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Multicomponent Adsorption of Chloroform, Carbon Tetrachloride, and 1,1,1-Trichloroethane on Soils

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Competitive adsorption of carbon tetrachloride, chloroform, and 1,1,1-trichloroethane from aqueous solutions onto soils was investigated. The experimental data were measured through batch equilibration studies in conjunction with gas chromatography/mass spectrometer analysis. Equilibrium isotherms were generated on three soil samples with different compositions. Competitive effects were analyzed by comparing single-component isotherms to binary and ternary solute isotherms and were quantified in terms of selectivity of an individual compound with respect to another constituent in the mixture. Influence of cosolvent was examined by generating single and multiple solute sorption isotherms from 25% (volume) and 50% (volume) methanol−water solutions. Isotherm linearity was observed, even in the vicinity of saturation, indicating constant retardation rate during the subsurface transport. The order of equilibrium uptake capacity of different soils was consistent with the order of their specific surface areas as determined through nitrogen adsorption. Competitive sorption from multisolute solutions was within a selectivity range of 1.17−2.22. While the contaminant properties determined the order of competition, soil properties determined its quantification. An opposite relationship between the organic matter content and the selectivity for the compound with higher polarity was observed. In the presence of cosolvent, soil's equilibrium capacity significantly decreased as the volume fraction of methanol increased. Furthermore, competition among the solutes decreased, exhibiting a selectivity range from 1.01 to 2.07. High adsorption tendency of the cosolvent on soil and increased solubility of the contaminant species in the mixed solvent are the dominant factors for the variations.

Introduction

Halogenated organic solvents are widely used as degreasing/cleaning agents as well as in production of polymers, fertilizers, pesticides, and pharmaceuticals. Many of these chemicals, including carbon tetrachloride, chloroform, and 1,1,1-trichloroethane, are aliphatic chlorinated organic compounds that have been identified as priority substances by the U.S. EPA in several regions. To assess the potential for them reaching ground water, the kind of physical and chemical processes that occur in the subsurface must be understood.

Sorption processes, in combination with physicochemical properties, play a major role in determining the mobility and the fate of a pollutant in soil. More precisely, soil sorption determines to what extent a compound will vaporize from soil surface or will be transported by water or any other solvent to ground water. The main focus of research on soil sorption has been on single-solute behavior. Studies including multisolute behavior are limited (Kaiser and Zech, 1997; Trania, 1991; Wood et al., 1990; Lee et al., 1989; Zachara, 1987; Mokraurer, 1989). Contaminating solutes are often released to the subsurface environment as multicomponent mixtures rather than a single-solute waste stream. The sorption behavior of a single compound may be changed when other contaminants present in the media compete for the available sorption sites, and previously adsorbed chemicals can be remobilized by an increase in the concentration of competing compounds that are strongly adsorbed. Furthermore, when present in sufficient quantities, cosolvents may exert considerable influence on the distribution of solutes between the soil and the aqueous phase, changing predominantly the aqueous nature of the subsurface. Application of findings from aqueous systems may lead to erroneous results and are inadequate to describe organic contaminant sorption and migration associated with these systems. Thus, any realistic consideration of the chemical fate of a given pollutant requires information on the sorption characteristics of the individual compound as modified by other pollutants in the mixture.

The objective of the work reported herein was to examine the multisolute adsorption equilibrium of chloroform, carbon tetrachloride, and 1,1,1-trichloroethane, on three soil samples with different chemical/physical properties. This objective was achieved by conducting aqueous phase single, binary, and ternary solute batch sorption studies in the absence and in the presence of a cosolvent (methanol). The results are expected to provide insight to the interactions between multisolute systems and soil, that can be used in risk assessment and contaminant removal studies.

Experimental Section

Materials. Chloroform and carbon tetrachloride were obtained from Aldrich Co. and had purities of 99.8% and 99.9+%, respectively. 1,1,1-Trichloroethane with 99.8% purity was supplied by Fisher Scientific Co. Soil samples obtained from Times-Beach−Missouri (2.4% organic matter, 11.4% sand, 35.2% silt, 33.4% clay, 44.14 m^2/g specific surface area, 17.69 Å average pore diameter, pH: 6.9), Visalia−California (1.7% organic matter, 45.1% sand, 35.2% silt, 21.7% clay, 25.33 m^2/g specific surface area,

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15.99 Å average pore diameter, pH: 8.1), and Eglin−Florida (1.6% organic matter, 91.7% sand, 6.3% silt, 2.0% clay, 23.28 m^2/g specific surface area, 14.08 Å average pore diameter, pH: 4.7) were used as adsorbents. Specific surface area of each soil sample was determined with a BET sorptometer-surface area analyzer by using nitrogen gas at liquid nitrogen temperature (−195.8 °C). BET area calculation was based on the projected area of a nitrogen molecule (16.2 $Å^2$). Aqueous solutions were prepared with double distilled water. Methanol, that was used in preparation of mixed solvents, was HPLC grade obtained from Fisher Scientific Co. with 99.9% purity.

