

SORPTION AND DESORPTION PROCESSES AFFECTING  
THE ENRICHMENT OF THE FLUOROCARBONS  
 $\text{CCL}_2\text{F}_2$  AND  $\text{CCL}_3\text{F}$  IN GROUND WATER

by

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## ABSTRACT

Field measurements of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in ground water have shown that concentrations in recharge areas may be higher than those in water at equilibrium with the atmosphere. This research tested the hypothesis that sorption and desorption of fluorocarbons from grain surfaces in response to changes in soil moisture content are responsible for this enrichment. Soil slurry experiments were performed to determine whether aqueous fluorocarbon concentrations increased when water came into contact with dry soils. In all slurries, the aqueous  $\text{CCl}_3\text{F}$  concentration increased significantly, whereas the  $\text{CCl}_2\text{F}_2$  concentrations increased in all but two of the slurries. The percent increase of both compounds correlated well with soil properties such as percent clay and percent organic matter.

Column experiments were carried out to obtain distribution coefficients ( $K_d$ ) for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  on dry soils. These values were 3.02 and 3.20  $\text{cm}^3/\text{g}$ , respectively, and the values for  $K_d$  on saturated sand were 0.67 and 0.360  $\text{cm}^3/\text{g}$  for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ , respectively. The difference in magnitude of  $K_d$  for saturated and dry media suggests that significant amounts of both fluorocarbons desorb from grain surfaces when dry soil is wetted, causing enrichment of aqueous fluorocarbon concentrations.

## INTRODUCTION

The presence of the fluorocarbons  $\text{CCl}_3\text{F}$  (Freon 11) and  $\text{CCl}_2\text{F}_2$  (Freon 12) in ground water has been studied as a potential tool for establishing relative ground-water ages and for identifying recharge areas [Thompson and Hayes, 1979]. These compounds have been manufactured as propellants, refrigerants, and solvents and have been released to the atmosphere in large quantities since the late 1930s. The cumulative release of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  was estimated by McCarthy, Bower, and Jesson [1977] from industrial data, and direct atmospheric measurements have been made by several groups [Heidt et al., 1975; Grimsrud and Rasmussen, 1975; Hester, Stephens, and Taylor, 1975; Pack et al., 1977; Penkett et al., 1979; Singh et al., 1979; Rasmussen, Khalil, and Dalluge, 1981]. The work of McCarthy et al. [1977] showed an exponential increase in atmospheric fluorocarbon levels, which has been supported by later research. Precipitation at equilibrium with the recent atmosphere therefore contains more fluorocarbons than did earlier precipitation, and consequently, the concentrations in recently recharged waters are higher than those in older waters. At any one time, ground water near the recharge area will contain more fluorocarbons than older water that has moved some distance down the flow path in isolation from the atmosphere.

The correlation between ground-water age and  $\text{CCl}_3\text{F}$  concentration was studied by Thompson and Hayes [1979], who compared  $\text{CCl}_3\text{F}$  concentrations in ground water with tritium data from Hot Springs



National Park in Arkansas and the Edwards aquifer near San Antonio, Texas. With the exception of the anomaly discussed below, their results showed that water with low tritium concentrations, indicating the predominance of relatively old water, also had low  $\text{CCl}_3\text{F}$  concentrations. Similarly, water with high tritium concentrations had greater amounts of  $\text{CCl}_3\text{F}$ .

The basic assumption in the work of Thompson and Hayes in developing the technique of fluorocarbon dating of ground water has been that the concentration of fluorocarbons in recharge waters is at equilibrium with the partial pressure in the atmosphere at the time of recharge, and therefore that change in atmospheric concentrations over time is the dominant factor controlling concentrations present in ground water. However, field measurements of anomalously high  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  concentrations in ground water indicate that the time of equilibration with the atmosphere is not the only major variable controlling aqueous fluorocarbon concentrations. For example,  $\text{CCl}_3\text{F}$  concentrations up to 40 times greater than those in water at equilibrium with the atmosphere were measured in the northeastern portion of the Edwards aquifer by Thompson and Hayes [1979] in an area that seemed to be remote from any potential contamination sources. Isolated measurements in ground water by Thompson [1981] at various places in Arizona have shown similar anomalies where no industrial or municipal contamination appeared likely.

In addition to anomalous aqueous fluorocarbon concentrations, soil gas measurements have occasionally shown  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  concentrations greater than those present in the atmosphere. Soil gas

measurements made in the upper 14 meters of soil near Gascoyne, North Dakota, showed  $\text{CCl}_2\text{F}_2$  concentrations 8 times greater than atmospheric levels and  $\text{CCl}_3\text{F}$  concentrations 11 times greater [Thompson, Russell, and Earp, 1979]. These data provide additional evidence that enrichment of fluorocarbons takes place in the subsurface as a natural phenomenon.

The mechanisms responsible for the observed enrichment of fluorocarbons in ground water and in soil gases must be understood to maximize the information obtained from studies of ambient fluorocarbons in ground water. With this purpose in mind, the aim of this research was to evaluate the hypothesis that the high concentrations may be accounted for by natural processes of sorption and desorption of fluorocarbons from the soil surface, occurring in response to wetting and drying sequences experienced by soils in recharge areas.

## ADSORPTION AS A FUNCTION OF SOIL COMPOSITION AND MOISTURE CONTENT

The sorption of organic chemicals onto soil materials depends on both the properties of the sorbate molecule and on the properties of the soil. The properties of the sorbate molecule determine which soil characteristics play a major role in sorption. Important molecular parameters influencing sorption include polarity, polarizability, and molecular weight [Okamura and Sawyer, 1971; Bohn, Prosocki, and Eckhardt, 1980]. In a study of hydrocarbon sorption on soil-packed columns, Bohn et al. [1980] found that retention increased with molecular weight and unsaturation of the hydrocarbon and decreased with branching. Molecules with a strong permanent or induced dipole are attracted to mineral components of the soil that bear local charges, whereas nonpolar molecules have a greater affinity for neutral surfaces provided by soil organic matter.

### Soil Organic Matter

The correlation between sorption of nonpolar, hydrophobic compounds and soil organic matter has often been noted [Bailey and White, 1964; Swoboda and Thomas, 1968; Osgerby, 1970; Hamaker and Thompson, 1972; Saltzman and Yaron, 1972; Karickhoff, Brown, and Scott, 1979; Hassett et al., 1980]. The mechanisms of sorption onto soil organic material are not well understood. A common assumption is that sorption is a surface phenomenon and, as such, the amount of sorption depends on the surface area available to sorbates. The

correlation between sorption and the organic component of soil is thus attributed to the high surface area characteristic of organic matter. Nonspecific physical sorption, caused by electrostatic forces between the adsorbate and the adsorbent, is generally presumed to be the major mechanism of sorption of un-ionized species onto soil organic matter [Osgerby, 1970]. Alternatively, Chiou, Peters, and Freed [1979] suggested that sorption of organic solutes may be a solubility partitioning process between the sorbate and the soil organic component rather than a surface phenomenon. Finally, consideration of solute-solvent interactions may provide another clue regarding the forces that govern sorption of organic solutes. Hydrophobic sorption, discussed by Horvath and Melander [1978] is based on the repulsion of nonpolar solutes by water rather than on attraction between the solute and the solid material. From a study of the sorption of dibenzothiophene by soils, Hassett et al. [1980] concluded that the linear partition coefficient was significantly correlated with the organic carbon content of the soils and discussed the possibility that sorption of dibenzothiophene is a result of the hydrophobic effect.

The sorption of fluorocarbons, as nonpolar organic molecules, may be expected to follow the same trends as similar molecules and sorb preferentially onto soil organic materials. Brown [1980] injected two fluorocarbons ( $\text{CCl}_3\text{F}$  and  $\text{CBr}_2\text{F}_2$ ) onto three saturated columns packed with Ottawa sand, Yolo sandy loam, and crushed coal. The fluorocarbons were retained more on the Yolo sandy loam than on the sand, but the greatest retention was exhibited by the crushed coal. Brown's results indicate that fluorocarbons, like other hydrophobic organic

compounds, have a strong tendency to sorb on or in organic components of soil.

### Soil Moisture Content

The tendency of organic pesticides to become more toxic as soil moisture increases has been noted in the literature. Upchurch [1957] found that diuron was more toxic to cotton under moist soil conditions than under dry, possibly indicating that concentrations in soil water increase as diuron molecules are replaced at sorption sites by water itself. Barlow and Hadaway [1956] and Harris [1964] found that the bioactivity of several pesticides was greater in moist soils than in dry soils, explaining the investigators' results on the basis of competition for sorption sites between water and the pesticide.

More recently, Okamura and Sawyer [1973] studied the retention of normal alkanes and halomethanes on two soils and on two silica-based chromatographic packing materials (Chromosorb W and Porasil C) as a function of moisture content. They found that the halomethanes but not the alkanes exhibited a decrease in retention with decreasing water content on the two soils and on the Chromosorb W over most of the moisture range. The trend was reversed on the Porasil C, which the investigators attributed to alteration of the silica surface. These results are contrary to what has been previously reported. The difference may represent different retention mechanisms. Okamura and Sawyer suggested four mechanisms for sorption in a moist soil system: (1) sorption onto the water surface, (2) sorption by the nonwetted surface, (3) sorption by a solid surface covered with water, and (4)

sorption by a surface altered by a single layer of water molecules becomes a new surface. Okamura and Sawyer's results are consistent with mechanisms (1), (3), and (4), whereas the results of previous studies suggest that sorption of organic compounds occurs primarily on dry surfaces and is inhibited by competition with water molecules.

