（51） **Predictive Model for Adsorption of Volatile Organic Chemicals on Soils**

揮発性有機化合物の土壌への吸着予測モデル

Toshiko Yamaguchi[1], Tjalfe Poulsen[1], Per Moldrup[2], and Takehiko Fukushima[1]

山口登志子 [1], Tjalfe Poulsen[1], Per Moldrup[2], 福島武彦 [1]

ABSTRACT; Adsorption of volatile organic chemicals (VOC's) directly onto the soil minerals at low soil-water contents is an important process. The direct adsorption of VOC vapors can increase the total adsorption capacity of the soil by several orders of magnitude. Vapor sorption can therefore cause high VOC fluxes out of the soil during periods with increasing soil-water contents. Models for predicting VOC sorption, including vapor sorption, as a function of water content and other soil properties are therefore valuable, for example for evaluating VOC volatilization and exposure risk at polluted soil sites. A new model for estimating trichloroethylene (TCE) sorption from BET-N_2 soil surface area and from soil clay content was developed based on TCE sorption data from 22 different porous media. The new TCE sorption model was tested against independent TCE sorption data for two Japanese soils (a sand and a clay loam). The data were measured by a recently developed gas chromatography micro-column (GCMC) method. The VOC sorption model well predicted TCE retardation (sorption) as a function of soil-water content. The new VOC sorption model can be useful, for example when designing soil vapor extraction systems that are used for clean-up of VOC polluted soil sites.

Keywords; VOC sorption, micro-column experiments, predictive models, soil surface area, soil clay content.

INTRODUCTION

Adsorption of volatile organic chemical (VOC) vapor directly onto dry surfaces of clay minerals strongly influences transport and distribution of VOC in the soil [12, 15]. At low water contents, the VOC sorption capacity is typically orders of magnitude higher than near water saturation [10]. During rainfall after a very dry period, all of the adsorbed VOC vapor will suddenly be released (desorbed). This can potentially result in massive VOC mass fluxes to the atmosphere at polluted soil sites [12-13]. Both soil and VOC properties control the vapor sorption. Knowledge of the mechanisms that control vapor sorption is needed to be able to predict vapor sorption capacity. For use in risk assessment and in contaminant transport calculations, simple models for predicting VOC vapor sorption from easy-to-measure soil properties are very useful.

Several recent studies have focused on measurement of VOC sorption coefficients in soils and soil minerals. Most of the studies have used trichloroethylene (TCE) as the sorbing VOC [2, 8-9, 10, 12-13, 16-18]. A model for TCE sorption based on two basic sorption parameters and additional expressions to estimate these parameters from soil cation exchange capacity (CEC) were presented by Poulsen et al. (1998) [13]. However, since vapor sorption capacity is strongly related to soil surface area and clay content [11], the CEC is probably not the best parameter for predicting VOC vapor sorption.

Therefore the main objective of this study is to develop a better and more conceptually correct model for predicting VOC sorption as a function of

soil-water content. In our new model, the sorption parameters are predicted from soil surface area and clay content.

MATERIALS AND METHODS

Two soils from Japan, a sand and a clay loam (soils 23 and 24 in Table 1), were used to measure TCE sorption coefficients as a function of soil-water content. Measurements were conducted using a transient-state, gas chromatography micro-column (GCMC) method [19-21]. A similar measurement system has since been presented [14]. A schematic of the experimental set-up is shown in Fig. 1
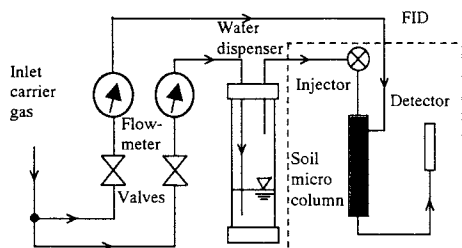

Figure 1. Gas chromatography micro-column (diameter 1.0 cm, length = 25 cm). Experimental set-up for measurement of VOC vapor breakthrough curves and sorption coefficients as function of soil-water content [19), 21)].

