

The Influence of Relative Humidity on the Adsorption of Toluene by Soils — Interpretation with the Adsorption Energy Distribution Functions.

Chih-yu Chen^{*}, Shian-chee Wu^{**}

^{*}Department of Environmental Engineering, Foo Yin Institute of Technology,
Taliao, Kaohsiung Hsien, Taiwan, R.O.C.

^{**}Graduate Institute of Environmental Engineering, National Taiwan University,
No. 71 Chou-shan Rd., Taipei, 10770, Taiwan, R.O.C.

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Abstract

It has been shown that the VOC adsorption capacity of soil decreases significantly with increasing relative humidity levels in the vapor phase. It might be due to the competition of adsorption sites by water molecules on the soil surfaces. Generally, the surface of nature adsorbents, such as soil and clay mineral, is highly heterogeneous owing to their complex chemical composition and irregularities of physical structure. It is necessary to describe the adsorption phenomena of nature adsorbent microscopically. Based on gas-solid adsorption isotherm, the energy distribution function of sorbing sites on soil surface were constructed. The variation of adsorption energy distribution function reveals that the adsorption energy for water was higher than that for toluene and, therefore, the soil surface would prefer to adsorb water vapor rather than toluene vapor. In addition, the adsorption energy of water vapor shifts towards the lower side at higher relative humidity level. It appears that the water vapor is condensed onto the surface. It is found that the previously adsorbed water molecules modified the soil surface and changed the energy spectrum of the adsorption sites. The shift of the adsorption energy spectrum to lower adsorption energy is the reason of the suppression of the soil uptake of organic vapors by water vapor. ©1998 Elsevier Science Ltd. All rights reserved

Introduction

Adsorption is one of the most important processes affecting the fate of volatile organic compound (VOC) in the vadose zone. There has been many articles discussing the effects of relative humidity on the adsorption of VOC on soils. The adsorption capacity of VOC of soil was reported to decrease significantly with increasing relative humidity in the vapor phase^{1,2}. The suppression of the soil uptake of VOC by water vapor has been explained by different affinity of organic vapor and water molecules to the soil mineral surface and organic matter. However, the extent to which the adsorbed water vapor modifies the surfaces of soils is determined by the vapor pressure of water (i.e. relative humidity) and the characteristics of the sorbing site. It has been suggested that the surfaces of nature adsorbents, soils and clay minerals, are highly heterogeneous owing to their complex chemical composition and the irregularities of their physical structure³. The adsorption energy between adsorbent and adsorbate reflects the intrinsic property of an adsorption site on the surface. Therefore, the adsorption energy can be a measurable property to describe the tendency of association of sorbent and sorbate and be used to categorize the adsorbing sites³. In addition, the distribution of the amount of adsorbing

sites according to their adsorbing energy level (similar to a probability density function) could be a quantitative description of the heterogeneity of the surface in the respect of adsorption tendency.

The objective of this study is to explore the mechanisms of the suppression of uptake of organic vapors by humidity and to establish a model which can explain the change in the adsorption behavior of soil surface before and after the sorption of water vapor.

Materials and Methods

Soil properties: Two soils, slate alluvial soils and diluvium red soils, were sampled and air-dried in the laboratory at room temperature prior to use. The moisture content of the air-dried soil was determined gravimetrically (oven-drying at 103.5°C for 24hr). The soil-pH was measured in a 1:1 (w/w) solid-deionized water mixture⁴. The organic carbon content of the soil was obtained by using the Walkley-Black procedure⁵. The cation-exchange capacity (CEC) of the soil was determined with the method proposed by Rhoades⁶. The mechanical analysis was conducted by pipette method⁷. The specific surface area of the soils was determined by BET nitrogen adsorption method with a porosimeter (Micromeritics Instrument Corporation, ASAP2000). The basic properties of the two soils are listed in Table 1. Soil samples were crushed by a wooden hammer and particles smaller than 0.84 mm were collected and packed into a glass tube.

