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Dynamic Analysis of Sorption of Volatile Organic Compounds in Water

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Chlorinated and brominated volatile organic compounds are among the groundwater pollutants creating major environmental problems. In this study, dynamic behavior of certain volatile organic compounds in water was investigated by using a novel moment technique. Adsorption equilibrium constant and the penetration length of tracers were evaluated by the first absolute and the second central moment expressions derived for a pulse-response system. In order to obtain adsorption equilibrium constant and penetration length, pulse-response experiments were carried out with different tracers in a one-sided adsorption cell at 30°C. The adsorption equilibrium constants at the gas-water interface were calculated for 1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride. This study showed that the adsorption equilibrium constant and the penetration length values could be successfully evaluated using the one-sided adsorption cell moment technique. The adsorption equilibrium constant for 1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride were found to be 0.30, 0.49, and 0.54 cm^3/cm^2, respectively.

Keywords Dynamic analysis; Moment technique; Sorption; VOCs; Water

Introduction

Industrial, urban, agricultural, and nuclear wastes contaminate groundwater and subsurface soil. Contamination of soil and water by textile effluents is also an important environmental problem (Manzoor et al., 2006). Transportation of pollutants in the groundwater depends strongly upon sorption characteristics of such compounds in wet soil. A three-phase mathematical model was developed and adsorption equilibrium of contaminants was analyzed by Sen et al. (2004). Kinetics of water sorption on loose grains of a composite sorbent was investigated and the pore diffusivity of water was reported by Aristov et al. (2006). One of the most important environmental problems is the contamination of groundwater by chlorinated and brominated volatile organic compounds (VOCs). The effects of VOCs on soil and water were studied by number of researchers in recent years (Yasyerli et al., 1999; Dogu et al., 1996; Jury et al., 1990; McCoy and Rolston, 1992; Unger et al., 1996; Tata et al., 2003). Gas chromatographic techniques were frequently used for the investigation of adsorption and diffusion in packed columns. In one of the earlier studies on this technique, Schneider and Smith (1968) improved gas chromatography theory and showed that effective diffusion and adsorption equilibrium parameters could be

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experimentally evaluated in packed-bed systems using the moment technique. Application of the moment technique to a single-pellet system was originally proposed by Dogu and Smith (1975) for the study of intra-pellet rate processes. It was shown that a pulse response technique could be used with the Wicke-Kallenbach type of diffusion cell to determine effective diffusivities in catalyst pellets. The one-sided single-pellet moment technique developed in our earlier publication, Yasyerli et al. (1999), allowed more effective evaluation of adsorption equilibrium and rate parameters.

In this study, moment expressions were presented for reversible and irreversible adsorption processes. Also, the effect of relative humidity on diffusion and adsorption was investigated by Yasyerli et al. (1999), using ethyl bromide as tracer in different clays. It was emphasized that amount of water in the pores of the soil had a significant effect on the mechanism of diffusion and adsorption processes. Besides dissolution of such VOCs in the water layer covering pore surfaces, adsorption at the gas-water and water-mineral surface are expected to contribute to the sorption process. The significance of adsorption at the gas-water surfaces of wet soil was experimentally shown in our earlier publication (Yasyerli et al., 1999).

A screening model that evaluates the relative volatilization losses of a number of organic compounds under standard soil conditions was introduced by Jury et al. (1990). In that study, the compound was assumed to move by vapor or liquid diffusion and by mass flow under the influence of steady upward or zero water flow while undergoing first-order degradation and linear equilibrium adsorption. The results showed that those certain compounds may volatilize from deep subsurface locations or even groundwater unless the soil surface is sealed to prevent gas migration. Four different mathematical models were presented by McCoy and Rolston (1992) for convective transport of gases in moist porous media. These models were capillary tubes, porous and nonporous particles, and particles with water-filled pores. In that analysis of sorption of organic gases on a partially saturated soil, adsorption on dry mineral surfaces, dissolution into adsorbed water films, and adsorption on the gas-water and water-solid interfaces should be considered. In the work of Unger et al. (1996) different possible mechanisms of sorption on a moist soil were discussed. In many cases, linear equilibrium relations were assumed for VOC adsorption on the gas-mineral surfaces, and Henry's law was used for dissolution into the liquid film.

