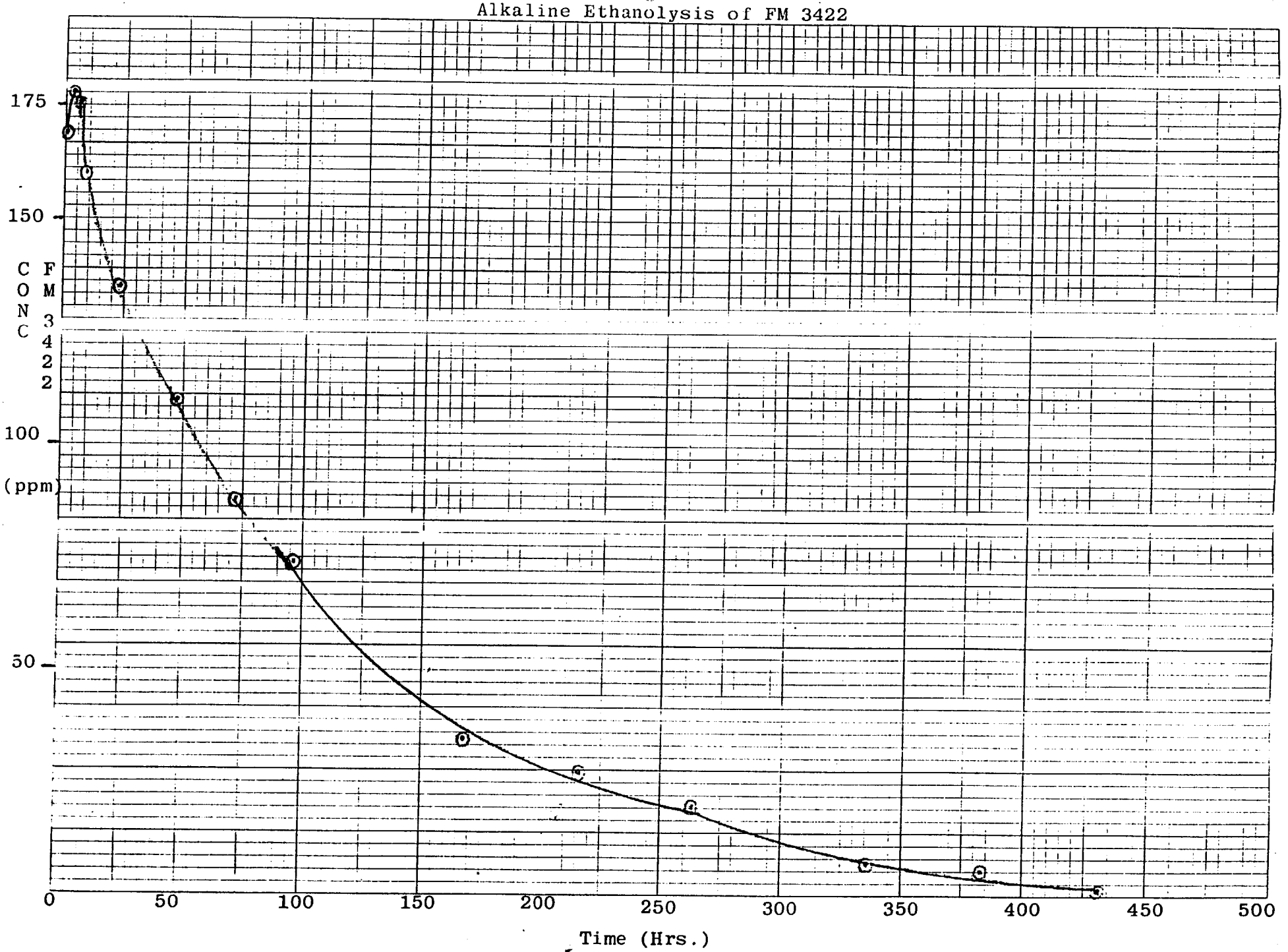
A plot of $\ln_{10} C$ versus time gives a slope of -0.004;

Since $k = -2.303$ (slope) then
$k = -2.303 \times -0.004 = 9 \times 10^{-3}\ hr^{-1}$

$$\text{half life} = t_{\frac{1}{2}} = \frac{1}{k} \cdot \ln 2 = \frac{0.693}{9\times10^{-3}} = 77 \text{ hrs.}$$

Figure 4

Alkaline Ethanolysis of FM 3422



FM 3422 Sorption onto Soil (46269-50)

Sorption-desorption soil studies were conducted by S. K. Welsh, and the results are given in Table 2.