Table 1. Basic properties of slate alluvial soils and diluvium red soils.

	slate alluvial soils	diluvium red soils
soil fraction, %		
clay	23.0	40.6
silt	46.0	46.0
sand	31.0	13.4
pH	7.4	4.3
CEC, cmol/Kg	6.0	3.4
organic carbon content, %	0.95	1.56
moisture content, %	0.42	1.43
specific surface area (BET/N ₂)(m ² /g)	9.57	30.6

Adsorption of toluene at different relative humidity level: The uptake of toluene from gas phase were carried out using a sorption apparatus at room temperature under different relative humidity levels and different toluene concentrations. Vapors from the organic vapor generator and the water vapor generator were combined and mixed with dry nitrogen gas to obtain appropriate relative humidity and toluene concentration in gas flow. The relative humidity of the gas flow was monitored continuously by an electronic relative humidity calibrator (VASALA, HMC20/HMP20B). The gas samples were collected with a gas-tight syringe and analyzed for the organic vapor concentration by a gas chromatograph equipped with flame ionization detector (HP5890A). After the vapor system had reached a steady state with constant relative humidity and organic vapor concentration, the soil column was connected to the outlet of the mixing chamber. Normally, a contact time of about 24 hours was required for establishing sorption equilibrium. The amount of organic vapor sorbed by soil at varying organic vapor concentration at a fixed relative humidity was determined by extracting the soil with dichloromethane and analyzing with a gas chromatograph.

Adsorption of water vapor: A soil column was connected to the sorption apparatus and purged with nitrogen until the relative humidity of the effluent was below detectable limit. Then the soil column was weighted and connected to a nitrogen gas flow with certain humidity. Sorption equilibrium was assumed

reached when the weight of soil column did not change in about 24 hours. The amount of water vapor sorbed by soil column was determined by the difference of weights.

Estimation of adsorption energy distribution function: If the adsorption energy distribution function of adsorbate-adsorbent pairs, $F(\epsilon)$, can be determined, the overall adsorption isotherm will be the integration of a number of local isotherms, which describe the sorption behavior of a group of sorption pairs with identical sorption energy, weighted by the distribution function³:

$$\theta_i(p) = N_a(p)/N_m = \int_{\epsilon_{\min}}^{\epsilon_{\max}} \theta_i(p, \epsilon) F(\epsilon) d\epsilon, \quad (1)$$

where the $N_a(p)$ (cc/g or mg/g) is the experimentally measured total amount of adsorbed VOC at vapor pressure, p , N_m (cc/g or mg/g) is the monolayer adsorption capacity, ϵ (kJ/mole) is the adsorption energy, $\theta_i(p, \epsilon)$ is the local adsorption isotherm for the specific group of adsorbing center with same sorption energy ϵ , and ϵ_{\min} is the minimum adsorption energy assumed to be equal to energy of condensation of adsorbate⁸. The energetic heterogeneity of an adsorbing surface is then characterized by the distribution function $F(\epsilon)$ (mole/kJ) normalized to unity. Three adsorption isotherms have been frequently used to represent the local adsorption isotherm, which are Langmuir equation, Fowler-Guggenheim equation and BET equation³. It is also assumed that the local adsorption isotherms are of the same type for any adsorption energy level.

An exponential adsorption isotherm has been used to describe the overall adsorption isotherm for heterogeneous surfaces⁹:

$$\ln N_a(p) = \ln[\theta_i(p)N_m] = \sum_{j=0}^m B_j [RT \ln(p/p_s)]^j \quad (2)$$

where the p_s is the saturated vapor pressure. This equation was derived with the methods of statistical mechanics to describe the average number of particles in the surface phase of an adsorption system¹⁰. $F(\epsilon)$ can be solved by substituting this exponential adsorption isotherm, equation (2), into equation (1) and using the method of condensation approximation⁹. The relationship giving pressure p versus adsorption energy ϵ is $\epsilon = -RT \ln(K_o p)$, in which K_o is a constant¹¹. The function $F(\epsilon)$ can be evaluated as^{3,9}