Sources contributing to occurrence of VOCs in wastewater can be broadly characterized as water supply, industries, commercial establishments, household and consumer products, surface runoff, and chemical and biogenic reactions that occur during water and wastewater treatment. For example, carbon tetrachloride and trichloroethylene are used as industrial solvents and can be found in wastewaters discharged from degreasing, dewaxing, and other types of industrial cleaning operations. Chloroform is formed during water and wastewater disinfection and is also used to manufacture household products such as liniments, degreasers, and cough medicine. The chlorine bleach used in washing machines can also form chloroform (Tata et al., 2003).

The significance of sorption prior to dissolution was shown in our recent publication (Yasyerli, 2004). Sorption of ethyl bromide in water was investigated by the moment technique and its adsorption equilibrium constant was obtained. The dynamic technique was also used for the investigation of sorption characteristics of H_2 and N_2 gases in activated carbon having three different particle sizes (Erdogan

and Kopac, 2007). The adsorption equilibrium constants and heats of adsorptions of H_2 and N_2 gases were evaluated by Erdogan and Kopac (2007). In another study by Kopac et al. (1996) the single-pellet moment technique was used for the investigation of the reaction of SO_2 with activated soda.

In the present study, sorption of volatile organic compounds and the penetration length of tracers in water were investigated by using this technique in the one-sided adsorption cell. The one-sided single-pellet dynamic procedure developed in our previous work (Yasyerli, 2004) was used to investigate adsorption of VOCs and the penetration length at the gas-water interface by using first absolute and second central moments simultaneously.

Method and Theory

In this work, pulse-response experiments were carried out in the one-sided adsorption cell. A schematic diagram of the experimental system is shown in Figure 1. In this study, a premeasured amount of deionized water was put into the one-sided adsorption cell. The upper-end face of water was exposed to a flow of inert gas (helium). The cell was designed in such a way that the chamber above the water surface can be assumed as perfectly mixed. Details of the method and the experimental setup were reported elsewhere (Yasyerli et al., 1999; Dogu et al., 1996). Pulses of adsorbing tracers (1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride) were injected into the carrier gas flowing through the upper chamber and the response peaks were detected by a thermal conductivity detector (TCD) connected to the exit stream.

In our earlier study (Yasyerli, 2004), theoretical expressions were derived for the moments of the response curves using two different models. In the first model (Model 1), adsorption of VOC on the water surface was neglected. In this model, dissolution into the water layer was taken into consideration. In the second model (Model 2), adsorption at the gas-water interface and dissolution into the water were both considered. As discussed in our earlier work, adsorption at the gas-liquid

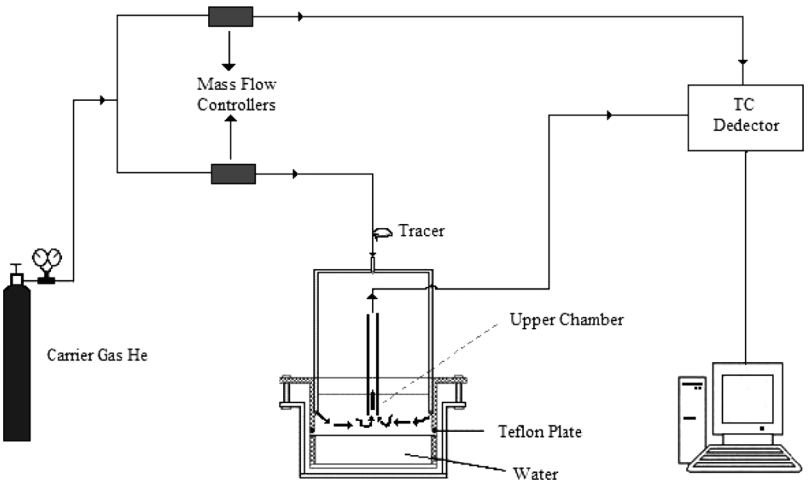


Figure 1. Schematic diagram of the experimental system.

interface was quite significant in such systems, and Model 2 was a much better representation of the system. For this model, model equations can be obtained as follows.

