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Predicting VOC Vapor Sorption from Soil Surface Area and Clay Content

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Introduction

Volatile organic contaminant (VOC) vapor sorption to soil minerals at low moisture contents strongly affects the amount of VOC retained in the soil. At low moisture contents, VOC sorption capacity is often orders of magnitude higher than near saturation. Vapor sorption is therefore an important contaminant transport mechanism. In this study a new model for predicting VOC sorption as function of moisture content based on available TCE sorption data was developed, and possible relationships between TCE sorption parameters and those for other chemicals were investigated.

Model development

The vapor sorption distribution coefficient K_D' between the gas phase concentration (g/cm^3 air) and the total concentration in the combined water and solid phases (g/cm^3 soil) is,

$$\text{Log}(K_D'(w)) = \text{Log}\left(\frac{K_D'(0) K_H}{K_D}\right) e^{-\alpha w} + \text{Log}[\beta(w)] \quad (1)$$

$$\beta(w) = \frac{K_D}{K_H} + \frac{w}{K_H}$$

where $K_D'(0)$ (cm^3/g) = K_D' at zero moisture content, w = soil gravimetric moisture content ($\text{g H}_2\text{O}/\text{g soil}$), K_D = hydrophobic sorption coefficient (cm^3/g), K_H = Henry's constant, α describes the decrease in K_D' with increasing w for low moisture contents (vapor sorption), and β describes sorption for high moisture contents (hydrophobic sorption). Figure 1 shows an example of K_D' and soil-water potential (ψ) as function of volumetric water content (θ , cm^3/cm^3) for sorption of toluene onto a Danish soil, Lundgaard sandy loam.

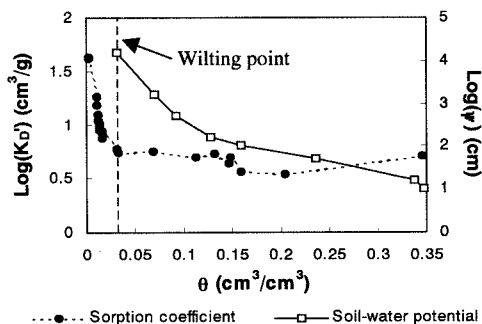


Figure 1. Toluene sorption coefficient (K_D') as function of moisture content for Lundgaard soil.

Vapor sorption generally becomes important at soil-water contents below the wilting point as also indicated in Fig. 1.

Keywords: Vapor phase sorption, distribution coefficients, soil moisture content, soil specific surface area, organic chemicals.
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Parameters α and $K_D'(0)$ for TCE were estimated independently from soil specific surface area (SA) and clay content using TCE sorption data for 31 soils. SA measured using both the BET N_2 method and the ethylene glycol monoethyl ether (EGME) method were considered where available.

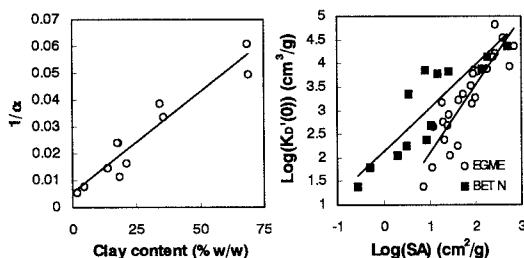


Figure 2. Relationship between soil properties and TCE sorption: a) $1/\alpha$ as function of clay content and b) $K_D'(0)$ as function of SA.

A strong correlation between $1/\alpha$ and clay content was observed.

$$\alpha = 1/(0.00077 \text{ Clay} + 0.0043) \quad r^2 = 0.91 \quad (2)$$

This correlation is illustrated in Fig. 2a. TCE vapor sorption coefficient $K_D'(0)$ was strongly correlated with both SA_{EGME} and $\text{SA}_{\text{BET N}_2}$.

$$\text{Log}(K_D'(0)) = 1.42 \text{Log}(\text{SA}_{\text{EGME}}) + 0.68, \quad r^2 = 0.80 \quad (3)$$

$$\text{Log}(K_D'(0)) = 0.91 \text{Log}(\text{SA}_{\text{BET N}_2}) + 2.1, \quad r^2 = 0.78 \quad (4)$$

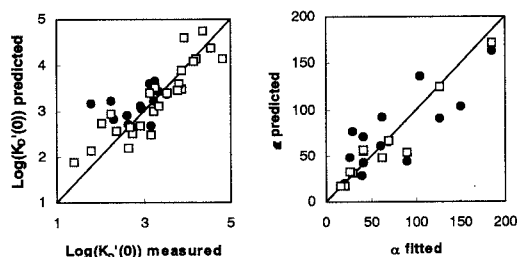


Figure 3. Measured and predicted values of α and K_D' by the Poulsen et al. (1998) model (dark symbols) and the model proposed here (white symbols): a) $\text{Log}(K_D'(0))$, b) α .