$$F(\epsilon) = \left[\sum_{j=1}^m j B_j (\epsilon_{\min} - \epsilon)^{j-1} \right] \exp \left[\sum_{j=1}^m B_j (\epsilon_{\min} - \epsilon)^j \right], \quad (3)$$

where B_j are defined as heterogeneity coefficients, which characterize the structural and surface heterogeneity of a solid⁸. To evaluate B_j for the local isotherm interpreted by BET model, equation (2) was modified by several researchers⁸. The experimental adsorption data was approximated by the logarithmic polynomial

$$N_a(p)(1-x) = \exp \left\{ \sum_{j=0}^m B_j [RT \ln(y/p_s)]^j \right\}, \quad (4)$$

where $x = p/p_s$ and $y = x/(1-x)$. The coefficient B_0 was related to the monolayer adsorption capacity $N_m \equiv \exp(B_0)$. In this study the adsorption isotherm of toluene vapor at different relative humidity levels and water vapor will be fitted with equation (4) by adjusting the values of B_j s. The estimates of B coefficients will be substituted into equation (3) to calculate adsorption energy distribution function, $F(\epsilon)$.

Results and discussion

The adsorption isotherm of toluene vapor at different relative humidity levels for these two soils are shown in Figures 1 and 2. The adsorption of toluene vapor by soils is significantly suppressed by water vapor

to only about half of that at very low humidity. These results are similar to those in previous studies^{1,2}. It is believed that the water molecules and toluene molecules compete simultaneously for the adsorption sites on soil surface. The experimental results reveal that the interaction between water vapor and soil surface is stronger than that between toluene vapor and soil surface. Some adsorption sites which would adsorb toluene vapor are occupied by water molecules and the adsorption capacity for toluene vapor is suppressed. The adsorption capacity of diluvium red soil is higher than that of slate alluvial soil. The difference coincides with the difference of the specific surface area of these two soils. The specific surface area of diluvium red soils (about 30 m²/g) is larger than that of alluvial slate soils (about 10 m²/g). The adsorption isotherm of water vapor on these two soils are shown in Figure 3. The sorption capacity of diluvium red soil for water vapor is larger than that of alluvial slate soil as well.

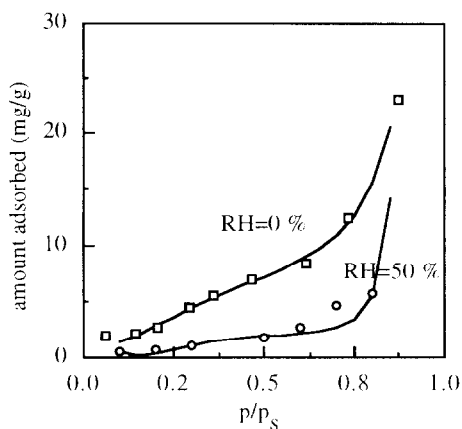


Fig.1. The adsorption isotherm of toluene on slate alluvial soils at different relative humidity. The solid curves are the best fit using equation (4).

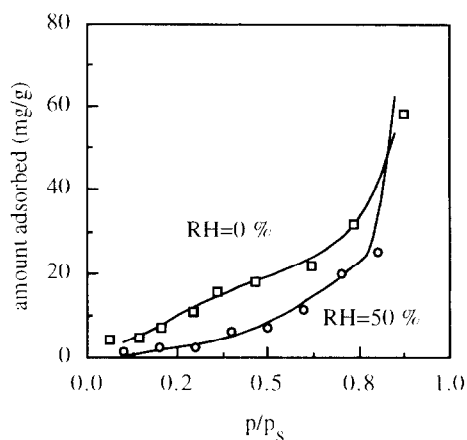


Fig.2. The adsorption isotherm of toluene on diluvium red soils at different relative humidity. The solid curves are the best fit using equation (4).