The species conservation equation for the tracers in the water layer within the one-sided adsorption cell is:

$$\frac{\partial C_L}{\partial t} = D_{AB}\frac{\partial^2 C_L}{\partial z^2} \tag{1}$$

In Equation (1), C_L corresponds to concentration of tracer in the water.

In this model, adsorption at water surface as well as dissolution into the water layer was taken into account. The mass conservation equation for the tracers injected as a pulse into the upper chamber of the adsorption cell includes an adsorption term in the gas-water interface:

$$-FC_A + D_{AB}\left(\frac{\partial C_L}{\partial z}\right)_{z=0} A = V_t\frac{dC_A}{dt} + K_{gl}A\frac{dC_A}{dt} \tag{2}$$

For a finite thickness of water in cell, boundary and initial conditions for Equations (1) and (2) were expressed as:

$$C_A = C_L K_H \quad \text{at } z = 0 \tag{3}$$

$$\frac{\partial C_L}{\partial z} = 0 \quad \text{at } z = L \tag{4}$$

$$C_A = C_o \quad \text{at } t = 0 \tag{5}$$

$$C_L = 0 \quad \text{at } t = 0 \tag{6}$$

Here, K_H is Henry's law constant of the tracer at the gas-water interface and L corresponds to the penetration length of tracers within the liquid. Solution of Equations (1) and (2) in the Laplace domain with boundary and initial conditions expressed in Equations (3)–(6) gives the following expression (Yasyerli, 2004) for the Laplacian of C_A as:

$$\overline{C}_A = \frac{C_o\tau\left(\frac{AK_{gl}}{V_t}+1\right)}{\left[\left(\frac{AD_{AB}}{K_H FL}\right)\left(\left(\frac{s}{D_{AB}}\right)^{1/2}L\right)\tanh\left(\left(\frac{s}{D_{AB}}\right)^{1/2}L\right)\right] + s\left(\tau\frac{AK_{gl}}{F}\right)+1} \tag{7}$$

Here, τ represents space time in the upper chamber of the cell, ($\tau = V_t/F$).

Moments of the response curves were defined as:

$$m_n = \int_0^\infty t^n C_A(t)dt = (-1)^n \lim_{s\to 0}\frac{d^n\overline{C}_A}{ds^n} \tag{8}$$

First absolute and second central moment were defined as:

$$\mu_1 = \frac{m_1}{m_0} = \frac{\int_0^\infty C_A(t)tdt}{\int_0^\infty C_A(t)dt} \tag{9}$$

$$\mu_2' = \frac{m_2}{m_0} - \left(\frac{m_1}{m_0}\right)^2 = \frac{\int_0^\infty C_A(t-\mu_1)^2 dt}{\int_0^\infty C_A(t)dt} \tag{10}$$

Zeroth (m_0), first absolute (μ_1), and second central moment (μ_2') expressions, corresponding to response peaks measured at the outlet of the upper chamber of the adsorption cell, were derived from the above definition of nth moment. These moment expressions derived are given below:

$$m_o = C_o\tau \tag{11}$$

$$\mu_1 = \tau + \left(\frac{AL}{K_H} + AK_{gl}\right)\frac{1}{F} \tag{12}$$

$$\mu_2' = \tau^2 + \left[\left(\frac{AL}{K_H} + AK_{gl}\right)\frac{1}{F}\right]^2 + \left[\frac{2}{3}\frac{L^3A}{D_{AB}} + \frac{2AL\tau}{K_H} + 2K_{gl}\tau A\right]\frac{1}{F} \tag{13}$$

