Adsorption (2013) 19:241–250
DOI 10.1007/s10450-012-9446-7

The effect of organic sorbates on water associated with environmentally important sorbents: estimating and the LFER analysis

Mikhail Borisover

Received: 16 September 2012 / Accepted: 23 November 2012 / Published online: 6 December 2012

Abstract The effect of organic sorbates on the water associated with naturally occurring sorbents is of significant interest since it probes the hydration of a sorbate-specific microenvironment and its role in a compound partitioning between various environmental compartments. This effect was described in a thermodynamically strict way by converting the sorption isotherms of organic vapors on variously hydrated sorbents into the derivatives relating the change in the amount of water associated with a sorbent to the change in the amount of an organic sorbate. Further, these derivatives were analyzed by means of the Linear Free Energy Relationship (LFER). The analysis included the sorption data for various organic vapors on such environmentally important sorbents as quartz, metal oxides, calcite, clay minerals and humic acid. From the LFER analysis it followed that (i) organic sorbate polarizability contributions from n- and π-electrons resulted in driving water into the sorbent phase; (ii) the increasing volume of the organic compounds involved expelling water molecules; (iii) the increasing hydrogen-bond acidity and basicity of organic sorbates resulted in expelling water from inorganic surfaces but in enhancing hydration of the humic phase. In contrast to inorganic surfaces, when sorbed on strongly hydrated humic acid, the majority of organic sorbates containing oxygen, nitrogen or sulfur atoms drive water into the sorbent phase. Several molecules of water may need to be cosorbed by a humic sorbent for each sorbed molecule of an organic compound thus supporting the possibility of the concomitant participation of a number of water molecules in organic sorbate–humic matter interactions.

Keywords Sorption · Organic compounds · Distribution · Hydration effect · Mineral surfaces · Humic matter

1 Introduction

Interactions of organic molecules with various inorganic and organic sorbents presented in soils, sediments and aerosols may be influenced by sorbent-water interactions and *vice versa*. Both effects are of fundamental interest for understanding the mechanisms of organic compound sorption on naturally occurring sorbent phases and for characterizing the distribution of organic molecules between various environmental compartments. So, numerous studies have documented the interactions of organic molecules with mineral phases and inorganic surfaces (Rhue et al. 1989; Ong and Lion 1991; Thoms and Lion 1992; Goss and Schwarzenbach 2002; Goss et al. 2003), soils (Yaron and Saltzman 1972; Chiou and Shoup 1985; Pennell et al. 1992; Unger et al. 1996), and natural organic matter (NOM) (Graber and Borisover 1998; Niederer et al. 2006a; Graber et al. 2007; Borisover et al. 2011) in terms of equilibrium sorption isotherms measured at varied water activity levels. These multiple data elucidated the effect of sorbent hydration on organic compound sorption. However, determining the effect of sorbed organic molecules on water sorption, at environmentally relevant conditions, is much more challenging and may become hardly possible. For example, little is known on the quantitative effect of organic sorbates, at their low uptakes typical in various environmental scenarios, on the amount of water associated with such sorbents as quartz, metal oxides, clays, NOM.

Nevertheless, this effect is of very interest. It probes the changes in the hydration status of a sorbent microenvironment that is specific for a given organic sorbate rather than of

---

M. Borisover (✉)
Institute of Soil, Water and Environmental Sciences, The Volcani Center, POB 6, Bet Dagan 50250, Israel
e-mail: vwmichel@volcani.agri.gov.il

the whole sorbent, and, thus, examines the role of this hydration status in a compound partitioning between various environmental compartments. It can help to better elucidate variable water–organic sorbate interrelations, which range from organic sorbate-water competition on certain mineral surfaces (Ong and Lion 1991; Goss and Eisenreich 1996; Goss and Schwarzenbach 2002) to water-enhanced interactions of organic sorbates with NOM and clays (Hayes and Mingelgrin 1991; Borisover and Graber 2004; Taraniuk et al. 2009). Testing the hydration status of the organic sorbate-specific microenvironment should be also helpful for revealing the extent of the cooperativity of water molecules in their involvement into organic sorbate interactions with such an environmentally important sorbent as NOM (Graber et al. 2007; Borisover et al. 2011). Further, the quantitative effect of sorbed organic molecules on water sorption can be linked to the properties of molecular sorbates, e.g., the molecular size, shape, and presence and type of functional groups, thus shedding light on molecular mechanisms of sorption and contributing to the better prediction of distribution of organic compounds between various environmental phases.

In general, because of the requirement for thermodynamic consistency, equilibrium data describing interactions of two different sorbates with a sorbent are not independent of one another in a system containing both sorbing components (e.g., Rudzinski et al. 1995; Cernik et al. 1996; Rusch et al. 1997; Kinniburgh et al. 1999). Therefore, by using equilibrium sorption isotherms of vapors of organic compounds measured at varied water activity levels, it should be possible to determine, in a thermodynamically strict, model-free way, the effect of organic sorbates on sorbent-water interactions.

Consequently, the objective of the present study was twofold: (1) on the basis of the known effect of relative humidity on organic vapor–sorbent interactions, to estimate the effect of sorbed organic molecules on the water sorption by environmentally important sorbents; and (2) to examine the relations between this effect of organic sorbates on sorbent-associated water and the molecular descriptors of organic molecules. The necessary thermodynamic relationships paving the way for quantifying the effect of organic sorbates on the amount of sorbent-associated water were derived and applied to experimental equilibrium sorption data obtained from the literature on such sorbents as quartz, metal oxides, calcite, clay minerals and humic acid. The present analysis appears to be the first attempt to evaluate, in a model-free way, the effect of organic sorbates on the water sorption by environmentally meaningful inorganic and organic phases from the effect of the gas phase humidity on vapor sorption of organic compounds.