If sorption of organic compounds is inhibited by the presence of water, desorption should occur when the moisture content of the soil increases, resulting in higher aqueous concentrations of the compound. The magnitude of this effect will depend on the mechanism of sorption as well as on the soil composition because it affects the amount of fluorocarbon sorbed onto the soil surface. If physical sorption is dominant, the weak bond strength should readily allow desorption of fluorocarbons to permit the establishment of a stronger bond between water and the soil. However, if solution partitioning of fluorocarbons between soil organic matter and the aqueous phase is the dominant factor, the effect of an influx of water will depend on the equilibrium partitioning between fluorocarbons, soil organic matter, and water and will not necessarily lead to increased concentrations. Sorption in this case will not be completely reversible, as it is in physical sorption.

Variation in soil composition with consequent variation in the amount of fluorocarbons sorbed will also affect the degree of enrichment by desorption. In media such as sand, which has relatively little affinity to sorb organic solutes, aqueous enrichment is potentially less noticeable than in more sorptive media.

## SOIL SLURRY EXPERIMENTS

To determine whether the aqueous concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  could be increased when water came into contact with dry soils, a series of experiments was performed in which the fluorocarbon concentration of distilled water was measured before and after the addition of different types of soils.

### Experimental Procedure

Samples of eight Arizona soils were obtained from the Department of Soils, Water, and Engineering at The University of Arizona. Information about the composition of these soils is given in Table 1. The soils were sieved twice through 4- and 6-mm sieves to mix the soils from which the individual samples were drawn. All soils were air dry and the amount of fluorocarbon absorbed onto them was assumed to be at equilibrium with the atmosphere, inasmuch as no attempt was made to store them in a fluorocarbon-free environment or to remove the fluorocarbons by treatment such as baking. Water samples were analyzed on a Varian model 3700 gas chromatometer equipped with a special water sample-handling system [Thompson and Hayes, 1979].

The experimental procedure was as follows:

1. Distilled water at  $11^\circ\text{C}$  was analyzed for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ .
2. One hundred grams of soil were placed in a beaker, which had been well rinsed with distilled water to remove any absorbed

TABLE 1. Composition of Soils Used in Soil Slurry and Column Experiments

Soil		Composition (%)		
Name	Type	Clay	Organic Matter	Sand
Laveen	loam	22.0	1.1	42.6
Mohall	clay loam	21.5	0.5	55.0
Clover Springs	silty clay loam	37.8	3.4	0.3
Grabe	silt loam	14.9	1.7	35.8
Camorro	loamy sand	6.2	1.6	79.9
Guest	clay	32.6	1.2	31.7
Pima I	silty clay loam	32.6	1.0	29.6
Vinton	loamy sand	9.3	0.5	76.9
Molokai	clay	39.2	1.4	12.4



fluorocarbons, and 200 ml of distilled water were added to the soil to make the slurry or muddy-water mixture.

3. The beaker was shaken gently to mix without causing turbulence, the sediment was allowed to settle, and the supernatant liquid was analyzed for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ . Three samples were taken from each of the eight mixtures.

### Experimental Results

The mean concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  measured in the soil slurries as well as the percent concentration increase above the concentration in distilled water are reported in Table 2. The results of individual measurements are reported in Appendix A. Three aspects of these results will be discussed. First, the general trend of increase in aqueous fluorocarbon concentrations after mixing with soils is discussed and an explanation of the results is proposed. Second, the magnitude and duration of the concentration increase for  $\text{CCl}_3\text{F}$  is compared with that for  $\text{CCl}_2\text{F}_2$ . Finally, the relationships between the percent increase of each compound and the soil composition is explored.

As illustrated in Figures 1 and 2, marked increases in aqueous concentrations of  $\text{CCl}_3\text{F}$  were measured for each of the soil slurries. Increases of aqueous  $\text{CCl}_2\text{F}_2$  were detected in all but two of the slurries. A logical explanation is that suggested by other researchers to account for increased pesticide toxicity at high moisture levels [Barlow and Hadaway, 1956; Upchurch, 1957; Harris, 1964; and Bailey and White, 1964]. As nonpolar, hydrophobic compounds,  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  have a weaker attraction for the soil surface than does water

TABLE 2. Mean Fluorocarbon Concentrations in Slurries and Percent Increase over Concentrations in Distilled Water

Soil Slurry	Mean $\text{CCl}_3\text{F}$ (ng/L)	Percent Increase	Mean $\text{CCl}_2\text{F}_2$ (ng/L)	Percent Increase
Laveen	$3.54 \pm 0.08^a$	471	$0.51 \pm 0.47^a$	-3.7
Mohall	$1.37 \pm 0.30$	122	$0.78 \pm 0.53$	46.7
Clover Springs	$6.06 \pm 0.29$	857	$1.29 \pm 0.41$	144
Grabe	$2.91 \pm 0.08$	370	$0.70 \pm 0.02$	32.7
Camorro	$3.00 \pm 0.37$	381	$0.83 \pm 0.48$	56
Guest	$3.03 \pm 0.04$	389	$1.03 \pm 0.05$	93
Pima I	$6.69 \pm 0.22$	981	$0.71 \pm 0.08$	34.6
Vinton	$1.13 \pm 0.13$	83	$0.52 \pm 0.18$	-2.8
Distilled water	$0.62 \pm 0.20$		$0.53 \pm 0.37$	

a. Confidence intervals shown are one standard deviation.

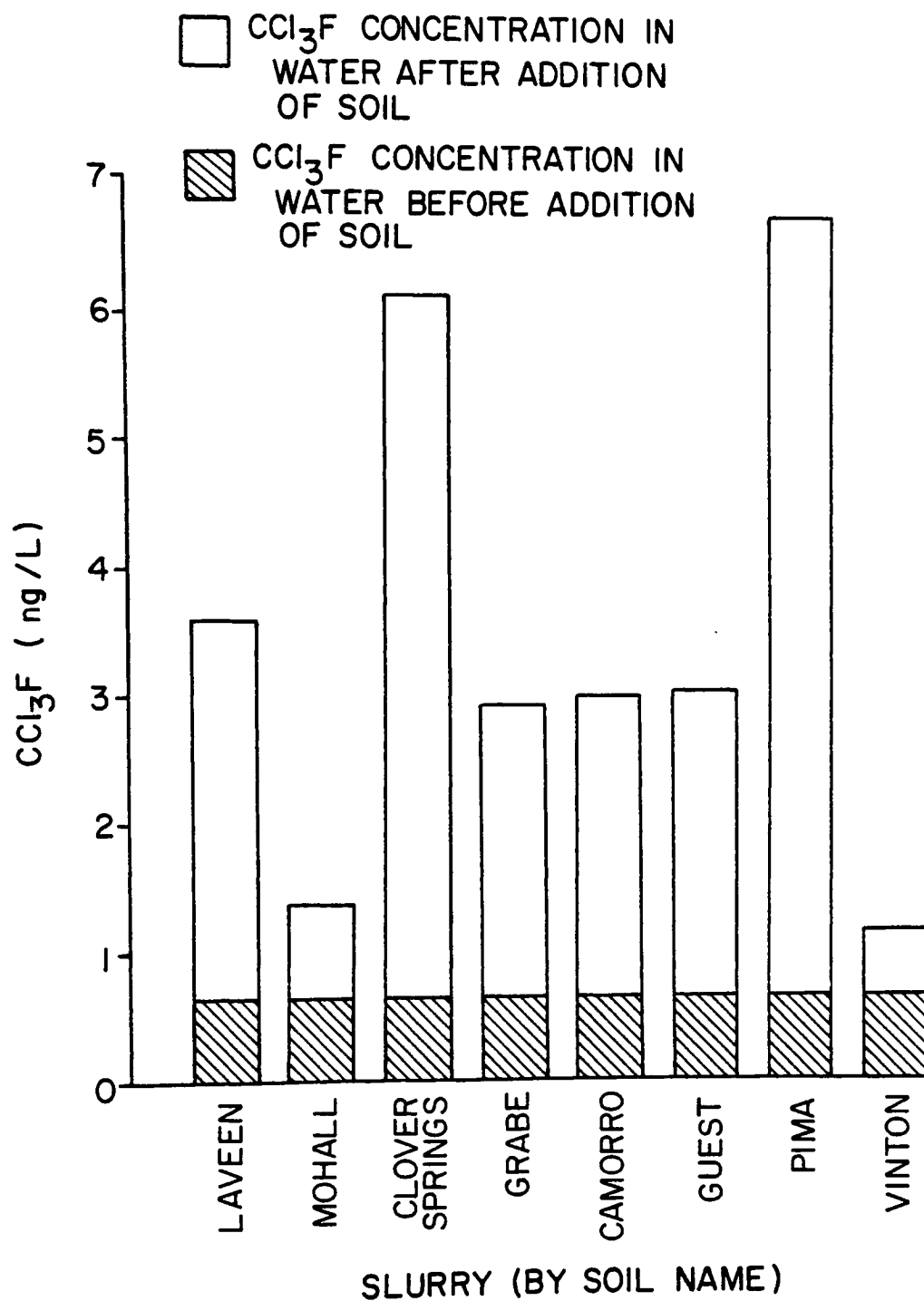


Figure 1. Concentration of CCl<sub>3</sub>F in Water before and after Addition of Soil