Soil TLC (48277-30)

Various types of soil were ground and sieved, and that fraction of 262 micron size was saved for TLC studies (42669-42). An intimate mixture of 150 g of 262 micron size greenhouse soil (sandy loam) with 80 ml of water was well slurried and spread onto 10 x 20 cm glass plates using an in-house designed spreader (designed by J. W. Belisle, A. Mendel, and G. Guthrie). The plates were allowed to air dry. A plate was spotted 2 cm from the bottom with radiolabeled-FC-95, -FC-143, and-FM 3422. The samples were those used earlier for water solubility studies. The plate was air-dried and developed 100 mm from the original spot in the ascending mode with water in a filter paper-lined TLC developing tank previously equilibrated with water for one day. The development required nearly two hours and the air-dried plate was then autoradiographed (13). Results showed that FC-143 and FM 3422 did not leave the origin (R_f=0). The spot, due to FC-95, was extremely faint for visualization but appears not to have migrated either (R_f=0).

Preliminary Studies on Samples from Bionomics Labs

A. Examination of Foil-lined Caps for Interferences (46269-50)

Four foil-lined caps which Bionomics Labs uses to seal bottles containing samples were screwed onto four clean bottles containing 25 ml of deionized water. The bottles were mechanically shaken for 4 hours, and the combined 100 ml of water was extracted with ethyl acetate. This extract was concentrated and chromatographed. No apparent interference for FM 3422 was noted. This extract was then spiked with FM 3422 to confirm no interference at the retention time of FM 3422.

B. Examination of Standards and Controls Prepared at Bionomics Lab

Personnel from Bionomics Labs prepared standard solutions of FM 3422 in water, then submitted one-liter samples of these standards and controls to us for analyses. The respective sample was extracted with ethyl acetate and the organic extract was concentrated to 10 ml. An aliquot was used then for GC analyses, and the results are summarized in Table 3 (Notebook 46269-50).

Table 2

Sorption-Desorption Studies on FM 3422*

Sample	Day	FM 3422 (ppm)	Day	FM 3422 (ppm)	Day	FM 3422 (ppm)
32A	2/22/78	0.01	2/23/78	<0.002	2/24/78	0.002
32B	2/22/78	0.01	2/23/78	0.002	2/24/78	0.002
56A	2/22/78	0.01	2/23/78	0.003	2/24/78	<0.002
56B	2/22/78	0.22	2/23/78	0.005	2/24/78	<0.002
100A	2/22/78	0.22; 0.20	2/23/78	0.014; 0.019	2/24/78	<0.002
100B	2/22/78	0.19; 0.21	2/23/78	0.010; 0.011	2/24/78	<0.002
BKA	2/22/78	0.48; 0.51	2/23/78	0.044; 0.035	2/24/78	
BKB	2/22/78	0.49	2/23/78	0.029; 0.029	2/24/78	

*See interoffice memo of S. K. Welsh to D. L. Bacon, FC Project, Soil Adsorption, Sept. 22, 1977 for methodology.

Table 3

Analyses for FM 3422 (in ppb) in Bionomics Samples

Sample I.D.	Theoretical Conc. (ppb)	Determined
A5609	20	20.8; 19.8
A5610	20	19.8; 20.6
A5611	10	10.2; 9.9
A5612	10	9.7; 10.1
A5613	5	5.2; 5.2
A5614	5	4.8; 5.1
A5615	2.5	2.5; 2.6
A5616	2.5	1.2; 1.3
A5617	1.25	(a)
A5618	1.25	(a)
A5619	Control A	<0.1
A5620	Control B	<0.1
A5621	Solvent Control A	<0.1
A5622	Solvent Control B	<0.1
A5670	1.25	1.1; 1.0(b)
A5670	1.25	1.0; 1.6(b)

(a) received broken in shipment; (b) replaces original samples A5617; A5618

C. Examination of Water Samples for Possible Interferences of FC-143 (46269-53)

As done in Part B above, seven samples of water, received from Bionomics Labs were extracted with ethyl acetate, followed by diazomethane methylation and gas chromatography to determine if the water and the various containers holding samples may present interferences for the analysis of FC-143. All samples appeared to be free of interferences in the GC region for FC-143 analysis.