Procedure. Experimental methods of study for adsorption from solutions are based on the determination of the concentration of a solute in a solution before and after this solution is brought into contact with the adsorbent. While adsorption equilibrium is being established, the solution is vigorously shaken to ensure uniformity. After the equilibrium is established, the sample is separated or filtered before the final concentration is measured. In the present study, adsorption of the chlorinated hydrocarbons was estimated from the change in solute concentration on exposure of the solution to soil as outlined below.

Prior to the experiments the soil samples were oven dried and kept in a desiccator. 1,1,1-Trichloroethane, carbon tetrachloride and chloroform were dissolved in distilled water to form aqueus solutions of various concentrations, based on typical concentration range in industrial waste streams, 1−15 mg/L (Stenzel, 1993). Solutions were prepared by dilution from a saturated solution. Prior to the experiments, each concentration level was double checked by GC-mass analysis for accuracy. In preparation of binary and ternary solutions, the initial concentration of each component in the mixture was identical with its concentration in the single-solute mixture so that the competition effect could be compared. Amber glass serum bottles (40 mL) with Teflon-lined septa were used as experiment containers. A soil:solution volume ratio of about 1:7 (volume) was chosen to provide optimum contact (Roy et al., 1991). In a typical experiment, approximately 5 g of soil sample and 35 mL of solution were added to the serum bottle. Special attention was paid to eliminate the headspace. Initially, a wide initial concentration range, up to 90% of aqueous solubility, was tested on Missouri soil. It was observed that the isotherms were essentially linear, showing no indication of curvature even at concentrations approaching saturation. Therefore, the equilibrium uptake values for the rest of the experimental studies were determined using a much lower initial concentration range, based on typical concentrations in industrial waste water.

Each measurement was carried out at constant temperature (20 °C), until the equilibrium is reached, in a reciprocating shaker bath fitted with a thermostat. The system was shaken at a rate that ensured that all soils were mixed well with the solution during the experiment. The equilibrium time was found from the kinetic batch studies, that varied from 36 to 40 h for different pairs. To ensure complete equilibration, a 48 h shaking period was employed.

At the end of the shaking period, the samples were directly centrifuged in serum bottles in order to prevent volatilization. The supernatant was removed from the bottle by using a syringe and was taken for concentration measurement. The equilibrium (final) concentrations were measured with a gas chromatograph/mass spectrometer (Perkin-Elmer-Qmass 910). Experimental results were validated by running duplicate samples and carrying out duplicate concentration measurements.

Table 1. Single−Solute Linear Isotherm Constants (*K*) and Normalized Isotherm Constants (K^1)

soil sample	compd	$K/(\mu g\ g^{-1}\ mg^{-1}\ L)$	$K^1/(mmol/m^2)$	standard error
Missouri	$CHCl_3$	2.133	4.027	0.034
	$C_2H_3Cl_3$	1.804	1.352	0.040
	CCl_4	1.695	0.301	0.039
California	$CHCl_3$	1.941	6.388	0.078
	$C_2H_3Cl_3$	1.592	2.080	0.053
	CCl_4	1.483	0.459	0.061
Florida	$CHCl_3$	1.763	6.257	0.027
	$C_2H_3Cl_3$	1.338	1.885	0.029
	CCl_4	1.123	0.375	0.012

In the study of cosolvent effect, methanol/water solutions containing 25% and 50% methanol (by volume) were prepared and the above procedure was repeated.

In calculating the adsorption equilibrium uptake, it was assumed that the solution was uniformly distributed throughout the pores of the adsorbent and the supernatant and that any decrease in the concentration of solute in the mixture was due to the adsorption by soil. Since the environmental concentration levels of the contaminant solutes are usually in the ppm range, as in the present work, the total solution volume was assumed to remain constant. To check the validity of this assumption, the volume of the supernatant was measured for a few samples. No noticeable change was observed within the accuracy provided by the experimental instrumentation.

Results and Discussion

Adsorption equilibrium isotherms describing the binding tendencies of chloroform, carbon tetrachloride, and 1,1,1-trichloroethane on three well characterized soil samples were measured at 20 °C. Although soil temperature varies due to climatic changes and depth, 20 °C may represent a typical soil temperature for the most part of the year in several regions. For all chlorinated hydrocarbons examined, the isotherms were essentially linear, showing no indication of curvature at even concentrations approaching saturation. This implies constant retardation factor for subsurface transport.

The results of single-solute isotherm studies are presented in Table 1 for each solute−soil pair. The Henry's isotherm constants (*K*) were calculated in the standard manner, namely the ratio of the amount of contaminant adsorbed in micrograms per gram of soil to the equilibrium concentration in mg/L.

