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# Effects of humidity and soil organic matter on the sorption of chlorinated methanes in synthetic humic-clay complexes

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## Abstract

Vapor-phase sorption is the most influential process governing the transport and the fate of volatile organic compounds in soil. To understand the influence of both soil organic content and the humidity of soil on the vapor sorption is an important process for degradation processes. The single-pellet moment technique was used to investigate sorption and diffusion of trichloromethane (TCM) and carbon tetrachloride (CTC) at varying relative humidities (0–80%) of synthetic humic-clay complex pellets consisting of clay (montmorillonite) and different amounts of organic matter (humic acid). The effective diffusivities of TCM and CTC did not show a noticeable change with moisture and humic acid content. On the other hand, with increasing humic acid content of clay at 0% relative humidity, an appreciable decrease of the equilibrium sorption constants of the tracers (TCM, CTC) was found because of the blockage of some sites of the mineral surfaces and especially micropores by the humic acid. The presence of water also reduced dramatically the sorption of TCM and CTC on synthetic humic-clay complexes. Above 20% relative humidity, the sorption coefficient of TCM and CTC varied only slightly with humic acid content. It was concluded that the sorption of TCM and CTC in synthetic humic-clay complexes was strongly effected by the moisture and humic acid content. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Single-pellet technique; Adsorption in soil; Diffusion in soil; Organic content of soil; Moist soil

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## 1. Introduction

Vapor-phase sorption is the most influential process governing the transport and the fate of volatile organic compounds (VOCs) in soil. The sorption of volatile organic pollutants in soils is strongly influenced by the physical and chemical composition of the soil, such as mineral type and organic carbon content. The moisture content in the soil, as well as the amount and type of clay and humus, play important roles in adsorption and partition processes [1–4].

Clay–mineral surfaces are assumed to be the dominant sorption sites for VOCs in dry soils. However, with an increase in relative humidity, soil organic matter, as a partitioning medium for VOCs is more important than clay–mineral surfaces [5,6]. Many researchers have dealt with natural soils, each of different compositions [1,7–9,11]. How VOCs interact with soil organic matter–soil mineral matter–water complex from these studies is very difficult to understand because many factors vary simultaneously (types and composition of soil's mineral and organic fractions). In this study, using synthetic humic-clay complexes prepared with known humic acid content circumvented this difficulty.

Numerous studies [1–11] have concentrated on VOCs transport and sorption on dry and wet soils. Jin and Jury [12] investigated the dependence of gas diffusion coefficient on soil properties. Batterman et al. [13] measured gas-phase diffusion coefficients at a wide range of water contents, and observed a nonlinear relationship between air-filled porosity and effective gas-phase diffusion coefficients. The effect of soil moisture content on vapor-phase sorption of VOCs was studied using a headspace method, and a model was developed to predict organic vapor sorption by Unger et al. [9]. Rutherford and Chiou [14] studied high-organic-content soils to clarify the effect of the drying–wetting cycle on VOC uptake. Their observations showed that water saturation reduced the sorption (partition) efficiency of organic matter, but this reduction is relatively small when compared with the almost complete suppression by water of adsorption on mineral surfaces. The influence of adsorbent (hematite, corundum, and lime), adsorbate (alkanes, aromatic and chloroaromatic compounds, alcohols, ketones, and ethers), temperature and relative humidity on the adsorption equilibrium was investigated with chromatographic method by Goss and Eisenreich [5]. An exponential reduction in the equilibrium adsorption coefficient was observed as the relative humidity was increased from 30 to 90% [5]. The partitioning of VOCs between soil water and the gas phase in the unsaturated zone was also examined by Washington [15]. The effect of the sorption process on the diffusion of VOCs in moist soil was examined by Cabbar and McCoy [16].

Thus far, a significant amount of research has been reported for the diffusion and the sorption of VOCs on wet and dry soils. Vapor sorption in soils is an important process for special degradation process. However, the current knowledge of this process is still limited and needs further research. A comprehensive understanding of the vapor adsorption of VOC on soil–water system will contribute to the development of effective soil remediation technologies.

