

# SORPTION OF ORGANIC POLLUTANTS FROM VAPOR PHASE: THE EFFECTS OF NATURAL SOLID CHARACTERISTICS AND MOISTURE CONTENT

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## ABSTRACT

The sorption of trichloroethylene (TCE) from vapor phase onto natural solids was investigated by batch sorption experiments. The effects of natural solid characteristics and moisture content on the sorption of TCE vapor were evaluated. As natural solids, six different US EPA soils and sediments were used. The moisture content of each natural solid was adjusted at four different values, including oven-dried condition. The linear sorption coefficients of TCE from the vapor phase ( $K_d'$ ) were about one to four orders of magnitude greater than those from the aqueous phase. The  $K_d'$  values for the oven-dried natural solids had poor correlation to the organic carbon content of natural solids. These results indicated that the sorption of TCE vapor was not controlled by the organic carbon referenced hydrophobic sorption. The  $K_d'$  values for the oven-dried natural solids, however, correlate well with the cation exchange capacity (CEC) and swelling clay content of natural solids. The interaction of TCE molecules with the exchangeable cations on natural solid surface could be a dominant sorption mechanism. The  $K_d'$  values decreased with increasing the moisture content of natural solids. The water on natural solid surface interferes the vapor-phase sorption of TCE onto the surface cations.

## KEYWORDS

Sorption; linear sorption coefficients; batch sorption experiments; vapor phase; volatile organic compounds; trichloroethylene; organic carbon content; cation exchange capacity; swelling clay content; moisture content.

## INTRODUCTION

Environmental pollution by organic compounds has been of growing concern due to their widespread utilization by industrial, agricultural, and domestic users. Evaluating the transport, potential biological effects, and ultimate fate of organic compounds requires knowledge of the sorption behavior of the organic compounds onto the natural solids (e.g., soils, sediments, and aquifer materials).

Much effort has been toward understanding the sorption of variety of hydrophobic organic compounds onto natural solids from aqueous phase. The vast majority of organic compounds investigated were non-ionic hydrophobic organic compounds of limited water solubility ( $< 10^{-3}$  M) (Karickhoff, 1981, 1984). For those non-ionic hydrophobic organic compounds, the sorption to natural solids from aqueous phase is dominated by "organic carbon referenced hydrophobic sorption". Sorption isotherms are linear if the concentration of organic compound in aqueous phase is below  $10^{-5}$  M or below one half of the aqueous phase solubility (whichever is lower) (Karickhoff, 1981, 1984; McCarty *et al.*, 1981). For natural solids, the organic matter constituent dominates the sorption of non-ionic hydrophobic organic compounds. Sorption coefficients normalized to the organic carbon content of natural solids ( $K_{OC}$ ), are relatively

independent of other natural solid and aqueous phase characteristics. The sorption onto the organic matter can be *a priori* estimated from the hydrophobicity of organic compounds based on the Linear Free Energy Relationships (Leo *et al.*, 1971; Chiou *et al.*, 1981, 1982, 1983; Karickhoff, 1981, 1984; Schwarzenbach and Westall, 1981; Miller *et al.*, 1985), as indicated by the 1-octanol/water partition coefficient ( $K_{ow}$ ) (Figure 1).