The TCE sorption experiments were performed on a GC containing a small column (length 25 cm, diameter 1.0 cm) packed with soil. A spike of TCE vapor was injected into the column using a non-reactive carrier gas (helium). The TCE breakthrough curve was detected using a flame ionization detector (FID). Comparison of the TCE breakthrough curve to the breakthrough curve for a non-sorbing tracer (methane) enabled determination of the adsorption coefficient for the TCE. The delay of the adsorbing TCE gas compared to the non-adsorbing methane gas directly gives the retardation factor (R). The TCE adsorption coefficient can then be calculated from the R value. A water dispenser installed in front of the injector and column enabled adjustment of the gas humidity and soil-water content during the experiment [19), 21)]. The advantage of the micro-column method is that it is relatively easy to obtain a large number of measurements at different soil-water contents. This is difficult using batch methods where each measurement requires a significantly longer time to carry out. For very dry soils VOC gas transport through the micro-column becomes very slow because of the extremely high vapor sorption. The micro-column method is therefore less useful for measuring sorption coefficients at or close to zero water content. However, the GC micro-column method seems

optimal for measuring VOC sorption and retardation within the soil-water content interval of interest for e.g. soil vapor extraction systems for clean-up of VOC contaminated soil sites. Determination of N_2-BET surface area (SA_{BET}) was carried out for 10 soils. For eight of the soils, prior measurements of TCE vapor sorption properties were also available [10]. Physical characteristics of the 10 soils are given in Table 1 (soil 8, 10, 12, 13, 16-19, and 23-24). The soils were initially air dried and passed through a 2.0 mm sieve. Prior to surface area determination all soils were oven dried at 105 °C for 24 hours and used without any further pre-treatment. Soil surface area was determined by N_2 gas adsorption by fitting the Braunauer-Emmett-Teller (BET) equation to the measured N_2 gas adsorption data following the procedure by Braunauer et al. (1938) [3)].

THEORY

The total VOC sorption coefficient, K_D' (cm^3/g), describes partitioning of VOC between the gas phase and the rest of the soil system. Normally, K_D' as a function of soil-water content is given by [13)],

$$K_D' = K_{sg} + \frac{K_D}{K_H} + \frac{w}{K_H \, \varphi \, \rho} \qquad (1)$$

where K_{sg} and K_D are solid/vapor and solid/aqueous phase VOC partitioning coefficients (cm^3/g), w (= θ/ρ_b) is the gravimetric water content (g H_2O/g dry soil), θ is the volumetric soil-water content (cm^3 H_2O/cm^3 wet soil), ρ_b is the soil bulk density (g dry soil/cm^3 wet soil), K_H is the dimensionless Henry's constant (= 0.38 for TCE [10)]), φ is the aqueous activity coefficient, and ρ is the water density (g/cm^3). It should be noted that this concept of partitioning coefficients only is valid at low VOC relative vapor pressures, i.e., where VOC adsorption is linearly related to the vapor pressure. At high vapor pressures, the BET theory can be used instead to describe the non-linear VOC adsorption isotherm over the full range of relative vapor pressures [1, 4)].

MODEL DEVELOPMENT

A general model for the total VOC sorption coefficient, K_D', can be developed by rewriting Eq. [1] to [10, 13)],

$$Log(K_D'(w)) = Log\left(\frac{K_D'(0) \, K_H}{K_D}\right) e^{-\alpha w} + Log[\beta(w)]$$
where $\qquad\qquad$ (2a)
$$\beta(w) = \frac{K_D}{K_H} + \frac{w}{K_H \, \varphi \, \rho} \qquad (2b)$$

and where $K_D'(0)$ (cm^3/g) is the value of K_D' at zero moisture content, α is a parameter that describes the decrease in K_D' with increasing w in the low water content region, and β describes sorption in the high water content region. The first part of Eq. (2a) describes the VOC partitioning between the dry soil mineral surfaces and the soil gas phase. The second part of Eq. (2a) describes the VOC partitioning between the soil organic matter and the soil water. Equation (2) assumes equilibrium VOC sorption and low relative VOC vapor pressures [10].

In this study we propose a physically based model where α and $K_D'(0)$ in Eq. (2) are estimated from soil surface area and clay content. Measurements of TCE sorption coefficients as a function of soil-water content for 22 different porous materials (soils 1 – 22 in Table 1) were used to develop and test the new TCE sorption model.