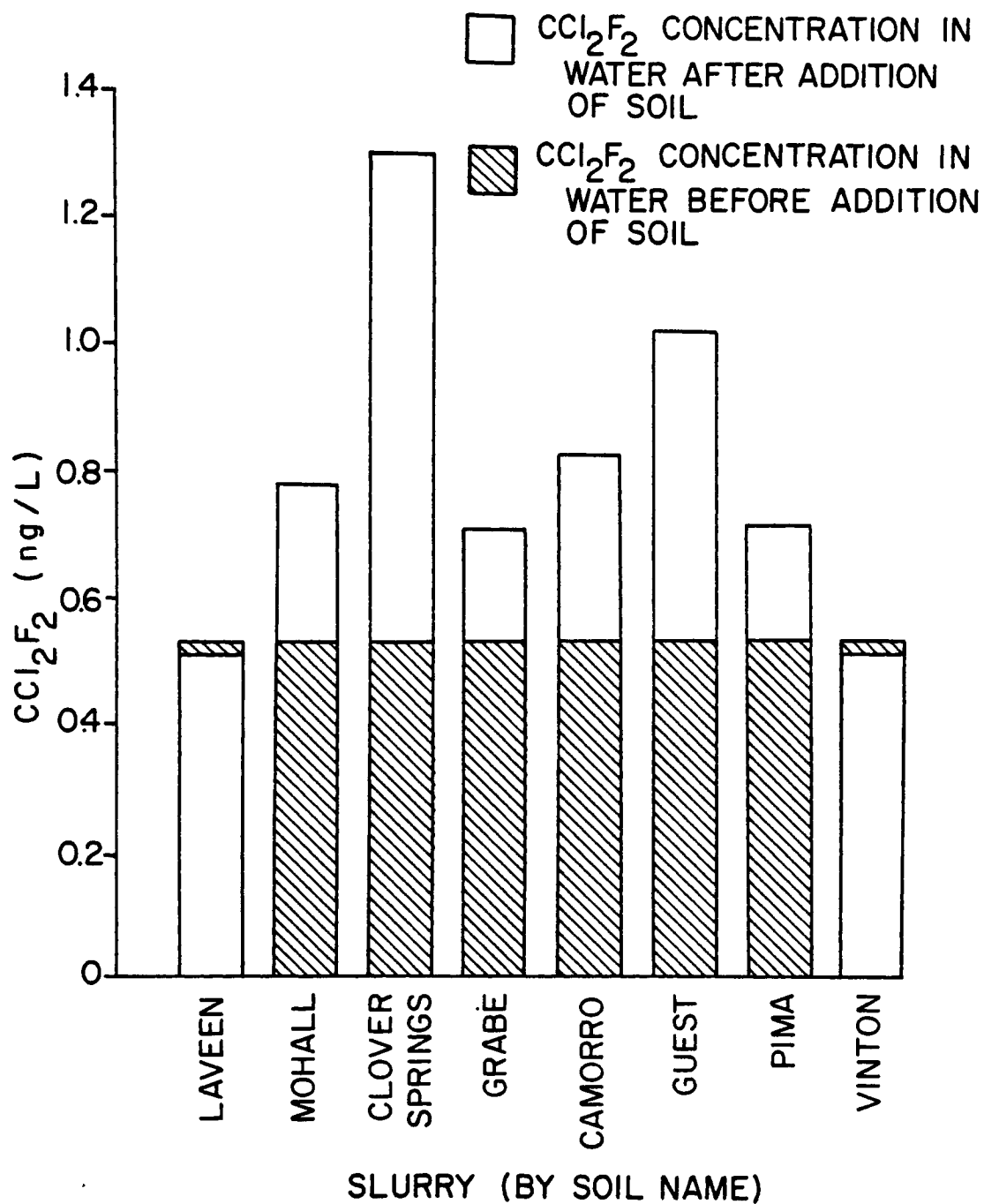


Figure 2. Concentration of  $\text{CCl}_2\text{F}_2$  in Water before and after Addition of Soil

itself. When water is introduced to an air-dry system, fluorocarbons are displaced from sorption sites and forced into solution. Comparison of the dipole moments ( $\mu$ ) of water,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_3\text{F}$ , which are measures of the permanent polarity of a molecule, shows that water is much more polar ( $\mu = 1.87$ ) [Weast, 1979, p. E-66] than  $\text{CCl}_3\text{F}$  ( $\mu = 0.45$ ) or  $\text{CCl}_2\text{F}_2$  ( $\mu = 0.51$ ) [Weast, 1979, p. E-63]. Inasmuch as most soil materials are polar or carry a local charge, the electrostatic bond between the soil surface and water itself is stronger than that between the soil and fluorocarbon molecules. This conceptual scheme assumes that sorption is a surface phenomenon caused by nonspecific electrostatic attraction between the sorbate and the sorbent.

#### Magnitude and Duration of Concentration Increase

For all slurries, the percent increase of  $\text{CCl}_3\text{F}$  was greater than that of  $\text{CCl}_2\text{F}_2$ . Two possible explanations are that (1)  $\text{CCl}_2\text{F}_2$  is more strongly bonded to the soil surface than  $\text{CCl}_3\text{F}$ , so that less is displaced by water or (2) more  $\text{CCl}_3\text{F}$  than  $\text{CCl}_2\text{F}_2$  is sorbed onto the dry soils, so more is desorbed when water is introduced. The only evidence in favor of the first hypothesis is that  $\text{CCl}_2\text{D}_2$  is less soluble in water than  $\text{CCl}_3\text{F}$  (Table 3). As a consequence, a molecule of  $\text{CCl}_2\text{F}_2$  would be more likely than a molecule of  $\text{CCl}_3\text{F}$  to remain bonded to the soil surface, owing to the hydrophobic effect. However, other molecular characteristics provide evidence that there may have been less  $\text{CCl}_2\text{F}_2$  initially sorbed on the soil. Polarizability gives an indication of the strength of the nonspecific bond between a compound and charged matrix. The more polarizable the sorbate, the greater its propensity to

TABLE 3. Molecular Characteristics of  $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CClF}_3$ 

Compound	Molecular Weight <sup>1</sup> (g)	Dipole Moment <sup>2</sup> (debye)	Molar Refraction <sup>3</sup> ( $\text{cm}^{-3}$ )	Boiling Point <sup>1</sup> (°C)	Aqueous Solubility <sup>4</sup> (wt %)
$\text{CClF}_3$	104.66	--	10.9	-81.4	0.009
$\text{CCl}_2\text{F}_2$	102.91	0.51	15.9	-29.79	0.028
$\text{CCl}_3\text{F}$	137.37	0.45	20.9	23.82	0.011

<sup>1</sup>Weast [1979, pp. E-34-E-35].

<sup>2</sup>Weast [1979, p. E-63].

<sup>3</sup>Calculated from additive contributions, data from Weast [1979, p. E-356].

<sup>4</sup>At 25°C, 1 atm [Weast, 1979, pp. E-34-E-35].

develop an induced dipole that would strengthen the sorbate-sorbent bond. It has been shown that heats of adsorption for some molecules, including  $\text{CCl}_2\text{F}_2$ , are proportional to their polarizabilities [Kiselev, 1970]. The molar refraction of a molecule is directly proportional to its polarizability, and this relationship has been used to compare the sorptivity of different compounds onto dry Graphon, salt-modified alumina and salt-modified porous silica beads [Okamura and Sawyer, 1971]. The molar refractions of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  are 20.9 and 15.9, respectively, which indicates that  $\text{CCl}_3\text{F}$  has a greater heat of adsorption than  $\text{CCl}_2\text{F}_2$  and therefore less  $\text{CCl}_2\text{F}_2$  is likely to have been initially sorbed onto the dry soil.

The hypothesis that more  $\text{CCl}_3\text{F}$  is initially sorbed onto soils is also supported by evidence obtained from normal gas chromatographic

analysis. Less  $\text{CCl}_2\text{F}_2$  than  $\text{CCl}_3\text{F}$  is retained on virtually all chromatographic column-packing materials, whether they are true adsorbents such a molecular sieve and graphitized carbon black or support materials coated with liquid organic films. The lesser sorption of  $\text{CCl}_2\text{F}_2$  in the gas-phase systems may be attributed to its weak cohesive forces, indicated by its low boiling point, molecular weight, and polarizability in comparison to  $\text{CCl}_3\text{F}$ .

The duration as well as the magnitude of the enrichment effect is greater for  $\text{CCl}_3\text{F}$  than for  $\text{CCl}_2\text{F}_2$ . In four of the eight slurries, the concentration of  $\text{CCl}_2\text{F}_2$  decreased over the sampling period, but the concentration of  $\text{CCl}_3\text{F}$  showed only slight random fluctuations in all slurries. This is probably due to the greater solubility of  $\text{CCl}_3\text{F}$ , which makes it less susceptible to volatilization.