These correlations are shown together with the measured data in Fig. 2b. Predictions of $K_D'(0)$ and α by Eqs. (2), and (3) were compared to measured data for the 31 soils. Model predictions are plotted against measured data in Fig. 3a and b, respectively. For comparison predictions by the most

recent vapor sorption model (Poulsen et al. 1998, Journal of Environmental Engineering, vol 124:146-155) are also plotted in Fig. 3. The Poulsen et al. model uses soil cation exchange capacity (CEC) rather than clay content and specific surface area for predicting sorption coefficients.

Model validation

Additional TCE vapor sorption data for 2 Japanese soils (Masa, Andosol), measured during this study, not included in the model development, were used to test the two vapor sorption models. Predictions by the new model were determined using measured values of $S_{\text{ABET N}_2}$, clay content, and K_D for the two soils together with Eqs. (1), (2), and (4). Results are plotted in Fig. 4 in terms of retardation factor (R).

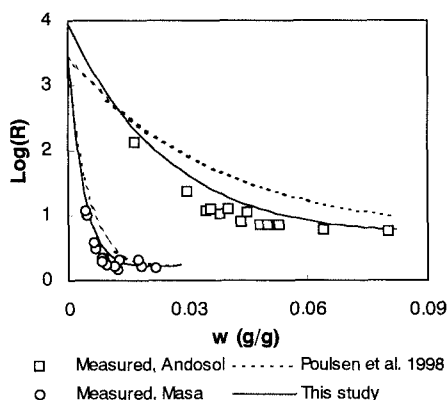


Figure 4. Measured and predicted Log (R) by the Poulsen et al. (1998) model and the new model for Masa, and Andosol.

$$R(w) = 1 + \frac{K_D(w) \rho_b}{\varepsilon} \quad (5)$$

where ε = volumetric soil-air content (cm^3/cm^3). In both cases, the new model gave improved predictions of $R(w)$ compared to the Poulsen et al. (1998) model (Fig. 4).

Implications for other VOC's

Previous studies indicate that vapor sorption behavior of other organic chemicals is similar to that of TCE. Two additional data sets for sorption of two other chemicals on Yolo loam were compared to TCE sorption data for the same soil to illustrate relations between sorption parameters. Measured values (w , $\log(R(w))$) for the three data sets are plotted in Fig. 5. In each soil all chemicals show the same approximate rate of decrease in $R(w)$ with w for low moisture contents. Predictions of R using the α -value for TCE ($= 41.6$), and measured values of $K_D'(0)$ and K_D , were calculated using Eq. (2). Results are plotted in Fig. 5. In all cases, model predictions are in close agreement with measured data, indicating that α is almost independent of the chemical type, but depends only on soil properties.

A parameter offering additional insight into sorption parameters relations for different chemicals is the ratio of retardation factors (R) for different chemicals. The ratio $R_{\text{TCE}/R_{\text{toluene}}}$ is shown as a function of the number of

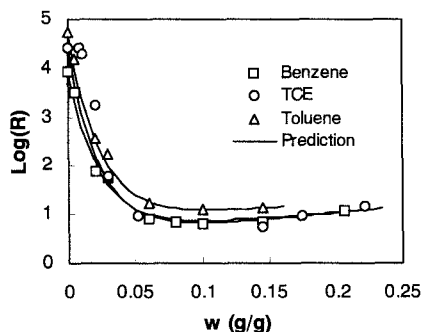


Figure 5. Measured and predicted values of Log(R) as function of w for benzene, TCE and toluene onto Yolo.

molecular layers of water coverage for Yolo in Fig. 6. The range is divided into three regions at one and three layers of water molecules. Ratios of retardation factors appear relatively constant in region I controlled by vapor phase sorption. In region III controlled by hydrophobic sorption, the ratio is also constant at a different level. Region II is a transition zone where $R_{\text{TCE}}/R_{\text{toluene}}$ changes smoothly between the values in region I and III. Region II is also the zone where sorption changes from being controlled by vapor sorption to being controlled by hydrophobic sorption.

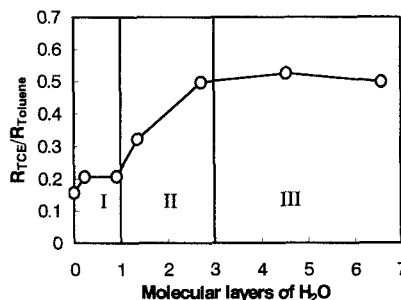


Figure 6. Ratio of retardation factors for TCE and toluene as function of number of molecular layers of water coverage for Yolo loam.

Conclusion

A new model for predicting TCE vapor and hydrophobic sorption in soils as function of moisture content based on soil surface area and clay content was developed and tested. Improved prediction accuracy compared to existing models was found. Further results indicate that the model concept can be used to predict sorption coefficients for other organic chemicals. However additional measurements are required in to accurately establish relationships between sorption parameters for different chemicals and soil types.

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