$K_D'(0)$ is strongly correlated with soil total surface area [9-10]. This is due to that VOC sorption occurs mainly on soil mineral surfaces but not on the soil organic matter when the soil is completely dry (w=0). Measurements of SA_{BET} for 13 soils for which both $K_D'(0)$ and SA_{BET} were available (Table 1, soils 8, 10, and 12-22) were used to develop an expression for predicting $K_D'(0)$,

$$Log(K_D'(0)) = Log(SA_{BET}) + 2.1, \; r^2 = 0.77 \qquad (3)$$

where $K_D'(0)$ has units of cm^3/g and SA_{BET} has units of m^2/g. The correlation is shown together with the measured data in Fig. 2.
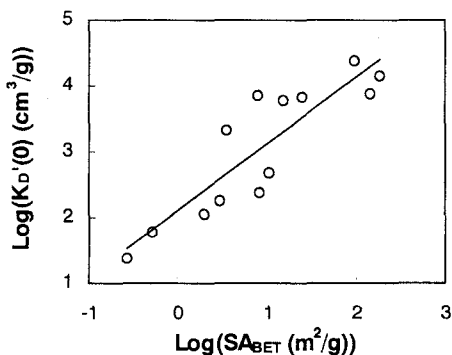

Figure 2. Sorption coefficient $K_D'(0)$ for trichloroethylene (TCE) as function of BET-N_2 soil surface area (SA_{BET}) for 13 soils.

Due to competition between VOC vapor and water vapor for the sorption sites, more water is needed to cover mineral surfaces in soils with high SA and clay content, and the slope (and thus α) of the $K_D'(w)$ curve will therefore be smaller. A highly significant correlation between $1/\alpha$ and soil clay content was obtained (correlation coefficient $r^2 = 0.91$), using 11

soils for which both α and clay content were available (Table 1, soils 1-11),

$$\alpha = \frac{1}{0.00077 \; Clay + 0.0043}, \; r^2 = 0.91 \qquad (4)$$

The correlation (Eq. (4)) is shown in Fig. 3.

In cases where a measurement of soil surface area, SA_{BET}, is not available, an approximate value may be estimated from soil clay content. A relationship for estimating SA_{BET} from clay content was developed, using data for 8 soils in Table 1 (marked with †), 12 soils from [6], 7 soils from [8], and unpublished data for additional 25 soils,

$$Log(SA_{BET}) = 1.3 Log(clay) - 0.8, \; r^2 = 0.81 \qquad (5)$$
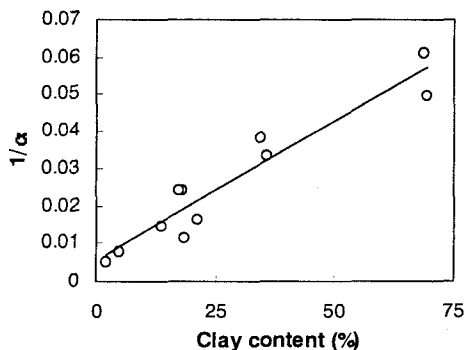
This relationship is plotted in Fig. 4.

Figure 3. Sorption parameter α for TCE as function of clay content for 11 soils.
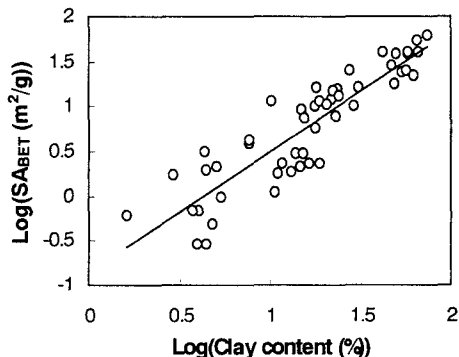

Figure 4. Indirect prediction approach: Relationship between soil surface area SA_{BET} and clay content for 52 soils.

We call this the 'indirect prediction approach' because it uses a predicted and not a directly measured value of SA_{BET} to estimate TCE adsorption. The variability of the data in Fig. 4 is likely due to

that the soil clay fraction consists of different types of clay minerals in the different soils. This is also the reason for the relatively large variability of the data in Fig. 2 ($K_D'(0)$ as a function of SA_{BET}). Although our new model is physically based and therefore an improvement compared to previous models, our new model has a relatively large uncertainty especially in estimating $K_D'(0)$. Therefore, if high prediction accuracy is wanted, we strongly recommend a direct measurement of the $K_D'(0)$ parameter.