#### Correlation between Fluorocarbon Enrichment and Soil Composition

The percent increase of aqueous  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  over the concentrations present in distilled water correlates with both percent organic matter and percent clay present in the soil. The correlation coefficients for the percent increase of  $\text{CCl}_3\text{F}$  with percentage of clay and organic matter were 0.7 and 0.6, respectively. The same correlations for  $\text{CCl}_2\text{F}_2$  with the percentage of clay and organic matter were 0.6 and 0.8, respectively. A weak correlation also exists between the percent organic matter and percent clay, which makes it difficult to definitively separate the effects of these two factors. However, the trend toward greater percent increase of aqueous fluorocarbons with clay and organic content of soils suggests that sorption of the

fluorocarbons is a surface phenomenon, because the surface area available for sorption increases with the percentage of both components.



## EQUILIBRIUM DISTRIBUTION OF FLUOROCARBONS

One approach to studying the changes in aqueous fluorocarbon concentrations that occur when dry soil is saturated involves analysis of the equilibrium distribution of fluorocarbons in both dry and saturated soil systems. If the amount of fluorocarbon sorbed onto a given medium is much greater under dry than under saturated conditions, the new equilibrium concentration must be reached through the release of some fluorocarbon molecules from sorption sites when the medium becomes saturated with water. This will result in an increase in aqueous fluorocarbon concentrations such as that measured in the soil slurries and in the field.

The key parameter to consider in this analysis is the distribution coefficient,  $K_d$ , defined for linear adsorption as

$$K_d = \frac{dS}{dC}$$

where  $S$  is the mass of solute adsorbed per mass of solid,  $K_d$  is the linear distribution coefficient, and  $C$  is the concentration of the solute. The assumption of linear adsorption requires that  $K_d$  be independent of concentration, i.e., that an arithmetic plot of  $S$  versus  $C$  be linear and that sorption and desorption reactions be rapid and reversible [Freeze and Cherry, 1979, p. 403]. At the extremely low fluorocarbon concentrations measurable with the electron-capture detector, this assumption is probably valid. For a soil-air system, the amount of fluorocarbon sorbed onto the soil is proportional to the concentration present in the

soil air, where the constant of proportionality is  $K_{dsa}$ . Similarly, the amount of fluorocarbon sorbed onto the soil in a saturated system is proportional to the concentration present in the water. Under this condition, the constant of proportionality is  $K_{dsw}$ .

It is evident that the magnitude of the distribution coefficient for each system is a major control on the amount of fluorocarbon sorbed on the solid surface. If  $K_{dsa}$  is much larger than  $K_{dsw}$ , more fluorocarbons are sorbed under dry than under saturated conditions, and excess fluorocarbons will go into solution causing enrichment.

#### Determination of Distribution Coefficients

Distribution coefficients were measured or calculated to determine whether the coefficients for  $CCl_3F$  and  $CCl_2F_2$  in soil-air and soil-water systems were sufficiently different to cause notable enrichment of aqueous fluorocarbon concentrations. In addition to the coefficients for these two systems, those for an air-water system were measured as a function of temperature to establish the concentrations of fluorocarbons in water at equilibrium with the atmosphere.

#### Soil-Air System

The distribution coefficients  $K_{dsa}$  for three fluorocarbons,  $CCl_3F$ ,  $CCl_2F_2$ , and  $CClF_3$ , were calculated from the retardation equation using results from chromatographic column studies in which the fluorocarbons were injected onto columns packed with dry soils. The  $CClF_3$  was included to provide additional information about the

mechanism of sorption by permitting correlation of the sorptive properties of boiling point and molecular weight.

The retardation equation, which assumes linear adsorption and has been used to calculate distribution coefficients for saturated systems [Davis and DeWiest, 1966] is:

$$V_i = \frac{V_w}{1 + K_d \frac{\rho_b}{n}} \quad (1)$$

where  $V_i$  = velocity of the solute  
 $V_w$  = velocity of the water  
 $\rho_b$  = bulk density of adsorbent  
 $n$  = porosity.

Modified for column studies using tracers in the gas phase, the equation becomes

$$t_i = \frac{t_w}{1 + \frac{\rho_b}{n} K_d}$$

where  $t_i$  = retention time of sample gas  
 $t_w$  = retention time of nonsorbed species.

The retention times ( $t_i$  and  $t_w$ ) were obtained from the phase column experiments and the porosity, and bulk density for each column was obtained from column geometry and mass measurements. The experiments were performed on soil columns packed with silica, sand and a variety of natural soils.

The soils were chosen to represent different soil characteristics affecting sorption. The Clover Springs soil is from the White Mountains and contains levels of organic matter that are among the highest found in Arizona. The Vinton soil is from an irrigated area and is representative of a sandy soil with relatively low organic content. The unique characteristic of the Molokai soil is its high iron oxide content (23%) [Alesii, Fuller, and Boyle, 1980]. The silica sand provided a pure silica system and a basis for relating the results of this study to those of previous studies. The soils were obtained from the University of Arizona's Department of Soils, Water, and Engineering, and the sand was acquired from the Crystal Silica Company in Oceanside, California. The soil types, column densities, and porosities are given in Table 4.

The natural soils were altered as little as possible in preparation and column packing to maintain their characteristics. Soils were passed twice through 2-mm sieves to remove the large clods and organic

TABLE 4. Soil Column Data

Packing Material	Column Length (cm)	Column ID (cm)	Column Volume (cm <sup>3</sup> )	Mass of Solids (g)	Bulk Density (g/cm <sup>3</sup> )	Porosity
Silica sand	33.7	0.61	9.82	15.79	1.61	0.39
Vinton	37.5	0.75	16.55	23.89	1.44	0.46
Clover Springs	37.5	0.75	16.55	22.18	1.34	0.49
Molokai	37.5	0.75	16.55	17.99	1.09	0.59

fragments and to mix the sample well. The sand was prepared by sieving between 60- and 80-mesh sieves and rinsing twice with a hexane-methanol-acetone succession to remove soluble organic films.

The arrangement of the experimental apparatus is shown schematically in Figure 3. Nitrogen carrier gas flowed through the soil column and a magnesium perchlorate desiccant cartridge to the electron capture detector. The nitrogen flow rate was controlled with a valve installed in the line upstream from the soil column and was measured several times during the analysis with a stopwatch and calibrated glass syringe. The soil column was immersed in a constant temperature bath, maintained at 30°C. The gas samples were injected with a gas-tight syringe through a rubber septum at the upstream end of the column, as shown in Figure 3.

The three fluorocarbons,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ , and  $\text{CClF}_3$ , were injected sequentially onto each column. Sample gas concentrations in the parts per million range (g sample/g air) were achieved by a serial dilution procedure. The final concentration of sample gas and the sample size injected onto a soil column depended on whether the detector responded to the initial injection or whether the gas was completely retained by the soil. Extremely low concentrations eluted rapidly from the Vinton column, whereas the same concentration injected onto the Clover Springs column failed to produce a peak at the output end. The concentration was then increased until a peak was seen. Retention times for the gases on the various soil columns are given in Table 5. Sample size and concentration for each injection are recorded in Appendix B.

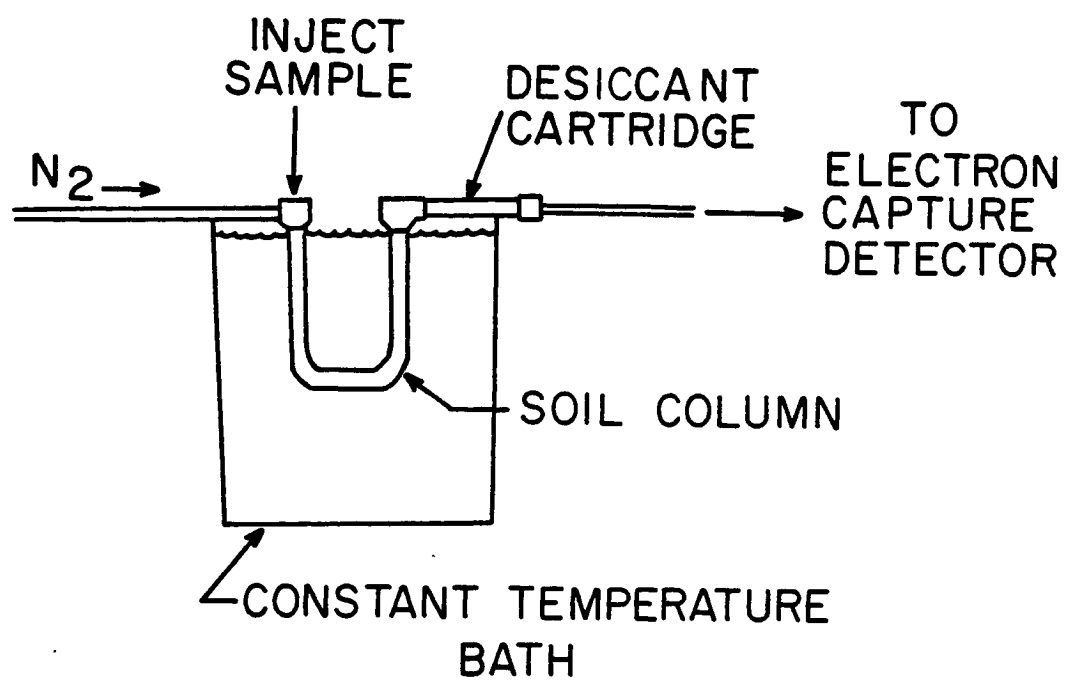


Figure 3. Experimental Apparatus for Air-dry Column Studies

The porosity of the soil packed in the column was determined from the relation

$$n = 1 - \frac{\rho_b}{\rho_s}$$

where  $\rho_s$  is particle density. A particle density of 2.65 g/cm<sup>3</sup> was assumed, and the bulk density was measured after packing the column. The porosities calculated by this method, listed in Table 4, are within the expected range of 0.3–0.6 found for many soils [Hillel, 1971, p. 11]. The porosity may have been increased by soil preparation and column packing procedures and is undoubtedly higher than that of undisturbed soils. In any case, if a lower porosity is used, the value of  $K_d$  remains within the same order of magnitude, and the conclusions of this study are not significantly altered.