As can be observed from Table 1, all soils adsorbed appreciable quantities of choroform in comparison to 1,1,1-trichloroethane and carbon tetrachloride, while carbon tetrachloride was adsorbed in the least amount. In contrast to the claims for the strong impact of solute's aqueous solubility on sorption (Chiou et al., 1979), the Henry's isotherm constants were not inversely correlated with the corresponding solubilities. Adsorption increased as the dipole moment of the solute increased. This implies that chloroform interacts significantly with the binding sites on the soil samples. Consequently, the strong positive interaction between the surface and the adsorbate overcomes even a fairly strong solute−solvent interaction. It should be noted that the same trend was observed in a previous investigation (Chen, 1993), in that vapor-phase adsorption of the same chlorinated hydrocarbon−soil pairs was studied. Furthermore, the trend was positively correlated with

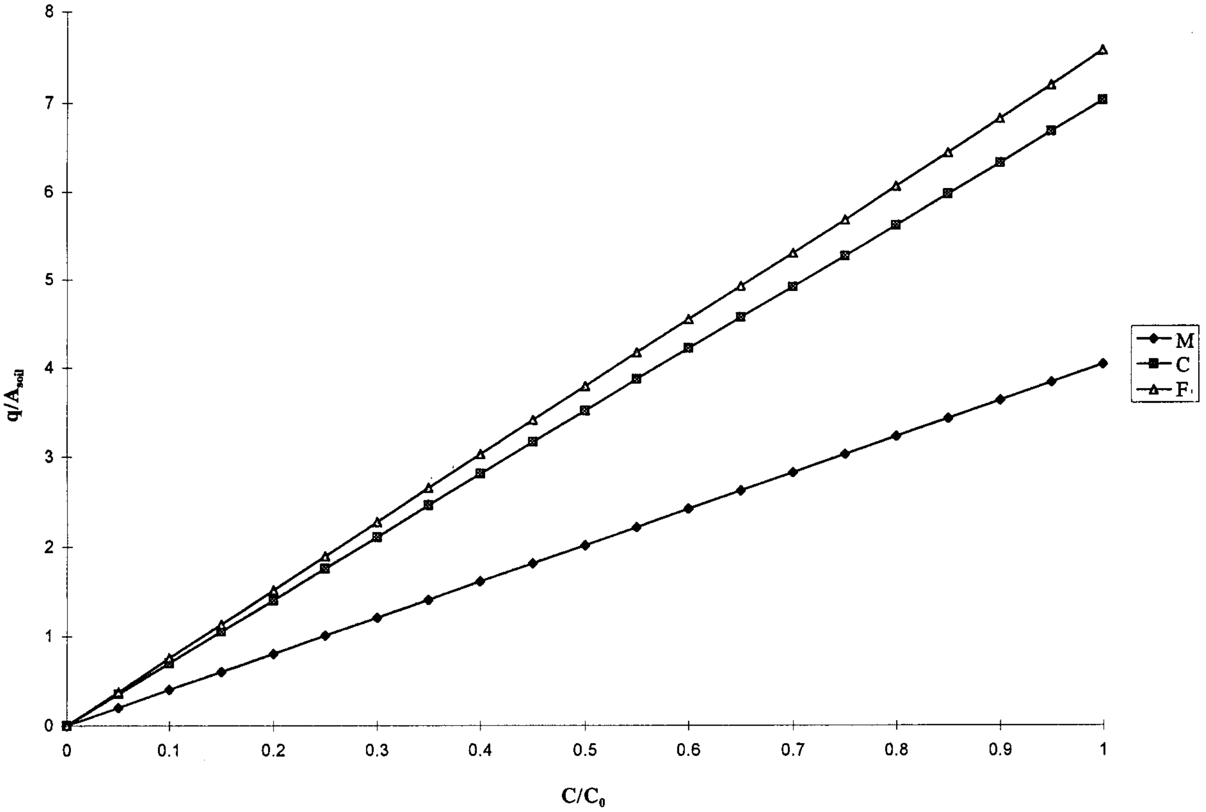

Figure 1. Normalized adsorption isotherms of chloroform on different soils.

the heat of adsorption values, a direct indication of the strength of binding forces reported.

The isotherms of a specific solute on three soils were qualitatively similar, but equilibrium uptakes corresponding to the same equilibrium concentration were different. On the basis of Henry's isotherm constants (*K*), different soils adsorbed the same solute with the following order: Missouri > California > Florida. Since adsorption is a surface phenomena, the uptake capacity of a specific soil depends on its specific surface area and pore size as well as the size of the adsorbate molecule. Earlier studies imply that the mineral content and the organic matter provide most of the surface area available for adsorption. As the clay percentage increases or the fraction of organic matter becomes small, adsorption to inorganic mineral surface becomes significant (Chiou et al., 1979). The specific surface areas reported in the Materials section exhibit the following trend: Missouri > California > Florida. Therefore the order of adsorption uptake, for all pollutants, was expected to follow the same trend. This is exactly reflected through the *K* values reported in Table 1.

To negate the differences in saturation solubility and specific surface area on the adsorption, normalized (reduced) isotherms were also constructed from

$$q/A_{\mathrm{soil}} = K^{\mathrm{I}}(C/C_0) \qquad (1)$$

where q/A_{soil} is the equilibrium uptake per unit area of soil (mmol/m^2), C and C_0 are the equilibrium and the saturation concentrations, respectively, and K^{I} is the normalized isotherm constant. The normalized isotherms of different sorbates on different soils are illustrated in Figures 1−3, and the normalized isotherm constants, K^{I}, are reported in Table 1 along with *K* values. Accordingly, adsorption on per unit area of different soils exhibits the following trend: Florida > California > Missouri. This trend is the opposite of the one obtained from *K* values. On the basis of these observations and a previous investigation (Chiou et al., 1979), it is reasonable to suggest that the clay and organic matter content provide most of the suface area for adsorption, that in turn increases the total adsorption uptake. On the other hand, silt−sand portion of the soils have higher adsorption potential for organic compounds.