Studies on FC-95:

To Determine if FC-95 is Sorbed On/In Containers (47703-20, -22, -24)

Three 0.20-ml samples of ^{14}C FC-95 (aqueous solutions saturated by the Veith technique (42669-30)) were transferred to scintillation vials to which 15-ml Aquasol^{R} was added in each case. These control samples were labeled C-1, C-2, and C-3. Ten milliliters of the ^{14}C FC-95 saturated solution was transferred to each of the following containers: Polypropylene (PP), polyethylene (PE), polycarbonate (PC), and glass (G). Each container was tightly capped and allowed to stand at room temperature for one week, at which time the solutions were transferred to glass jars. The various containers were rinsed twice with 2-ml water and the rinses added to the respective jar. By pipet, 0.2 ml of the solution was transferred from the jar into a scintillation vial. This was repeated two times to generate three samples from each jar. Aquasol^{R} was added to each scintillation vial and then counted (13). These vials were labeled PP-1, PP-2, etc. Each of the saved containers from above was rinsed a first and a second time with 4 ml of methanol, and each rinse was transferred to a separate, clean vial. By pipet, 1 ml of the respective methanol rinse above was transferred to each of three scintillation vials containing Aquasol^{R} and then counted. The samples were labeled using the notation above, but the letter F for first rinse and S for the second rinse was added to the designation, e.g., PPF-1 indicates polypropylene container, first methanol rinse of the first sample, while GS-2 indicates a glass container, second methanol rinse of the second sample. The results are summarized in Table 4: Polypropylene was the first container of choice followed by polyethylene.

Studies on FC-143:

To Determine if FC-143 is Sorbed On/In Containers (47703-30, -37; 49400-51)

This experiment was performed essentially like that for FC-95, with the exception that the polycarbonate containers were not investigated. Various solvents attack polycarbonate (e.g., ethyl acetate). Control samples C-1, C-2, and C-3, as well as the 500-ppm ^{14}C FC-143 solution were transferred to polypropylene (PP)-, polyethylene (PE)-, and glass (G)-containers. Each container was tightly capped and allowed

Table 4

Sorption Studies on FC-95 (Labeled)

Part 1: Scintillation Counting on Samples

Sample	dpm	Conc. mg/l FC-95	µg absolute	Avg. µg
C-1	15,163	266	2660	
C-2	16,058	282	2820	2750
C-3	15,735	276	2760	
PP-1	11,294	198	2770	
PP-2	10,523	184	2580	2730
PP-3	11,585	203	2840	
PE-1	11,278	198	2770	
PE-2	11,808	207	2900	2870
PE-3	11,994	210	2940	
PC-1	11,493	201	2810	
PC-2	11,558	203	2840	2790
PC-3	11,138	195	2730	
G-1	11,840	208	2910	
G-2	11,252	197	2760	2850
G-3	11,760	206	2880	

Part 2: Scintillation Counting on Rinses

PPF-1	15.9	0.06	0.24	
PPF-2	16.8	0.06	0.24	0.19
PPF-3	7.22	0.02	0.08	
PPS-1	5.80	0.02	0.10	
PPS-2	<Background	0.00	0.00	0.03
PPS-3	<Background	0.00	0.00	
			Avg. Total	0.27
PEF-1	50.5	0.18	0.72	
PEF-2	60.5	0.21	0.84	0.71
PEF-3	40.5	0.14	0.56	
PES-1	26.1	0.09	0.45	
PES-2	4.66	0.02	0.10	0.37
PES-3	31.0	0.11	0.55	
			Avg. Total	1.08

Table 4 (continued)

Sample	dpm	Conc. mg/l FC-95	µg absolute	Avg. µg
PCF-1	1829	6.41	25.6	
PCF-2	1865	6.54	26.2	26.4
PCF-3	1958	6.86	27.4	
PCS-1	270.3	0.95	4.75	
PCS-2	294.0	1.03	5.15	4.78
PCS-3	254.0	0.89	4.45	
			Avg. Total	31.18
GF-1	140.9	0.49	1.96	
GF-2	140.6	0.49	1.96	1.99
GF-3	146.1	0.51	2.04	
GS-1	126.8	0.44	2.20	
GS-2	118.6	0.42	2.10	2.17
GS-3	125.5	0.44	2.20	
			Avg. Total	4.16

to stand at room temperature for one week, at which time the solutions were transferred to glass jars. The various containers were rinsed twice with 2 ml of water and the rinses added to the respective jar. By pipet, 0.2 ml of the solution was transferred from the jar into a scintillation vial. This was repeated two times to generate three samples from each jar. Aquasol^R was added to each vial and then counted. These vials were labeled PP-1, PP-2, etc. Each of the saved containers from above was rinsed a first and a second time with 4-ml methanol, and each rinse was transferred to a separate, clean vial (in the case for the glass container, 3 ml rather than 1 ml of methanol was used for the first transfer, thus GF-2 contained 1 ml of rinse and GF-3 had to be eliminated). By pipet, 1 ml of the respective methanol rinse above was transferred to each of three scintillation vials containing Aquasol^R and then counted. The samples were labeled with the notation mentioned earlier. The results are given in Table 5. Polypropylene, the container of choice, was used in subsequent experiments.