2 Thermodynamic background

A sorbent S (with a constant mass m_S and a given surface area) is considered to be in equilibrium with a gas phase containing two compounds, A and W, e.g., an organic sorbate and water, respectively, that can interact with the sorbent. The scenario of interest is when interactions of compounds A and W with sorbent S occur at constant values of temperature T, pressure P (controlled by a "non-interacting" inert gas) and chemical potential of component W, μ_W. In the sorbent phase (which includes also the sorbent/gas interface) μ_W is defined by the molar amounts n_i of both sorbed components A and W, for a given sorbent mass:

$$d\mu_W = \left(\frac{\partial \mu_W}{\partial n_A}\right)_{T,P,n_W,m_S} dn_A + \left(\frac{\partial \mu_W}{\partial n_W}\right)_{T,P,n_A,m_S} dn_W \tag{1}$$

Molar amounts n_A and n_W of sorbed components A and W, respectively, correspond to the excesses determined by the difference between the total amount of a component in the system and its gas phase concentration multiplied by the gas phase volume. When $d\mu_W = 0$,

$$\left(\frac{\partial n_W}{\partial n_A}\right)_{T,P,\mu_W,m_S} = -\left(\frac{\partial \mu_W}{\partial n_A}\right)_{T,P,n_W,m_S} \Big/ \left(\frac{\partial \mu_W}{\partial n_W}\right)_{T,P,n_A,m_S} \tag{2}$$

If we consider the Maxwell relation for the sorbent phase

$$\left(\frac{\partial \mu_W}{\partial n_A}\right)_{T,P,n_W,m_S} = \left(\frac{\partial \mu_A}{\partial n_W}\right)_{T,P,n_A,m_S}$$

where μ_A is the chemical potential of component A, Eq. (2) is transformed into Eq. (3):

$$\left(\frac{\partial n_W}{\partial n_A}\right)_{T,P,\mu_W,m_S} = -\left(\frac{\partial \mu_A}{\partial \mu_W}\right)_{T,P,n_A,m_S} \tag{3}$$

Since the gas phase is equilibrated with sorbent S and may be considered ideal, μ_A and μ_W are related to the partial vapor pressures of components A and W (p_A and p_W, respectively):

$$\begin{aligned} \mu_A &= \mu_A^0(T) + RT \ln p_A \\ \mu_W &= \mu_W^0(T) + RT \ln p_W \end{aligned} \tag{4}$$

where $\mu_A^0(T)$ and $\mu_W^0(T)$ are standard chemical potentials of components A and W in the gas phase. The amount n_A of component A associated with the sorbent may be linked to its partial vapor pressure in the ideal gas phase, p_A, by its distribution coefficient, $K_{d,A}$:

$$n_A/m_S = K_{d,A} \times p_A \tag{5}$$

Thus, by using Eqs. (4) and (5), Eq. (3) is converted into Eq. (6):

$$\left(\frac{\partial n_W}{\partial n_A}\right)_{T,P,\mu_W,m_S} = \left(\frac{\partial \ln K_{d,A}}{\partial \ln p_W}\right)_{T,P,n_A,m_S} \qquad (6)$$

Thus, Eq. (6) suggests the way to quantify the effect of organic sorbates on the amount of sorbent-associated water, based on the effect of water vapor partial pressure on the coefficient of the compound A distribution between the sorbent and the gas phase (at a constant concentration of compound A in the sorbent phase). Obviously, considering the distribution of water between a sorbent and the ideal gas phase similarly to that described for component A by Eq. (5), the left side of Eq. (6) can be immediately used to characterize the effect of the sorbed concentration of component A on the water distribution coefficient. Within the assumptions on equilibrium and the ideality of the gas phase, Eq. (6) are not limited by the type of sorbent or the nature of components A and W. If the partial pressures in Eq. (4) were replaced with the concentrations of components in a solution, then Eq. (3) would generate the expression used for studying mutual relations in binding of ligands with macromolecules (Cantor and Schimmel 1980).

The amount of component A associated with the sorbent may be sufficiently low that the distribution coefficient $K_{d,A}$ in Eqs. (5) and (6) does not depend on the concentration of component A in the sorbent phase. Such a concentration-independent $K_{d,A}$ determined for various organic sorbates on diverse mineral sorbents was related to the gas phase relative humidity by the following empirical equation (Goss 1992; Goss and Eisenreich 1996):

$$\ln K_{d,A} = \text{const} + D \times \frac{p_W}{p_W^{sat}} = \text{const} + \frac{D \times RH}{100} \qquad (7)$$

where p_W and p_W^{sat} are the partial vapor pressure and saturated vapor pressure of component W, i.e., water, respectively; RH is the relative humidity of the gas phase, i.e., $\frac{p_W}{p_W^{sat}} \times 100$. At any specific T and P, const and the coefficient D are determined for a given organic sorbate on a given sorbent and do not depend on the relative humidity for a certain range of $\frac{p_W}{p_W^{sat}}$ values (usually above 30 % of the gas phase relative humidity). The coefficient D does not depend on: (i) whether concentrations or partial pressures are used to represent the organic compound in the gas phase; and (ii) the units used for expressing partial pressure and concentrations of a sorbate. When the dependence expressed in Eq. (7) is valid, Eq. (6) can be transformed into Eq. (8):

$$\left(\frac{\partial n_W}{\partial n_A}\right)_{T,P,\mu_W,m_S} = D \times \frac{p_W}{p_W^{sat}} = \frac{D \times RH}{100} \qquad (8)$$

Thus, the coefficient D relates the relative humidity with the effect of sorbed organic molecules on the amount of sorbed water. In fact, D reflects the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ obtained by extrapolating Eq. (8) to 100 % relative humidity. This thermodynamic rationalization of the parameter D of the previously established Eq. (7) appears to be one important result of this analysis.