Competitive sorption studies were carried out in two steps. First, the sorption isotherms of $CHCl_3$−CCl_4, $CHCl_3$−$C_2CH_3Cl_3$, and $C_2CH_3Cl_3$−CCl_4 binary pairs on three soils were generated. The results were evaluated in terms of binary solute linear isotherm (K_b) and normalized isotherm (K_b^{I}) constants, relative distribution coefficients (K_b/K and $K_b^{\mathrm{I}}/K^{\mathrm{I}}$) and selectivities. Then, ternary solute isotherms ($CHCl_3$, $C_2CH_3Cl_3$, CCl_4) were measured and analyzed in terms of ternary solute isotherm (K_m) and linear isotherm (K_m^{I}) constants, relative distribution coefficients (K_m/K and $K_m^{\mathrm{I}}/K^{\mathrm{I}}$) and selectivity of an individual compound with respect to another constituent in the mixture. The intent was to observe the influence of the additional species on the previously studied binary pairs.

The binary distribution coefficients (K_b and K_b^{I}), presented in Tables 2−4, are significantly lower than the single-solute coefficients (K and K^{I}). However, they followed a similar trend on a specific soil: $CHCl_3 > C_2CH_3Cl_3 > CCl_4$. The magnitude of decrease in K_b, that can be deducted from the relative distribution coefficients (K_b/K and $K_b^{\mathrm{I}}/K^{\mathrm{I}}$) of Tables 2, 3, and 4, is different for each compound with the following order: $CHCl_3 < C_2CH_3Cl_3 < CCl_4$. This order is inversely related to their polarity, that suggests that different molecules are inclined to compete for the same site on soil minerals primarily because of their different polarity.

The multisolute linear isotherm (K_m) and normalized isotherm (K_m^{I}) constants are presented in Table 5. As expected, K_m and K_m^{I} values are substantially lower than

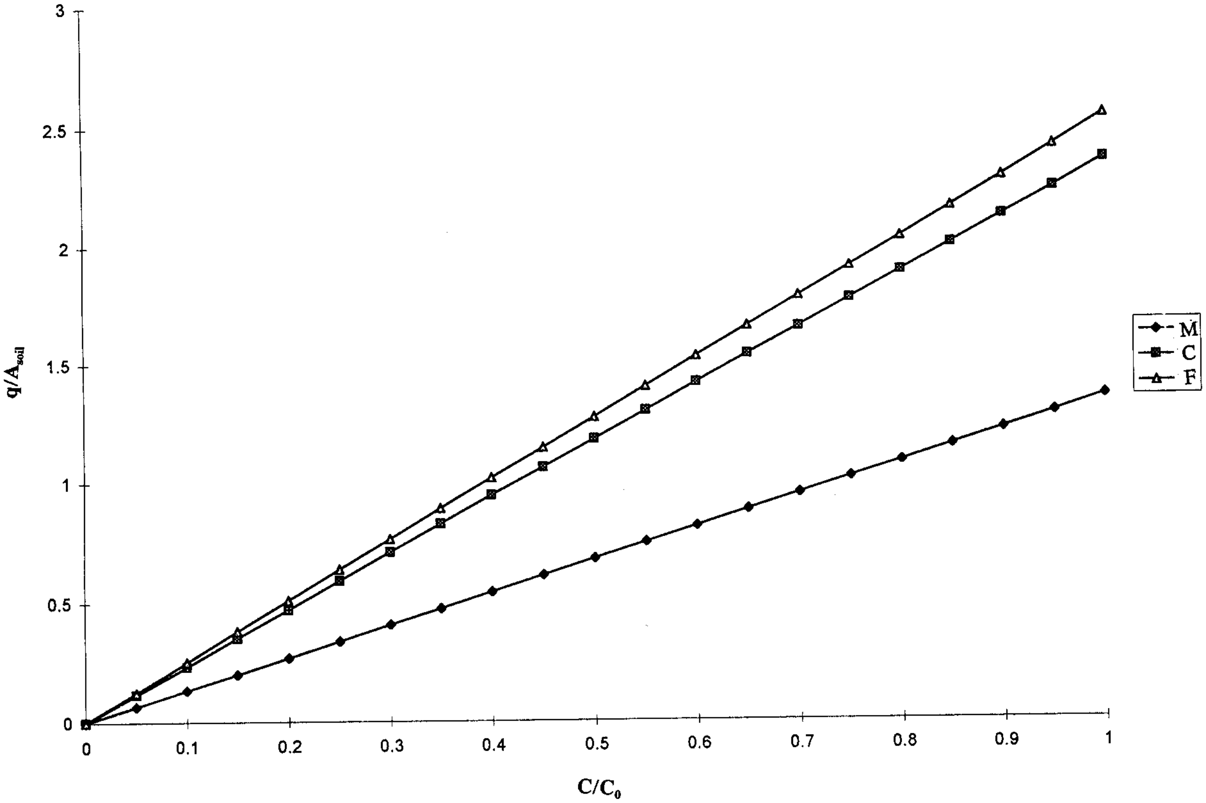

Figure 2. Normalized adsorption isotherms of 1,1,1-trichloroethane on different soils.