The single-pellet moment technique has been used extensively for the measurement of effective diffusivities of nonadsorbing and adsorbing gases, and adsorption equilib-

rium constants in porous catalyst pellets [17,18]. Later, it was shown that the single-pellet moment technique could be successfully used to evaluate tortuosity factors for diffusion in catalyst [19], and the effective thermal conductivity of a monolithic ceramic catalyst support [20]. More recently, Cabbar et al. [10,11,21] modified and applied this technique to investigate adsorption and diffusion of volatile organic contaminants in soil.

In the present study, the single-pellet moment technique was used to investigate the influence of both soil organic content and the humidity of synthetic humic-clay complex pellets on the sorption behavior of trichloromethane (TCM) and carbon tetrachloride (CTC). It was the goal of this work to expand our understanding of the vapor sorption process that depends on many factors including moisture, and the organic carbon content.

## 2. Materials and experimental method

TCM (Merck) and CTC (Merck) tracers were chosen as representative VOCs. Synthetic humic-clay complex was composed of montmorillonite-type clay (natural) and humic acid (Fluka). The origin, composition and some other properties of the natural clay samples were identical with those reported in the previous publications [10,21]. For adjustment of the percentages of humic acid in clay, a precalculated amount of humic acid was dissolved in water with the addition of minimum required amount of 0.1 N KOH. This solution was added to a hot-stirred suspension of clay and mixed, then evaporated to dryness, crushed and sieved. In the preparation of clay-humic complexes containing different percentages of organic carbon, a procedure similar to the one reported by Cabbar et al. [21] and Rebhun et al. [22] was used.

Cylindrical pellets measuring 3.15 mm in length and 13.9 mm in diameter were then made by pressing these powders using a ring-shaped stainless steel pellet holder. The small piece of moist clay prepared by crushing cylindrical pellet, which was saturated with a carrier gas at the desired relative humidity, and placed into the sample cell of the sorptometer. A Dewar flask containing liquid nitrogen was placed around the sample cell. The gas containing 30% nitrogen in helium flowed over this sample at liquid nitrogen temperature and in 2 to 3 min adsorption was complete. The surface areas at different relative humidities (Table 1) were measured by this procedure in a Quantachrome Monosorb apparatus. Pore-size distributions were determined with a Quantachrome 60 mercury porosimeter. Total porosity of 2% and 5% humic acid-clay pellets determined from porosimeter data were 0.41 and 0.39, respectively. In the preparation of the humic-clay pellets, the sample weight was adjusted to have an apparent density of 1.3 g/cm<sup>3</sup>. The pellet was placed into the single-pellet diffusion cell. In the single-pellet moment technique, the single-pellet diffusion cell was placed into the oven of the gas chromatography (Gow Mac Series 350). Details of cell and the experimental procedure are available in the literature [10,17].

Carrier gas (helium) with the desired relative humidity was passed over both faces of the humic-clay pellet (Fig. 1). Adjustment of the relative humidity of the carrier gas was achieved by splitting the gas stream from the helium cylinder into two streams, and passing one through a water saturator. Dry and saturated streams were then mixed. A

Table 1  
Humic-clay pellets surface areas at different relative humidities

% Relative humidity	Surface area (m <sup>2</sup> /g)		
	Pure clay <sup>a</sup>	2% Humic-clay pellet	5% Humic-clay pellet
0	40.6	36.9	32.5
5	32.1	27.8	25.3
20	29.4	25.6	22.7
40	25.7	22.9	20.4
60	22.9	22.7	19.5
80	22.4	20.3	18.9
90	22.0	nd <sup>b</sup>	nd <sup>b</sup>

<sup>a</sup>From Cabbar et al. [10].