3 Results and discussion

3.1 Sorption of organic and water molecules from the gas phase on mineral surfaces

An exponential change in the concentration-independent distribution coefficients $K_{d,A}$ with increasing relative humidity, as follows from Eq. (7), was observed for sorption of vapors of polar and non-polar organic compounds on such mineral sorbents as quartz, clay minerals, calcite (calcium carbonate), hematite (α-Fe_2O_3), and corundum (α-Al_2O_3)(Goss 1992, 1993; Goss and Eisenreich 1996). Water sorption hysteresis in the systems studied was absent or had no impact on the $K_{d,A}$ values that were considered to reflect the equilibrium distribution of organic molecules between the gas and sorbent phases. By means of Eq. (8) and the reported D values, the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ was calculated for some organic sorbates on various mineral sorbents equilibrated at 80 % relative humidity, i.e., $\frac{p_W}{p_W^{sat}} = 0.8$ (Table 1). The relative humidity level of 80 % was selected as being close to the high humidity end of the gas phase moisture range in which Eq. (7) was observed. The important conclusions can be derived from the data shown in Table 1:

(1) The $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ values are negative and range between −0.9 and −4.2 for various sorbate/sorbent pairs. The negative sign of the $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ derivative could be attributed to organic sorbate-water competition for sorption sites on inorganic surfaces such that the addition of an amount of an organic sorbate may involve a few-times-larger change in the molar amount of the sorbent-associated water (at constant chemical potential of water, i.e., constant relative humidity). However, the direct interactions of diverse organic compounds with inorganic surfaces above relative humidity of 30 % were considered to be barely relevant (Goss 1992; Goss and Eisenreich 1996); rather, organic sorbate interactions at hydration water surfaces were assumed to control the sorbent/gas distribution of organic molecules (Goss et al. 2003). If the latter is true, then, the negative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ derivative could reflect competition between an organic sorbate and water for "sorption sites" at hydration water surfaces.

(2) The $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ values present in Table 1 are sensitive to the nature of the inorganic surface and the structure of the organic sorbates. The influence of the latter may not necessarily be obvious. For example, if the

Table 1 The derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ calculated for various organic sorbates on diverse mineral sorbents equilibrated at 80 % relative humidity[a]

Sorbent	Relative humidity range, %	Temperature, °C	Organic sorbates				
			n-Hexane	*n*-Nonane	*o*-Dichlorobenzene	Diethyl ether	Acetone
Quartz sand[b]	30–90	70	na[c]	−2.6	−2.7	−3.8	−4.2
Corundum (α-Al_2O_3)[d]	40–80	60	na	na	−1.0	na	−0.9
Hematite (α-Fe_2O_3)[d]	40–80	70	na	−2.0	−1.9	−1.4	−1.5
Calcite ($CaCO_3$)[d]	40–80	60	na	−1.4	−1.7	−1.1	na
Ca-kaolinite[e]	40–80	70	−1.4	na	na	−2.9	na
Na-kaolinite[e]	40–80	70	−1.4	na	na	−2.6	na
Ca-bentonite[e]	40–80	70	−3.7	na	na	na	na

[a] Typically, the errors associated with the calculated values are in the range between 5 and 15 %

[b] The *D* values used in Eq. (8) for calculating the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ are from Goss (1992)

[c] "na" means "not available"

[d] The *D* values are from Goss and Eisenreich (1996)

[e] The *D* values are from Goss (1993)

sorption of organic molecules and water on a surface followed the ideal competitive Langmuir model, then the derivative defined by Eq. (6) would not depend on the nature of the organic sorbate and its affinity to interact with a sorbent; it would be controlled only by water partial pressure. It can be seen from the data in Table 1 that the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at a relative humidity of 80 % might vary over a threefold to fourfold range with different sorbents, e.g., for diethyl ether between quartz sand and calcite, or for acetone between quartz sand and corundum, with the maximal values observed on quartz sand and Ca-bentonite. On quartz sand, hydrogen-bond accepting acetone and diethyl ether exhibited greater ability to eliminate hydration water than larger (and less polar) *n*-nonane and *o*-dichlorobenzene. On hematite the opposite was found: *n*-nonane and *o*-dichlorobenzene were more effective in "rejecting" hydration water than acetone or diethyl ether. To summarize, the diverse values of the *D* parameter in Eq. (7) provided a quantitative measure of the varied ability of organic molecules to expel water molecules from the sorbent phase.

In order to describe the variable influence of organic sorbate structure on the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$, the Linear Free Energy Relationship (LFER) analysis (Abraham et al. 1994; Pool 2003) was applied to the *D* values from Eq. (7). Although the *D* values originally were obtained for a specific range of relative humidity—typically, between 40 % and 80 %—formally they represent the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ (or $(\frac{\partial \ln K_{d,A}}{\partial \ln p_W})_{T,P,n_A,m_S}$) obtained by extrapolating Eq. (8) to the water vapor saturation point, i.e., relative humidity of 100 %. Since LFER is applicable for examining logs of distribution coefficients between the gas and a condensed medium (Abraham et al. 1994), according to Eq. (6) it could be also applicable to the derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$. The specific LFER used for analysis of the *D* values is determined by Eq. (9):

$$D = c + eE + sS + aA + bB + l \log L^{16} \qquad (9)$$

In Eq. (9) E, S, A, B and $\log L^{16}$ are the molecular descriptors of organic sorbates; their numerical values are from Abraham et al. (1994). E is the compound's excess molar refraction, which describes polarizability contributions from n- and π-electrons; S is the compound's dipolarity/polarizability; A and B are the hydrogen-bond acidity and basicity, respectively; L^{16} is the gas/*n*-hexadecane partitioning coefficient; c is a constant. With regard to the distribution between the gas and the bulk condensed medium, the last term in Eq. (9) was considered to reflect, in part, dispersion interactions and the cavity formation; $\log L^{16}$ is strongly related to the volume of organic compounds. The physicochemical meaning of molecular descriptors used in Eq. (9) is detailed in Abraham et al. (1994) and Pool (2003).