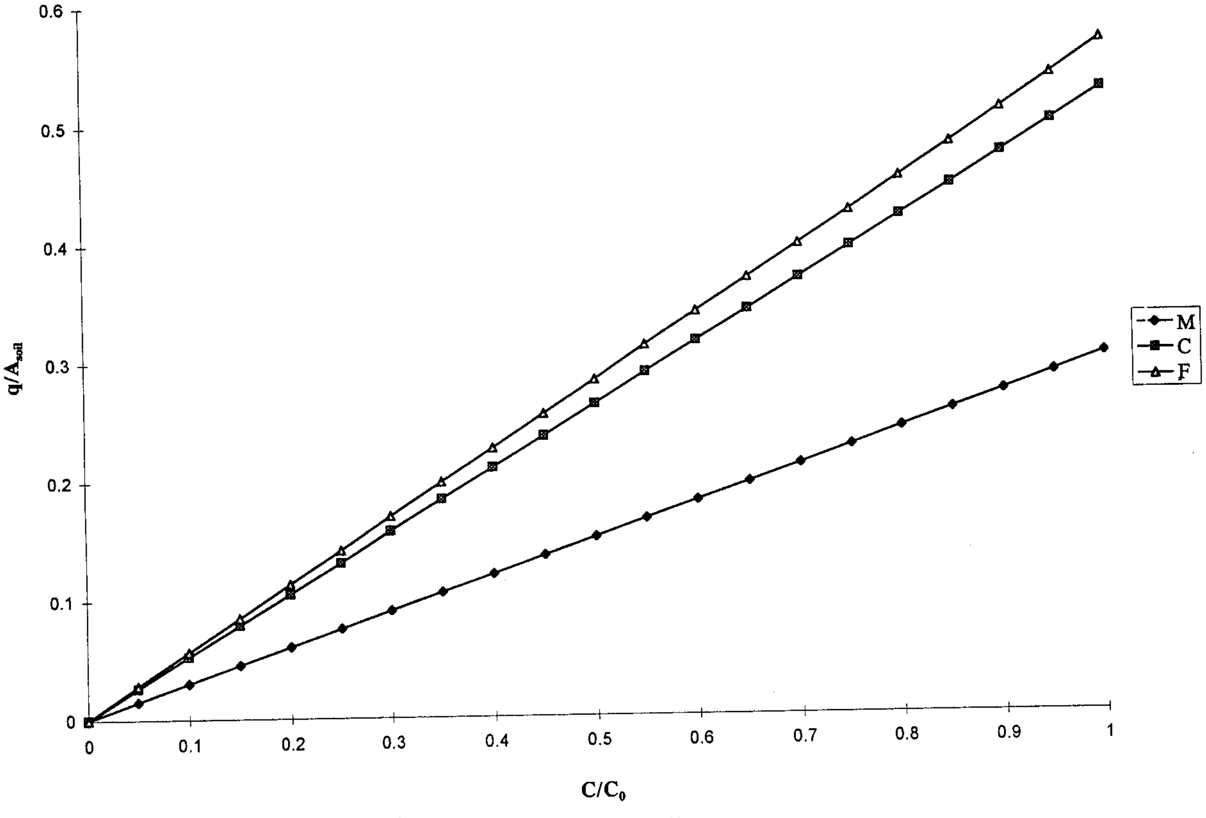

Figure 3. Normalized adsorption isotherms of carbon tetrachloride on different soils.

the K_b and K_b^I values. However, they followed the same trend, both for their magnitude and for the decrease in their magnitudes. These results confirm that the polarity of the compound, rather than its aqueous solubility, dominates the competitive adsorption in soils.

The selectivity information is presented in Table 6. Accordingly, chlorinated aliphatic hydrocarbons compete moderately for the sites available for adsorption on soil, within a selectivity range from 1.17 to 2.22. It is also clear that while the adsorbate properties determine the nature

Table 2. Binary-Solute Linear Isotherm Constants (K_b) and Normalized Isotherm Constants (K_b^I) of $CHCl_3$ and CCl_4

soil sample	compd	K_b/(μg g^{-1} mg^{-1} L)	K_b^I/ (mmol/m^2)	standard error	K_b/K (or K_b^I/K^I)
Missouri	$CHCl_3$	1.179	2.226	0.030	0.53
	CCl_4	0.813	0.144	0.017	0.48
California	$CHCl_3$	1.128	3.705	0.028	0.58
	CCl_4	0.734	0.259	0.011	0.49
Florida	$CHCl_3$	0.844	4.18	0.018	0.47
	CCl_4	0.410	0.137	0.008	0.36