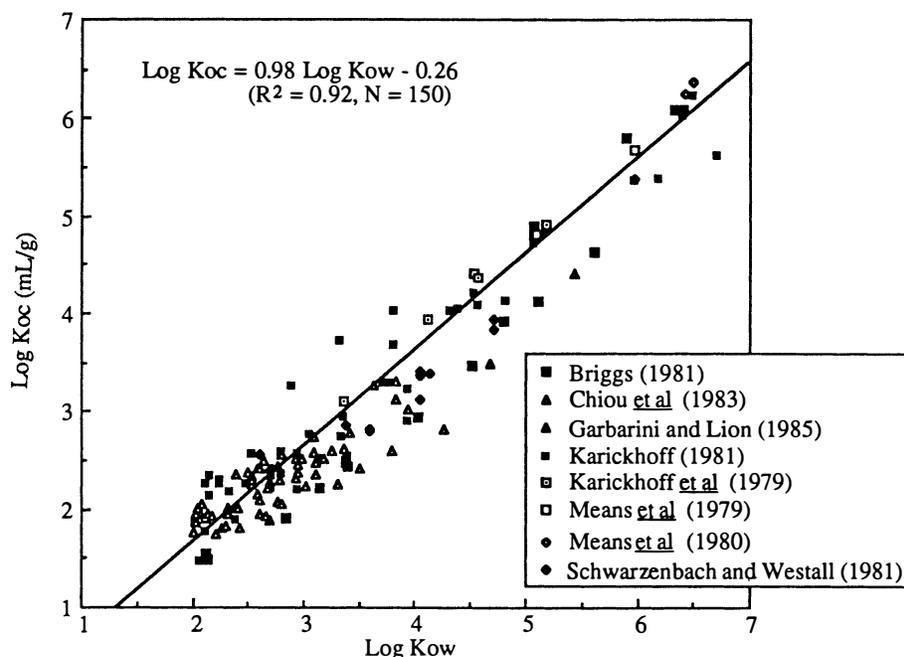


Figure 1. Correlation between observed sorption coefficients ( $K_{oc}$ ) and 1-octanol/water partition coefficients ( $K_{ow}$ ).

The mechanisms of sorption of organic compounds—including neutral (non-ionic and non-polar), ionic, and polar species—onto natural solids from aqueous phase have been summarized by several investigators (Mortland, 1970, 1985; Hamaker and Thompson, 1972; Khan, 1972; Stevenson, 1972; Harter, 1977; Voice and Weber, 1983). An organic compound may be sorbed by the various sorptive mechanisms:

1. Interactions between an organic ion and the electrical double layer
2. Ion exchange
3. Coordination by surface metal cations
4. Ion-dipole interaction
5. Hydrogen bonding
6. Van der Waals-London forces
7. Hydrophobic interaction

Due to the heterogeneous nature of natural solids, it is difficult to evaluate the relative importance of the various sorption mechanisms. Actual sorption processes probably involve varying degrees of several types of interactions, but often one type predominates (Hamaker and Thompson, 1972; Voice and Weber, 1983).

The sorption mechanisms (1) and (2) are not important for the non-ionic organic compounds. Coordination by exchanged metal cations is important when the organic compound is an electron donor (Lewis base) relative to water, such as amines (Mortland, 1970, 1985; Stevenson, 1972). The ion-dipole interaction between charged surface and the uncharged non-ionic organic compound is also expected to be negligible in aqueous solution. Finally, hydrogen bonding is considered to be an insignificant contribution to the sorption (Mortland, 1970, 1985).

These arguments lead to the conclusion that the sorption of non-ionic organic compounds from aqueous phase results primarily from van der Waals-London forces reinforced by the hydrophobic interaction. The combined effect of these two mechanisms is often referred to as hydrophobic sorption (Hamaker and Thompson, 1972; Voice and Weber, 1983). The thermodynamic driving force for the hydrophobic sorption is the increase in entropy which occurs upon dehydration of the organic molecules. In the aqueous phase, the non-ionic organic molecule is surrounded by an envelope of structured water molecules. As the organic molecule is transferred from the aqueous phase to the non-aqueous solid phase, the structural envelope of water molecules breaks down and the entropy of the system increases (Hamaker and Thompson, 1972; Horvath *et al.*, 1977, 1978; Chiou *et al.*, 1979; Schwarzenbach and Westall, 1981; Voice and Weber, 1983).

Many hydrophobic chlorinated organic compounds, such as TCE, tetrachloroethylene (PCE), and trichloroethane (TCET), volatilize when they are released to the environment due to their low boiling points. For these volatile organic compounds, the sorption from vapor phase must be considered. The organic carbon referenced hydrophobic sorption is, however, not applicable to the vapor-phase sorption. And the investigations on the vapor-phase sorption onto natural solids are, however, generally lacking. Under oven-dried conditions, vapor-phase sorption coefficients have been shown to be highly correlated with specific surface area (Ong and Lion, 1991). The sorption is greatly affected by the amount of moisture present in the system (Ong and Lion, 1991).