Equations (11), (12), and (13) include contributions of all dead volumes in the injection and detection lines and in the upper chamber. In order to eliminate these effects, another set of pulse-response experiments was repeated with a Teflon plate placed over the upper face of the water, under the same experimental conditions. The moment expressions corresponding to this case are:

$$m_{0t} = C_0\tau \tag{14}$$

$$\mu_{1t} = \tau \tag{15}$$

$$\mu_{2t}' = \tau^2 \tag{16}$$

The corrected first absolute and second central moments were found by taking the differences of the moments obtained without and with the Teflon plate placed over the water layer (Yasyerli, 2004). The corrected first absolute moment and second central moment expressions are:

$$\mu_{1c} = \left(\frac{AL}{K_H} + AK_{gl}\right)\frac{1}{F} \tag{17}$$

$$\mu_{2c}' = \left[\left(\frac{AL}{K_H} + AK_{gl}\right)\frac{1}{F}\right]^2 + \left[\frac{2}{3}\frac{L^3A}{D_{AB}} + \frac{2AL\tau}{K_H} + 2K_{gl}\tau A\right]\frac{1}{F} \tag{18}$$

The zeroth moment expressions are the same for the case of a Teflon plate placed over the water layer and the case without the Teflon plate if the adsorption mechanism of the tracer is reversible.

The corrected first absolute moment has a linear dependence on $1/F$. The slope of μ_{1c} versus $1/F$ graph includes the gas-liquid adsorption equilibrium and Henry's constants. In principle, the K_{gl} value may be evaluated from the experimental first absolute moment only if the dimensionless Henry's constants for VOCs are known. But another unknown parameter is the length of adsorption or penetration length. The adsorption equilibrium constant and the penetration length parameters can be calculated by the simultaneous analysis of the corrected first absolute moment and the corrected second central moment expressions. The corrected second central moment expression can be rearranged as follows:

$$Y = \mu_{2c}' - \mu_{1c}^2 = \left[\frac{2}{3}\frac{L^3A}{D_{AB}} + \frac{2AL\tau}{K_H} + 2K_{gl}\tau A\right]\frac{1}{F} \tag{19}$$

The difference between the second central moment and corrected first absolute moment has a linear dependence on 1/F. The gas-liquid adsorption equilibrium constant and the penetration length of tracers may then be evaluated from the simultaneous analysis of slopes of μ_{1c} versus 1/F and Y versus 1/F curves.

Furthermore, penetration of tracers may be evaluated in another way. If the adsorption equilibrium constant of a tracer is large, then a long tail of the response peak is expected. The adsorbing tracer may not penetrate all through the total length of the water layer within the duration, t_1, of a pulse-response experiment. The penetration time into the water layer can be defined by the first moment of the response peak that would be measured if a detector had been placed at z = L. This first moment expression (μ_{1p}) can be derived for a reversible adsorption process as follows:

$$\mu_{1p} = \frac{m_1}{m_0} = \mu_1 + \frac{L^2}{2}\left(\frac{1}{K_H D_{AB}}\right) \tag{20}$$

This equation was obtained from the moment definitions given in Equation (8) and the solution of Equations (1)–(6) in the Laplace domain for $\overline{C}_L$. In Equation (20) μ_1 is the first absolute moment (Equation (12)) of the response peak measured at the outlet of the sorption cell.

The penetration length (L) of a tracer within the water layer may be characterized as the distance from the top surface of the water in which the first moment of the tracer within the water, μ_{1p}, is equal to the duration of a pulse-response experiment (t_1). An expression for L may be written by taking $\mu_{1p} = t_1$ in Equation (20):

$$L = \sqrt{2(t_1 - \mu_1)(K_H D_{AB})} \tag{21}$$

The response curve tail approaches to zero at t_1. The adsorption equilibrium constant at the gas-water interface (K_{gl}), penetration length, and t_1 values for tracers are given in Table III. In this Table, t_1 values are given at low and high carrier gas flow rate ranges. Values of penetration length (L) determined from Equations (17), (18), and (21) are also shown in Table III.