Table 3. Binary-Solute Linear Isotherm Constants (K_b) and Normalized Isotherm Constants (K_b^I) of $CHCl_3$ and $C_2H_3Cl_3$

soil sample	compd	K_b/(μg g^{-1} mg^{-1} L)	K_b^I/ (mmol/m^2)	standard error	K_b/K (or K_b^I/K^I)
Missouri	$CHCl_3$	1.303	2.456	0.047	0.61
	$C_2H_3Cl_3$	0.847	0.635	0.026	0.47
California	$CHCl_3$	1.252	4.150	0.037	0.65
	$C_2H_3Cl_3$	0.789	1.031	0.020	0.50
Florida	$CHCl_3$	1.205	4.277	0.035	0.68
	$C_2H_3Cl_3$	0.542	0.754	0.019	0.40

Table 4. Binary-Solute Linear Isotherm Constants (K_b) and Normalized Isotherm Constants (K_b^I) of CCl_4 and $C_2H_3Cl_3$

soil sample	compd	K_b/(μg g^{-1} mg^{-1} L)	K_b^I/ (mmol/m^2)	standard error	K_b/K (or K_b^I/K^I)
Missouri	CCl_4	0.914	0.162	0.016	0.54
	$C_2H_3Cl_3$	1.137	0.852	0.026	0.63
California	CCl_4	0.858	0.266	0.009	0.57
	$C_2H_3Cl_3$	1.075	1.404	0.023	0.67
Florida	CCl_4	0.710	0.237	0.024	0.62
	$C_2H_3Cl_3$	0.938	1.322	0.014	0.70

Table 5. Ternary-Solute Linear Isotherm Constants (K_m) and Normalized Isotherm Constants (K_m^I)

soil sample	compd	K_m/(μg g^{-1} mg^{-1} L)	K_m^I/ (mmol/m^2)	standard error	K_m/K (or K_m^I/K^I)
Missouri	$CHCl_3$	0.920	1.732	.0.024	0.43
	$C_2H_3Cl_3$	0.710	0.527	0.020	0.39
	CCl_4	0.607	0.108	0.012	0.36
California	$CHCl_3$	0.555	1.852	0.014	0.29
	$C_2H_3Cl_3$	0.401	0.520	0.011	0.25
	CCl_4	0.334	0.101	0.012	0.22
Florida	$CHCl_3$	0.490	1.752	0.008	0.28
	$C_2H_3Cl_3$	0.317	0.434	0.007	0.23
	CCl_4	0.242	0.079	0.005	0.21

Table 6. Selectivity (S) Information[a]

soil type	B/T	S_{1-2}	S_{1-3}	S_{2-3}
Missouri	B	1.54	1.45	1.24
	T	1.30	1.52	1.17
California	B	1.58	1.54	1.25
	T	1.38	1.66	1.20
Florida	B	2.22	2.05	1.32
	T	1.54	2.07	1.31

[a] 1 = $CHCl_3$; 2 = $C_2CH_2Cl_3$; 3 = CCl_4. B = in binary mixture; T = in ternary mixture.

Table 7. Single-Solute Linear Isotherm Constants (K_c) and Normalized Isotherm Constants (K_c^I) for Methanol−Water Systems at $f_c = 0.25$

soil sample	compd	K_c/(μg g^{-1} mg^{-1} L)	K_c^I/ (mmol/m^2)	standard error	K_c/K (or K_c^I/K^I)
Missouri	$CHCl_3$	1.113	2.101	0.027	0.52
	$C_2H_3Cl_3$	1.080	0.809	0.020	0.49
	CCl_4	0.985	0.175	0.012	0.41
California	$CHCl_3$	0.909	2.992	0.044	0.47
	$C_2H_3Cl_3$	0.880	1.150	0.042	0.41
	CCl_4	0.862	0.267	0.016	0.39
Florida	$CHCl_3$	0.767	2.752	0.038	0.43
	$C_2H_3Cl_3$	0.722	1.018	0.007	0.40
	CCl_4	0.709	0.237	0.005	0.36

Table 8. Single-Solute Linear Isotherm Constants (K_c) and Normalized Isotherm Constants (K_c^I) for Methanol−Water Systems at $f_c = 0.50$

soil sample	compd	K_c/(μg g^{-1} mg^{-1} L)	K_c^I/ (mmol/m^2)	standard error	K_c/K (or K_c^I/K^I)
Missouri	$CHCl_3$	0.566	0.107	0.038	0.26
	$C_2H_3Cl_3$	0.504	0.378	0.017	0.28
	CCl_4	0.492	0.087	0.023	0.29
California	$CHCl_3$	0.468	1.540	0.034	0.24
	$C_2H_3Cl_3$	0.419	0.547	0.026	0.26
	CCl_4	0.407	0.126	0.031	0.27
Florida	$CHCl_3$	0.424	1.505	0.038	0.24
	$C_2H_3Cl_3$	0.358	0.504	0.017	0.27
	CCl_4	0.352	0.118	0.003	0.31