<sup>b</sup>Not determined.

three-way valve was used to introduce this gas into the single-pellet cell or to a trap. The relative humidity of the carrier gas stream was determined with magnesium perchlorate traps. The split ratio of the streams determined the final relative humidity and could be modified by adjusting two flowmeters. The experiments were performed at 0, 5, 20, 40, 60 and 80% relative humidities. Before starting the experiments, 3 h were allowed to establish steady-state conditions. Convective transport through the humic-clay pellet was prevented by adjusting the pressures at the pellet ends to be equal. These experiments were carried out by injecting a 1.00- $\mu$ l pulse containing the sorbing or diffusing component (TCM, CTC) into the stream flowing over the upper face of the synthetic

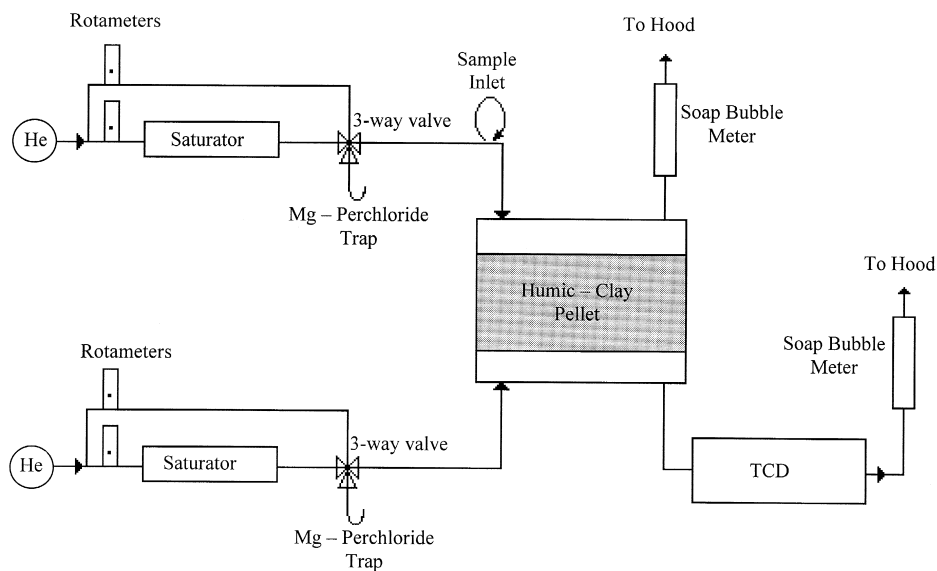


Fig. 1. Experimental setup.

humic-clay pellets which contained 2 and 5% humic acid and moisture (from 0% to 80% relative humidity). The response peak was measured with a thermal conductivity detector placed in the stream leaving the lower face of the pellet (Fig. 1). Response curves were detected at several lower-face-stream flow rates at 30°C. Time delay of the response curve depends on effective diffusivity and sorption equilibrium constants of the tracer (TCM and CTC) in the humic-clay pellet. Initial experiments for testing the sorption reversibility of TCM and CTC material balances were performed, and it was concluded that sorption was reversible. A small tracer amount (1.00- $\mu$ l pulse) was used to ensure sorption linearity, which was also confirmed with different-sized pulses.

### 3. Theory

The differential mass balance for the transport of diffusing component (TCM and CTC) within the moist humic-clay pellet can be expressed as

$$(\rho_p K_{\text{obs}} + \varepsilon_p) \frac{\partial C_A}{\partial t} = D_e \frac{\partial^2 C_A}{\partial x^2} \quad (1)$$

here,  $D_e$  corresponds to the effective diffusion coefficient of the tracer in the pellet,  $\varepsilon_p$  is the total porosity of the pellet,  $\rho_p$  is pellet density, and  $K_{\text{obs}}$  is the observed sorption coefficient which lumped all partitioning effects together. In the presence of water, the organic vapors' sorption might occur by the following mechanisms; (1) adsorption from the vapor phase to the pure mineral surface, (2) adsorption on the surface of a water film that is adsorbed on the mineral, (3) dissolution into an adsorbed water film and soil organic carbon [5,7,8]. The observed sorption coefficient ( $K_{\text{obs}}$ ) lumps each process above. The use of the observed sorption coefficient can be assumed to be valid for very low concentrations of the tracer (TCM and CTC). Because adsorption linearity can be assumed for small tracer concentrations, a moment analysis can easily be performed [17,18]. The  $n$ th moment of the response peak at  $x = L$  is defined as

