The Air/Surface Adsorption Equilibrium of Organic Compounds Under Ambient Conditions

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The environmental fate of volatile and semivolatile organic pollutants strongly depends on their partitioning between the gas phase and condensed phases. This partitioning includes absorption in bulk phases like water or organic matter and adsorption on ambient surfaces. Often, the latter process is neglected due to the limited knowledge of adsorption as compared to absorption. The first part of this work discusses how the adsorption equilibrium can be assessed as a function of surface and adsorbate properties, temperature, and relative humidity. It is shown that the traditional approach of correlating adsorption constants with the volatility of the considered compounds or with their octanol/air partitioning does not provide a reasonable understanding of the experimental data. Instead, a model is needed that is based on a simple description of the relevant intermolecular interactions. The second part of this work analyses the relative importance of adsorption to surfaces for the overall sorption of airborne organic compounds in the environment. This discussion is focused on gas/particle partitioning and on the exchange between soil surfaces and the atmosphere.

KEY WORDS: fate-modeling, gas/particle partitioning, mineral surfaces, relative humidity, volatilization, water surface

I. INTRODUCTION

The environmental fate of volatile and semivolatile organic compounds strongly depends on their partitioning between air and condensed phases

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like aerosols, rain, fog, snow, soil surface, and vegetation that are in contact with the air. Such sorption processes can slow down the long-range transport of compounds in the atmosphere. Transformation processes also are strongly affected by the partitioning between air and condensed phases. Phototransformation for example occurs in air and aqueous phases but not in phases that cannot be penetrated by light (e.g., soil). A good understanding of thermodynamic partition equilibria of organic pollutants is therefore the basis for a good understanding of their environmental fate.

The complex fate of organic compounds in the environment is usually described with mathematical models that combine the available information on transport, partitioning, and transformation. These models are usually based on the assumption that the partitioning of organic compounds occurs mainly as absorption between bulk phases like water, air, and various organic phases like organic matter in soils and sediments, organic aerosols, and biota. The adsorption equilibrium between air and surfaces, however, has usually been neglected in such models.* Only studies that deal specifically with sorption to aerosols[1−3] or dry soils[4−12] have also discussed adsorption as a potential partition process. The main reason for the neglect of adsorption lies in the limited conceptual understanding of this process and in a lack of quantitative data. In order to close this gap we have measured many hundred adsorption constants during the last decade.[13−23] For these measurements we varied systematically all relevant factors that have an influence on the adsorption equilibrium (i.e., type of compound, type of surface, relative humidity and temperature). The following review is mainly based on these data. Of course, many others have also reported adsorption constants of organic compounds on ambient surfaces[4,9,24−30] that will be referred to. However, the first part of this review (Section II) that discusses a conceptual model for the adsorption equilibrium focuses on data that (a) were measured in the linear range of the adsorption isotherm, (b) can be normalized to the specific surface area of the adsorbent, (c) were measured at ambient relative humidity, and (d) are numerous enough to allow conclusions about the influence of relevant factors. References that deal with the sorption of organic vapors on complex soils or aerosols were not considered because these data do often not allow a clear distinction between adsorption and absorption and the sorbing media is not clearly defined.[6,8,31−40]

Section II of this article gives an overview of the experimental data and presents a conceptual model for a simple qualitative understanding and a good quantitative prediction of air/surface adsorption constants. Section III

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*For the following discussion of sorption between air and other phases it is essential to distinguish between adsorption and absorption: adsorption is the partitioning between a bulk phase—here the gas phase—and an interface—here the surface of a solid or liquid medium. Absorption is the partitioning between a bulk phase and another liquid or "solid" bulk phase.

of this review discusses the relevance of adsorption for the fate of organic compounds in various environmental settings.

II. EQUILIBRIUM ADSORPTION CONSTANTS—EXPERIMENTAL DATA AND A CONCEPTUAL MODEL

A. Experimental Determination of Adsorption Constants

There are two different experimental approaches for the determination of adsorption constants between the gas phase and a surface: (1) In batch experiments the adsorbing compound (= adsorbate) is introduced into a closed system, where it partitions between the gas phase and the sorbent before its concentration is analyzed in one or both phases; (2) in dynamic experiments the sorbent is used as stationary phase in a gas chromatographic system and the observed retention of a compound is a function of its sorption behavior. If sorption occurs in the linear part of the isotherm and if equilibrium is achieved, then adsorption constants can be directly determined from the retention volume. The retention volume is determined from the retention time and the pressure-corrected flow rate of the carrier gas. In this work only the second method was used because it gives fast and highly reproducible results, especially for low gas phase concentrations. This chromatographic method is limited to rather volatile compounds. However, an extrapolation to less volatile compounds is possible as soon as the influence of the various functional groups in a molecule on the adsorption energy is understood. The experimental details are described in refs.,[13−15,21,22] and works cited there.

B. Conceptual Model for Equilibrium Adsorption Constants

Obviously, the extent of adsorption of a given compound to a specific surface depends on the surface area and the affinity between the surface and the compound. The specific surface area of a sorbent can usually be determined by the standard N_2-BET adsorption method. This allows one to normalize all experimental adsorption constants to the surface area of the sorbent. Typical specific surface areas are in the range of 0.1–1 m^2/g for sand, 1–5 m^2/g for aluminum oxides, iron oxides, and lime, 10–20 m^2/g for kaolinite, and up to several hundred square meters per gram for activated charcoal and other artificial adsorbents. Adsorption data normalized to the surface area only depend on the affinity between the compound and the surface and can be used for relative comparisons and thermodynamic interpretations. Therefore, adsorption constants used here have the following form:

$$K_{i\,\text{surf/air}} \equiv \frac{\text{amount of compound } i \text{ per surface area}}{\text{amount of compound } i \text{ per volume of air}} \left(\frac{m^3}{m^2} \right)$$

1. CORRELATION WITH SATURATED LIQUID VAPOR PRESSURE

Experimental sorption constants have often been related to the saturated (liquid) vapor pressure ($p_{iL}*$) of the respective compounds in the following form:

$$\log K_{i\,\text{surf/air}} = a(\log p_{iL}{}^{*}) + \text{constant} \qquad (1)$$

This approach is used for adsorption and absorption from air to all kinds of sorbent phases. The idea behind this widely used empirical approach is that sorption coefficients of various compounds for the same sorbent could be predicted from their p_{iL}^{*}. However, it is not at all obvious why a general linear relationship of this form should exist. The saturated vapor pressure, p_{iL}^{*}, depends on the intermolecular interactions in the pure liquid phase of i whereas the sorption equilibrium depends on the interactions between the compound i and the sorbent phase. Indeed, one generally finds that Eq. (1) only works within a given compound class (because these compounds exhibit similar interactions), while different compound classes require different correlations (Figure 1) (see ref. 41 for a detailed discussion).

As another disadvantage, Eq. 1 only works for a specific sorbent because the properties of the sorbent are hidden in the regression coefficients a and the constant instead of being represented by sorbent specific parameters in the equation. Hence not only every compound class but also every sorbent requires a new correlation with new values for a and c. This is illustrated in Figure 2, where different regressions are needed to describe the
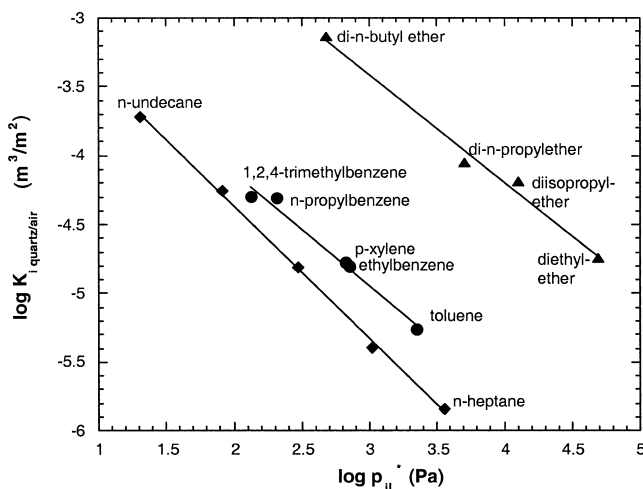

FIGURE 1. Double-logarithmic plot of adsorption constants measured on quartz at 70% relative humudity (rh) and 15°C[21] plotted versus the respective saturated liquid vapor pressure p_{iL}^{*} at 15°C.
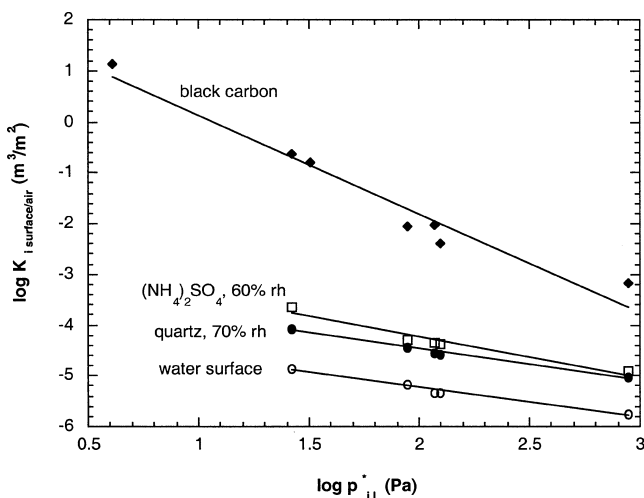
FIGURE 2. Adsorption constants of chlorobenzenes on various surfaces plotted as a function of vapor pressure (all data at 15°C). Experimental adsorption constants taken from refs. 21–23 and 42.

adsorption of chlorobenzenes on various surfaces that may occur as aerosol surfaces in the atmosphere. Equation (1) can also not describe or explain the influence of relative humidity on adsorption (data shown later). The same principle problems occur in correlations that use the log octanol/air partitioning as a predictor variable. Hence, it appears that Eq. (1) contributes rather little to our understanding of the sorption equilibrium and its applicability in the prediction of adsorption coefficients is very limited. A much better understanding can be developed by explicitly considering the intermolecular interactions that govern the adsorption equilibrium.