### RESEARCH OBJECTIVE

Given the above limited data, the objective of this research is to investigate the effects of natural solid characteristics and moisture content on the sorption of volatile organic compounds from vapor phase. Additional information on the vapor-phase sorption would enhance the present ability to predict the fate of volatile organic compounds in natural environments.

### EXPERIMENTAL METHODOLOGY

#### Materials

TCE was selected as the subject for the investigation because it is one of the most common volatile organic pollutants. The TCE was purchased from Nacalai Tesque (99.5%), and used without further purification. High purity distilled deionized water from a Milli-Q system was used throughout the research.

Natural solids consist of heterogeneous mixture of various solid components (e.g., organic matter, clay minerals, and metal oxides), all of which have the possibility of involving the sorption. In this research, six natural solids (soils and sediments) collected by US EPA (i.e., EPA-6, -9, -14, -15, -22, and -23) were selected (Hassett *et al.*, 1980). They provide a wide range of characteristics that have been shown to affect the degree of sorption of organic compounds (Table 1). Two of the most important characteristics for the selection were organic carbon and swelling clay contents, which range from 0.11 to 2.38 wt% and 10.1 to 60.8 wt%, respectively.

TABLE 1 Characteristics of the US EPA Natural Solids

Solid	pH (1:1)	CEC (meq/100 g)	Organic Carbon (wt%)	Swelling Clay (wt%)	Specific Gravity
EPA-6	7.83	33.01	0.72	60.8	2.6992
EPA-9	8.34	12.40	0.11	16.3	2.7217
EPA-14	4.54	18.86	0.48	13.8	2.7536
EPA-15	7.79	11.30	0.95	10.1	2.6927
EPA-22	7.55	8.53	1.67	14.8	2.6995
EPA-23	6.70	31.15	2.38	57.6	2.6520

#### Batch Sorption Experiment

The headspace technique developed by Peterson *et al.* (1988) was employed to measure the TCE vapor-phase sorption coefficients. The batch sorption experiments were carried out in 50 mL (nominal volume)

borosilicate glass bottles. The natural solids were weighed into the bottles, and the bottles were immediately sealed with Teflon-lined rubber septa and aluminum crimp caps. A 0.05 mL of TCE vapor taken from the headspace over pure liquid TCE at 20°C was injected to each bottle with a 0.5 mL gas-tight syringe. The initial relative vapor pressure of TCE was 0.073%. The natural solids and vapor were equilibrated in dark at 20°C for 24 hours. A rotating tumbler (30 rpm.) was used for the mixing, since it has better reproducibility than other mixing systems (Clunie and Giles, 1957; Diamondstone *et al.*, 1982; Roy *et al.*, 1985).

After the equilibration, 0.5 mL of the gaseous headspace was withdrawn with a 1 mL gas-tight syringe and analyzed by a mass fragmentgram method with a gas chromatography/mass spectroscopy (GCMS) (Shimazu QP-1000) equipped with a column of Shimazu CBP20-S50-050 (0.50 µm film, 50 m x 0.33 mm ID). The column temperature was held at 50°C for the first 1 min, then increased to 100°C at 20°C/min. The flow rate of He carrier gas was set at 30 mL/min.

Sorption coefficients ( $K_d'$ ) are determined by the slope of the following relationship:

$$\frac{C_{G1} \cdot V_{G1}}{C_{G2} \cdot V_{G2}} = K_d' \frac{M}{V_{G2}} + 1 \quad (1)$$

Equation (1) can be obtained by equating the mass balance relationships for bottles with natural solids to control bottles without natural solids (Peterson *et al.*, 1988). In Equation (1),  $M$  is the oven-dried mass of the natural solids (masses used ranged from 0.05 to 4 g depending upon the moisture content of natural solids),  $C_{G1}$  and  $C_{G2}$  are the headspace concentrations or equivalently the GCMS signals for a control bottle and a sample bottle, respectively, and  $V_{G1}$  and  $V_{G2}$  are the volumes (mL) of the control bottle (measured as 68.55 mL) and the available gas volume (*i.e.*, total volume less volume of natural solids) of a sample bottle, respectively.