Multiple linear regression analysis based on Eq. (9) was applied to the *D* values provided for various organic sorbates on a given variously hydrated sorbent; then, the statistically less significant regressors, i.e., with $p > 0.05$, were removed, and the data were refitted. The LFER coefficients, i.e., c, e, s, a, b and l, for various sorbents are shown in Table 2. It should be clear also that these LFER coefficients obtained from the analysis of the *D* values cannot be indiscriminately compared with those coefficients obtained from the LFER analysis of distribution coefficients of organic sorbates on a given hydrated sorbent. Table 2 lists also the correlation coefficients *R*, the *P* values and the *F* values for the multiple LFER regressions, the number of compounds

Table 2 The coefficients[a] and statistical parameters of the LFER model (Eq. (9)) applied to the analysis of the D values reflecting the extrapolated derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at 100 % relative humidity for the sets of organic sorbates in a series of mineral sorbents[b]

Sorbent	c	e	s	a	b	l	p[c]	$R/F/P$[d]	RMSE[e]	N[f]
Quartz sand	2.23 ± 0.96	3.46 ± 0.63	-2.67 ± 0.51	–	-7.68 ± 1.08	-1.33 ± 0.24	<0.001	0.96/24.0/0.000	0.23	13
Corundum[g]	0.27 ± 0.34	–	–	-2.28 ± 0.46	-1.58 ± 0.40	-0.34 ± 0.06	<0.01	0.90/11.8/0.003	0.13	12
Hematite[h]	-0.13 ± 0.49	–	–	–	-1.42 ± 0.57	-0.51 ± 0.11	<0.05	0.88/14.7/0.002	0.16	12
Calcite[i]	-0.70 ± 0.32	–	–	–	–	-0.26 ± 0.08	0.025	0.81/10.1/0.025	0.16	7
Ca-kaolinite	-0.53 ± 0.41	2.48 ± 0.66	-2.87 ± 0.67	–	-2.54 ± 0.57	-0.60 ± 0.14	<0.01	0.93/15.1/0.000	0.22	15
Na-kaolinite	-1.13 ± 0.24	1.45 ± 0.48	-1.82 ± 0.42	–	-2.45 ± 0.28	-0.26 ± 0.10	<0.05	0.98/43.5/0.000	0.10	11
Ca-bentonite	-0.67 ± 0.81	–	–	–	–	-1.48 ± 0.30	0.0017	0.88/24.4/0.002	0.33	9

[a] The coefficients c, e, s, a, b and l are defined in Eq. (9). "±" corresponds to one standard error

[b] The sources of the D values for a series of organic sorbates, the experimental temperatures and the relative humidity ranges are the same as reported for each mineral sorbent in Table 1

[c] p is the statistical significance level for each of the coefficients of Eq. (9) except the intercept c

[d] R is the correlation coefficient; F denotes the F-test; P is the statistical significance level of the multiple regression

[e] Root mean squared error

[f] Number of organic compounds included in the analysis

[g] α-Al_2O_3

[h] α-Fe_2O_3

[i] $CaCO_3$

included, and the root mean squared errors (RMSE). The sources of the D values of organic sorbates, the experimental temperatures and the relative humidity ranges are the same as indicated for each mineral sorbent in Table 1. The LFER-fitted D values, or $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at 100 % relative humidity, for various sorbates on different sorbents are plotted in Figs. 1 and 2 against the determined D values. Figures 1 and 2 show that there is good correspondence between the determined D values and those fitted with the LFER (Eq. (9)). Based on Table 2, the following points should be noted:

(1) The coefficients e, s, a, b, and l do not invert their signs among all the inorganic sorbents considered. For example, for all the inorganic sorbents, b and l are negative, which indicates that with increasing hydrogen-bonding basicity and increasing molecular size of organic sorbates, the ability of organic molecules to displace hydration water increases. The negative s values observed for sorption on quartz sand and kaolinites indicate that the compound's dipolarity also contributes to the effective displacement of sorbent-associated water molecules.

(2) Interestingly, the e coefficients—when statistically significant—are positive. Within the framework of Eq. (9), this indicates that the polarizability contributions from n- and π-electrons of sorbing organic molecules increase the amount of sorbent-associated water. This positive effect seems to be less clear than the negative displacing effect; it needs further investigation.

(3) The hydrogen-bonding acidity effect represented by the coefficient a is less common. It was observed only with sorption on corundum Al_2O_3 and also was negative: sorption of organic molecules capable of hydrogen-bonding acidity involves a release of sorbent-associated water.

Despite the use of a limited dataset for the present analysis, the applicability of this specific LFER (Eq. (9)) for characterizing the D values (or $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at 100 % relative humidity) is much wider. This follows from the earlier successful LFER application carried out for the $K_{d,A}$ values of many organic compounds on various mineral surfaces at certain relative humidities (Goss and Schwarzenbach 2002; Goss et al. 2003). For example, distribution coefficients of a diverse set of 50 organic vapors were measured on quartz, calcite and corundum at certain relative humidities and described by means of the LFER approach (Goss and Schwarzenbach 2002). In that application the LFER compound's attributes were limited by use of only the three sorbate descriptors: A, B and L^{16}. The surface parameters deduced from this fitting were examined as functions of relative humidity (Goss et al. 2003).

Therefore, the LFER in its original form, i.e., including five molecular descriptors (Abraham et al. 1994), should provide an even better description of the variability of the $K_{d,A}$ values among sorbates on a given mineral surface at a certain relative humidity. Hence, one may anticipate that this LFER model should be also suitable for describing the ef-