2. AN ADSORPTION MODEL BASED ON INTERMOLECULAR INTERACTIONS

The constant, $K_{i\,12}$, which describes the partition equilibrium of a compound i between two phases 1 and 2 is related to the free energy of transfer, $\Delta G_{i\,12}$, of 1 mole i from a fixed position in phase 1 to a fixed position in phase 2 by the following equation[43] (R, gas constant; T, absolute temperature):

$$\log K_{i\,12} = -\Delta G_{i\,12}/(2.303RT) + \text{constant} \tag{2}$$

The constant in Eq. (2) depends on the units of $K_{i\,12}$ and the chosen standard state. In the case of the adsorption equilibrium between air and a surface, $\Delta G_{i\,\text{surf/air}}$ is determined solely by the intermolecular interactions between the compound i and the surface, since interactions in air are negligible (ideal gas assumption). Two kinds of interactions must be considered for nonionic

organic molecules*: (1) omnipresent, nonspecific van der Waals interactions and (2) specific electron donor–acceptor (EDA) interactions that only occur if the adsorbate i and the surface posses complimentary electron donor–acceptor functions. Here, only weak EDA interactions (mostly H bonds) are considered because this work only deals with reversible physisorption.[†] Strong EDA interactions where the reaction partners exchange or share electrons are not considered.

With these two kinds of interactions and with the standard state of adsorption defined by de Boer,[44,45] Eq. (2) can be written as:

$$\log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2) = -\left(\Delta G_{i\,\text{surf}}^{\text{vdW}} + \Delta G_{i\,\text{surf}}^{\text{EDA}}\right)/(2.303RT) - 8.47 \qquad (3)$$

Both kinds of interactions (van der Waals and EDA) are attractive; that is, their contributions to $\Delta G_{i\,\text{surf/air}}$ are negative. These interactions can be quantified by a rather simple approach. The van der Waals activity as well as the electron donor and acceptor activities of the adsorbate i and the surface are quantified by separate parameters (vdW, ED, and EA). The product of the complimentary parameters yields a number proportional to the respective component of the free energy of adsorption (for details see the discussion in ref. 19). Hence, Eq. (3) can be written as:

$$\log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2) = a(\text{vdW}_i)(\text{vdW}_{\text{surf}}) + b(\text{ED}_i)(\text{EA}_{\text{surf}})$$
$$+ c(\text{EA}_i)(\text{ED}_{\text{surf}}) - 8.47 \qquad (4)$$

The coefficients a, b, and c are scaling factors that depend on the specific scales used for vdW_i, vdW_{surf}, ED_i, EA_i; EA_{surf}, and ED_{surf}; a, b, and c also contain the term $2.303RT$ from Eq. (3) and depend on temperature. The interaction parameters in Eq. (4) are general placeholders that can be replaced by specific parameter scales as discussed in the following.

Parameters to Quantify van der Waals Interactions. In an earlier work, the logarithm of the subcooled liquid vapor pressure ($\log p_{i\text{L}}^*$) was used as a scale for the van der Waals properties of organic compounds, vdW_i.[20] This has the advantage that vapor-pressure data are widely available and that the resulting equation can directly be compared to the simpler empirical approach in Eq. (1), which also uses the saturated vapor pressure as a parameter.[20] However, this approach can obviously not be applied for compounds that have EDA interactions in their pure phase (e.g., alcohols,

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*In case of highly charged surfaces, interactions between the surface charge and uncharged organic molecules also have to be taken in account. However, these interactions can be neglected for surface potentials typically found in the natural environment (−15 to −60 mV).

[†]In contrast, chemisorption involves the formation of a covalent bond between the adsorbate and the surface and is reversible only at high temperatures.

carboxylic acids, amines), because their vapor pressure does not represent van der Waals interactions alone. A better alternative is the logarithmic hexadecane/air partition constant ($\log K_{i\,\text{hexadecane/air}}$), which is used in the following. For all compounds this constant is proportional to their ability to interact by van der Waals interactions. Data can be found in the literature.[46−49]

In order to replace the general surface parameter vdW_{surf} in Eq. (4) by a quantitative scale, one can use the square root of the van der Waals component of the surface free energy ($\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$).[20] For nonassociated liquids $\gamma_{\text{surf}}^{\text{vdW}}$ is identical with the surface tension. For associated liquids $\gamma_{\text{surf}}^{\text{vdW}}$ can be determined from the interfacial tension with alkanes. The $\gamma_{\text{surf}}^{\text{vdW}}$ of solids is derived from contact angle measurements with alkanes.[50,51] Table 1 shows a number of $\gamma_{\text{surf}}^{\text{vdW}}$ values gathered from the literature.

The data in Table 1 as well as other data in the literature show that $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ values for organic surfaces always lie between 4.2 and 7 $(\text{mJ/m}^2)^{0.5}$. This finding is useful for back-of-the-envelope calculations of adsorption constants, as shown later.

Parameters for EDA Interactions. Electron donor–acceptor properties of organic molecules have been quantified by Abraham and coworkers in comprehensive scales. In these scales the variable $\Sigma\alpha_{i2}^{\text{H}}$ describes the H-donor (= e-acceptor) property and $\Sigma\beta_{i2}^{\text{H}}$ describes the H-acceptor (= e-donor) property of a compound i immersed in a liquid bulk phase whose molecules serve as interaction partners.[60] These relative scales were derived from fitting absorption data of the respective compound between various organic bulk phases and water or air. Here, these scales are used to quantify the EDA properties of compounds adsorbing on a surface. The H-donor variable and the H-acceptor variable both equal zero for alkanes that do not interact by EDA interactions.

Unfortunately, no appropriate quantitative scales for the EDA properties of surfaces, EA_{surf} and ED_{surf}, are available. In earlier papers[19,20,61] we used scales of van Oss,[50] which he had introduced for the calculation of contact angles and interfacial tensions. However, there are some fundamental reasons why these scales may be questionable.* Therefore, we set up new scales for

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*The scale of van Oss[50] implies that the water molecules in the surface layer of a bulk water phase have the same capability to interact by EDA interactions with their horizontal neighbors as with other molecules across the interface. However, EDA interactions strongly depend on the orientation of molecules. A surface water molecule that is in an ideal orientation for EDA interactions with its neighboring water molecules in the surface plane cannot at the same time be in an ideal orientation for EDA interactions across the interface. Hence, the EDA component of the water surface tension cannot be a correct measure for the EDA interaction capability of a water surface *across* the interface. For the same reason (i.e., the variable orientation of surface molecules in liquid surfaces depending on the position of the strongest EDA interaction partner) the measurement of EDA surface parameters with bipolar liquids as suggested by van Oss[50] may not lead to a consistent scale.