$$m_n = \int_0^\infty C_A(L, t) t^n dt \quad (2)$$

After Laplace transformation of the partial differential equation (Eq. (1)) with the boundary conditions at  $x = 0$  (where  $C_A = M\delta(t)$ ) and at  $x = L$  (where  $-AD_e\{\partial C_A/\partial x\} = FC_A$ ), the resulting ordinary differential equation can be solved. Here, the initial condition is  $C_A(x, t = 0) = 0$ . Dogu and Smith [17,18] discussed the details of the boundary conditions and the assumptions.

Theoretical moment expressions are obtained using the following relation between  $n$ th moment and Laplacian of the tracer at  $x = L$ :

$$m_n = (-1)^n \lim_{s \rightarrow 0} \frac{d^n(\bar{C}_A)_{x=L}}{ds^n} \quad (3)$$

The zeroth moment expression corresponds to the area under the response curve and for each tracer it is

$$m_0 = \frac{M}{1 + \frac{L}{AD_e} F} \quad (4)$$

where  $A$  is end-face area of pellet,  $L$  is pellet length,  $F$  is lower-face stream volumetric flow rate, and  $M$  is input-pulse strength. A linear relation between the zeroth moment and the lower-face flow rate can be obtained by taking the inverse of Eq. (4),

$$\frac{M}{m_0} = 1 + \frac{L}{AD_e} F. \quad (5)$$

The strength of the input pulse ( $M$ ) was measured independently by placing an impermeable teflon plate over the pellet, and determining the response peak leaving the top chamber of the single pellet cell. The area under the response curve of this peak corresponds to  $M$ . According to Eq. (5), the slope of the inverse of the zeroth moment vs. the lower-face flow rate curve is a function of the effective diffusion coefficient.

The first moment (retention time) is

$$\mu_1 = \frac{m_1}{m_0} = \frac{L^2 \left( 3 \frac{A}{L} D_e + F \right)}{6 D_e \left( \frac{A}{L} D_e + F \right)} \left[ \varepsilon_p + \rho_p K_{\text{obs}} \right] \quad (6)$$

where the first absolute moment,  $\mu_1$ , corresponds to time delay of the response curve.

Experimental values for moments (the zeroth and the first absolute moment) (Eq. (2)) for TCM and CTC were obtained by numerical integration of the response data at the outlet of the lower-face stream of carrier gas. The effective diffusion coefficients for TCM and CTC on humic-clay pellets were determined by regression from the slopes of linear plots of  $M/m_0$  vs. the lower-face flow rate (Eq. (5)). The observed sorption coefficients ( $\rho_p K_{\text{obs}}$ ) of TCM and CTC were evaluated from of Eq. (6) and the experimental data.

#### 4. Results and discussion

The effective diffusion coefficients obtained by the analysis outlined above for humic-clay pellets are given in Table 2 together with the values given for pure clay reported by Cabbar et al. [10]. The effective diffusivities of TCM and CTC did not show a noticeable change with moisture and humic acid content. These effective diffusivities correspond to macropore diffusion coefficients. The macropore effective diffusion coefficient is a strong function of macropore structure. These experimental results indicate that humic acid and also water filled micropore and caused a decrease in surface area (Table 1), but did not change the macropore structure of the pellet significantly.

Table 2

Effective diffusivity of trichloromethane (TCM) and carbon tetrachloride (CTC) in humic-clay pellets

% Relative humidity	Effective diffusion coefficient ( $\text{cm}^2/\text{s}$ )			
	Tracer	Pure clay <sup>a</sup>	2% Humic-clay pellet	5% Humic-clay pellet
0	TCM	0.015	0.010	0.011
0	CTC	0.019	0.014	0.014
80	TCM	0.014	0.008	0.009
80	CTC	0.016	0.012	0.011

<sup>a</sup>From Cabbar et al. [10].