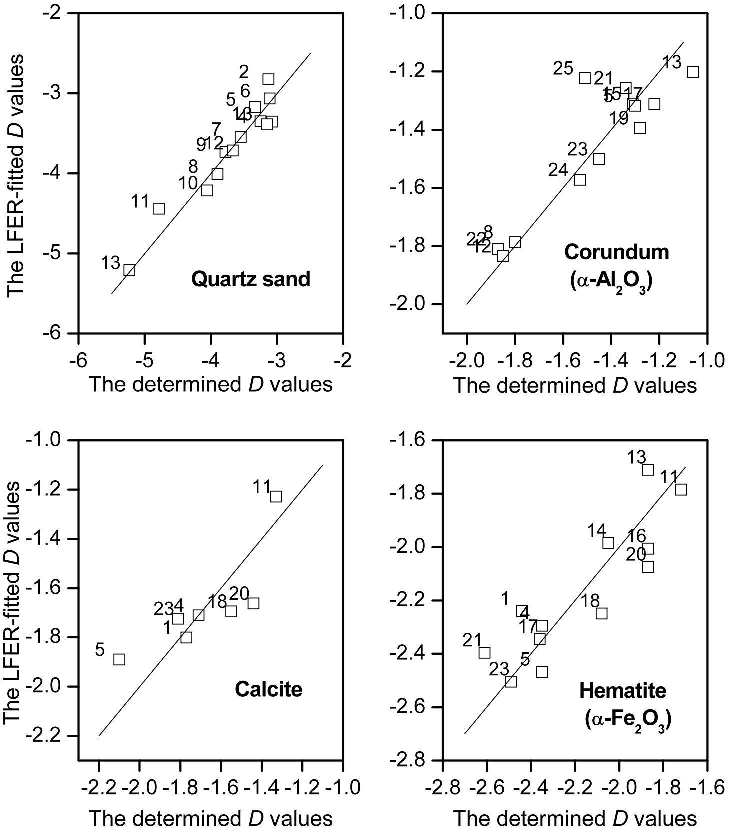

Fig. 1 The LFER-fitted *D* values reflecting the extrapolated derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at 100 % relative humidity are plotted against experimentally determined *D* values. The sorbents are indicated on the plots. Key to chemical compounds: *1*, *n*-nonane; *2*, *m*-dichlorobenzene; *3*, *m*-xylene; *4*, *p*-xylene; *5*, *o*-dichlorobenzene; *6*, 1,3,5-trichlorobenzene; *7*, 1,2,4-trichlorobenzene; *8*, naphthalene; *9*, 1,2,3-trichlorobenzene; *10*, acetonitrile; *11*, diethyl ether; *12*, ethanol; *13*, acetone; *14*, *n*-octane; *15*, *n*-decane; *16*, toluene; *17*, *o*-xylene; *18*, ethylbenzene; *19*, propylbenzene; *20*, chlorobenzene; *21*, *p*-dichlorobenzene; *22*, 1,2,3,4-tetrachlorobenzene; *23*, anisole; *24*, pyridine; *25*, ethylacetate. The *solid straight line* corresponds to the 1:1 ratio between fitted and determined *D* values

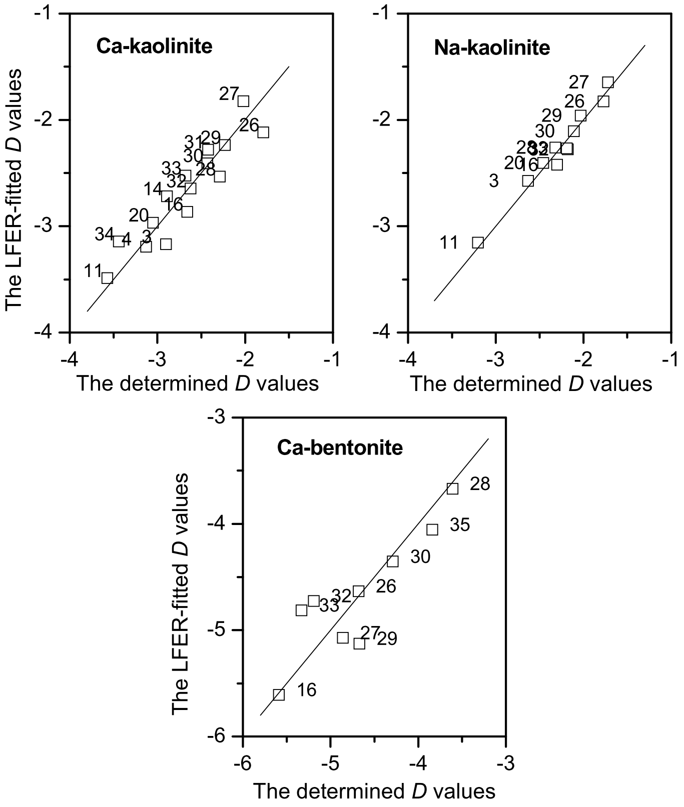

Fig. 2 The LFER-fitted *D* values reflecting the extrapolated derivative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at 100 % relative humidity are plotted against experimentally determined *D* values. The sorbents are indicated on the plots. Chemical compounds numbered from 1 to 25 are explained in the caption to Fig. 1; also included here are: *26*, *n*-hexane; *27*, cyclohexane; *28*, dichloromethane; *29*, trichloroethylene; *30*, chloroform; *31*, tetrachlorethylene; *32*, 1,1,1-trichloroethane; *33*, benzene; *34*, 1,2-dichloroethane; *35*, *trans*-1,2-dichloroethylene. The *solid straight line* corresponds to the 1:1 ratio between fitted and determined *D* values

Table 3 The coefficients[a] and statistical parameters of the LFER model (Eq. (9)) applied to the analysis of the D values determined from the experimental sorption data[b] on Leonardite humic acid by means of Eq. (10) for two ranges of relative humidity (RH) at 15 °C

RH range, %	c	e	a	b	l	p[c]	$R/F/P$[d]	RMSE[e]	N[f]
0.01–45	-0.12 ± 0.55	1.51 ± 0.43	2.50 ± 0.75	–	-0.47 ± 0.15	<0.002	0.58/11.5/0.000	1.11	73
70–98	0.70 ± 0.75	–	–	4.63 ± 0.93	-0.31 ± 0.15	<0.05	0.63/22.7/0.000	1.35	73

[a] The coefficients c, e, a, b and l are defined in Eq. (9). "±" corresponds to one standard error

[b] The original sorption data used for determining the D values are from Niederer et al. (2006a)

[c] p is the statistical significance level for each of the coefficients of Eq. (9) except the intercept c

[d] R is the correlation coefficient; F denotes the F-test; P is the statistical significance level of the multiple regression

[e] Root mean squared error

[f] Number of compounds included in the analysis

fect of sorbing organic molecules on the amount of sorbent-associated water, i.e., $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$, or, correspondingly, on the coefficients describing water distribution between the gas phase and mineral sorbents, for a wide range of organic sorbates and mineral sorbent surfaces.