The adsorption data for each set of adsorption experiments was transformed into the form like equation (4). Several sets of B_j s with different number and value were obtained from the regression of adsorption data with a statistic software StatView. Each set of B_j s was used to characterize the adsorption behavior at different pressure with equation (4), an overall adsorption isotherm. Table 2 lists the results of B_j s. Figures 1, 2 and 3 show that the logarithmic polynomial can describe adsorption data well with a set of B_j s. The monolayer adsorption capacity, N_m , is calculated from B_1 . The cross-sectional area occupied by a toluene molecule and a water molecule is estimated with the method proposed by Tremaine & Gray¹². With these two values the specific surface area of soils could be estimated. Both the monolayer adsorption capacity, N_m , and specific surface area of soils are listed in Table 3.

Table 2. The B_j s for each set of adsorption experiments.

adsorbent	adsorbate	B_0	B_1	B_2	B_3	B_4	B_5
slate alluvial soil	toluene (RH=0%)	1.271	-0.012	-0.031	-0.000875	0.0003627	-0.0001335
	toluene (RH=50%)	-0.162	0.161	0.055	0.003	-0.005	-0.001
	water	1.759	-0.111	-0.012	0.002	-0.0003173	
diluvium red soil	toluene (RH=0%)	2.239	-0.035	-0.03	0.01	0.0001612	-0.0002066
	toluene (RH=50%)	1.356	0.312	-0.041	-0.019	0.001	0.0001
	water	2.567	-0.118	-0.007	0.003	-0.0003499	

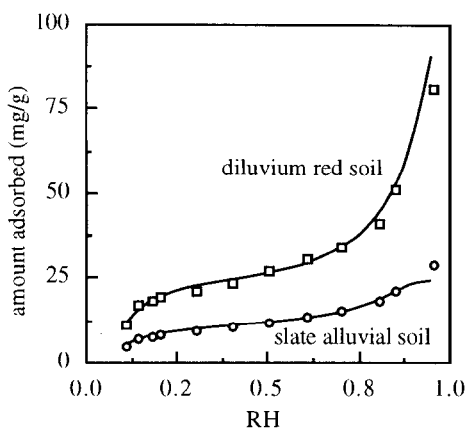


Fig.3. The adsorption isotherm of water vapor on two different soils. The solid curves are the best fit using equation (4).

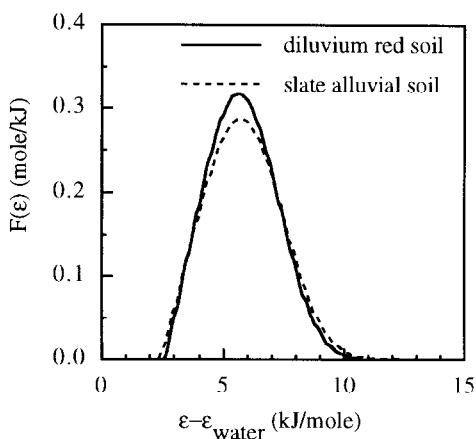


Fig.4. The adsorption energy distribution function for water-slate alluvial soil pair and water-diluvium red soil pair.

It is found that the specific surface areas obtained from different adsorbates are different. The specific surface area obtained from toluene vapor is smaller than that from water vapor. The specific surface area obtained from toluene vapor under a higher relative humidity is smaller than that at very low humidity. This suggests that part of soil surface was occupied by water vapor and the probing toluene could only access the surface sites which were not occupied by water vapor. The specific surface area estimated from water vapor is much greater than that measured with BET/N₂ procedure. The discrepancy may be due to the unique property of water molecules. Mitchell¹³ classified the possible mechanisms of soil-water interaction into hydrogen bonding, hydration of exchangeable cations, attraction by osmosis, charged surface-dipole attraction and attraction by London dispersion force. Spósito & Prost¹⁴ suggested that the first stage of water adsorption by clay was the solvation of the exchangeable cations by either three or more water molecules. They further pointed out that these hydration states corresponded to interlamellar *c* axis spacing large enough to accommodate either one or two layers of adsorbed water molecules. These results in the literature and from this study as well suggest that the water vapor could create new space to accommodate more water molecules inside soils and result in extra monolayer adsorption. Therefore, the specific surface area of soils estimated from the monolayer adsorption capacity of water vapor is different from the specific surface area from BET/N₂ method and needs to be redefined.