TABLE 1. Square Root of the van der Waals Component of the Surface Free Energy of Various Surfaces

Surface	$\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ $(mJ/m^2)^{0.5}$	Temperature (°C)	Reference
Organic surfaces			
n-Octanol	5.24	20	50
Glycerol	5.83	20	50
Thiodipropionitrile	7.06	25	52
Squalane	5.40	23	51
White oil	5.38	25	53
Teflon	4.23	20	50
Polypropylene	5.07	20	50
Polyethylene	5.74	20	50
Polystyrene	6.48	20	50
Polyvinyl chlorid	6.56	20	50
Glucose	6.50	20	50
Paraffin wax	5.05	?	53
Birch wood meal	6.62	50	54
Silica grafted with hexadecanol	6.22	20	55
Inorganic surfaces			
Water	4.67	20	53
Ice	5.44	0	50
TiO_2 (anatase)	8.69	25	56
SiO_2	8.80	25	56
Copper	7.69	25	57
Copper, partly oxidized	8.13	25	57
Lead	9.91	25	57
Lead, partly oxidized	10.1	25	57
Iron	10.4	25	57
Iron, partly oxidized	10.5	25	57
$\alpha-Al_2O_3$	~10	60	58
Elemental carbon			
Carbon fibers [a]	6.82	29	59
Graphite	10.7–11.5	25	53, 56

[a]Depending on the pretreatment of the fibers, significantly different values have been reported in the literature.

the EDA properties of surfaces. Of course, the alkanes again define one end of this scale; that is, their values of EA_{surf} and ED_{surf} equal zero. The water surface, which has EDA properties significantly different from zero, can serve as a reference to define the slope of these new scales (here at 15°C because this is closer to ambient temperatures than the typical standard temperature of 25°C). The values of EA_{water} and ED_{water} were arbitrarily set equal to unity (note that an absolute scaling of EDA properties is neither possible nor required). The decision to set $EA_{\text{water}} = ED_{\text{water}}$ also is completely arbitrary. Hence, if EDA surface parameters of other surfaces are determined according to this scale (see later discussion) they must be understood as

being relative to the water surface, which was chosen as a reference. *Note*: The characterization of van der Waals and EDA properties of a surface by a single and constant parameter each implies that this surface is homogeneous and that the orientation of the surface molecules is fixed. The validity of these assumptions is discussed later.

With the specific parameters discussed above Eq. (4) can be rewritten as:

$$\log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2) = a(\log K_{i\,\text{hexadecane/air}})\sqrt{\gamma_{\text{surf}}^{\text{vdW}}} + b(\Sigma\beta_{i2}^{\text{H}})\text{EA}_{\text{surf}}$$
$$+ c(\Sigma\alpha_{i2}^{\text{H}})\text{ED}_{\text{surf}} - 8.47 \qquad (5)$$

In order to determine the unknown coefficients *a–c* it is necessary to fit Eq. (5) to a sufficiently large data set of experimental adsorption constants, $\log K_{i\,\text{surf/air}}$, for a surface whose surface parameters, $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$, EA$_{\text{surf}}$, and ED$_{\text{surf}}$, are known and different from zero. A first attempt was made in an earlier work[20] with experimental adsorption constants of 32 organic compounds on a water surface.[27] However, these data as well as others published in the literature[24–26,62] are limited in their diversity. Therefore, we recently determined a larger and much more diverse data set of adsorption constants on a water surface.[22] These data agree nicely with those from the literature where they overlap. (*Note*: In these experiments the totally observed sorption was a mixture of absorption and adsorption. Hence, the experiments had to be conducted with different water volumes so that adsorption could be singled out by extrapolation to zero absorption.

3. APPLICATION OF THE MODEL TO ADSORPTION AT THE WATER SURFACE

Equation (5) was fitted to experimental adsorption constants of 60 organic compounds with very different van der Waals and EDA properties. The compounds include the following compound classes: alkanes, alkenes, alkynes, halogenated alkanes and alkenes, alkylated and halogenated aromatic compounds, ethers, aldehydes, ketones, esters, alcohols, and nitro aromatic and thio compounds. Experiments were conducted at 15°C because this is closer to ambient temperatures than 20 or 25°C. The fit gave the following result $(r^2 = .93)$[22]:

$$\log K_{i\,\text{water surf/air}} (\text{m}^3/\text{m}^2)$$

$$= (0.136 \pm 0.003)\left(\log K_{i\,\text{hexadecane/air}}\sqrt{\gamma_{\text{water}}^{\text{vdW}}}\right) + (5.13 \pm 0.15)(\Sigma\beta_{i2}^{\text{H}})\text{EA}_{\text{water}}$$
$$+ (3.67 \pm 0.27)(\Sigma\alpha_{i2}^{\text{H}})\text{ED}_{\text{water}} - 8.47 \qquad (6)$$

The values used for the surface parameters of water at 15°C are EA$_{\text{water}} = 1$, ED$_{\text{water}} = 1$ (see earlier discussion), and $\sqrt{\gamma_{\text{water}}^{\text{vdW}}} = 4.7$ mJ/m^2.[50] The values of $\log K_{i\,\text{hexadecane/air}}$ (at 25°C), $\Sigma\beta_{i2}^{\text{H}}$ and $\Sigma\alpha_{i2}^{\text{H}}$ were taken from the

literature.[47,60] It is not intuitive that log $K_{i\,\text{hexadecane/air}}$ values at 25°C are used to predict adsorption constants at 15°C. However, the log $K_{i\,\text{hexadecane/air}}$ values are only needed as a relative scale and since $\Delta H_{i\,\text{hexadecane/air}}$ is proportional to log $K_{i\,\text{hexadecane/air}}$ (see data in ref. 63) this relative information does not change with temperature. Hence, the log $K_{i\,\text{hexadecane/air}}$ scale at any ambient temperature can be chosen as van der Waals parameter for the adsorbates. Of course, the fitted coefficient a depends on the temperature that is eventually chosen. Here, the log $K_{i\,\text{hexadecane/air}}$ scale at 25°C is used because this is the temperature for which literature values are avaible.

Figure 3a shows that Eq. (6) fits very diverse data set of absorption costants on a water surface sufficently well. In contrast, a correlation with log p_{iL}^* according to Eq. (1) exhibits a large scatter (Figure 3b).

The fitted coefficients a–c in Eq. (6) only depend on temperature and on the scales that have been used to describe the interaction properties of compounds and surfaces. After they have been determined from the fit of one data set for one surface they should work in general. Hence, the general Eq. (7) should allow the prediction of adsorption coefficients of any compounds on any surfaces at 15°C if the required interaction parameters are known. Note that the temperature dependence of $\gamma_{\text{surf}}^{\text{vdW}}$ is small—about -0.7 (mJ/m^2) per 10°C[64]—so that it does not matter whether values for 15, 20, or 25°C are used:

$$\log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2) = 0.136 \; \log K_{i\,\text{hexadecane/air}}\sqrt{\gamma_{\text{surf}}^{\text{vdW}}} \tag{7}$$

$$+ 5.13\big(\Sigma\beta_{i2}^{\text{H}}\big)\text{EA}_{\text{surf}} + 3.67\big(\Sigma\alpha_{i2}^{\text{H}}\big)\text{ED}_{\text{surf}} - 8.47$$

An independent validation of the van der Waals part of Eq. (7) was performed for a number of organic surfaces for which literature values for
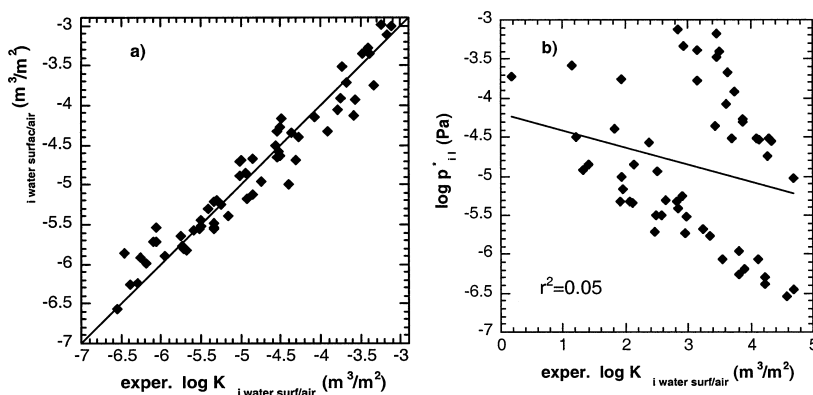

FIGURE 3. Experimental adsorption constants on a water surface (15°C),[22] plotted (a) versus values fitted with Eq. (6) and (b) versus saturated liquid vapor pressures.
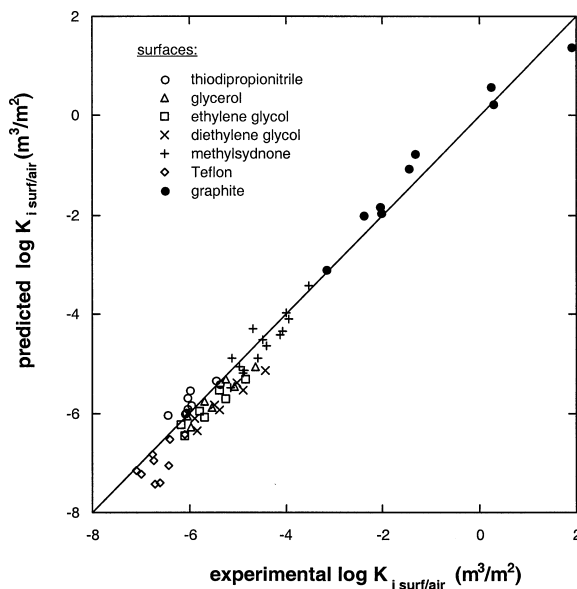
FIGURE 4. Comparison of adsorption constants from the literature (extrapolated to 15°C) with those calculated from Eq. (7). Experimental adsorption constants and enthalpies and the surface parameters required for the prediction were taken from the following references: 42, 65–70 and 50, 52, 53, 68, respectively.