3.2 Sorption of organic and water molecules from the gas phase on natural organic matter

The study by Niederer et al. (2006a) presented the systematic examination of the effect of gas phase relative humidity on equilibrium sorption of a large set of organic compounds on Leonardite humic acid which could be considered as a NOM model. Therefore, these previously collected data could be useful for estimating the effects of diverse organic molecules on humic acid-associated water. Four levels of relative humidity expressed as percentages of the $\frac{p_W}{p_W^{sat}}$ values were examined by Niederer et al. (2006a) at 15 °C: < 0.01, 45, 70, and 98 %. No general linear relations between $\ln K_{d,A}$ and relative humidity were found throughout the studied relative humidity range. However, because of the relatively modest influence of sorbent hydration on the measured distribution coefficients, the variability of $\ln K_{d,A}$ within a narrow range of relative humidity can be assumed to follow the linear $\ln K_{d,A}$ vs. $\frac{p_W}{p_W^{sat}}$ relationship described by Eq. (7). Therefore, based on the previously reported $K_{d,A}$ values (Niederer et al. 2006a), in the present work the D value for each organic sorbate was determined for the lowest and highest ranges of relative humidity, i.e., 0.01 to 45 %, and 70 to 98 %, respectively, by means of Eq. (10):

$$D = \frac{\Delta \ln K_{d,A}}{\Delta (p_W/p_W^{sat})} \tag{10}$$

where Δ denotes the change over the relative humidity range.

The determined D values also were analyzed by using LFER (Eq. (9)). Figure 3 shows the plots of the LFER-fitted D values against the determined ones. From the full list of 90 compounds studied by Niederer et al. (2006a), 17 compounds comprising long-chain alkanes, cycloalkanes, alkenes, cycloheptanone, di-n-pentyl ether, 1-chlorooctane, chloroacetone, 2,4-pentanedione and dimethyl succinate were omitted because of lack of the relevant LFER descriptions. The overall LFER fits of the D values were characterized by low R values, especially, for the low relative humidity range (Fig. 3a). Since during the data fitting some terms of the whole LFER relationship (9) were found statistically non-significant, i.e., with the coefficient-associated $p > 0.05$, they were omitted, and the data were refitted. Table 3 summarizes the statistically significant coefficients of the refitted LFER models and theirs statistical parameters.

It is clear from Fig. 3a that the D values in the lower range of relative humidity varied between -4 and $+3$. The positive D values indicate that even at relatively low hydration of humic acid (associated with low gas phase relative humidity) interactions of organic molecules with this sorbent are accompanied by increase in the sorbent hydration. Organic compounds not containing oxygen, nitrogen or sulfur atoms, i.e., hydrocarbons and their halogen-substituted derivatives (Fig. 3a), are characterized by the negative D values (associated with the negative extrapolated derivatives $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ at 100 % relative humidity; Eq. (8)). This selection of hydrocarbons and their halogen-substituted derivatives as a separate subgroup of organic compounds was based on a previous analysis of the thermodynamics of distribution between the gas phase and hydrated NOM, in which these compounds were demonstrated to undergo mostly non-specific, van-der-Waals interactions with NOM (Borisover and Graber 1997). Therefore, in the lower range of relative humidity, the interactions of hydrocarbons and their halogen-substituted derivatives with the sorbent expel the water molecules associated with humic acid. This tendency is contributed by negative l coefficients in the LFER equation (Table 3), i.e., the expelling of the water molecules associated with humic acid increases with increasing vol-

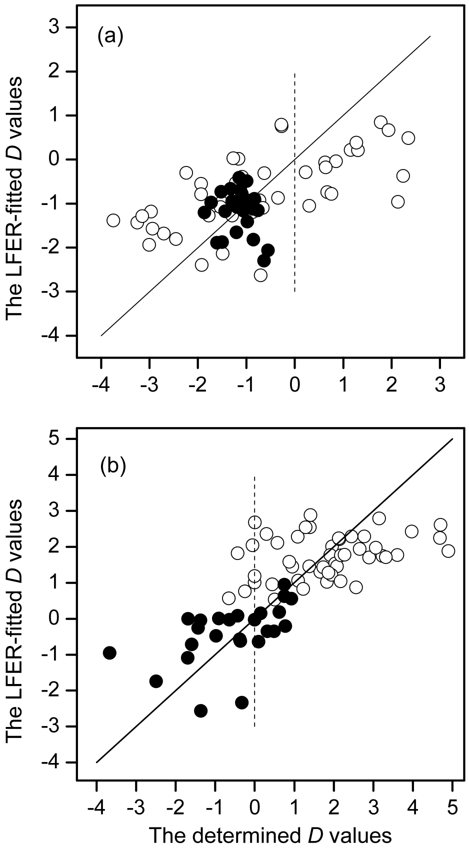

Fig. 3 Sorption of 73 organic compounds on Leonardite humic acid. The LFER-fitted D values are plotted against the D values determined from the experimental data by means of Eq. (10). (**a**) The relative humidity range is between 0.01 and 45 %. The LFER fit is characterized by $R = 0.58$, $F = 6.68$, $P < 0.0001$. (**b**) The relative humidity range is between 70 and 98 %. The LFER fit is characterized by $R = 0.72$, $F = 14.49$, $P < 0.00001$. *Black-filled circles* represent saturated, non-saturated, aromatic hydrocarbons and their halogen-substituted derivatives. *Open circles* represent organic compounds containing oxygen, nitrogen or sulfur atoms, i.e., mostly alcohols, phenols, ketones, esters, ethers, nitro-substituted compounds, and carboxylic acids. The *solid straight line* corresponds to the 1:1 ratio between fitted and determined D values. The *vertical dashed line* separates sorbates with the negative D values from those with positive D values

ume of the organic compounds and/or their increasing capability of dispersion interactions. Organic compounds containing oxygen, nitrogen or sulfur atoms may give rise to both negative and positive derivatives (Fig. 3a). This means that, in terms of the negative $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ derivative or capability to expel water molecules from the humic acid sorbent, in the lower range of relative humidity there is no straightforward differentiation between non-polar (or low-polar) compounds such as, e.g., hydrocarbons, and organic compounds containing oxygen, nitrogen or sulfur atoms. The latter group of compounds is capable of specific interactions, e.g., hydrogen bonding, with NOM. Positive values of the $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ derivative are contributed by polarizability that arises from the presence of n- and π-electrons and by hydrogen-bond acidity (Table 3).