Four different moisture content values, which ranged from 0 to 11.1%, were used. For the adjustment of the moisture content of natural solids, the natural solids were first dried in an oven at 105°C for 24 hours. Then, a required amount of water was added and mixed for 24 hours with the rotating tumbler (30 rpm.).

## RESULTS AND DISCUSSION

Sorption is generally regarded as a rapid process (times to reach equilibrium of minutes to a few hours) and equilibration time of 24 hours are frequently used because of its convenience. Karickhoff (1980, 1984), however, reported that true sorption equilibrium may require weeks (to months) to achieve. The equilibration time in batch sorption experiments should be the time interval in which the system reaches chemical equilibrium and the concentrations of the products and reactants cease to change with respect to time. In this research, an operational definition of equilibrium suggested by US EPA (1982) was adopted, that is, the equilibrium time should be the minimum amount of time needed to establish a rate of change equal to or less than 5 % per 24 hour interval. Preliminary investigation on the kinetics indicated that this operational definition was satisfied within 24 hours (Figure 2). Therefore, the equilibration time of 24 hours was used in this research for the batch sorption experiments.

Linear Sorption Isotherms were observed for the vapor-phase sorption of TCE onto the natural solids, as indicated in Figure 3. The slope of the straight line was determined by fit to Equation (1). Table 2 summarizes the vapor-phase sorption coefficients of TCE ( $K_d'$ ) under various moisture contents. The sorption coefficients from aqueous phase ( $K_d$ ), which are estimated from the Equation shown in Figure 1 with  $K_{ow}$  of TCE ( $\log K_{ow} = 2.29$ ), are also given in Table 2. The values of  $K_d'$  are about one to four orders of magnitude greater than those of  $K_d$  for all six natural solids under the moisture contents tested in this research. Therefore, the organic carbon referenced hydrophobic sorption cannot be used as a predictor of  $K_d'$ .

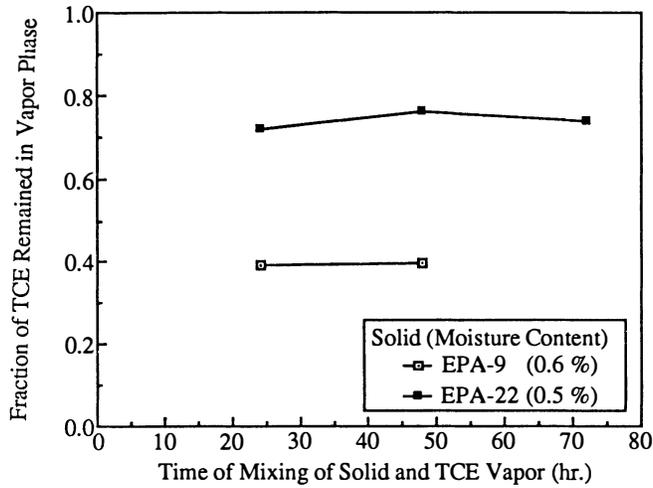


Figure 2. Kinetics of trichloroethylene (TCE) vapor-phase sorption by the EPA solids.

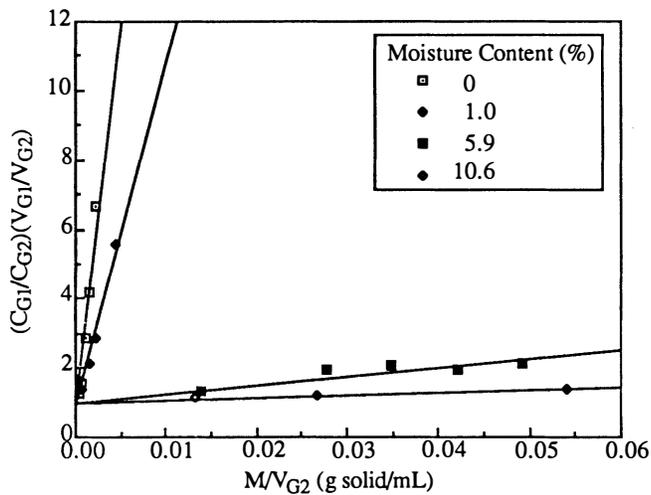


Figure 3. Sorption of trichloroethylene (TCE) at various moisture content onto EPA-6.