of the competition, soil properties determine its quantification. Although all selectivities from the ternary solute mixture are in accordance with the polarity of the compounds, selectivities of $CHCl_3$−$C_2H_3Cl_3$ and $CHCl_3$−CCl_4 from the binary solute mixtures display a slightly different trend. Since carbon tetrachloride is nonpolar, chloroform would have been expected to have higher selectivity with respect to carbon tetrachloride (as in the case of ternary mixture). This behavior can be attributed to the aqueous solubilities of the compounds. The solubility of chloroform is 8.3 times that of carbon tetrachloride, while it is only 2.22 times that of 1,1,1-trichloroethane. The substantial difference in the solubilities result in a higher tendency for chloroform to stay in the aqueous phase for the $CHCl_3$−CCl_4 pair with respect to other cases. Nevertheless, the selectivity in favor of chloroform (1.45) implies the dominance of the polarity effect.

Further examination of Table 6 shows that selectivity of a compound from the same mixture is different on different soils. In all cases, the selectivity for the compound with higher polarity increased on different soils with the following order: Missouri < California < Florida. This trend is opposite to the organic matter content of the soils, suggesting that inorganic (mineral) constituents of the soil are more selective to the polar compounds. Thus, in soils with low organic matter, higher competition among the organic contaminants should be expected. However, total sorption capacity will tend to be low. These findings support Wang et al.'s (1993) claim related to sorption of toxic organic compounds on waste water solids. Accordingly, the degree of competition depends on whether partitioning or adsorption dominates the sorption. For compounds whose sorption uptake is primarily that of adsorption, the competition will be significant; for compounds whose sorption uptake is primarily that of partitioning, the competition effect will be negligible.

Influence of cosolvent was investigated by generating single solute and ternary solute sorption isotherms from 25% and 50%, by volume, methanol−water solutions. The results of the single solute studies, in terms of single solute linear isotherm (K_c) and normalized isotherm (K_c^I) constants are presented in Tables 7 and 8, where f_c is the volume fraction of methanol. As one can see, the general trend is that as the volume fraction of cosolvent increases, the equilibrium uptake for chlorinated hydrocarbons decreases significantly. Similar observations were made by previous investigators (Rao et al., 1985) who studied the adsorption of pentachlorophenol from ethanol−water solution on soil. They attributed the decrease of the equilibrium uptake entirely to the increase of the solubility of the compound in the solution. Although solubility is a con-

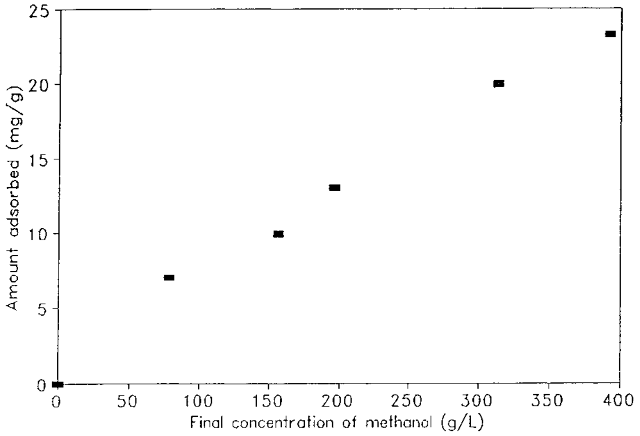

Figure 4. Methanol adsorption on Missouri soil.

Table 9. Ternary-Solute Linear Isotherm Constants (K_{cm}) and Normalized Isotherm Constants (K_{cm}^I) for Methanol−Water Systems at f_c = 0.25

soil sample	compd	K_{cm}/(μg g^{-1} mg^{-1} L)	K_{cm}^I/ (mmol/m^2)	standard error	K_{cm}/K_m (or K_{cm}^I/K_m^I)
Missouri	$CHCl_3$	0.369	0.695	0.048	0.40
	$C_2H_3Cl_3$	0.255	0.189	0.023	0.36
	CCl_4	0.201	0.036	0.046	0.33
California	$CHCl_3$	0.195	0.651	0.051	0.35
	$C_2H_3Cl_3$	0.124	0.161	0.037	0.31
	CCl_4	0.099	0.030	0.052	0.30
Florida	$CHCl_3$	0.157	0.561	0.027	0.32
	$C_2H_3Cl_3$	0.085	0.116	0.044	0.27
	CCl_4	0.058	0.019	0.061	0.24

Table 10. Ternary-Solute Linear Isotherm Constants (K_{cm}) and Normalized Isotherm Constants (K_{cm}^I) for Methanol−Water Systems at f_c = 0.50

soil sample	compd	K_{cm}/(μg g^{-1} mg^{-1} L)	K_{cm}^I/ (mmol/m^2)	standard error	K_{cm}/K_m (or K_{cm}^I/K_m^I)
Missouri	$CHCl_3$	0.258	0.486	0.053	0.28
	$C_2H_3Cl_3$	0.168	0.125	0.031	0.24
	CCl_4	0.132	0.024	0.022	0.22
California	$CHCl_3$	0.105	0.352	0.049	0.19
	$C_2H_3Cl_3$	0.052	0.068	0.036	0.13
	CCl_4	0.036	0.011	0.041	0.11
Florida	$CHCl_3$	0.109	0.210	0.043	0.12
	$C_2H_3Cl_3$	0.024	0.035	0.016	0.08
	CCl_4	0.014	0.005	0.027	0.06

tributing factor, it is believed that the decrease of the equilibrium uptake is caused by methanol adsorption on soil. As shown in Figure 4, methanol was adsorbed significantly on soil, decreasing the chlorinated hydrocarbon adsorption. Thus, for waste streams containing substantial amount of cosolvent, chlorinated hydrocarbons are likely to reach the ground water. For aqueous wastes on the other hand, they will be adsorbed by soil.