The distribution coefficients recorded in Table 5 were calculated using the calculated porosity and the retention times of the fluorocarbons observed in the column studies. Due to the extreme sorptive capacity of the Molokai soil, the only fluorocarbon to elute detectably from an input concentration of 0.4 ppm was CCl<sub>2</sub>F<sub>2</sub>. The  $K_{dsa}$  for CClF<sub>3</sub> and CCl<sub>3</sub>F on the Molokai column could not be calculated.

There was no apparent correlation between the degree of sorption as measured by  $K_{dsa}$  and the percent clay and organic matter present in the soil. This may be due to the influence of a third soil component such as metallic oxides that was not taken into consideration in the analysis.

TABLE 5. Distribution Coefficients and Retention Times for  $\text{CClF}_3$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CCl}_3\text{F}$  on Air-dry and Saturated Columns

Column	$\text{CClF}_3$			$\text{CCl}_2\text{F}_2$			$\text{CCl}_3\text{F}$		
	$t_w$ (min)	$K_{dsa}$ ( $\text{cm}^3/\text{g}$ )	$t_s$ (min)	$t_w$ (min)	$K_{dsa}$ ( $\text{cm}^3/\text{g}$ )	$t_s$ (min)	$t_s$ (min)	$K_{dsa}$ ( $\text{cm}^3/\text{g}$ )	$t_s$ (min)
	<u>Air-dry Columns</u>								
Silica sand	0.18±0.004	2.52	2.12±0.07	0.17±0.01	3.20	2.04±0.05	0.18±0.01	3.02	2.03±0.05
Clover Springs		0.52		0.27±0.02	2.93	2.02±0.53		12.77	
Vinton	0.25±0.01	0.31	0.48±0.01	0.22±0.01	3.96	2.95±0.02	0.21	39.60	26.24
Molokai				0.25±0.01	109	12.6 ±0.5			
	<u>Saturated Column</u>								
Silica sand					0.360			0.067	



For each column, there was a good correlation between  $K_{dsa}$  and the molecular weights, boiling points, and molar refractions of the three fluorocarbons (Figures 4-6). For physical sorption, in which nonspecific van der Waals forces dominate, the extent of adsorption is related to the strength of the cohesive forces. The molecular weight and boiling point of a compound determine the magnitudes of these forces and have been shown to correlate well with the degree of sorption where the mechanism is physical sorption [Bohn et al., 1980; Glasstone and Lewis, 1960]. The direct relationship between sorption and molar refraction suggests that the more polarized molecules are the most highly sorbed onto dry materials [Okamura and Sawyer, 1971].

#### Air-Water System

Inasmuch as  $CCl_2F_2$  and  $CCl_3F$  are gases under normal temperatures and pressures, they are partitioned between the gas and dilute aqueous phases according to Henry's law [Stumm and Morgan, 1970]:

$$(CCl_3F_{AQ}) = K_{H_1} p_{CCl_3F}$$

$$(CCl_2F_2_{AQ}) = K_{H_2} p_{CCl_2F_2}$$

where  $p$  = partial pressure of the solute gas in the atmosphere

$K_{H_1}$  = Henry's law coefficient for  $CCl_3F$

$K_{H_2}$  = Henry's law coefficient for  $CCl_2F_2$

The values of  $K_{H_1}$  and  $K_{H_2}$  as functions of water temperature were determined by analyzing equal volumes of air and standing water in which the  $CCl_2F_2$  and  $CCl_3F$  concentrations were assumed to be at

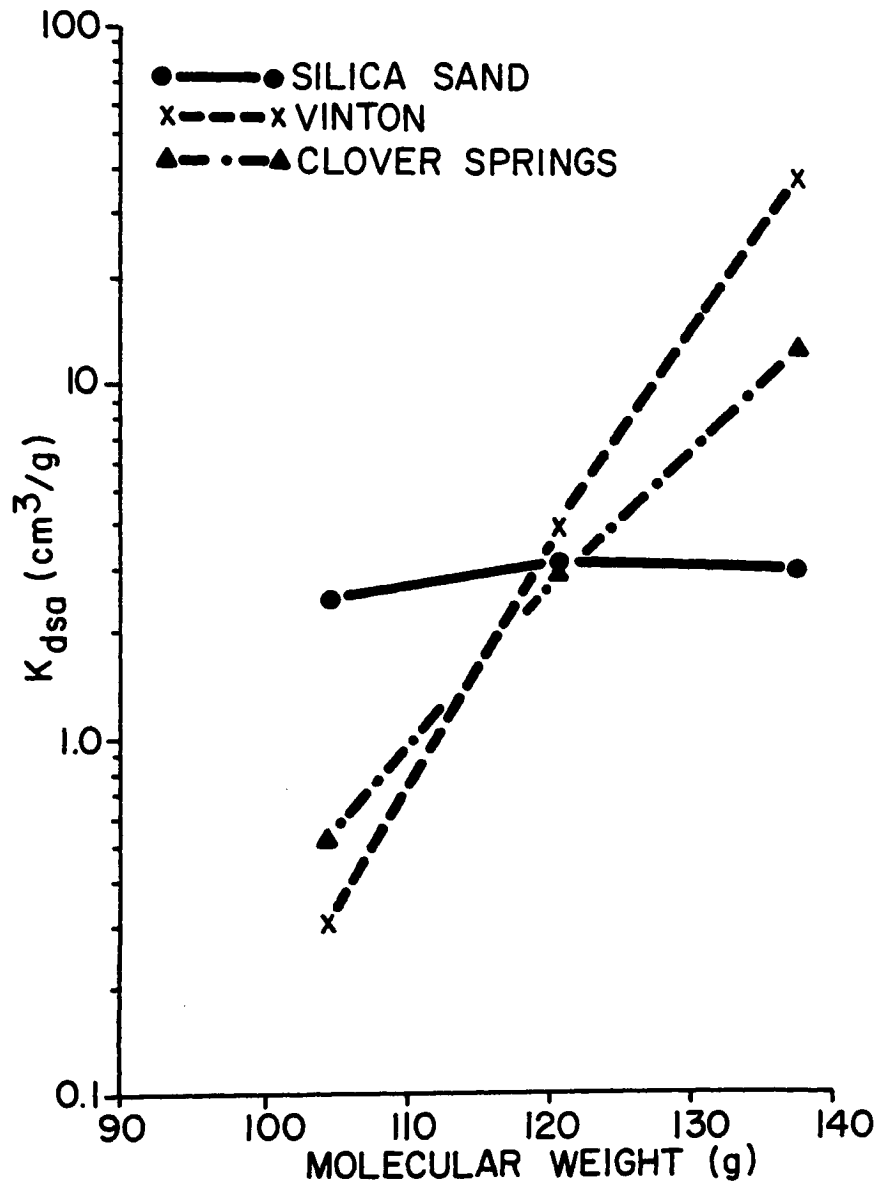


Figure 4. Variation of  $K_{dsa}$  with Molecular Weight of Adsorbent.  
 -- Data from Weast [1979, pp. E-34-E-35]