TABLE 2 TCE Vapor Phase Sorption Coefficients under Different Moisture Content ( $K_d'$ ) and Estimated Aqueous Phase Sorption Coefficients ( $K_d$ )

Solid	Sorption Coefficient				
	$K_d'$ (mL/g)	$K_d$ (mL/g)	$K_d'$ (mL/g)	$K_d$ (mL/g)	$K_d$ (mL/g)
EPA-6	2,196.9 (0)	989.0 (1.0)	25.3 (5.9)	7.2 (10.6)	0.69
EPA-9	410.2 (0)	249.0 (0.6)	6.3 (1.7)	1.0 (5.0)	0.11
EPA-14	888.7 (0)	328.2 (1.1)	12.3 (3.8)	2.3 (8.2)	0.46
EPA-15	450.0 (0)	248.5 (0.5)	36.0 (1.6)	14.3 (4.7)	0.92
EPA-22	200.7 (0)	51.3 (0.5)	23.7 (1.3)	8.2 (4.7)	1.61
EPA-23	1,713.3 (0)	1,877.6 (1.5)	44.2 (5.2)	10.9 (11.1)	2.30

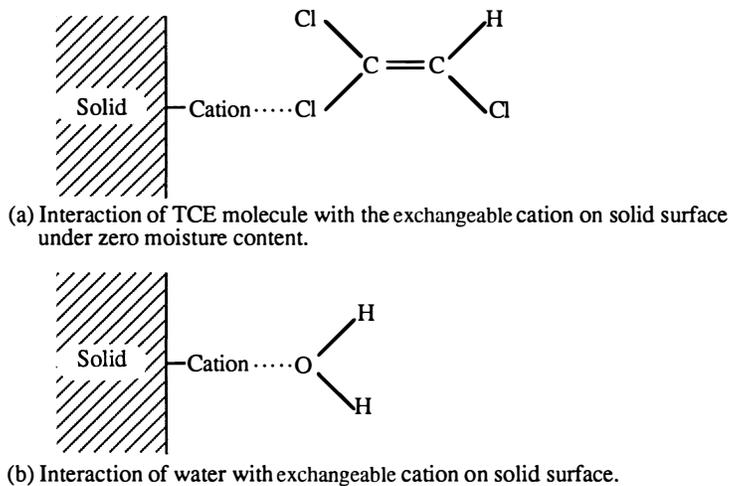
Values in the parentheses represent moisture content (%) of natural solids.

Table 3 provides the correlation coefficients of  $K_d'$  at oven-dried conditions to the natural solid characteristics. The organic carbon content of the natural solids had poor correlation. On the other hand, CEC and swelling clay content were highly correlated. Ong and Lion (1991) observed the highest correlation between the sorption of TCE vapor and specific surface area of natural solids under oven-dried conditions. Specific surface area measurements were not available during the course of this research. The specific surface area, in general, has high correlation to CEC and swelling clay content in natural solids. These results indicate that mechanisms other than hydrophobic sorption to the organic matter of natural solids must be considered when dealing with the sorption of TCE vapor. The TCE vapor may strongly interact with the mineral surfaces of natural solids.

**TABLE 3 Correlation Matrix (R) for TCE Vapor Phase Sorption Coefficients under Oven-Dried Conditions**

Solid Characteristics	Correlation Coefficient
pH (1:1)	0.11
CEC (meq/100 g)	0.99
Organic Carbon (wt%)	0.22
Swelling Clay (wt%)	0.94

The high correlation of  $K_d'$  under oven-dried conditions to CEC of natural solids implies that the interaction of TCE molecule with the exchangeable cation on natural solid surface may be an important sorption mechanism [Figure 4 (a)]. The ability of water to compete with TCE molecules for sorption sites, and hence to substitute for the TCE molecules at the exchangeable cation, is probably the source of the apparent decrease in the amount of TCE vapor sorbed by natural solids [Figure 4 (b)]. In order to make a final conclusion, however, further investigation with other volatile organic compounds (e.g., PCE and TCET) must be necessary.