$\sqrt{\gamma_{surf}^{vdw}}$ and the adsorption constants of organic compounds were found. The comparison of the adsorption constants calculated from Eq. (7) (without any further fitting) and from the literature show good agreement for adsorption constants that cover almost 10 orders of magnitude (Figure 4).

Unfortunately this validation is limited to cases where only van der Waals interactions take place because EDA surface parameters, EA_{surf} and ED_{surf}, were not available. Recently, the adsorption constants of 40–55 organic compounds have been measured on 6 minerals (quartz, kaolinite, bentonite, talc, $CaCO_3$, and α-Al_2O_3) and 4 salts (NaCl, KNO_3, $(NH_4)_2SO_4$, NH_4Cl) at 15°C and at different relative humidities.[21,23] The evaluation of these data sets with Eq. (7) using the surface parameters as fitting parameters gave results very consistent with those for the bulk water surface (details are discussed below). Figure 5 shows the comparison between fitted and experimental data for these data. This indicates that Eq. (7) also works in those cases where EDA interactions play an important role. The compounds include the following compound classes: alkanes, alkenes, alkynes, halogenated alkanes and alkenes, alkylated and halogenated aromatic compounds, ethers, aldehydes, ketones, esters, alcohols, and nitro aromatic compounds.

In all data sets for water, mineral surfaces, and salts, the deviation between fitted and experimental data was less than a factor 2 for 80% of the compounds. This performance is good enough for most practical
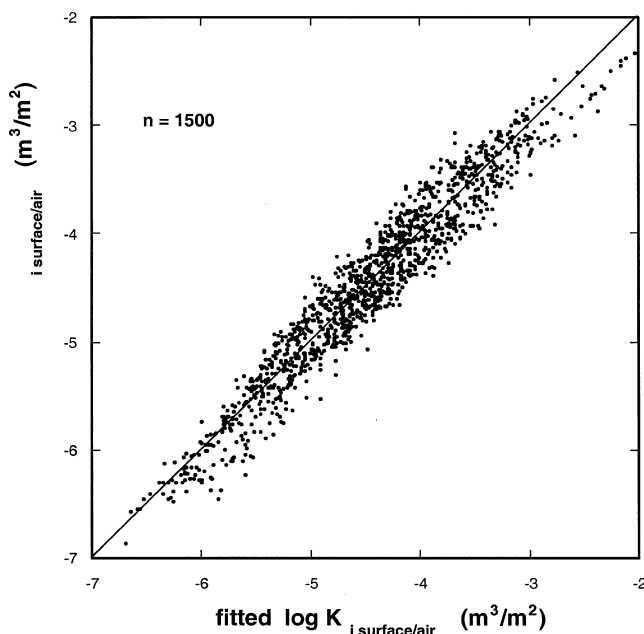
FIGURE 5. Comparison between measured and fitted adsorption constants on 6 minerals and 4 salt surfaces at 15°C and 20–90% rh.[21,23]

applications. However, it must be noted that absorptive partitioning data between bulk organic phases and air are usually fitted much better by linear free energy relationships using Abraham's solvation parameters.[71–75] This difference cannot be explained by the smaller number of fitting parameters that have been used to explain the adsorption data [Eq. (7)]. The fits of the adsorption data cannot be improved significantly if Abraham's π_i parameter is included as an additional compound parameter in Eq. (7). This parameter, which is supposed to describe the dipolarity/polarizability of molecules, is usually needed for a good fit of absorption data. An improvement can also not be obtained by substituting the constant in Eq. (7)—which is set to −8.47 according to de Boer's standard state[44]—by a fitting parameter. Instead, the reason for the different performance may be due to the fact that Abraham's solvation parameters were actually derived from fitting absorption data. Intermolecular interactions strongly depend on the distance between the interacting molecules, which in turn depends on their three-dimensional structure. This information is implicitly contained in Abraham's solvation parameters, and hence one could expect that these parameters are not ideal for describing adsorption on a surface. This is further corroborated by the fact that the observed deviation between fitted and experimental values is systematic for any given compound on all tested surfaces (see Table 2). Hence, it should eventually be possible to derive adsorption parameters

TABLE 2. Comparison of Fitted and Experimental Adsorption Constants for Selected Surfaces, Relative Humidities, and Compounds

Adsorbate	Experimental $K_{i\,\text{surf/air}}$/fitted $K_{i\,\text{surf/air}}$									
	CaCO$_3$		Kaolinite		$\alpha-\text{Al}_2\text{O}_3$		Quartz		NaCl,	
	40%	90%	45%	80%	40%	90%	45%	90%	20%	Water
Dipropylether	0.51	0.56			0.61	0.62	0.79	0.52	0.39	0.59
Diisopropyl ether	1.16	1.10	1.05	0.97	1.02	1.16	1.44	0.86	0.56	1.16
Tetrahydro furane	0.59	0.63	1.08	0.73	0.62	0.66	0.89	0.82	0.67	0.62
Ethyl acetate	2.12	2.19		2.27	2.64	2.44	3.34	2.11		2.47
2,2,2-Tri fluoroethanol	2.02	2.34			2.40	2.24	3.82	3.03		2.51
Ethylbenzene	0.65	0.67	0.77	0.66	0.67	0.63	0.68	0.68	0.56	0.77
Indane	0.43	0.43	0.47	0.50	0.40	0.41	0.25	0.43	0.29	0.48
Naphthalene		0.55	0.45		0.54	0.55		0.70	0.48	0.46
Bromobenzene	0.95	0.90	0.94	0.86	0.79	0.74	0.72	0.97	1.00	0.86
Cyclooctane	0.44	0.41	0.48	0.49			0.26	0.31	0.61	0.43
Anisole	0.70	0.76	1.00	0.78	0.80	0.74	0.57	0.64	0.57	0.86
Benzaldehyde	1.66	1.63			1.73	1.71		1.73	1.75	1.47

Note. The similarity of the deviations on different surfaces indicates that much of the remaining uncertainty in the compound variability could be reduced by improved interaction parameters for the compounds.

for the van der Waals and EDA properties of adsorbates that would give much better fits of the adsorption data than the solvation parameters used here.

Another possible cause for the observed scattering could be expected to come from the changing orientation of the water molecules in the surface layer. In contrast to surface molecules in a solid surface, these water molecules could principally change their orientation in order optimize their interactions with the various adsorbates. Thus one would expect the orientation of the surface water molecules to differ if the adsorbate is apolar or a strong e-donor or e-acceptor. Such a surface of water molecules could then not be described correctly by constant EDA surface parameters. This problem would express itself in a systematic deviation of experimental and fitted [with Eq. (7)] data for compounds with different EDA properties. However, such a systematic deviation could not be found in any of our data sets. One may therefore conclude that the assumption of constant surface properties holds for the surface of bulk water and adsorbed water films independent of the type of adsorbate molecule.

We conclude that Eq. (7) can serve as a valuable tool to describe the compound- and surface variability of adsorption constants. Since Eq. (7) is based on a very diverse set of compounds it should allow the prediction of adsorption constants for compounds other than those used in the experiments without much additional error. (Limitations that apply are discussed in II.B.6 and II.B.7.) In contrast to Eq. (7), the correlation of adsorption constants with log p_{iL}^* [Eq. (1)] only describes a small part of the compound

variability (e.g., Figure 3b) and provides no information on the influence of the surface. In the following, the influence of two other factors, temperature and relative humidity, on adsorption will be addressed.

4. INFLUENCE OF RELATIVE HUMIDITY ON ADSORPTION AT MINERAL SURFACES

Water molecules and organic molecules in the air principally compete for the same adsorption sites on surfaces. On hydrophilic surfaces (e.g., most mineral oxides except talc, salts) the adsorption of water is hardly influenced by competing organic compounds because the water concentration in air is much higher and the affinity of water to hydrophilic surfaces is much stronger than that of organic molecules. The latter is due to the strong H bonds between water and hydrophilic surfaces. The following heats of immersion give an impression of the respective strength of interaction: rutile (TiO_2) in water (-550 mJ/m^2), in ethanol (-397 mJ/m^2), in butylamine (-330 mJ/m^2), and in hexane (-135 mJ/m^2).[76] For the immersion of quartz in different liquids the following values were obtained: in water (-1993 mJ/g), in pyridine (-1649 mJ/g), in benzene (-817 mJ/g), and in hexane (-549 mJ/g).[77]

Figure 6 shows a typical adsorption isotherm for water on a hydrophilic mineral oxide (adapted from data in refs. 16, 78–82). These surfaces are usually covered with 1–2 molecular layers of water at 30% relative humidity (rh). The adsorbed water increases to about 5–10 molecular layers at 90% relative humidity (rh).