Solubility of FC-95 in Water (47703-15)

The Veith technique (6) for saturating water with organics was conducted using radiolabeled FC-95 as described in Notebooks 287103-5 and 42669-30. Three 0.25-ml samples were withdrawn from the saturator at 0, 1, 2, 4, 6, 24, and 48 hours. The samples were placed in scintillation vials to which 15 ml of Aquasol^R was added, and counts were taken on the Nuclear Chicago scintillation counter (Agrichem). The solubility results are tabulated below:

Hr.	mg/l FC-95
0	0
1	226
2	238
4	282
6	280
24	292
48	291

Avg. (Hrs. 4-48) = 286

Quantitation of FC-95 by the Methylene Blue Method (47703-44)

FC-95 was quantitated by the methylene blue method for methylene blue-active substances as detailed in Standard Methods for the Examination of Water and Wastewater (10). Known concentrations of FC-95 (100 ml, see below) were added to each of five separatory funnels followed by 25 ml of methylene blue reagent and 10 ml of chloroform. The funnels were shaken for one-half minute and the contents were allowed to separate. The desired organic phase was withdrawn through glass wool and collected. The percent transmission of the organic phase was determined after the Spectronic 20 instrument was first calibrated (652 nm) with chloroform. The concentration versus percent transmission is shown in Table 6 and illustrated in Figure 1.

Table 5

Sorption Studies on FC-143 (Labeled)

Part 1: Scintillation Counting on Samples

Sample	dpm	Conc. mg/l FC-143	µg absolute	Avg. µg
C-1	34,456	534	5340	
C-2	34,521	535	5350	5350
C-3	34,599	536	5360	
PP-1	24,829	385	5390	
PP-2	24,560	381	5334	5325
PP-3	24,190	375	5250	
PE-1	23,664	367	5138	
PE-2	24,078	373	5222	5143
PE-3	23,409	362	5068	
G-1	24,962	387	5418	
G-2	25,546	396	5544	5465
G-3	25,002	388	5432	

Part 2: Scintillation Counting on Rinses

PPF-1	293	0.91	3.6	
PPF-2	270	0.84	3.4	3.6
PPF-3	296	0.92	3.7	
PPS-1	21.5	0.07	0.35	
PPS-2	20.9	0.06	0.30	0.35
PPS-3	25.3	0.08	0.40	
			Avg. Total	3.95
PEF-1	16,936	52.5	210	
PEF-2	17,268	53.5	214	213
PEF-3	17,430	54.0	216	
PES-1	859	2.7	13.5	
PES-2	849	2.6	13.0	13.0
PES-3	802	2.5	12.5	
			Avg. Total	226
GF-1	13,530	14.0	56.0	
GF-2	4,414	13.7	54.8	55.4
GS-1	124	0.38	1.9	
GS-2	129	0.40	2.0	1.0
GS-3	126	0.39	2.0	
			Avg. Total	57.4

Table 6

FC-95 by Methylene Blue

Concentration of FC-95 (ppm)	% Transmission
0.0	100
0.06	76
0.12	56
0.20	40
0.40	17

Note that FC-95 can be quantitated in this range; however, the limitations are that any methylene blue-active substances such as anionic surfactants or other sulfonic acids will present a positive interference.