RESULTS AND DISCUSSION

Predictions of $K_D'(0)$, α, and $K_D'(w)$ by the new model, Eqs. (2), (3), and (4), were compared to measured data for soils 1 – 22 (Table 1). If SA_{BET} was not measured, it was estimated from clay content using Eq.(5). The root mean square error (RMSE) was used as a measure of model prediction accuracy,

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_{i,measured} - X_{i,predicted})^2} \quad (6)$$
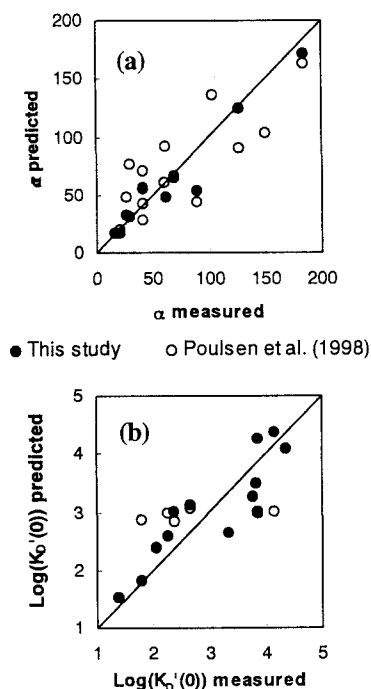

● This study   ○ Poulsen et al. (1998)

Figure 5. Measured and predicted values of TCE sorption parameters by the Poulsen et al. (1998) model [13] and the new model proposed in this study: (a) Log ($K_D'(0)$), and (b) α.

where X_i is the i'th parameter value, and n is the total number of data points.

For all three parameters, $K_D'(0)$, α, and $K_D'(w)$, the RMSE was calculated for both the new VOC sorption model based on SA_{BET} and clay content and the old VOC sorption model [13] based on CEC. We therefore only used the data sets (soils) where both models could be applied. The RMSE values for the three parameters were $K_D'(0)$: (0.86 and 0.68), α: (0.01 and 0.005), and $K_D'(w)$: (0.53 and 0.49) where the first number is for the Poulsen et al. model [13] and the second number is for the new model. Model predictions of $K_D'(0)$ and α are plotted against measured data in Fig. 5.

Additional TCE vapor sorption data for soils 23 and 24 were used to test the accuracy of the two models. Predicted values of $K_D'(w)$ were calculated with the Poulsen et al. model [13] using the measured values of CEC and K_D (Table 1). Predictions by the new model were calculated either using measured SA_{BET}, clay content, and K_D from Table 1 together with Eqs. (2), (3) and (4) (direct approach), or using measured values of clay content to estimate SA_{BET} by Eq.(5) and subsequently by Eq.(3) (indirect approach). The results are presented in Fig. 6 in terms of the retardation factor (R) determined as,

$$R(w) = 1 + \frac{K_D'(w)\,\rho_b}{\varepsilon} \quad (7)$$

where ε is the air-filled porosity (cm^3/cm^3). R expresses the retardation (reduced mobility) of the adsorbing VOC compared to a conservative, non-adsorbing (R=1) tracer[20-21].

————— Direct approach   ○ Andosol
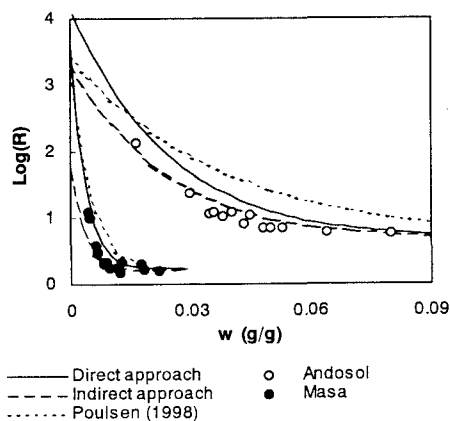— — — Indirect approach   ● Masa
· · · · · · Poulsen (1998)

Figure 6. Measured and predicted values of retardation factor (R) by the Poulsen et al. (1998) model [13] and the model proposed in this study for Masa (soil 23) and Andosol (soil 24) using SA_{BET} (direct approach) and clay content (indirect approach), shown as a function of gravimetric soil-water content (w).

Both when using the direct and the indirect (Eq.(5)) approach, the model developed in this study gave increased prediction accuracy for R(w), whereas the old model [13] underestimated the value of α, resulting in overestimation of R(w) for most of the measured data points. It is interesting to note that the indirect approach (using soil clay content to estimate $K_D'(0)$) gave improved predictions compared to the direct approach (using soil surface area to estimate $K_D'(0)$) for both soils, see Fig. 6. This may indicate that clay content is a better parameter than surface area to estimate $K_D'(0)$, especially as clay content is much easier to measure than surface area. Combining Eqs. (3) and (5) gives,

$$Log(K_D'(0)) = Log(-0.8 + 1.3Log(Clay)) + 2.1 \quad (8)$$

This predictive model, Eq. (8), for TCE sorption onto completely dry soil from the very easy-to-measure clay content seems to provide better overall predictions of vapor sorption (Fig. 6 indirect approach) and should be further tested when more VOC sorption data become available.