While the adsorption of water is hardly influenced by competing organic vapors, the adsorption of organic molecules on hydrophilic surfaces strongly depends on the presence of adsorbed water. For organic molecules it is energetically most favorable to adsorb at surface sites, where they do
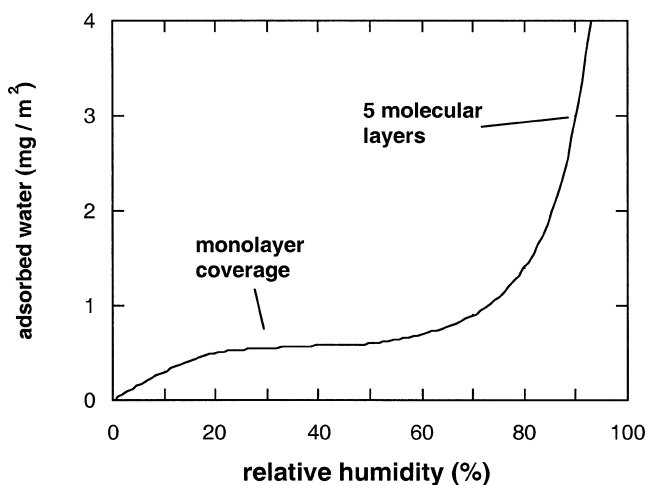

FIGURE 6. Typical adsorption isotherm for water on a mineral oxide.

not have to replace strongly bound water molecules. As a consequence, an adsorption of organic molecules directly on the mineral surface can only occur at low rh (<30%). At higher humidities organic molecules adsorb on top of the adsorbed water layer. Of course, this has consequences for the interactions of the adsorbed molecule. Van der Waals and EDA interactions decay exponentially with distance between the interaction partners and therefore are strongest with next neighbors. The values of $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ in Table 1 indicate that the van der Waals interactions of a dry mineral surface are much stronger than those of a water surface. Hence, organic compounds whose interactions are usually dominated by van der Waals forces experience a decrease in their interaction energy with the surface as relative humidity increases. Between 0 and about 30% rh this decrease is mainly caused by the decreasing number of adsorption sites on the pure mineral surface. At relative humidities above 30% this decrease is caused by the increasing thickness of the water film that separates the adsorbed organic molecules from the pure mineral surface so that water instead of the mineral surface becomes the main interaction partner of the adsorbed organic molecule. All experimental data do, indeed, show the expected decreasing adsorption constants with increasing humidity for all tested organic compounds on various hydrophilic mineral surfaces.[4,9,13,14,16,21,29,83−85]* Between 30 and 90% rh this decrease is found to follow an exponential relationship.[13,14,16,21] A typical example is shown in Figure 7.

Figure 7 also suggests that the adsorption constants of a given compound on various mineral surfaces fall together when extrapolated to 100% rh and that this value would be identical to the adsorption on a bulk water surface. Figure 8, a and b, shows this comparison for a large and diverse set of compounds on three mineral surfaces.[21] An agreement between the adsorption constants on mineral surfaces extrapolated to 100% rh and the adsorption on a bulk water surface does indeed exist for the nonpolar compounds, which are dominated by van der Waals forces (Figure 8a). However, compounds that can form strong EDA interactions with the surface reveal a small but significant deviation from this behavior (Figure 8b). The same effect can be seen even more clearly in the surface parameters of the minerals that are deduced from these data (see next paragraph for these values and a further discussion).

Surface Parameters of Inorganic Surfaces as a Function of Relative Humidity. The adsorption data measured in earlier work for 12 to 16 organic compounds on 5 different minerals at elevated temperatures had clearly

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*Below 90% rh, absorption in the adsorbed water film is negligible. However, at rh >90% the adsorbed water film becomes so thick that absorption may dominate the overall sorption behavior of a compound. In this case, an increase of the overall sorption constant with increasing humidity can be observed for some compounds at rh >90.%.[9,21,22,86,87]
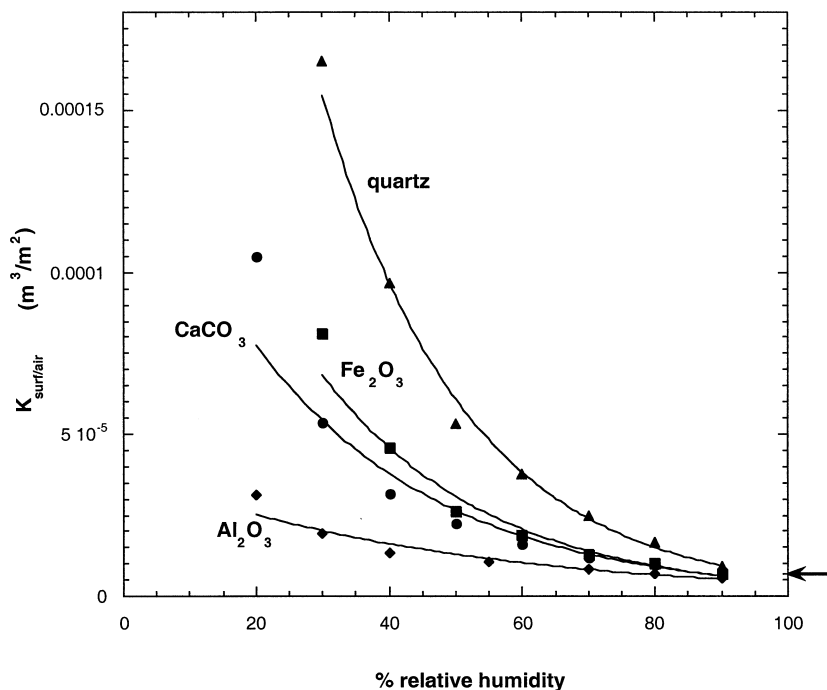
FIGURE 7. Adsorption constants of 1,2-dichlorobenzene on various minerals measured at different relative humidities (data from refs. 13, and 16 extrapolated from 70 to 15°C). The arrow on the right-hand side marks the adsorption constant of 1,2-dichlorobenzene on a bulk water surface.[22]

FIGURE 8. Adsorption constants at 15°C on mineral surfaces extrapolated to 100% rh[21] compared to the respective adsorption constants measured on a bulk water surface[22] (15°C): (a) nonpolar compounds (e.g., alkanes, halogenated and alkylated aromatic compounds); (b) polar (oxygen containing) compounds.

FIGURE 9. The van der Waals property, $\sqrt{\gamma_{surf}^{vdW}}$, of various inorganic surfaces as a function of relative humidity at 15°C[21,23] (relative standard deviation between 1 and 2%).

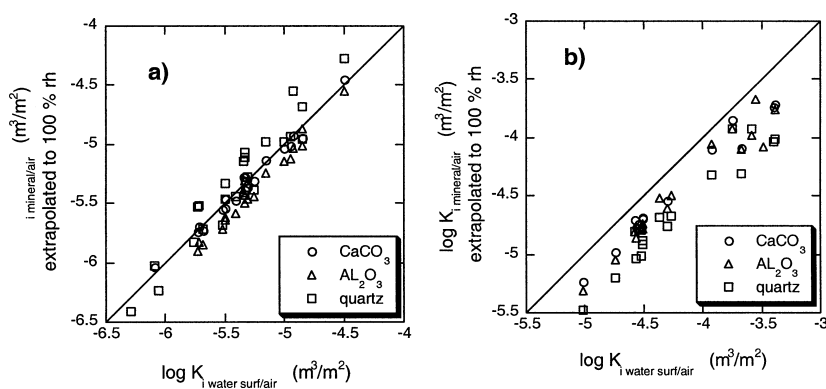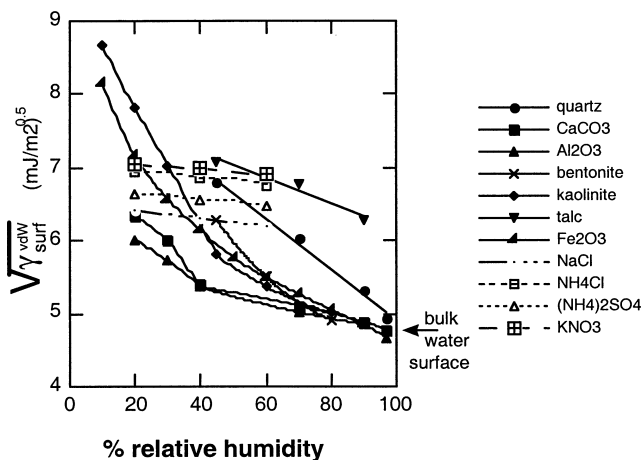shown an exponential influence of relative humidity.[13,14,16] However, a larger and more diverse data set measured at ambient temperatures was required for a reliable determination of all three surface parameters and for a comparison with the adsorption data on bulk water. Hence, the adsorption constants of 45–55 organic compounds were measured at 15°C on 6 minerals (quartz, $CaCO_3$ and α-Al_2O_3, kaolinite, bentonite, talc) and 4 salts [NaCl, KNO_3, NH_4Cl, $(NH_4)_2SO_4$] at 3 or 4 different relative humidities.[21,23] These data sets were evaluated with Eq. (7) using $\sqrt{\gamma_{surf}^{vdW}}$, ED_{surf}, and EA_{surf} as fitting parameters. The resulting values for the surface properties are shown in Figure 9 and Figure 10a and 10b as a function of relative humidity. For