Experimental Work

In this experimental study, pulse-response experiments were carried out with some VOCs as tracer such as 1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride. The amount of water placed into the cell was 12.5 mL. The cell was placed in a constant temperature oven. Helium was used as the carrier gas flowing over the water. The experimental system is shown in Figure 1. The flow rate of the helium was changed in the range of 1.1–5.0 cm^3/s. The volume of the upper chamber of the cell was 7.43 cm^3 and the surface of the water layer in the cell was 7.07 cm^2. Pulse-response experiments were conducted at 30°C by injecting 1.0 μL VOC as tracer into the carrier gas and by detecting the response peak using a thermal conductivity (TC) detector and response peak evaluated with PeakSimple 3.29 software. The experimental conditions are summarized in Table I. Another set of pulse-response experiments were performed with a Teflon plate placed over the water layer. The corrected moments were determined by using differences of the moments with and without the Teflon plate placed over the water layer. Further details of the one-sided adsorption

Table I. The experimental conditions

Detector	TC
Gas chromatograph	Gow-Mac Series 350
Detector temperature (K)	373
Injection temperature (K)	373
Cell temperature (K)	303
Carrier gas	He
Carrier gas flow range (cm^3/s)	1.1–5.0
Amount of water (mL)	12.5

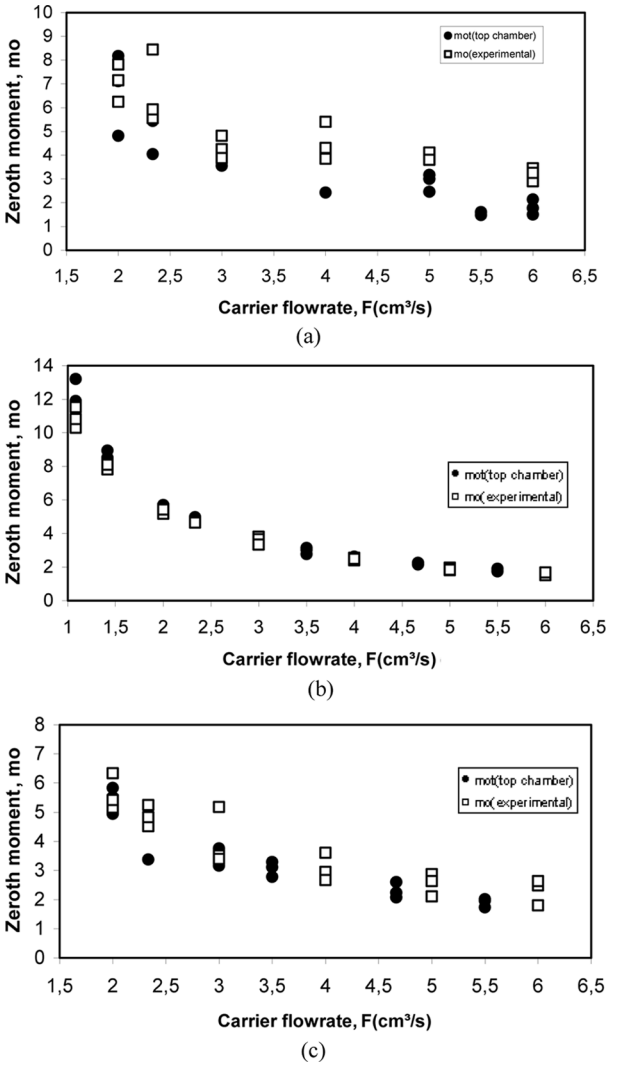


Figure 2. Zeroth moment data for (a) 1,2-dichloroethane, (b) 1,1,1-trichloroethane, and (c) carbon tetrachloride in water (T = 30°C).

cell were reported in our previous studies (Yasyerli et al., 1999; Dogu et al., 1996; Yasyerli, 2004).