In contrast, in the range of higher relative humidity (Fig. 3b) the same set of organic sorbates seems to be more differentiated. The vast majority of organic sorbates containing oxygen, nitrogen or sulfur atoms exhibit positive D values associated with positive extrapolated $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ derivatives at relative humidity of 100 % (Eq. (8)), and this indicates that interactions of these organic molecules with humic acid drive water into the humic acid phase. This "driving-in" effect is contributed positively by hydrogen-bond basicity, i.e., by the positive LFER-coefficient b (Table 3). A significant number of compounds comprising the subgroup of hydrocarbons and their halogen-substituted derivatives exhibits negative D values (Fig. 3b), which is consistent with the negative l coefficient (Table 3).

Interactions of organic compounds with NOM are generally considered as strongly contributed by intra-NOM sorption of organic molecules (Chiou et al. 1979; Brusseau and Rao 1989; Pignatello 2000). Therefore, mutual interrelationships between interactions of organic molecules and water with Leonardite humic acid hydrated in the high range of relative humidity could be considered as a proxy for the interplay of these interactions in fully hydrated NOMs. Indeed, sorption properties of a Leonardite humic acid in equilibrium with 98 % relative humidity were found to be in a good agreement with sorption properties of completely hydrated humic acid (Niederer et al. 2006b). In this case, the positive D values for multiple organic compounds (Fig. 3b) suggest that their sorption on NOM from aqueous solution is not associated with expulsion of water molecules from the hydrated NOM phase. In fact, the opposite effect should be expected: interactions of organic compounds containing oxygen, nitrogen or sulfur atoms with fully hydrated NOM should be associated with driving of water molecules into the NOM phase. The large D values determined, i.e., up to 5 (Fig. 3b) suggest that several molecules of water will be sorbed by NOM for each sorbed molecule of an organic compound.

Such a concomitant interaction of an organic compound and water with fully hydrated NOM was derived for interactions between carbamazepine and NOM from measurements of carbamazepine sorption by a variously hydrated NOM sorbent (Borisover et al. 2011). In contrast, sorption of less-polar organic compounds on hydrated NOMs may indeed result, with regard to NOM-associated water, in an "expulsion" effect, because for these compounds the D values (or the extrapolated $(\frac{\partial n_W}{\partial n_A})_{T,P,\mu_W,m_S}$ derivatives at 100 % relative humidity, Eq. (8)) are often negative (Fig. 3b). These differences between subgroups of organic compounds and, especially, the "driving-in" effect of organic sorbates containing oxygen, nitrogen or sulfur atoms on the association of water with NOM may be understood within the earlier concept regarding the interplay between penetration of organic molecules into the NOM phase and disruption of interactions between "linked" intra-NOM fragments in the presence of water or of an active organic solvent (Borisover et al. 2001; Borisover and Graber 2002). Intra-organic matter sorption of organic compounds is associated with disrupting specific intra-NOM interactions and may require the effective solvation (hydration) of NOM moieties which would drive water molecules into the NOM phase. This mechanism seems to be less effective for non-polar organic molecules that are not capable of disrupting specific interactions between intra-NOM fragments (Graber and Borisover 1998).

4 Conclusions

The effect of sorbed organic compounds on sorbent-associated water may be evaluated, in a model-free way, from the effect of relative humidity on equilibrium sorption isotherms of vapors of organic compounds and then can be examined by means of the LFER analysis. One interesting result of this evaluation is the understanding that a sensitivity of a mineral sorbent/gas phase distribution of an organic compound to the gas phase relative humidity may often be explained by one (extrapolated) relation between the changes in the sorbed quantities of water and an organic compound at 100 % relative humidity.

Among different examined sorbents including humic and inorganic matters, organic sorbate polarizability contributions from n- and π-electrons resulted in driving water molecules into the sorbent phase but the increasing volume of the organic compounds involved expelling water molecules from the sorbent phase. However, the response to the hydrogen-bond acidity and basicity of organic sorbates was differing between inorganic surfaces and humic acid matter. When the statistically meaningful effect of the hydrogen-bond acidity and basicity of sorbates was observed, it resulted in expelling water from inorganic surfaces and in enhancing hydration of the humic matter phase. Further, as distinct from sorption on inorganic surfaces, when sorbed on strongly hydrated humic acid, the majority of organic sorbates, which contain oxygen, nitrogen or sulfur atoms, drive water into the sorbent phase. This conclusion seems to be conceptually important for understanding the principles controlling the distribution of organic compounds between various environmental compartments with participation of highly hydrated NOM (e.g., as in wet soils and sediments): interactions of organic compounds containing oxygen, nitrogen or sulfur atoms with NOM may drive water into the NOM phase rather than expel it as would often be expected due to the anticipated organic sorbate/water competition. The analysis carried out suggested also that several molecules of water may need to be cosorbed by a humic sorbent for each sorbed molecule of an organic compound.

The described evaluation of the effect of sorbed organic compounds on the sorbent-associated water and the further LFER analysis of this effect may be extended to other types of the sorbents for which the sorption equilibrium of vapors of water and organic compounds can be quantitatively monitored.

Acknowledgements Comments of Dr. Kai-Uwe Goss of the Helmholtz Centre for Environmental Research GmbH, UFZ Department of Analytical Environmental Chemistry and of two reviewers are greatly appreciated.