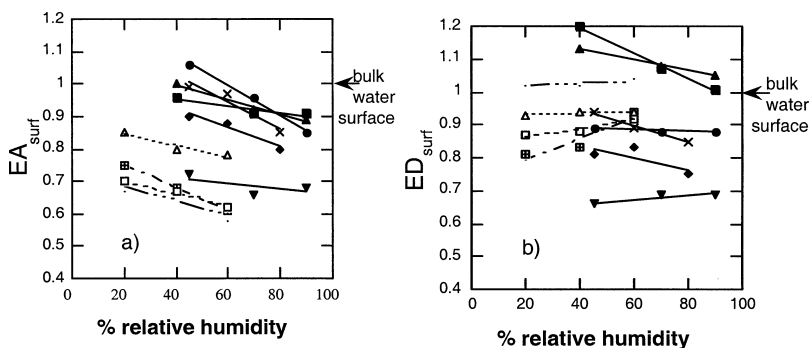**FIGURE 10.** (a) The electron-acceptor property, EA_{surf} (relative standard deviation around 5%), and (b) the electron-donor property, ED_{surf} (relative standard deviation between 15 and 20%) of various inorganic surfaces as a function of relative humidity at 15°C.[21,23] Symbols are the same as in Figure 9. (Figures reprinted with permission from ref. 23. Copyright SETAC, Pensacola, FL.)

TABLE 3. Contribution of van der Waals and e-Donor/Acceptor Interactions to log $K_{i\,\text{surf/air}}$ Exemplarily Shown for Selected Compounds on NaCl at 20% rh and 15°C [Data were Calculated from the Respective Terms in Eq. (7).]

Compound	log $K_{i\,\text{surf/air}}$	van der Waals	e-Donor/Acceptor	Constant
n-Nonane	−4.84	3.63	0	−8.47
p-Xylene	−4.44	3.34	0.69	−8.47
Benzaldehyde	−3.29	3.48	1.69	−8.47
Di-*n*-propyl ether	−3.95	2.57	1.95	−8.47
Aniline	−2.38	3.42	2.67	−8.47
Ethanol	−3.83	1.29	3.35	−8.47

the van der Waals surface properties (Figure 9) some of the values derived from the smaller data set are also included in order to give a more complete picture (i.e., data for minerals below 40% rh and all data for Fe_2O_3).

van der Waals Surface Properties. van der Waals interactions are the dominating interactions in the adsorption of all tested organic compounds except the small alcohols (see Table 3). Hence, the rh dependency of the adsorption constants is reflected primarily in the van der Waals surface parameters. The data show a strong decrease with rh for the hydrophilic minerals kaolinite, bentonite, quartz, and $CaCO_3$ and a weak decrease for talc and the salts.

The qualitative understanding of the van der Waals component of the surface free energy, $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$, is rather straightforward. The ability of a surface to interact with an adsorbate is dominated by the properties of its outermost molecular layer due to the exponential decrease of intermolecular interactions with distance.[88] Furthermore, it is known that the $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ values of dry mineral surfaces are in the range of 8–10 $(\text{mJ/m}^2)^{0.5}$ (see Table 2). Hence, it is reasonable that $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ values of hydrophilic minerals decrease from higher values at low relative humidities to the values of a bulk water surface [4.67 $(\text{mJ/m}^2)^{0.5}$] at 100% rh. Only for bentonite is a small deviation from this general behavior found. Extrapolation of the bentonite data suggests that the $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ value of water is already reached at about 90% rh. This can be explained by capillary condensation in the small pores of bentonite that causes water to adsorb in large amounts at around 90% rh water. For this water, the van der Waals parameter is hardly influenced by the underlying mineral any more and therefore is quite similar to bulk water.

The hydrophobic talc surface adsorbs less water and does not reach a multilayer water coverage at high relative humidity. Therefore, the values of $(\gamma_{\text{surf}}^{\text{vdW}})^{0.5}$ lie above those of a bulk water surface throughout the whole humidity range and show a weaker dependence on rh.

Salt surfaces are hygroscopic and adsorb large amounts of water even at low relative humidity so that the underlying solid salt has almost no influence on the surface properties of the adsorbed water film, even at relative humidities as low as 20%. This explains why almost no change of the $\sqrt{\gamma_{surf}^{vdW}}$ values with increasing humidity is observed for the salts. However, despite the thickness of the adsorbed water layer, the $\sqrt{\gamma_{surf}^{vdW}}$ values are considerably higher than that of pure water. This is due to the fact that the adsorbed water films form a saturated solution of the underlying salt. Although growing with increasing rh, these salt saturated water films do not show a considerable change of their van-der-Waals surface properties because there is enough salt available to keep the water film saturated.

In order to put our values further into perspective, it should be noted that among all surfaces Teflon [4.2 $(mJ/m^2)^{0.5}$] has the lowest $\sqrt{\gamma_{surf}^{vdW}}$ value, while black carbon [11 $(mJ/m^2)^{0.5}$] marks the upper end of the scale for ambient surfaces.

E-Donor/Acceptor Surface Properties. The e-acceptor properties (EA_{surf}) of all surfaces decrease with increasing humidity (Figure 10a). For the salts and the hydrophobic talc surface the absolute values are considerably smaller than that of a water surface over the whole humidity range, whereas EA_{surf}-values of the hydrophilic minerals are closer to that of water. The e-donor properties (ED_{surf}) of all surfaces exhibit less change with relative humidity and are closer to the values of the bulk water surface except for the talc surface that shows the lowest values (Figure 10b). The observed trend in the e-donor/acceptor properties of the surfaces is difficult to interpret. We have speculated that these properties depend on the orientation of the outermost water molecules in the adsorbed water film on the minerals.[21] Hence, these results may add an interesting detail to the discussion of the properties of water molecules close to hydrophilic surfaces which is an ongoing debate in surface science.[78,89−93] Extrapolation of the electron acceptor/donor properties of the hydrophilic minerals to 100% rh does not yield the values of the bulk water surface (in contrast to $(\gamma_{surf}^{vdW})^{0.5}$ values; see also Figure 8). This indicates that an estimation of adsorption constants between 90 and 100% rh with Eq. (7) requires an interpolation of the EDA surface properties measured at 90% for the specific surface and the value that is already known for the bulk water surface ($\equiv$100% rh). A simple extrapolation of EDA surface properties from lower relative humidities would be erroneous.

5. TEMPERATURE DEPENDENCE OF THE ADSORPTION EQUILIBRIUM

In general there is a strong decrease of adsorption with increasing temperature. For volatile organic compounds the adsorption constant changes by

a factor of 2–3 per 10°C. The quantitative description of the influence of temperature on the adsorption constant, $K_{i\,surf/air}$, is given by the van't Hoff equation[94]:

$$\log K_{i\,surf/air} = -\frac{\Delta H_{i\,surf/air} + RT_a}{2.303R}\frac{1}{T} + \text{constant} \qquad (8)$$

with $\Delta H_{i\,surf/air}$ the enthalpy of adsorption, R the gas constant, T the absolute temperature, and T_a the average temperature in the studied temperature range. Hence, a given adsorption constant can be extrapolated to other temperatures if $\Delta H_{i\,surf/air}$ is known and if it can be assumed to be constant over the considered temperature range. The adsorption enthalpy, $\Delta H_{i\,surf/air}$, depends on the adsorbate i and on the surface. The experimental determination of a specific $\Delta H_{i\,surf/air}$ requires the measurement of adsorption constants at different temperatures and an evaluation according to Eq. (8). This involves a considerable amount of experimental work so that alternative methods for estimating $\Delta H_{i\,surf/air}$ would be welcome. The plot in Figure 11 suggests that there is a linear relationship between $\Delta H_{i\,surf/air}$ and the corresponding values of log $K_{i\,surf/air}$ at a given temperature for various mineral surfaces, relative humidities and organic compounds. The reader is referred to ref. 18 for a further discussion of this relationship.

FIGURE 11. Plot of the experimental enthalpy of adsorption against the logarithm of the corresponding adsorption constants (extrapolated to 15°C) on different mineral surfaces at various humidities for compounds with very different polarity (adapted from ref. 18).