Results and Discussion

The zeroth moments for 1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride are given in Figure 2(a), 2(b), and 2(c), respectively. Results of pulse-response experiments conducted at 30°C with 1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride tracers showed that zeroth moments obtained with and without the Teflon plate placed over the water layer (m_{0t}, m_0) were very close for all tracers. It was shown that sorption was thus reversible for all tracers within the time scale of the pulse-response experiments.

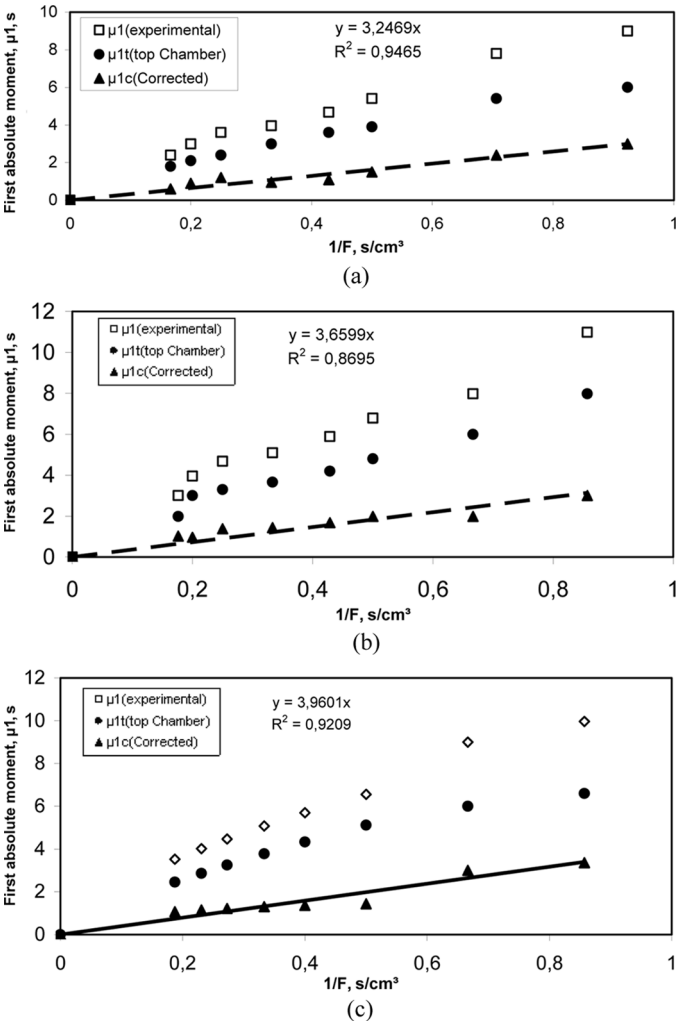


Figure 3. First absolute moment analysis; μ_1 vs. $1/F$ for (a) 1,2-dichloroethane, (b) 1,1,1-trichloroethane, and (c) carbon tetrachloride in water ($T = 30°C$).

Experimental values of first absolute moments obtained with and without a Teflon plate covering the water surface (μ_{1t} and μ_1, respectively) are shown in Figure 3. The corrected first absolute moments were evaluated by taking the differences of the moments obtained in the experiments carried out without and with the Teflon plate covering the water surface. The differences of μ_1 and μ_{1t} values 1,2-dichloroethane, 1,1,1-trichloroethane, and carbon tetrachloride are given in Figures 3(a), 3(b), and 3(c), respectively. Results reported in these figures showed that the relation between μ_{1c} and inverse flow rate (1/F) is linear, as predicted by Equation (17). Slopes of the μ_{1c} versus 1/F curves given in Figures 3(a), 3(b), and 3(c) were found to be 3.25 (with an R^2 value of 0.95) for 1,2-dichloroethane, 3.66 (with a R^2 value of 0.87) for 1,1,1-trichloroethane, and 3.96 (with a R^2 value of 0.92) for carbon tetrachloride respectively. There are three unknown parameters in