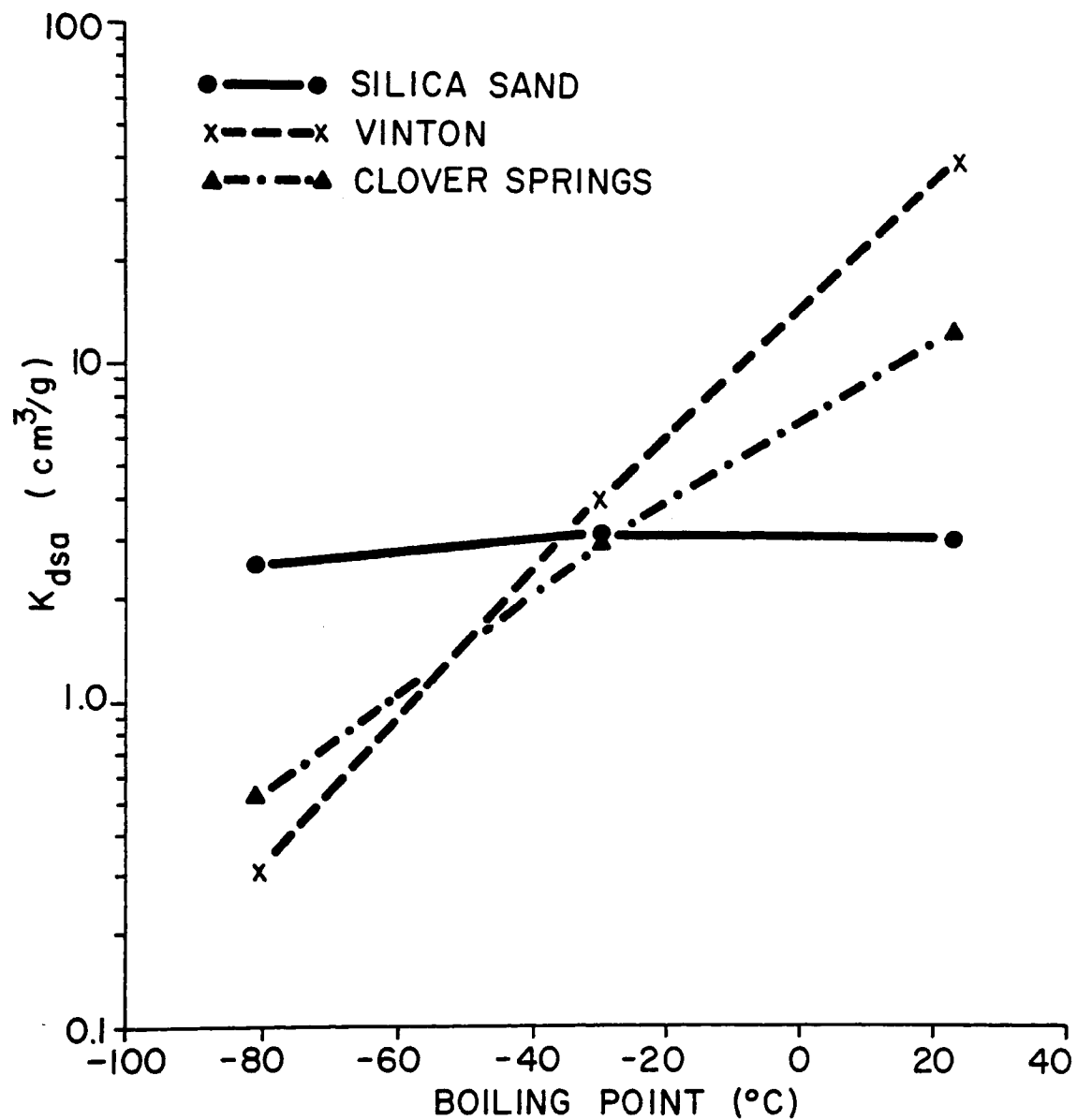


Figure 5. Variation of  $K_{dsa}$  with Boiling Point of Absorbent.  
 -- Data from Weast [1979, pp. E-34-E-35]

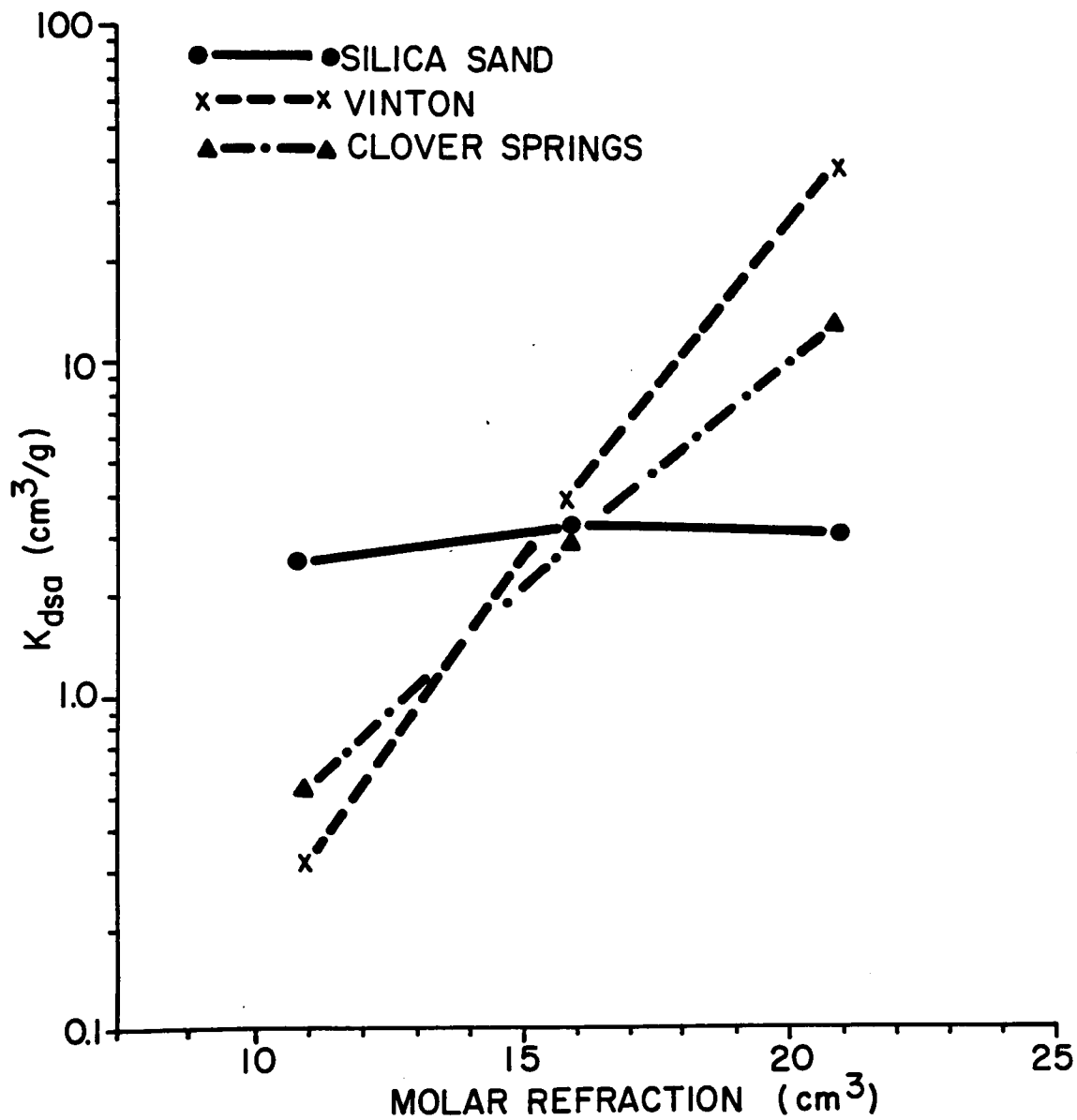


Figure 6. Variation of  $K_{dsa}$  with Molar Refraction of Adsorbent.  
 -- Molar refractions calculated from additive contributions; data from Weast [1979, p. E-356]

equilibrium with atmospheric levels. Because the measurements were made over a period of several months during which air temperatures ranged from 16°C to 30°C, the measurements of fluorocarbons in air were corrected to a standard temperature of 25°C.

The logarithm of the distribution coefficient is inversely related to the water temperature, as shown by the van't Hoff equation:

$$\ln K_{dsa} = \frac{-\Delta H}{RT} + C$$

where  $\Delta H$  = change in enthalpy of reaction

$R$  = gas constant

$T$  = absolute temperature.

Figures 7 and 8 show the temperature variation of the distribution coefficients for  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  for an air-water system. There is considerable scatter in these figures due to day-to-day operating conditions of the instrument, but the range of variation of the distribution coefficient is not large enough to substantially affect the outcome of this study.

#### Soil-Water System

The distribution coefficients for  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  on a saturated sand system were calculated from results obtained by Thompson and Stiles (1981), who conducted a column study in which several hydrocarbons and bromide were injection into a saturated sand column. The sand was obtained from the same source as that used in the soil-air experiments and was prepared in the same manner.