CONCLUSIONS

An improved model for predicting TCE vapor sorption parameters ($K_D'(0)$ and α) from soil clay content and BET-N_2 soil surface area is proposed. This model was developed using physical properties and TCE sorption data from 22 different porous media. Also, an expression for estimating soil BET-N_2 specific surface area from clay is suggested. The new model was tested against two additional independent data sets and yielded improved predictions in comparison with an existing model. As the highest model uncertainty is associated with the prediction of $K_D'(0)$, a single measurement of the sorption coefficient at zero water content ($K_D'(0)$) will often give significantly improved prediction accuracy. More measurements of sorption coefficients for different chemicals onto different soils are needed to further investigate this behavior and, also, to improve and generalize the presented vapor sorption model for other chemicals than TCE.

Table 1. Physical properties and sorption parameters for TCE onto 24 different porous media used in the development and testing of a new model for estimating TCE sorption parameters from soil properties.

Soil	Nr.	SA_{BET} m^2/g	K_d $cm^3\,g^{-1}$	Clay %	$K_d'(0)$ $cm^3\,g^{-1}$	α	CEC meq/100g	Reference
EPA-6	1	N/A	0.69	68.6	2196	16.4	33.0	17
EPA-23	2	N/A	2.30	69.1	1713	20.2	31.5	17
EPA-14	3	N/A	0.46	63.6	888	26.0	18.9	17
EPA-15	4	N/A	0.92	35.7	450	29.9	11.3	17
EPA-9	5	N/A	0.11	17.4	410	41.6	12.4	17
Yolo	6	N/A	0.58	18.0	3401	41.6	21.1	10
EPA-22	7	N/A	1.61	21.2	200	61.2	8.5	17
Ødum	8	3.7 †	1.21	13.7	174	68.5	14.0	10
Gila	9	N/A	0.30	18.4	1831	89.0	20.6	7
Lundgaard	10	0.7 †	0.69	4.8	60.8	126.5	8.8	10
Aquifer	11	N/A	0.1	2.0	1464	184.6	2.3	10
Jyndevad (56A)	12	0.3 †	N/A	3.9	24.3	N/A	9.3	10
Árlsev (60A)	13	1.8 †	N/A	10.9	110	N/A	11.4	10
Kaolinite	14	8.5	0.272	N/A	240	N/A	N/A	8
Fe Oxide	15	11.0	0.050	N/A	470	N/A	N/A	8
Rønhave (58A)	16	2.3 †	N/A	16.3	2174	N/A	13.4	10
Silstrup (64B)	17	15.4 †	N/A	23.5	6060	N/A	20.3	10
Roskilde (57D)	18	24.6 †	N/A	27.6	6579	N/A	29.3	10
Askov (54C)	19	7.9 †	N/A	23.2	7246	N/A	17.2	10
Al	20	143	0.011	N/A	7500	N/A	N/A	8
Coated Al	21	189	0.244	N/A	13800	N/A	N/A	8
Montmorillonite	22	515	0.308	N/A	23300	N/A	N/A	8
Masa	23	10.3	0.05	0.8	N/A	N/A	2.7	This study
Andosol	24	86.3	3.5	28.7	N/A	N/A	29.4	This study

† Measured during this study.
N/A: Not available.

REFERENCES

1)Amali, S., L. W. Petersen, D. E. Rolston, and P. Moldrup, "Modeling multicomponent volatile organic and water vapor adsorption on soils", *J. Hazard. Mater.*, 36, 89-108, 1994.

2)Batterman, S., A. Kulshrestha, and H. Cheng, "Hydrocarbon vapor transport in low moisture soils", *Environ. Sci. and Technol.*, 29, 171-180, 1995.

3)Braunauer, S., P. H. Emmet, and E. Teller, "Adsorption of gases in multimolecular layers", *J. Am. Chem. Soc.*, 60, 309, 1938.