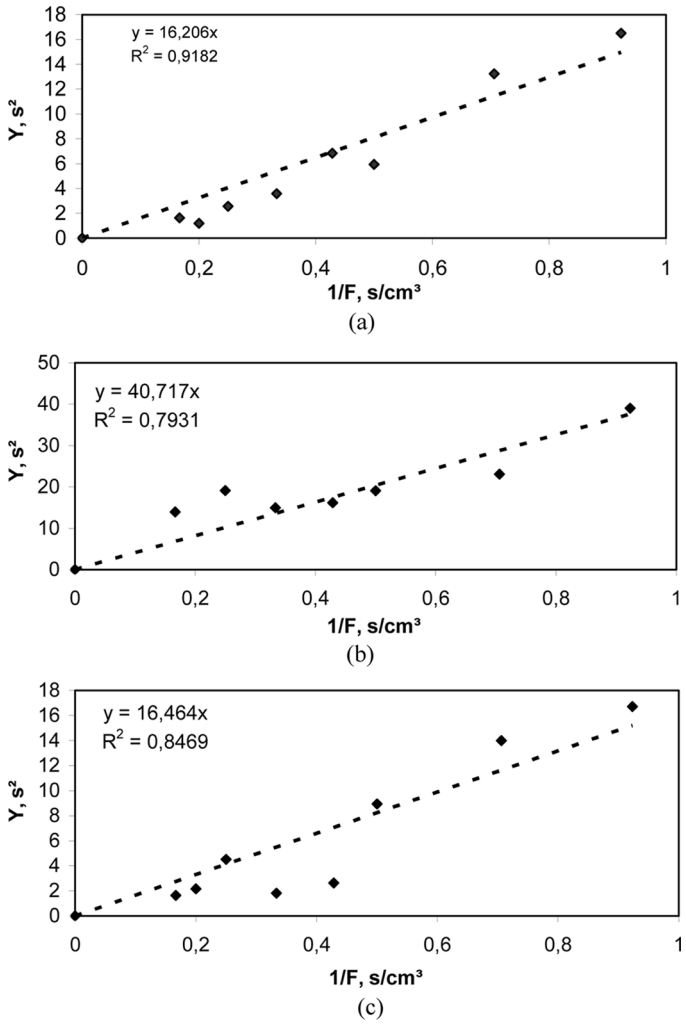


Figure 4. Second central moment analysis; Y vs. 1/F for (a) 1,2-dichloroethane, (b) 1,1,1-trichloroethane, and (c) carbon tetrachloride in water (T = 30°C).

Table II. Diffusion coefficients of gas in water for VOCs

Tracer	Formula	D_{AB} cm^2/s
1,2-dichloroethane	$C_2H_4Cl_2$	1.34×10^{-5}
1,1,1-trichloroethane	$C_2H_3Cl_3$	1.18×10^{-5}
Carbon tetrachloride	CCl_4	1.20×10^{-5}

Equation (17), namely Henry's constant, gas-liquid adsorption equilibrium constant, and penetration length. The K_H value of tracers in water could be taken from the literature (Jury et al., 1990; Munz and Roberts, 1989). In order to evaluate gas-liquid adsorption equilibrium constant and the penetration length, the first absolute moment data and second central moment data were used simultaneously.