With 5% humic acid–clay pellet, a gradual decrease of the first absolute moments of CTC was observed with an increase in relative humidity (Fig. 2). A similar behavior was observed in the case of CTC with 2% humic acid–clay pellet, and of TCM with 2 and 5% humic acid–clay of varying relative humidities. For comparison, typical data for TCM showing the variation of the first absolute moment with respect to lower-face flow rate with humic-clay pellets (at 0% and 80% relative humidity) is given in Fig. 3. Table 3 and Fig. 3 show that there was a significant difference in the first absolute moment with varying humic acid content of clay at 0% relative humidity. Under dry conditions, the observed sorption coefficient ( $\rho_p K_{\text{obs}}$ ) of 2% humic acid–clay pellet was about two times smaller than the corresponding value for pure clay obtained from earlier publication [10]. Present result for 5% humic acid–clay pellet was likewise four times smaller. This indicated that sorption was mainly on the clay (mineral) surfaces of dry pellets.

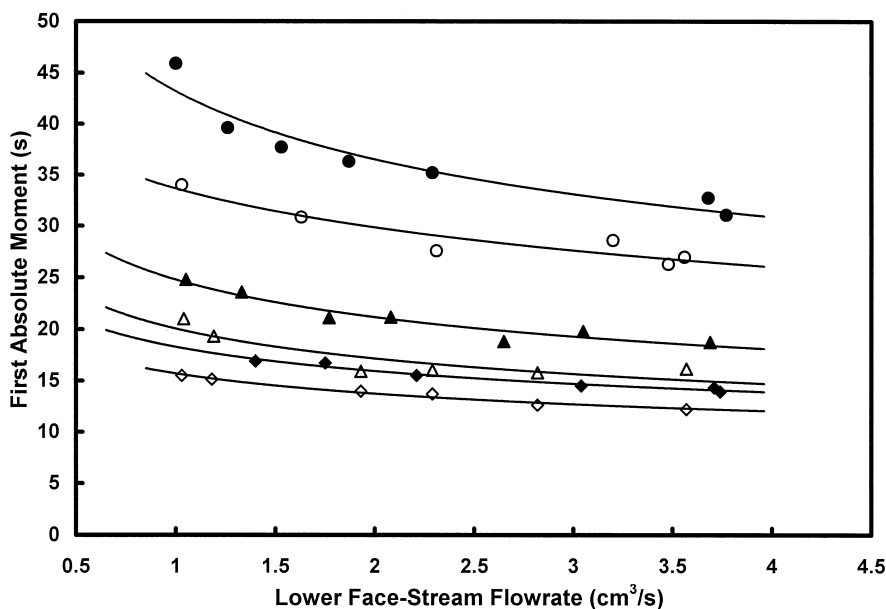


Fig. 2. First absolute moment values of carbon tetrachloride (CTC) on 5% humic-clay pellet: ●: 0% Relative humidity; ○: 5% Relative humidity; ▲: 20% Relative humidity; △: 40% Relative humidity; ◆: 60% Relative humidity; ◇: 80% Relative humidity.