References

Abraham, M.H., Andonian-Haftvan, J., Whiting, G.S., Leo, A., Taft, R.S.: Hydrogen bonding. Part 34. The factors that influence the solubility of gases and vapors in water at 298 K, and a new method for its determination. J. Chem. Soc. Perkin Trans. **II**, 1777–1791 (1994)

Borisover, M.D., Graber, E.R.: Specific interactions of nonionic organic compounds with soil organic carbon. Chemosphere **34**, 1761–1776 (1997)

Borisover, M., Graber, E.R.: Simplified Link Solvation Model (LSM) for sorption in natural organic matter. Langmuir **18**, 4775–4782 (2002)

Borisover, M., Graber, E.R.: Hydration of natural organic matter: effect on sorption of organic compounds by natural organic matter fractions vs. natural organic matter source material. Environ. Sci. Technol. **38**, 4120–4129 (2004)

Borisover, M.D., Reddy, M., Graber, E.R.: Solvation effect on organic compound interactions in soil organic matter. Environ. Sci. Technol. **35**, 2518–2524 (2001)

Borisover, M., Sela, M., Chefetz, B.: Enhancement effect of water associated with natural organic matter (NOM) on organic compound–NOM interactions: a case study with carbamazepine. Chemosphere **82**, 1454–1460 (2011)

Brusseau, M.L., Rao, P.S.C.: Sorption nonideality during organic contaminant transport in porous media. Crit. Rev. Environ. Control **19**, 33–99 (1989)

Cantor, C.R., Schimmel, P.R.: Biophysical Chemistry. Part III: The Behavior of Biological Macromolecules. Freeman, San Francisco (1980). Chap. 15

Cernik, M., Borcovec, M., Westall, J.C.: Affinity distribution description of competitive ion binding to heterogeneous materials. Langmuir **12**, 6127–6137 (1996)

Chiou, C.T., Shoup, T.D.: Soil sorption of organic vapors and effects of humidity on sorptive mechanisms and capacity. Environ. Sci. Technol. **19**, 1196–1200 (1985)

Chiou, C.T., Peters, L.J., Freed, V.H.: A physical concept of soil-water equilibria for nonionic organic compounds. Science **206**, 831–832 (1979)

Goss, K.-U.: Effects of temperature and relative humidity on the sorption of organic vapors on quartz sand. Environ. Sci. Technol. **26**, 2287–2294 (1992)

Goss, K.-U.: Effects of temperature and relative humidity on the sorption of organic vapors on clay minerals. Environ. Sci. Technol. **27**, 2127–2132 (1993)

Goss, K.-U., Eisenreich, S.J.: Adsorption of VOCs from the gas phase to different minerals and a mineral mixture. Environ. Sci. Technol. **30**, 2135–2142 (1996)

Goss, K.-U., Schwarzenbach, R.P.: Adsorption of diverse set of organic vapors on quartz, $CaCO_3$, and α-Al_2O_3 at different relative humidities. J. Colloid Sci. **252**, 31–41 (2002)

Goss, K.-U., Buschmann, J., Schwarzenbach, R.P.: Determination of the surface sorption properties of talc, different salts, and clay minerals at various relative humidities using adsorption data of a diverse set of organic vapors. Environ. Toxicol. Chem. **22**, 2667–2672 (2003)

Graber, E.R., Borisover, M.D.: Hydration-assisted sorption of specifically interacting organic compounds by model soil organic matter. Environ. Sci. Technol. **32**, 258–263 (1998)

Graber, E.R., Tsechansky, L., Borisover, M.: Hydration-assisted sorption of a probe organic compound at different peat hydration levels: the link solvation model. Environ. Sci. Technol. **41**, 547–554 (2007)

Hayes, M.H.B., Mingelgrin, U.: Interactions between small organic chemicals and soil colloidal constituents. In: Bolt, G.H., et al. (eds.) Interactions at the Soil Colloid-Soil Solution Interface, p. 352. Kluwer Academic, Dordrecht (1991)

Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borcovec, M., Benedetti, M.F., Avena, M.J.: Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. Colloids Surf. A, Physicochem. Eng. Asp. **151**, 147–166 (1999)

Niederer, C., Goss, K.-U., Schwarzenbach, R.P.: Sorption equilibrium of a wide spectrum of organic vapors in leonardite humic acid: experimental setup and experimental data. Environ. Sci. Technol. **40**, 5368–5373 (2006a)

Niederer, C., Goss, K.-U., Schwarzenbach, R.P.: Sorption equilibrium of a wide spectrum of organic vapors in leonardite humic acid: modeling of experimental data. Environ. Sci. Technol. **40**, 5374–5379 (2006b)

Ong, S.K., Lion, W.: Trichloroethylene vapor sorption onto soil minerals. Soil Sci. Soc. Am. J. **55**, 1559–1568 (1991)

Pennell, K.D., Rhue, R.D., Rao, P.S.C., Johnston, C.T.: Vapor phase sorption of para-xylene and water on soils and clay minerals. Environ. Sci. Technol. **26**, 756–763 (1992)

Pignatello, J.J.: The measurement and interpretation of sorption and desorption rates for organic compounds in soil media. Adv. Agron. **69**, 1–71 (2000)

Pool, C.F.: The Essence of Chromatography, pp. 15–18. Elsevier, Amsterdam (2003)

Rhue, R.D., Pennell, K.D., Rao, P.S.C., Reve, W.H.: Competitive adsorption of alkylbenzene and water vapors on predominantly mineral surfaces. Chemosphere **18**, 1971–1986 (1989)

Rudzinski, W., Nieszporek, K., Moon, H., Rhee, H.-K.: On the theoretical origin and applicability of the potential theory approach to predict mixed-gas adsorption on solid surfaces from single-gas adsorption isotherms. Chem. Eng. Sci. **50**, 2641–2660 (1995)

Rusch, U., Borcovec, M., Daicic, J., van Riemsdijk, W.H.: Interpretation of competitive adsorption isotherms in terms of affinity distributions. J. Colloid Interface Sci. **191**, 247–255 (1997)

Taraniuk, I., Rudich, Y., Graber, E.R.: Hydration-influenced sorption of organic compounds by model and atmospheric humic-like substances (HULIS). Environ. Sci. Technol. **43**, 1811–1817 (2009)

Thoms, S.R., Lion, W.: Vapor phase partitioning of volatile organic compounds—a regression approach. Environ. Toxicol. Chem. **11**, 1377–1388 (1992)

Unger, D.R., Lam, T.T., Schaeffer, C.E., Kosson, D.S.: Predicting the effect of moisture on vapor-phase sorption of volatile organic compounds by soils. Environ. Sci. Technol. **30**, 1081–1091 (1996)

Yaron, B., Saltzman, S.: Influence of water and temperature on adsorption of parathion by soils. Proc., Soil Sci. Soc. Am. **36**, 583–586 (1972)