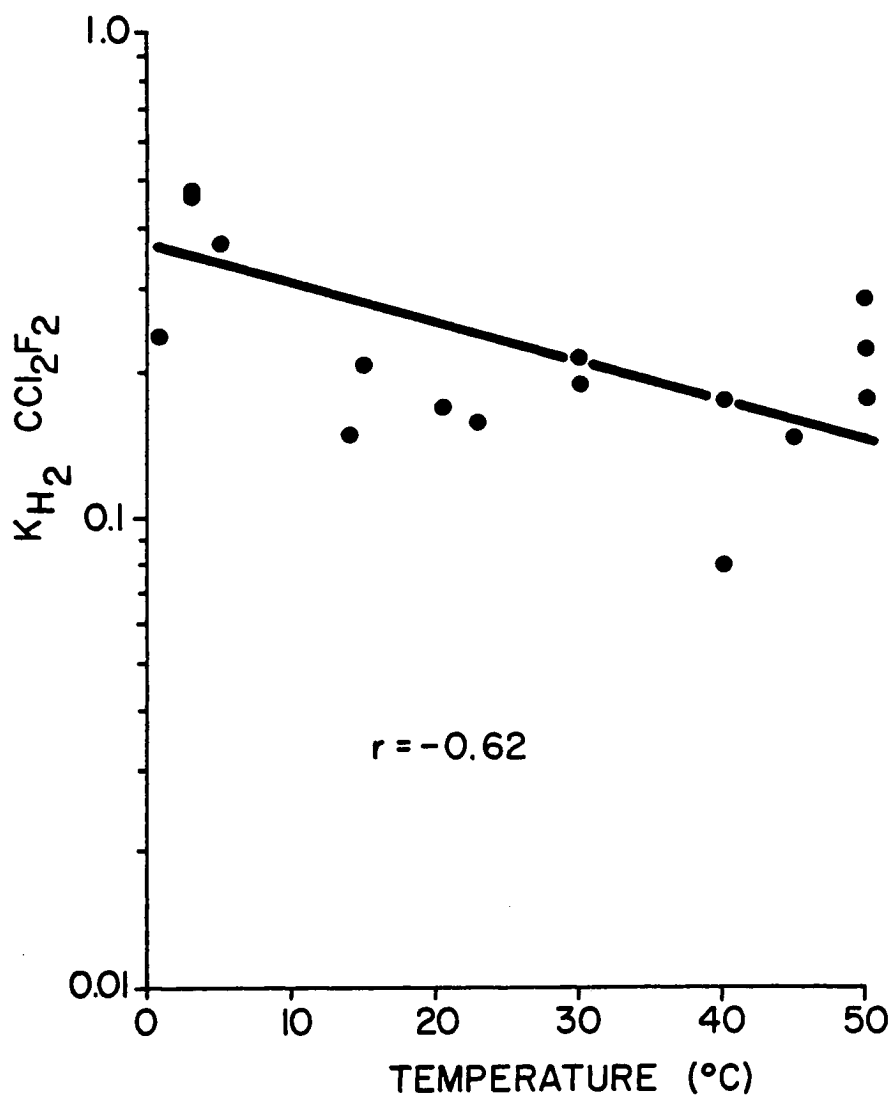


Figure 7. Correlation between  $K_{H_2}$  and Water Temperature for  $\text{CCl}_2\text{F}_2$

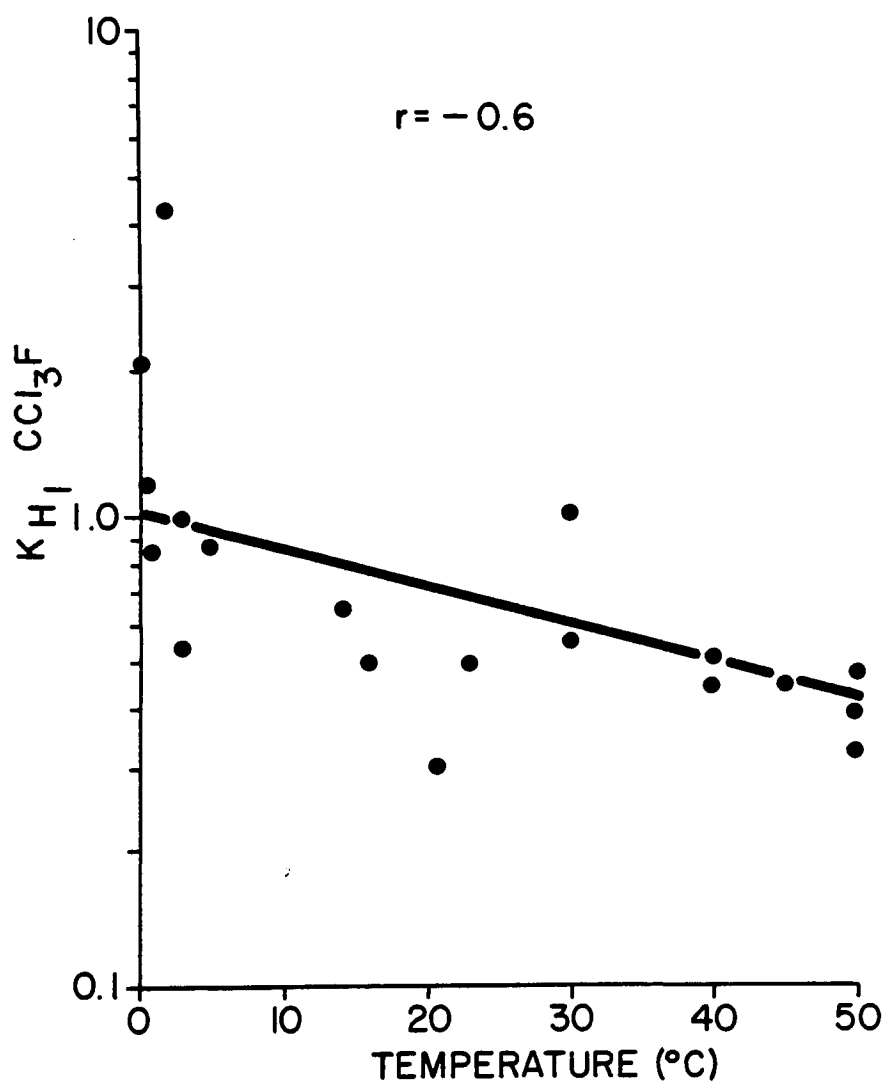


Figure 8. Correlation between  $K_{H_1}$  and Water Temperature for  $\text{CCl}_3\text{F}$

The distribution coefficients were calculated using equation (1). The values of these distribution coefficients are listed in Table 5. It is interesting to note the  $K_{dsw}$  value of  $0.067 \text{ cm}^3/\text{g}$  for  $\text{CCl}_3\text{F}$  determined by Thompson and Stiles [1981] is within  $0.002 \text{ cm}^3/\text{g}$  of the  $0.065 \text{ cm}^3/\text{g}$  determined by Brown [1980] in a similar study on saturated silica sand, despite the vast differences in the concentrations injected, which were in the parts per billion range in Brown's study and in the parts per million range in the work of Thompson and Stiles.

#### Discussion of Results

A comparison of the distribution coefficients determined for saturated and dry silica sand systems suggests that the observed enrichment of fluorocarbons in ground water may result from desorption from the soil surface. The difference between  $K_{dsa}$  and  $K_{dsw}$  ranges from one order of magnitude for  $\text{CCl}_2\text{F}_2$  to three orders of magnitude for  $\text{CCl}_3\text{F}$ . The significance of this difference may best be explained with an example in which the concentration of fluorocarbons in water that has saturated dry sand is calculated. First, the concentration of fluorocarbons sorbed onto dry sand at equilibrium with the atmosphere is determined using  $K_{dsa}$  and the values given by Rasmussen et al. [1981] for atmospheric  $\text{CCl}_3\text{F}$  ( $1.06 \times 10^{-12} \text{ g CCl}_3\text{F}/\text{cm}^3 \text{ air}$ ) and  $\text{CCl}_2\text{F}_2$  ( $1.6 \times 10^{-12} \text{ g CCl}_2\text{F}_2/\text{cm}^3 \text{ air}$ ) in the Pacific Northwest in January 1980. The concentrations are  $3.20 \times 10^{-12} \text{ g CCl}_3\text{F}/\text{g sand}$  and  $5.12 \times 10^{-12} \text{ g CCl}_2\text{F}_2/\text{g sand}$ . The fluorocarbon concentrations in water at equilibrium with these amounts sorbed onto the sand, calculated with the  $K_{dsw}$ , are  $4.78 \times 10^{-11} \text{ g CCl}_3\text{F}/\text{cm}^3 \text{ water}$  and  $1.42 \times 10^{-11} \text{ g}$



$\text{CCl}_2\text{F}_2/\text{cm}^3$  water. In comparison, the concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in water at  $30^\circ\text{C}$  at equilibrium with atmospheric levels are  $6.5 \times 10^{-13}$  g  $\text{CCl}_2\text{F}_2/\text{cm}^3$  water and  $3.68 \times 10^{-13}$  g  $\text{CCl}_2\text{F}_2/\text{cm}^3$  water.

These calculations show that the concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in water that has saturated silica sand are over 70 and 30 times, respectively, those of water at equilibrium with atmospheric levels. The enrichment of  $\text{CCl}_3\text{F}$  predicted with these distribution coefficients is reasonably close to that measured by Thompson and Hayes [1979] in Texas, where they detected  $\text{CCl}_3\text{F}$  concentrations about 40 times those in water at equilibrium with the atmosphere.

In this example, it has been assumed that water saturates the dry sand instantaneously and that there are only two phases between which fluorocarbons are partitioned at any one time. To apply this analysis to an actual recharge situation, it is necessary to assume that water moves through the soil as a saturated plug and that there is a well-defined boundary between the soil-air and soil-water systems. This assumption is valid for coarse or sandy soils that exhibit a relatively sharp wetting front [Hillel, 1971, p. 137]. For other soils in which there is a relatively wide fringe of partially saturated material during recharge, the fluorocarbon-rich water would tend to lose fluorocarbons to the soil atmosphere until equilibrium was reached.

## CONCLUSIONS

Anomalously high concentrations of fluorocarbons in ground water may be the result of desorption from soil surfaces during a recharge event when dry soils become saturated. The results of soil slurry experiments demonstrate that  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  concentrations in water are increased when water is mixed with dry soil. One possible mechanism of enrichment is that fluorocarbon molecules, due to their nonpolar nature, are less attracted to the polar soil surface than are the water molecules themselves. When dry soil is saturated, water molecules replace fluorocarbons at sorption sites. Fluorocarbons are forced into solution, increasing the aqueous concentrations.

Enrichment of aqueous fluorocarbon concentrations can be predicted by an analysis of changes in the equilibrium distribution of fluorocarbons when a dry soil becomes saturated with water. A comparison of the distribution coefficients describing the partitioning of these compounds within air-soil and water-soil systems shows that the concentration of fluorocarbons sorbed onto dry silica sand is much higher than the concentration sorbed onto saturated sand. When dry sand becomes saturated, fluorocarbon molecules go into solution until the new equilibrium distribution is reached.