The adsorption energy distribution function, calculated by equation (3), for water vapor sorbed by these two soils are shown in Figure 4. The normalized adsorption energy distribution curve is similar for the two soils, although the chemical composition and physical texture of the two soils are quite different. The adsorption energy distribution function for toluene sorbed by alluvial slate soil and diluvium red soil under different relative humidities are shown in Figure 5 and Figure 6. The shape of adsorption energy distribution changes significantly with the relative humidity in the vapor phase. It suggests that the water vapor modifies the soil surface and the probing toluene has quite different affinity for soil surfaces under different relative humidity. Modified surfaces were seen by the probing toluene and the shape of adsorption energy distribution curve was shifted to lower energy. The adsorption energy distribution curves at RH=0% and RH=50% (Figure 5 and Figure 6) show that the toluene were easily replaced by water molecules on the sites with sorption energy $\epsilon - \epsilon_{\text{toluene}}$ from 2 kJ/mole to 6 kJ/mole. However, a new group of sites with sorption energy close to

condensation energy were created which correspond to those unoccupied by water molecules or on the surfaces of newly formed water films. The extent of surface heterogeneity of soil surface decreased as more water molecules being adsorbed onto the soil surface. The water film prohibited the interaction between toluene and soil surfaces. In addition, Pennell¹⁵ proposed that the VOC would be condensed onto the interface of gas and liquid. So, the toluene would be condensed onto the water film when the concentration of toluene was high enough in vapor phase. The value of $\varepsilon - \varepsilon_{mir}$ decreased with an increase in the concentration of toluene in vapor phase. The amount of toluene condensed onto the water film increased with the increase of the toluene concentration in vapor phase. The condensation of toluene was recognized as adsorption by soil surface and the number of adsorption sites estimated by equation (2) at low adsorption energy region increased. Consequently, the adsorption energy distribution curve was raised under lower value of $\varepsilon - \varepsilon_{mir}$.

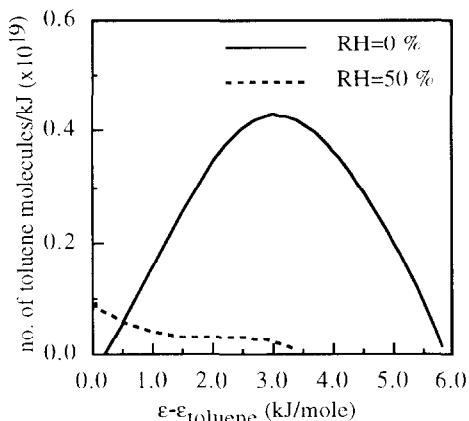


Fig.5. The adsorption energy distribution function for toluene-slate alluvial soil at RH=0% and 50%.

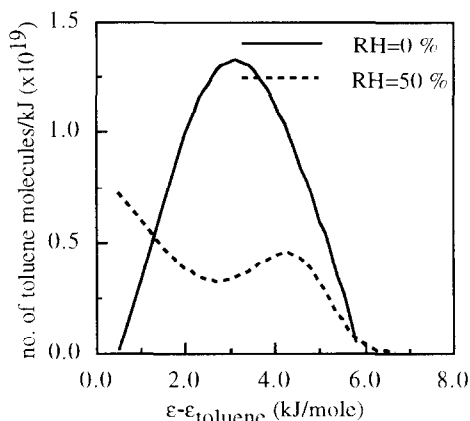


Fig.6. The adsorption energy distribution function for toluene-diluvium red soil at RH=0% and 50%.