GC Calibration and Recovery Studies on FC-143 (46269-34, -54)

The purpose of this work was to prepare absolute standards of FC-143 and to evaluate recovery from water. An internal standard of perfluorodecanoic acid (obtained from Dr. Jon Belisle, CRL) was prepared by weighing and dissolving 0.100 g of this acid into 100 ml of hexane (1000 ppm). A standard of 1000 ppm of FC-143 (lot 83) was made by weighing and dissolving 0.100 g of FC-143 in 100 ml of methanol. For acidification of aqueous solutions, 1 g of p-toluene sulfonic acid (PTSA) in 100 ml of methanol (10^4 ppm) was prepared, and 2-3 drops of this solution was added to extractants prior to diazomethane methylation. Samples prepared for GC was as follows: In a 20-ml vial was placed 5 ml benzene and in a second vial was placed 5 ml of 10% ether in hexane. Each vial was spiked with 20 µg of the FC-143 and with 20 µl of the internal standard. Three drops of PTSA were added to each vial followed by ethereal diazomethane. After 15 minutes of reaction time, excess diazomethane was removed (N_2 purge) and the samples were diluted to 10 ml (volumetric flask) followed by GC. Results showed that benzene was superior to ether-hexane as a solvent (larger integrator response). Furthermore, the electron capture response to FC-143 (as the methyl ester) was different from that to the perfluorodecanoic acid (as the methyl ester). Accordingly, various concentrations of both these acids were made, followed by methylation and gas chromatography. An average response factor was thus obtained. Hen, 0.1 and 1 ppm standards of FC-143 were prepared in water. The water sample, containing the internal standard acid, was benzene extracted, concentrated, acidified (PTSA), and methylated in the usual manner. GC of the samples showed recoveries of 93% and 100.4% for the 0.1 ppm solution and 90.9% and 99.4% for the 1 ppm solution.

TLC OF Biodegradation Studies on Radioactive FC-95, FC-143, and FM 3422 (47703; 6-14, 21, 25-27, -35; 39-43, 46)

Details of the biodegradation studies on labeled FC-95, FC-143, FM 3422, and controls are described in E. A. Reiner's report (14). In the present work, the nineteen samples each from sludge, water, and ethyl acetate extracts generated from biodegradation studies were applied directly to plates (20x20 cm, E. Merck GF 254 silica gel). The plates were developed in ethyl acetate then examined first by ultraviolet light (long and short wavelength) and then by autoradiography. The plates were exposed to Kodak x-ray film for one week, and the film was then developed and examined. Comparison with control samples indicated no significant differences.

In a second part of this experiment, a portion of the ethyl acetate extract from the various samples was methylated with diazomethane to convert any nonvolatile components to GC volatile species. Both the unmethylated and methylated samples were then analyzed by gas chromatography. No differences were noted between these and control samples. GC conditions are detailed in Notebook 47703-43.

Determination of the Solubility of N-Methyl FOSE Alcohol FM 3925 (48277-8; 46269-53; 42669-4)

About 20 g of FM 3925 Lot 505 was melted (steam bath) to obtain a homogeneous sample. The cooled, solid material, 200 mg, was dissolved in about 200 ml of reagent grade acetone, and this solution was added to precleaned 2 mm diameter solid glass beads contained in a beaker. Beads were precleaned successively with heptane, chloroform, acetone, water, methanol, and then air dried. The FM 3925 coated glass beads were placed in a glass column (350x18 mm) and supported by glass wool (pretreated with Glastreat^{R}). The end rubber stoppers were connected to Bev-Line V^{R} tubing and a peristaltic pump was used to circulate deionized water through the column. The entire setup was conducted in the dark in a temperature-controlled walk-in environmental room (18±1°). Prior to the start of this experiment, water was pumped for 5 hours through the setup, and this water was discarded. The purpose of this was to remove any impurities that would be as soluble as, or more soluble than, FM 3925. Fresh water was then placed into the system and at intervals (see Table 3), 100 ml (volumetric pipet) of water was withdrawn from the main 2-liter storage chamber. Each of the 100 ml samples was quantitatively transferred to a separatory funnel, and 10 ml of saturated aqueous sodium chloride was added followed by 15 ml of ethyl acetate. The mixture was extracted and the separated organic phase was quantitatively transferred to a 10-ml volumetric flask. The aqueous phase was reextracted with 4 ml of ethyl acetate, and the organic phase was added to the 10-ml volumetric flask whose volume was finally brought to the mark with ethyl acetate. An aliquot was used for gas chromatography using an electron capture detector and a six-foot (1.8 meters) column of Carbowax CW20M run at 180°. The results are reported in Table 3.

Table 3

Solubility of FM 3925 in Water

Time of Water Circulation (hrs.)	FM 3925 (ppm)
1	1.72; 1.82
2	1.90; 1.87
4	2.10; 2.17
6	2.33; 2.30
8	2.34; 2.35
24	2.17; 2.14

Avg. (Hrs. 4-24) = 2.3 ppm

The solubility of FM 3925 is forty-six times that of FM 3422. The retention time of FM 3925 is close to that of FM 3422, and the gas chromatographic patterns (see Figure 2 in reference 1) are essentially the same.