The greater the difference between the distribution coefficients for dry and saturated systems, the greater the effect of enrichment. Less enrichment would be expected for  $\text{CCl}_2\text{F}_2$  than for  $\text{CCl}_3\text{F}$  because the difference between the distribution coefficients for saturated and

dry systems is less for  $\text{CCl}_2\text{F}_2$  than for  $\text{CCl}_3\text{F}$ . This is consistent with the results of the soil slurry desorption experiments, which showed that the percent increase of  $\text{CCl}_2\text{F}_2$  in water after mixing with soils was markedly lower than the percent increase of  $\text{CCl}_3\text{F}$ .

Similarly, the highest aqueous concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  would be expected in regions where the antecedent moisture was very low, so that a high fluorocarbon concentration would be sorbed onto the soil prior to saturation. Thus, the greatest enrichment should be noticed in arid regions rather than in humid ones. More research is needed to determine the variation of  $K_d$  as a function of soil moisture and to evaluate the hypothesis that the enrichment is primarily an arid-region phenomenon.

The enrichment of fluorocarbon concentrations in ground water affects the use of fluorocarbons as tools for ground-water dating and identification of recharge areas. At this stage of research it is not possible to separate the effects of ground-water age and sorption-adsorption processes in determining the fluorocarbon concentration of ground water. Relative dating is meaningful, however, inasmuch as concentrations of  $\text{CCl}_2\text{F}_2$  and  $\text{CCl}_3\text{F}$  are highest where water contains recent recharge, decreasing with distance down the flow path.

## APPENDIX A

### DATA FROM SLURRY EXPERIMENTS

Conversions from peak areas to concentration units were based on values for atmospheric  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  in the Pacific Northwest in January 1980 ( $\text{CCl}_3\text{F}$  = 188 parts per trillion ( $10^{12}$ ), v/v;  $\text{CCl}_2\text{F}_2$  = 322 parts per trillion, v/v) from Rasmussen et al. (1981).

TABLE A-1. Concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ 

Sample	Concentration (ng/L)			
	$\text{CCl}_3\text{F}$	Mean $\text{CCl}_3\text{F}$	$\text{CCl}_2\text{F}_2$	Mean $\text{CCl}_2\text{F}_2$
<u>Laveen</u>				
1	4.414		1.185	
2	4.633		0.709	
3	4.493	$4.515 \pm 0.113$	0.694	$0.863 \pm 0.278$
<u>Mohall</u>				
1	2.201		1.696	
2	1.582		0.789	
3	1.475	$1.751 \pm 0.394$	0.417	$0.967 \pm 0.660$
<u>Clover Springs</u>				
1	7.313		1.052	
2	7.927		1.726	
3	7.972	$7.736 \pm 0.366$	2.048	$1.607 \pm 0.511$
<u>Grabe</u>				
1	3.631		0.888	
2	3.676		0.853	
3	3.840	$3.716 \pm 0.107$	0.893	$0.878 \pm 0.020$
<u>Camorro</u>				
1	4.329		1.597	
2	3.417		0.402	
3	3.643	$3.793 \pm 0.473$	1.096	$1.032 \pm 0.600$
<u>Guest</u>				
1	3.840		1.255	
2	3.828		1.230	
3	3.930	$3.868 \pm 0.056$	1.349	$1.280 \pm 0.064$
<u>Pima I</u>				
1	8.648		0.952	
2	8.755		0.732	
3	8.231	$8.546 \pm 0.276$	0.769	$0.883 \pm 0.099$
<u>Vinton</u>				
1	1.599		0.853	
2	1.453		0.684	
3	1.272	$1.441 \pm 0.163$	0.397	$0.645 \pm 0.233$

TABLE A-1. Concentrations of  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ --Continued

Sample	Concentration (ng/L)			
	$\text{CCl}_3\text{F}$	Mean $\text{CCl}_3\text{F}$	$\text{CCl}_2\text{F}_2$	Mean $\text{CCl}_2\text{F}_2$
<u>Distilled Water</u>				
1	0.749		0.674	
2	0.681		0.357	
3	0.664		0.367	
4	1.244		1.448	
5	0.614	$0.788 \pm 0.259$	0.456	$0.660 \pm 0.456$

APPENDIX B

DATA FROM AIR-DRY COLUMN STUDIES

TABLE B-1. Silica Sand Column

Sample Number	Sample		N <sub>2</sub> Flow Rate (ml/min)	Retention Time	
	Concentration (ppm) <sup>a</sup>	Size ( $\mu$ l)		Air (min)	Sample (min)
<u>CCl<sub>2</sub>F<sub>2</sub></u>					
1	0.38	50	80	0.17	2.00
2	0.38	100	80	0.17	2.00
3	0.38	100	80	0.17	2.10
4	0.38	100	80	0.18	2.02
5	0.38	50	80	0.18	2.00
6	0.38	50	80	0.17	2.10
mean				0.17 $\pm$ 0.01	2.04 $\pm$ 0.05
<u>CCl<sub>3</sub>F</u>					
1	0.22	10	80	0.18	2.02
2	0.22	10	80	0.19	2.00
3	0.22	10	80	0.18	2.10
4	0.22	10	80	0.18	2.0
mean				0.18 $\pm$ 0.01	2.03 $\pm$ 0.05
<u>CClF<sub>3</sub></u>					
1	0.17	100	80	0.19	2.10
2	0.17	100	80	0.18	2.10
3	0.17	100	80	0.18	2.00
4	0.17	200	80	0.18	2.20
5	0.17	200	80	0.18	2.13
mean				0.18 $\pm$ 0.004	2.12 $\pm$ 0.07

a. Parts per million (m/m)



TABLE B-2. Clover Springs Column

Sample Number	Sample		N <sub>2</sub> Flow Rate (ml/min)	Retention Time	
	Concentration (ppm) <sup>a</sup>	Size ( $\mu$ l)		Air (min)	Sample (min)
<u>CCl<sub>2</sub>F<sub>2</sub></u>					
1	0.8	100	80	0.27	1.74
2	0.8	100	80	0.25	1.42
3	0.8	100	80	0.28	2.41
4	0.8	100	80	0.29	2.52
mean				0.27 $\pm$ 0.02	2.02 $\pm$ 0.53
<u>CCl<sub>3</sub>F</u>					
1	0.9	100	80	0.28	
2	903	50	80	0.29	
3	903	100	80	0.29	
4	903	100	80	0.29	
<u>CClF<sub>3</sub></u>					
1	0.68	100	80	0.28	
2	681	50	80	0.28	
3	681	100	80	0.28	

a. Parts per million (m/m).

TABLE B-3. Vinton Column

Sample Number	Sample		N <sub>2</sub> Flow Rate (ml/min)	Retention Time	
	Concentration (ppm) <sup>a</sup>	Size ( $\mu$ l)		Air (min)	Sample (min)
<u>CCl<sub>2</sub>F<sub>2</sub></u>					
1	0.73	50	80	0.22	2.96
2	0.73	50	80	0.21	2.96
3	0.73	50	80	0.22	2.95
4	0.73	50	80	0.22	2.92
mean				0.22 $\pm$ 0.005	2.95 $\pm$ 0.02
<u>CCl<sub>3</sub>F</u>					
1	4.09 $\times$ 10 <sup>-6</sup>	100	76	0.21	26.24
<u>CClF<sub>3</sub></u>					
1	690	100	72	0.25	0.49
2	690	200	72	0.24	0.48
3	690	200	72	0.25	0.48
4	690	200	72	0.25	0.48
mean				0.25 $\pm$ 0.01	0.48 $\pm$ 0.01

a. Parts per million (m/m).

TABLE B-4. Molokai Column<sup>a</sup>No elution of  $\text{CCl}_3\text{F}$  and  $\text{CClF}_3$  at 100  $\mu\text{l}$  of 0.38 ppm gas mixture.

Sample Number	Sample		$\text{N}_2$ Flow Rate (ml/min)	Retention Time	
	Concentration (ppm) <sup>a</sup>	Size ( $\mu\text{l}$ )		Air (min)	Sample (min)
$\text{CCl}_2\text{F}_2$					
1	0.38	100	88	0.25	12.3
2	0.38	100	88	0.24	12.1
3	0.38	100	88	0.24	13.1
4	0.38	100	88	0.25	13.0
mean				$0.25 \pm 0.01$	$12.6 \pm 0.5$

a. Part per million (m/m).

APPENDIX C

DISTRIBUTION COEFFICIENTS FOR  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ ,  
AIR-WATER SYSTEM

Water Temperature (°C)	$K_d$ ( $\text{CCl}_3\text{F}$ ) ( $\text{CCl}_3\text{F}$ aq)/( $\text{CCl}_3\text{F}$ g)	$K_d$ ( $\text{CCl}_2\text{F}_2$ ) ( $\text{CCl}_2\text{F}_2$ aq)/( $\text{CCl}_2\text{F}_2$ g)
0.5	1.18	0.49
1	0.85	0.24
3	0.54	0.47
3	0.99	0.48
5	0.88	0.37
14	0.65	0.15
16	0.50	0.21
20.5	0.30	0.17
23	0.31	0.16
30	1.04	0.22
30	0.56	0.19
40	0.52	0.18
40	0.45	0.08
45	0.45	0.15
50	0.32	0.18
50	0.47	0.23
50	0.40	0.29

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