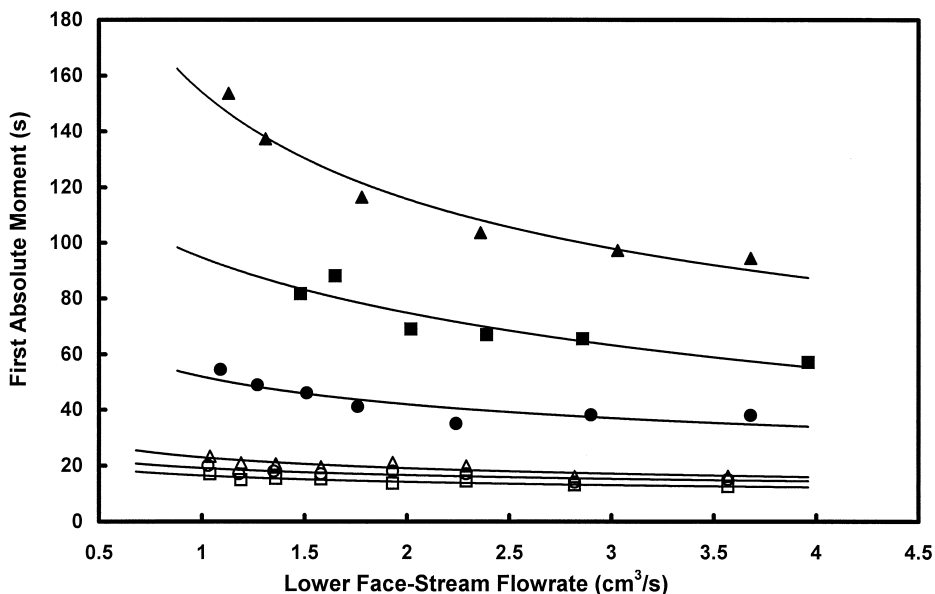


Fig. 3. First absolute moment values of trichloromethane (TCM) on humic-clay pellets:  $\blacktriangle$ : Pure Clay at 0% Relative Humidity;  $\blacksquare$ : 2% Humic-Clay at 0% Relative Humidity;  $\bullet$ : 5% Humic-Clay at 0% Relative Humidity;  $\triangle$ : Pure Clay at 80% Relative Humidity;  $\square$ : 2% Humic-Clay at 80% Relative Humidity;  $\circ$ : 5% Humic-Clay at 80% Relative Humidity.

Previous studies with soil, either natural or synthetic, showed decreasing sorption of organic vapors with increasing soil organic matter under dry conditions [6,21].

When a humic-clay pellet was exposed to a carrier gas containing water vapor, some of the micropores were filled by water and also some parts of the pore surface were covered. Water effectively competes with organic vapors for active sorption sites as the relative humidity increases, resulting in the suppression of the volatile organics (TCM, CTC) sorption. At relative humidities around 80%, the adsorbed water probably was thick enough to prevent the influence of the mineral and soil organic matter on

Table 3

The observed sorption coefficient of trichloromethane (TCM) and carbon tetrachloride (CTC) on humic-clay pellets at different relative humidities

% Relative humidity	The observed sorption coefficient (dimensionless)					
	Pure clay		2% Humic-clay pellet		5% Humic-clay pellet	
	TCM	CTC	TCM	CTC	TCM	CTC
0	92.0 <sup>a</sup>	90.0 <sup>a</sup>	40.33	36.3	21.4	21.8
5	56.9	39.9	23.6	21.6	16.03	15.65
20	15.7	9.7	14.39	9.95	13.19	9.49
40	11.3	5.8	10.93	6.32	10.78	7.21
60	8.3	4.8	7.61	5.05	6.73	5.49
80	7.2 <sup>a</sup>	3.6 <sup>a</sup>	4.44	3.38	4.04	3.50

<sup>a</sup>From Cabbar et al. [10].



adsorption. Therefore, the sorption of TCM and CTC on pure clay and synthetic humic-clay complexes was reduced dramatically in the presence of water vapor at high relative humidity (Figs. 1 and 2).

Below 20% relative humidity, the pore surface was not completely covered with water molecules; hence, the VOCs (TCM, CTC) could be adsorbed especially to the unoccupied fraction of the clay mineral surface some sites of which had already been covered with humic acid. At low relative humidities, a decrease in sorption capacity with the increase in humic acid was clearly seen (Table 3). When a certain film thickness is reached, sorption on mineral surface becomes less important. Therefore, above 20% relative humidity, an increase in humic acid content did not significantly change the sorption capacity. In this range of relative humidity, however, sorption capacity for TCM showed a gradual decreasing trend as it was observed in low relative humidity experiments and CTC exhibited slightly increasing sorption capacities with increasing humic acid content. Considering the experimental accuracy and the percentage variation in sorption capacity values, it may not be very suitable to make a definite claim for explaining these different trends, but it can be attributed to the difference in the molecular structure and the polarities of TCM and CTC. After all, it can safely be said that for relative humidities greater than 20% the change in the sorption capacities of both VOCs with increasing humic acid content is not very much appreciable. When the relative humidity approached 80%, the effect of humic acid content on sorption capacity almost disappeared. The first absolute moments of TCM were found to be nearly the same for all humic-clay complexes studied around 80% relative humidity (Fig. 3). The same behavior was also observed for CTC. The observed sorption coefficients ( $\rho_p K_{obs}$ ) of TCM and CTC at 80% relative humidity were found to be almost the same for the humic-clay pellets studied as it seen in Table 3.