REFERENCES

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(11) Taken from A. N. Welter's oral presentation to Commercial Chemicals personnel, Oct. 23, 1978; minutes of meeting, Oct. 31, 1978.

(12) C. F. Prutton and S. H. Maron, "Fundamental Principles of Physical Chemistry," Macmillan, 1951, Chapter 19.

(13) Agrichem Laboratory personnel are acknowledged for their help in autoradiography and scintillation studies.

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Attached are comments on the 3M Technical Report "Analytical Methodology and Support. Arthur Mendel, Project 9970612643 Fate of Fluorochemicals, Report No. 8, Jan. 17, 1979" made by Professor Stephen A. Boyd, Michigan State University, dated May 19, 1993.

Review of Technical Report Summary
Analytical Methodology and Support

Discussion and Results

The octanol-water partition coefficient of FM 3422 was reported as 6.6×10^6. There is a strong correlation between the octanol water partition coefficient and the solubility in water for organic solutes given by the equation (Chiou et al., 1982, Environ. Sci. Technol. 16:4-10).

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

This relationship would predict a supercooled liquid solubility of ca.47 ppb FM 3422 based on the K_{ow} value of 6.6×10^6. For the K_{ow} and S_w values to be compatible require that either FM 3422 is a liquid at room temperature or have a low melting point ($< 100°C$). If the m.p. is $> 100°C$ then the actual solubility should be lower ($\sim 10x$) than the predicted supercooled liquid solubility, i.e., about 5 ppb instead of 50 ppb. If the m.p. of MF 3422 is > 100 to 150°C then either the measured K_{ow} or S is probably wrong. The relationship referred to in the reports is by the same group (Chiou et al.) and I think this is a useful exercise. The line plotted in Fig. 2 looks a little different than the equation above. The main cautionary note is that these relationships predict the supercooled liquid solubility of solids. If the solid has a high m.p. (> 100 to 150°C) the actual water solubility may be substantially ($\sim 10x$) lower. When working with these equations, you need to plot the supercooled liquid solubility not the measured aqueous solubility of the solid. At any rate, it is a good estimate to give you an idea of where the experimental value should fall. It also emphasizes the importance and utility of obtaining accurate S_w and K_{ow} values.

Similar estimates of bioconcentration factors (BCF) can be obtained from empirical relationships between BCF and either K_{ow} or S_w, with each species (e.g., trout, guppie) yielding its own relationship. A unified relationship can be obtained by normalizing the BCF of a species by its lipid content, analogous to normalizing the soil sorption coefficient, K, to the soil organic carbon content to give K_{oc}. The normalized factor, BCF_1, is linear with S_w and K_{ow} on a log scale for different species of aquatic organisms (e.g., zooplankton, guppies, rainbow trout, catfish). The equation is:

$$\log BCF_1 = 0.899 \log K_{ow} + 0.623$$

(from Chiou, 1985, Environ. Sci. Technol. 19:57-62). This equation has the advantage of predicting BCF values for different species, as long as you know their lipid content.

As mentioned earlier, the soil TLC plates are of limited value. They didn't distinguish the mobilities of FC 95 and FC 143 versus FM 3422 despite the fact that the former two compounds have much lower soil sorption coefficients than the latter. Hence, the assay seems insensitive.

Experimental

The water solubility here is reported as 5 ppm or 100 times the 0.05 ppm value discussed above. This has to be determined accurately. Micelle formation may occur and result in this high apparent solubility; the compound likely has surfactant qualities judging from its structure. You should know if it forms micelles. This is easily done by measuring the critical micelle concentration (CMC). There are a variety of methods for this determination. Sorption of this compound by soil may be quite different above and below the CMC.

Water solubility determinations. The difference of 43 times in the water solubilities of FM 3925 are FM 3422 seems rather large considering the high degree of structural similarity.

Recommendation

1. Obtain an accurate water solubility for FM 3422 and 3925*.

2. Obtain an accurate octanol-water partition coefficient for FM 3422 and 3925*.

3. Determine if FM 3422 and 3925 form micelles, i.e., measure the critical micelle concentrations.

*A key reference describing methodology for determining water solubility and octanol-water partition coefficient is:

C.T. Chiou and D. W. Schmedding. 1980. Measurement and interpretation of octanol-water partition coefficient and water solubility of organic chemicals. Association of Official Analytical Chemists. Washington, D.C.