**Figure 4.** Model of trichloroethylene (TCE) vapor phase sorption onto solids. The surface hydration by water inhibits the sorption. The orientations of TCE and water molecules are not necessarily correct.

The influence of moisture content for the six natural solids is shown in Figure 5. The ordinate is the  $K_d'$  values at various moisture contents normalized with respect to  $K_d'$  at oven-dried condition of each natural solid. The sorption is decreased with increasing moisture content for all six natural solids. A possible reason is that sorption of water onto natural solids results in a decrease in sorption sites available for TCE vapor. It is, however, interesting to note that the decrease in the sorption is not necessarily consistent for all natural solids. For EPA-9 and -23, which respectively have the lowest and highest organic carbon contents among the six natural solids, show rapid and slow decreases, respectively. Although water is sorbed both by organic and mineral constituents of natural solids, the water sorbed by the organic matter may give less interference in the sorption of TCE vapor than that by the minerals.

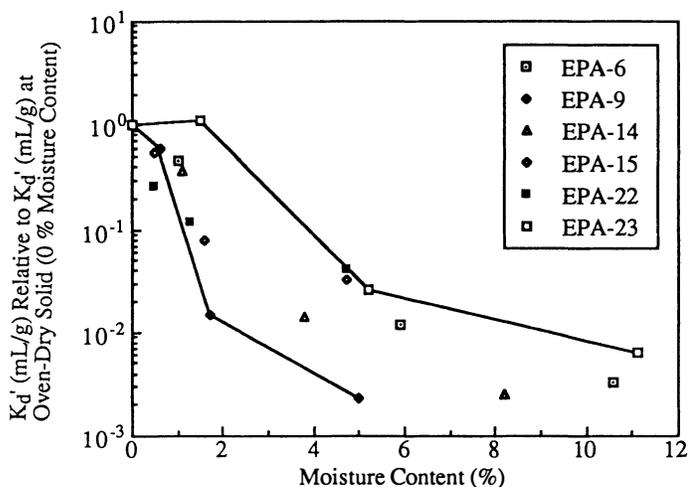


Figure 5. Effect of moisture content on TCE vapor phase sorption.

## CONCLUSIONS

The predominance of organic carbon in "controlling" the sorption of non-ionic hydrophobic organic compounds from the aqueous phase to natural solids of very different origins has been extensively documented. The generalized experimental observations have suggested that the sorption of those organic compounds results primarily from "hydrophobic sorption," and those compounds are sorbed predominantly by the organic matter of natural solids. The sorption coefficient for a natural solid consisting of multiple components can be reduced to a form containing only sorption to organic matter as the controlling phase.

This research indicates that the use of saturated sorption coefficients for TCE onto natural solids as an approximation for vapor phase sorption is not valid. The sorption of TCE vapor is controlled primarily by mineral constituents of natural solids, which is indicated by the high correlations of the sorption coefficients of TCE vapor to CEC and swelling clay content. Furthermore, the water sorbed by natural solids reduces the sorption of TCE vapor.

Overall, this research provides additional insights on the sorption of organic compounds onto natural solids. The practice of assuming the organic carbon referenced hydrophobic sorption for organic vapor should be avoided to obtain accurate predictions. Various natural solid characteristics (organic carbon content, particle size distribution, clay mineral composition [amount and type], pH, CEC, and specific surface area) are considered to affect the vapor phase sorption. Among them, CEC and swelling clay content may be the most important characteristics to the prediction. And the interaction of TCE molecule with the exchangeable cation on natural solid surface could be an important sorption mechanism. Further investigation is, however, required to make a final conclusion, since the combination of only one organic compound (TCE) and six natural solids was used in this research.

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