The observed sorption coefficients of TCM were different from CTC results because of differences of dipole moments. The polar VOCs have greater sorption capacities on soil mineral, soil organic matter, and water than nonpolar VOCs [1,2,11,14] in agreement with the present results.

From the evaluation of the present results it is concluded that sorption of TCM and CTC on humic-clay complexes is mainly on the dry clay surface. The presence of water reduced TCM and CTC uptake by synthetic humic-clay complexes. The conclusions reached here with the specific humic-clay complexes used in this work are in close agreement with the results reported by other researchers [1,2,5,6,14].

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## References

- [1] S. Batterman, A. Kulshrestha, H. Cheng, Environ. Sci. Technol. 29 (1995) 171.
- [2] C.T. Chiou, T.D. Shoup, Environ. Sci. Technol. 19 (1985) 1196.

- [3] A.S. Mayer, P.E.E. Carriere, C. Gallo, K.D. Pennell, T.P. Taylor, G.A. Williams, L. Zhong, *Water Environ. Res.* 69 (1997) 777.
- [4] K. Goss, *Environ. Sci. Technol.* 27 (1993) 2127.
- [5] K. Goss, S.J. Eisenreich, *Environ. Sci. Technol.* 30 (1996) 2135.
- [6] M. Chang, S. Wu, *Proc. 214th ACS National Meeting, Las Vegas, 1997, ACS, Division of Environmental Chemistry, 1997*, pp. 185–188.
- [7] K.D. Pennell, R.D. Rhue, P.S.C. Rao, C.T. Johnston, *Environ. Sci. Technol.* 26 (1992) 756.
- [8] C. Thibaud, C. Erkey, A. Akgerman, *Environ. Sci. Technol.* 27 (1993) 2373.
- [9] D.R. Unger, T.T. Lam, C.E. Schaefer, D.S. Kosson, *Environ. Sci. Technol.* 30 (1996) 1081.
- [10] H.C. Cabbar, N. Varol, B.J. McCoy, *AIChE J.* 44 (1998) 1351.
- [11] C. Cabbar, G. Dogu, T. Dogu, B.J. McCoy, J.M. Smith, *Environ. Sci. Technol.* 28 (1994) 1312.
- [12] Y. Jin, W.A. Jury, *Soil Sci. Soc. Am. J.* 60 (1996) 66.
- [13] S. Batterman, I. Padmanabham, P. Milne, *Environ. Sci. Technol.* 30 (1996) 770.
- [14] W. Rutherford, C.T. Chiou, *Environ. Sci. Technol.* 26 (1992) 956.
- [15] J.W. Washington, *Ground Water* 34 (1996) 709.
- [16] H.C. Cabbar, B.J. McCoy, *Environ. Prog.* 15 (1996) 159.
- [17] G. Dogu, J.M. Smith, *AIChE J.* 21 (1975) 58.
- [18] G. Dogu, J.M. Smith, *Chem. Eng. Sci.* 31 (1976) 123.
- [19] C.T. Wang, J.M. Smith, *AIChE J.* 28 (1983) 132.
- [20] K. Murtezaoglu, E. Oray, T. Dogu, G. Dogu, N. Saracoglu, C. Cabbar, *J. Chem. Eng. Data* 40 (1995) 720.
- [21] C. Cabbar, G. Dogu, T. Dogu, B.J. McCoy, *AIChE J.* 42 (1996) 2090.
- [22] M. Rebhun, R. Kalabo, L. Grossman, J. Manka, Ch. Rav-Acha, *Water Res.* 26 (1992) 79.