The linear regression of the data in Figure 11 yields ($n = 78$, $r^2 = .91$):

$$\Delta H_{i\,\text{surf/air}}(\text{kJ/mol}) = -10.2(\pm 0.4) \log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2, 15°\text{C}) - 89.6(\pm 1.9)$$

$$(9)$$

This fit has a relative standard error of 6% in the fitted $\Delta H_{i\,\text{surf/air}}$ and is sufficiently accurate for practical applications. Equation (9) can, of course, be converted to $\log K_{i\,\text{surf/air}}$ values at temperatures other than 15°C.

The data in Figure 11 show that a single regression line can fit data for different mineral surfaces. This may in part be due to the adsorbed water that covers all these mineral surfaces at relative humidities above 30% and that tends to level out the influence of the different pure mineral surfaces on the adsorption interactions. In order to check how universal this relationship is, it was compared to literature data for adsorption on the following organic surfaces: different carbon fibers (0% rh),[95] cellulose (>92% rh),[96] wood fibers (0% rh),[45] soot (70% rh),[97] glycerol,[67] and mono-, di-, and triethyleneglycol.[69,70] In these works the simultaneously occurring absorption in the organic phases had been separated from adsorption by extrapolation to zero absorption.

Although Figure 12 implies that the differences in the data sets for different organic surfaces are significant, all data still fall in the vicinity of the regression line for the mineral surfaces [Eq. (9)]. Hence, an overall regression
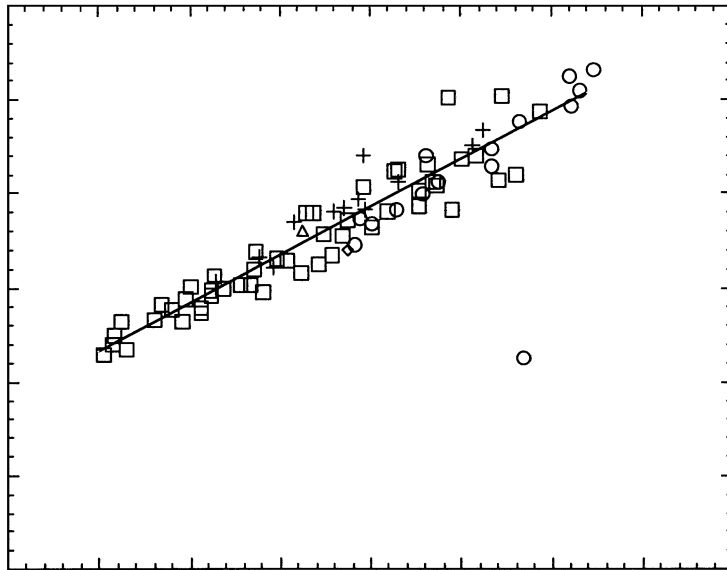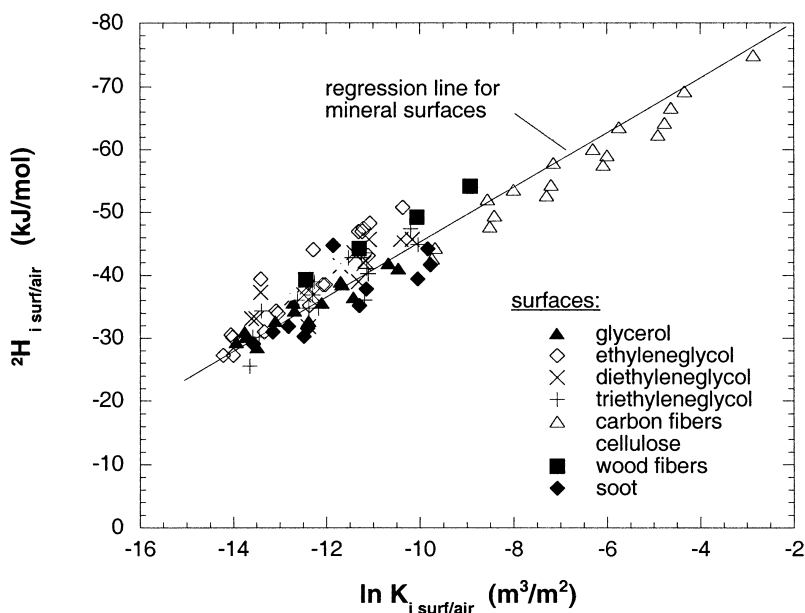

FIGURE 12. Plot of the experimental enthalpy of adsorption against the logarithm of the corresponding adsorption constants (extrapolated to 15°C) on different organic surfaces (adapted from ref. 18).

with all these data for mineral and organic surfaces can be derived ($n = 182$, $r^2 = .89$):

$$\Delta H_{i\,\text{surf/air}}(\text{kJ/mol}) = -9.83(\pm 0.28)\log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2, 15°\text{C}) - 90.5(\pm 1.4)$$

$$(10)$$

This regression fits the $\Delta H_{i\,\text{surf/air}}$ values with a standard error of 9%. While this is not as good as a specific regression for a particular surface (due to the wide range of surfaces used for its derivation), Eq. (10) can provide rough estimates of $\Delta H_{i\,\text{surf/air}}$ values for a wide range of surfaces for which no experimental enthalpies of adsorption are known and can even be used in cases were the surface has not been identified. It is interesting to note that the adsorption data for a bulk water surface deviate somewhat from this general pattern (for details see ref. 18). This deviation, however, can be neglected for most practical purposes. Hence, one can summarize that Eq. (9) and Eq. (10), which relate the logarithmic adsorption constants to their corresponding enthalpies of adsorption, are very useful practical tools for the temperature extrapolation of adsorption constants. There are probably few cases where the effort to measure a more accurate experimental value of $\Delta H_{i\,\text{surf/air}}$ would be worthwhile.

Some other factors that affect the adsorption equilibrium are discussed in the next paragraphs.

6. COMBINED INFLUENCE OF TEMPERATE AND RELATIVE HUMIDITY

Equation (9) allows the extrapolation of adsorption constants from 15°C to other temperatures at constant relative humidity. Together with Eq. (7) one can thus predict adsorption to surfaces for any combination of temperature and relative humidity. There is one interesting combination of both parameters that deserves a special discussion. This situation occurs if the temperature in a system changes while the absolute moisture content in the air remains constant (e.g., the exhaust gas from an incineration process will have various temperatures in different parts of the system while absolute moisture content remains the same). In this case, a change in temperature has two opposing effects on $K_{i\,\text{ads}}$. An increase in temperature will decrease adsorption, but at the same time it will also decrease relative humidity, which in turn amplifies adsorption. Obviously, it would be interesting to know whether one of these two opposing effects would generally be dominating on mineral surfaces. In a technical system, for example, one could optimize the cleaning efficiency of a particle filter by placing it in that part of the system where the maximum of all pollutants is sorbed to the particles. Beforehand, it is unclear whether this will be the high or the low temperature region. (*Note*: These considerations are, of course, only relevant if the particle phase is dominated by hydrophilic surfaces like minerals). A similar situation may occur on air–dry soil surfaces

during diurnal temperature changes if the absolute moisture content in the air stays constant.

Here are some rough estimations:

- Direct temperature effect: Compounds with a subcooled liquid saturated vapor pressure of 10^{-3} and 10^{-6} Pa at 25°C, respectively, exhibit enthalpies of adsorption of about -95 and -120 kJ/mol.[18] This corresponds to a decrease of the adsorption coefficients by a factor of 3.9 and 5.6, respectively, if the temperature is increased by 10°C at constant relative humidity.
- Indirect temperature effect: An increase in temperature from 15 to 25°C at constant absolute humidity corresponds to a decrease of relative humidity from 80% to 43% or from 50% to 27%. The van der Waals surface parameter is the only one that changes substantially with relative humidity. Compounds with $p_{i\mathrm{L}}^*$ of 10^{-3} and 10^{-6} Pa at 25°C exhibit log $K_{i\,\text{hexadecane/air}}$ values of about 10 and 13 at 25°C. Hence, one can calculate with Eq. (7) that adsorption for the 2 compounds will increase by a factor of 53 and 183, respectively, for an rh change from 80 to 43% and by factor of 11 and 22 for an rh change from 50 to 27%. Obviously, this indirect temperature effect strongly outweighs the direct temperature effect; that is, a temperature increase at constant moisture will lead to a strong increase in adsorption to hydrophilic surfaces. This important information is not at all intuitive.

7. STERIC FACTORS

There are a number of steric influences that are not incorporated in Eq. (7).