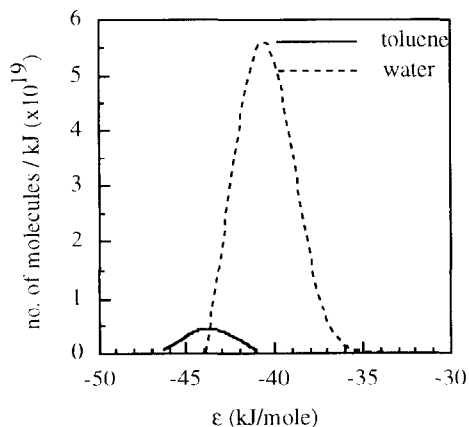


Fig.7. The adsorption energy distribution function for water and toluene vapor on slate alluvial soils.

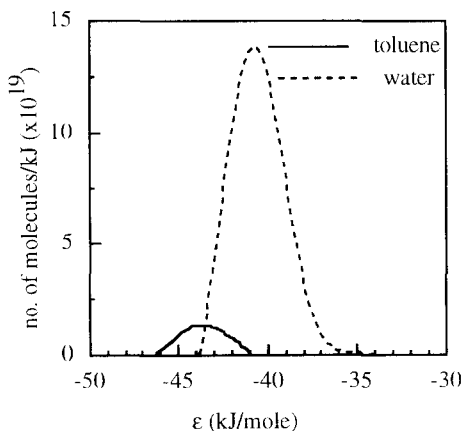


Fig.8. The adsorption energy distribution function for water and toluene vapor on diluvium red soils.

To further explain the mechanism of the adsorption of water and toluene onto the soil surfaces, the energy of condensation, ϵ_{\min} , for each one was estimated. Assuming that the vapor of adsorbate followed ideal gas law, the energy of vaporization of adsorbate at temperature T can be represented by

$$\Delta E_v = \Delta H_v - RT, \quad (5)$$

where ΔE_v is the energy of vaporization, ΔH_v is the enthalpy of vaporization, R is the gas constant, and T is the temperature. The energy of condensation, ϵ_{\min} , is the negative value of ΔE_v . The enthalpy of vaporization, ΔH_v , at temperature T can be estimated from ΔH_{vb} , the enthalpy of vaporization at boiling point T_b with the equation below¹⁶:

$$\Delta H_v = \Delta H_{vb} \left[\frac{1 - T/T_c}{1 - T_b/T_c} \right]^n, \quad (6)$$

where T_c is the critical temperature of adsorbate. The results of ϵ_{\min} for water and toluene are -46.3 kJ/mole and -46.8 kJ/mole, respectively. Replotting the adsorption energy distribution curves of these two soils for water and toluene with the ϵ_{\min} s was shown in Figure 7 and Figure 8. The curve for water occurs at the right-hand side of that for toluene. It means that the adsorption energy for soil adsorbing water was higher than that for toluene. The soil surface would prefer to adsorb water vapor rather than to adsorb toluene vapor. This result supports the previous suggestion that the water vapor may occupy the surface more easily than toluene and modify the surface.

Conclusion

The sorption capacity of diluvium red soil for water vapor is larger than that of alluvial slate soil as well. The specific surface area obtained for toluene vapor is smaller than that for water vapor. It is likely that the water vapor could create new space to accommodate more water molecules inside soils and result in larger monolayer adsorption capacity. The adsorption of toluene vapor by soils is significantly suppressed by water vapor. The probing toluene has quite different affinity for soil surface under different relative humidity levels. The shapes of the energy distribution functions for these two soil systems were significantly deviated when adsorption took place at different relative humidity levels. It is obvious that the surface of soil has been modified by moisture and the shape of adsorption energy distribution curve was shifted to lower energy. It is likely that there are two mechanisms resulting in the sorption capacity diminishing. Firstly, the adsorption center with higher adsorption energy is occupied by moisture first and the number of available adsorption center decreases. Secondly, the surface is modified by moisture to form a new surface and toluene molecules are not adsorbed easily by this new surface. Therefore, the adsorption monolayer capacity for toluene estimated by B at 50% relative humidity is lower than that under very low relative humidity.

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