Second central moment data obtained for all tracers are given in Figures 4(a)–(c). In these figures, the difference of corrected second central moment and square of first absolute moment, $\mu'_{2c} - \mu^2_{1c} = Y$, were plotted as a function of inverse flow rate. The relation between Y and 1/F gave the expected linear relation (Figure 4) for all VOCs. Slopes of the Y versus 1/F relation given in Figure 4(a), 4(b), and 4(c) were found to be 16.21 (with a R^2 value of 0.92) for 1,2-dichloroethane, 40.72 (with a R^2 value of 0.80) for 1,1,1-trichloroethane, and 16.46 (with a R^2 value of 0.85) for carbon tetrachloride, respectively. The second central moment expression (Equation (19)) includes all three unknown parameters. The diffusion coefficient of gas in liquid at 30°C was calculated from the Wilke-Chang equation using the association parameter for water $\Psi = 2.6$ (Bird et al., 2002). The calculated values of D_{AB} for all chemicals according to the Wilke-Chang equation are also shown in Table II. The unknown parameters, gas-liquid adsorption equilibrium constant and the penetration length, were evaluated by the simultaneous analysis of the corrected first absolute moment and the second central moment data. The values of penetration length (L) and gas-liquid adsorption equilibrium constant (K_{gl}) evaluated from this analysis are given in Table III. Results clearly showed the significance of the number of chlorine atoms in the tracer on the gas-liquid adsorption equilibrium constant. The gas-liquid adsorption equilibrium constant increases with an increase in chlorine numbers. Penetration length was also calculated by using Equation (21). Results reported in Table III showed that the penetration lengths calculated by the two methods are quite close to each other.

Table III. Results of the adsorption equilibrium constant at the gas-water interface (K_{gl}), penetration length (L), and duration of pulse-response experiment (t)

Tracer	K_{gl} (cm^3/cm^2)	L cm (From Equations (17) and (18))	L cm (From Equation (21))	t_1 (s)
1,2-dichloroethane	0.30	0.006	0.005–0.007	24–60
1,1,1-trichloroethane	0.49	0.040	0.031–0.045	32–72
Carbon tetrachloride	0.54	0.018	0.017–0.033	15–57

Conclusions

The dynamic technique is shown to be a very effective and simple method for analysis of the adsorption equilibrium constant and penetration length. The technique can also be used for the evaluation of Henry's constant if the thickness of the water layer is kept very small (smaller than the penetration length). Results of this study showed that detailed information could be obtained about the sorption mechanism of chlorinated volatile organic contaminants in water at 30°C using the one-sided moment technique. It was found that all the tracers obeyed the reversible adsorption mechanism within the time scale of pulse response experiments. Also, Henry's law constant and the diffusion coefficient of contaminant vapor in water (D_{AB}) may be effectively evaluated. It is concluded that the adsorption equilibrium constant at the gas-liquid interface and penetration length values are proportional to the number of chlorine of the contaminants. It was demonstrated that, with an increase in chlorine in the tracers, the adsorption equilibrium constant at the gas-liquid interface increased.

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Nomenclature

A	area of water surface, cm^2
C_A	concentration of the tracer in upper chamber
C_L	concentration of the tracer in the water
C_0	initial concentration of the tracer in upper chamber
D_{AB}	diffusion coefficient of gas in liquid, cm^2/s
F	flow rate of carrier gas, cm^3/s
K_{gl}	adsorption equilibrium constant at the gas-water interface, cm^3 of gas/cm^2 of liquid
K_H	dimensionless Henry's law constant for component distributed between gas and liquid, cm^3 of liquid/cm^3 of gas
L	penetration length of a tracer within the water layer, cm
s	Laplace variable, s^{-1}
t	time, s
z	axial direction in the water

Greek Letters

μ_1	first absolute moment, s
μ_{1c}	corrected first absolute moment, s
μ_{1p}	penetration time thorough the water, s
μ_{1t}	first absolute moment for the upper chamber, s
μ_2'	second central moment, s^2
μ_{2c}'	corrected second central moment, s^2
μ_{2t}'	second central moment for the upper chamber, s^2
τ	defined as V_t/F, s

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