In Tables9 and 10, linear isotherm (K_{cm}) and normalized isotherm (K_{cm}^I) for ternary solute adsorption from cosolvent solution have been compared with that of multisolute adsorption from aqueous solution (K_m and K_{cm}^I). As can be seen from these tables, in all cases, the change in K_{cm} for CCl_4 with respect to K_m is the largest, and the change of K_{cm} for $CHCl_3$ with respect to K_m is the smallest. The selectivity information in Table 11 shows that the competition among the chlorinated hydrocarbons decreases with the addition of cosolvent. These results suggest that the increased solubility of the compounds in the mixture counteracts the competition due to polarity. As a results, competition diminishes.

Table 11. Selectivity (*S*) Information for Soil−Water−Methanol Systems[a]

soil type	f_c	S_{1-2}	S_{1-3}	S_{2-3}
Missouri	0.00	1.30	1.52	1.17
	0.25	1.03	1.13	1.08
	0.50	1.12	1.15	1.02
California	0.00	1.38	1.66	1.20
	0.25	1.03	1.05	1.02
	0.50	1.11	1.15	1.03
Florida	0.00	1.54	2.07	1.31
	0.25	1.06	1.08	1.02
	0.50	1.18	1.20	1.01

[a] 1 = $CHCl_3$; 2 = $C_2CH_3Cl_3$; 3 = CCl_4.

Because the initial solute concentrations were not in a comparible range with the methanol solution (25% to 50 vol %), driving definite conclusions based on the selectivity for methanol were not feasible in the present work. A competitive aqueous phase sorption study among the chlorinated hydrocarbons and methanol (or a similar cosolvent) within a comparable initial concentration range can quantify the competition and clarify the involved mechanisms behind the substantial hindering effect of the cosolvent. Also needed is liquid−liquid ternary equilibrium data of methanol−water-chlorinated hydrocarbon systems for solubility quantification, that have not been located in the existing literature. This can lead to quantitative identification of the degree of significance of dissolution as a mechanism.

Literature Cited

Chen, C. H. Adsorption of Chlorinated Hydrocarbon Vapors on Soils. M.S. Thesis, University of Missouri−Columbia, 1993.

Chiou, T. C.; Peters, J. K.; Freed, H. V. A Physical Concept of Soil−Water Equilibria for Nonionic Organic Compounds. *Science* **1979** *206*, 831−832.

Kaiser, K.; Zech, W. Competitive Sorption of Dissolved Organic Matter Fractions to Soils and Related Mineral Phases. *Soil Sci. Soc. Am. J.* **1997**, *61:* (1), 64−68.

Lee, J.; Crum, J. R.; Boyd, S. A. Enhanced Retention of Organic Contaminant by Soils Exchanged with Organic Cations. *Environ. Sci. Technol.* **1989**, *23*, 1365−1372.

Mokraurer, J. E.; Kosson, D. S. Electrophysical Sorption of Single Carbon Halogenated Solvents onto Soil. *Environ. Prog.* **1989**, *8*, 1−5.

Rao, P. S. C.; Hornsby, A. G.; Kilcrease, D. P.; Nkedekiaz, P. Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems. *J. Environ. Qual.* **1985**, *14*, 376−383.

Roy, W. R.; Krapac, I. G.; Chou, S. F. J.; Griffin, R. A. *Batch Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals*; EPA/530-SW-006; U.S. EPA: Cincinnati, OH, 1991.

Stenzel, M. H. Remove Organics by Activated Carbon Adsorption. *Chem. Eng. Prog.* **1993**, March, 36−43.

Trania, S. J.; Onken, B. M. Cosorption of Aromatic N-Heterocycles and Pyrene by Smectites in Aqueous Solutions. *J. Contam. Hydrol.* **1991**, *7*, 237−259.

Wang, L.; Govind, R. Sorption of Organic Compounds on Wastewater Solids: Mechanism and Modelling. *Environ. Sci. Technol.* **1993**, *27*, 152−158.

Wood, A. L.; Bouchard, D. C.; Brusseau, M. L.; Rao, S. C. Cosolvent Effects on Sorption and Mobility of Organic Contaminants in Soils. *Chemosphere* **1990**, *21*, 575−587.

Zachara, J. M. Sorption of Binary Mixtures of Aromatic Nitrogen Heterocyclic Compounds on Subsurface Materials. *Environ. Sci. Technol.* **1987**, *21*, 397−402.

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