4)Chiou, C. T., and T. D. Shoup, "Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity", *Environ. Sci. and Technol.*, 19, 1196-1200, 1985.

5)Feller, C., E. Schouler, F. Thomas, J. Roullier, and A. J. Herbillon, "N$_2$-BET specific surface areas of som low activity clay soils and their relationships with secondary constituents and organic matter contents", *Soil Sci.*, 153, 293-299, 1992.

6)Gallez, A., A. S. R. Juo, and A. J. Herbillon, "Surface and charge characteristics of selected soils in the tropics", *Soil Sci. Soc. Am. J.*, 40, 601-608, 1976.

7)Ong, S. K., and L. W. Lion, "Effects of soil properties and moisture on the sorption of trichloroethylene vapor", *Water Res.*, 25, 29-36, 1991a.

8)Ong, S. K., and L. W. Lion, "Mechanisms for trichloroethylene vapor sorption onto soil minerals", *J. Environ. Quality*, 20, 180-188, 1991b.

9)Ong, S. K., and L. W. Lion, "Trichloroethylene vapor sorption onto soil minerals", *Soil Sci. Soc. Amer. J.*, 55, 1559-1568, 1991c.

10)Petersen, L. W., P. Moldrup, Y. El-Farhan, O. H. Jacobsen, T. Yamaguchi, and D. E. Rolston, "The effect of moisture and soil texture on the adsorption of organic vapors", *J. Environ. Quality*, 24, 752-759, 1995.

11)Petersen, L. W., P. Moldrup, O. H. Jacobsen, and D. E. Rolston, "Relations between soil specific surface area and soil physical and chemical properties", *Soil Sci.*, 161, 1-13, 1996a.

12)Petersen, L. W., Y. El-Farhan, P. Moldrup, D. E. Rolston, and T. Yamaguchi, "Transient diffusion and emission of volatile organic vapors in soils with fluctuating low water contents", *J. Environ. Quality*, 25, 1054-1063, 1996b.

13)Poulsen, T. G., P. Moldrup, T. Yamaguchi, J. W. Massmann, and J. Aa. Hansen, "VOC Vapor sorption in soil: Soil type dependent model and implications for vapor extraction", *J. Environ. Engrg.*, 122, 700-706, 1998.

14)Rodriguez-Maroto, J. M., C. Gomez-Lahoz, C. Vereda-Alonzo, F. Garcia-Herruzo, and R. A. Garcia-Delgado, "Experimental setup for the study of soil vapor extraction: A practical approach to determine sorption effect", *Wat. Sci. Tech.*, 8, 169-176, 1998.

15)Ryan, P. A., and Y. Cohen, "Diffusion of sorbed solutes in gas and liquid phases of low-moisture soils", *Soil Sci. Soc. Am. J.*, 54, 341-346, 1990.

16)Shimizu, Y., N. Takei, and Y. Tereshima, "Sorption of organic pollutants from vapor phase: The effects of natural solid characteristics and moisture content", *Water Sci. Tech.*, 26, 79-87, 1992.

17)Shimizu, Y., N. Takei, and Y. Tereshima, "Roles of solid components on the sorption of trichloroethylene (TCE) onto solids from the vapor phase", *Water Sci. Tech.*, 30, 1-11, 1994.

18)Unger, D. R., T. L. Lam, C. E. Schaefer, and D. S. Kosson, "Predicting the effects of moisture on vapor phase sorption of volatile organic compounds to soils", *Environ. Sci. Technol.*, 30, 1081-1091, 1996.

19)Yamaguchi, T., R. I. Farcasanu, P. Moldrup, L. W. Petersen, and D. E. Rolston, "Effects of soil-water content on adsorption of volatile organic chemicals in soils", *Proc. of the 2nd Int. Congr. on Envir. Geotechnics, Osaka, Japan,* 1125-1130, 1996.

20)Yamaguchi, T., H. Inoki, and P. Moldrup, "Gas chromatography micro-column method for measuring retardation of volatile organic chemical gas transport in soils", *Japan Society of Civil Engineering (JSCE) Journal of Environmental Systems and Engineering* VII-2, 13-22, 1997a.

21)Yamaguchi, T., T. Tanaka, R. I. Farcasanu, and P. Moldrup, "Retardation of volatile organic chemical gas transport in soils under different environmental conditions", *Japan Society of Civil Engineering (JSCE) Journal of Environmental Systems and Engineering* VII-2, 23-29, 1997b.