Three-Dimensional Structure of the Adsorbate. Molecules with a planar shape adsorb closer to a surface than nonplanar molecules. This implicates stronger interactions between the surface and planar molecules because van der Waals interactions increase with decreasing distance between the interaction partners.[88] The van der Waals parameter, log $K_{i\,\text{hexadecane/air}}$, in Eq. (7) does not account for these steric differences, as is illustrated in the examples in Figure 13. The planar *n*-alkanes exhibit a stronger adsorption than nonplanar cycloalkanes with the same log $K_{i\,\text{hexadecane/air}}$. The same principal behavior can be observed on other inorganic and organic surfaces.[21,23,69,70]

In Section II.B.3 it had already been discussed that the solvation parameters that are used in Eq. (7) to describe the compound properties are not optimally suited for the adsorption process and that this explains most of the remaining uncertainty in the fitted data (Figure 3a and Figure 5). This problem could be overcome by the development of a special scale of van der Waals and EDA interaction parameters for the adsorption process. This
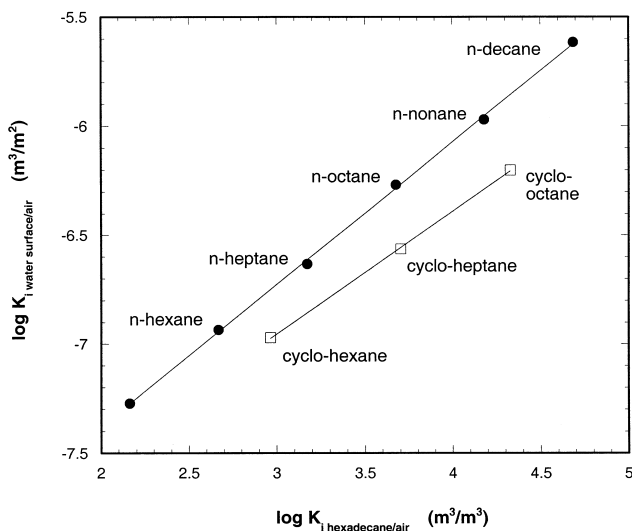
FIGURE 13. Adsorption constants of planar n-alkanes and nonplanar cycloalkanes on a water surface at 25°C[27] plotted versus log $K_{i\,\text{hexadecane/air}}$ (25°C) which is used as van der Waals parameter here.

would, however, require a much larger experimental data set than is currently available. Here, we continue to work with Abraham's solvation parameters since the results are good enough for practical purposes in environmental chemistry.

Orientation of the Adsorbate. EDA interactions require a direct contact between the e-donor and e-acceptor functional groups of the adsorbate and the surface. Molecules that possess more than one of these functional groups (e.g., many pesticides) may be sterically hindered to bring all of them in contact with the complimentary functional groups of the surface. Hence, the compound parameters $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ that describe the complete EDA interaction capacity of a molecule must be reduced. So far, there are no experimental data that would allow an assessment of this effect.

Micropores in the Adsorbent. Many organic molecules are too big to adsorb in micropores (<20 Å). This effect can be accounted for if the accessible surface area of an adsorbent is known. On the other hand, there are adsorbates that just fit neatly into the pores of an adsorbent (e.g., molecular sieves). This increases the contact area and thereby the van der Waals interaction energy up to a factor of two compared to adsorption on a planar surface. Consequently, the adsorption constant, which depends exponentially on the adsorption energy, increases enormously. This effect can be used to specifically adsorb a single gas (e.g., carbon dioxide) from a gas mixture. Such adsorption constants cannot be calculated with Eq. (7) unless the van der Waals parameters of the surface or the adsorbate are adjusted to account for this effect.

8. NONLINEAR ADSORPTION ISOTHERMS

A nonlinear adsorption isotherm occurs if the free energy of adsorption is not constant but changes with the concentration of the adsorbate. This can have two reasons: a heterogeneous surface or increasing adsorbate–adsorbate interactions at high surface coverage.

Heterogeneous Surfaces. Most solid surfaces (in contrast to liquid surfaces) exhibit chemical and morphological heterogeneity on a molecular scale. As a consequence there are adsorption sites with different interaction energies. This leads to nonlinear adsorption because high-energy adsorption sites are occupied before low-energy adsorption sites. The adsorption constant then is a function of the surface coverage, and the calculation of adsorption constants with Eq. (7) would require that the surface parameters were known as a function of surface coverage.[98] Fortunately, this problem does not occur with mineral surfaces at ambient conditions because the adsorbed water film levels out such heterogeneity. Hence, this effect needs not be considered here. Further information on the heterogeneity of dry minerals can be found in refs.[98-100]

High Surface Coverage. Nonlinear isotherms can also be caused by adsorbate–adsorbate interactions, which typically start to occur at a surface coverage above 10%. On minerals these isotherms usually follow a type II form.[4,29,101,102] However, since this situation does not occur at environmental background concentrations it is not further considered here.

It is interesting to note that it directly follows from the preceding discussion that adsorption isotherms on mineral surfaces should become increasingly linear with increasing hydration of the surface (i.e., increasing rh) because hydration (a) reduces the heterogeneity of the surface and (b) reduces the surface concentration of the adsorbate (at a given gas-phase concentration) due to weaker van der Waals interactions. Experimental data do indeed corroborate this conclusion.[4,101]

In the first part of this work a concept was outlined that allows a quantitative and qualitative understanding of those factors (surface properties, adsorbate properties, relative humidity, temperature) that determine the adsorption constants of organic compounds between air and various surfaces. In the following these results are used to identify situations in which the fate of organic compounds in the environment is substantially influenced by the adsorption equilibrium between air and surfaces.

III. THE IMPORTANCE OF THE ADSORPTION EQUILIBRIUM BETWEEN AMBIENT SURFACES AND AIR FOR THE OVERALL ENVIRONMENTAL FATE OF AIRBORNE ORGANIC COMPOUNDS

As mentioned in the introduction, the surface/air adsorption process is frequently neglected in the assessment of the environmental fate of organic

compounds. Generally, it is assumed that nonionic organic compounds mainly partition between the bulk phases air, water, and organic matter. This leaves us with some open questions that are discussed in the following:

- Is it justified that bulk phases like water or organic matter are only considered as absorptive media although they obviously possess a surface at which adsorption from the gas phase must take place to some degree?
- What is the relative importance of phases for which only adsorption but not absorption of organic compounds can occur (e.g., mineral surfaces, ice, snow, glassy organic polymers) compared to absorbing phases within a considered environmental system?

Before these questions are discussed it is necessary to point out some principal differences between adsorption and absorption which make it so important that both processes are treated separately:

- Compounds adsorbed on surfaces are available for reaction with hydroxyl radicals or direct photoreaction. This reactivity is strongly reduced inside organic bulk phases.
- For the adsorption equilibrium, kinetics can usually be neglected since the adsorption process itself is extremely fast. (*Note*: Chemisorption, i.e., the formation of a covalent bond between adsorbent and adsorbate, is not considered here.) In the case of absorption, kinetics may be considerably slowed down by the necessary molecular diffusion within the absorbing phase (through a liquid boundary layer or—in case of "solids," e.g., organic polymers—through the whole compartment). This may take months, as for absorption of PAHs in foliage.[103]
- Both processes also differ completely in the factors that determine the corresponding sorption capacity: The extent of adsorption depends on the surface area of the sorbent and on the affinity between the surface and the adsorbate. The latter is characterized by the adsorption coefficient normalized to surface area and has been discussed throughout Section II. The extent of absorption depends on the bulk amount (mass or volume) of the sorbent and on the absorption coefficient. Obviously, surface area and volume are completely different properties of a sorbent, and so are the adsorption and absorption coefficients of a compound, which depend on the strength of the intermolecular interactions. Figure 14 shows that both equilibrium coefficients do not correlate with each other for a given compound and sorbent. The reason lies in the cavity formation energy, which is a major free energy contribution in the case of absorption, while it does not play a role in the case of adsorption (for a more detailed conceptual discussion see refs. 41). Hence, a proper characterization of the sorption capacity of a sorbent depends on the kind of sorption process that is looked at.
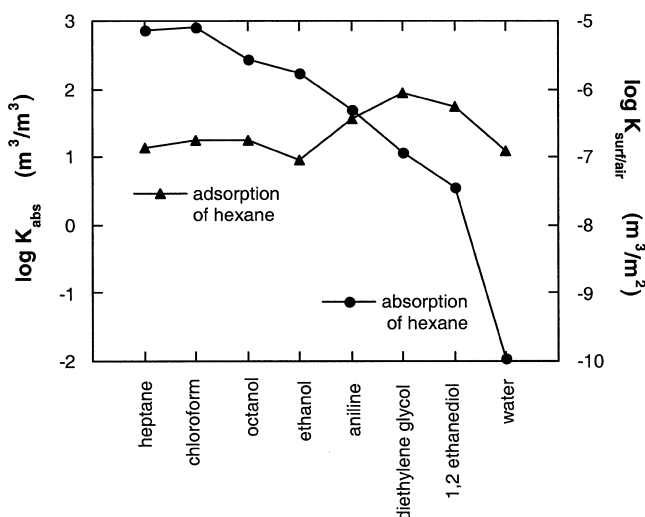
FIGURE 14. Adsorption and absorption constants of hexane on/in different sorbents at 25°C. The absorption coefficients are experimental values from ref. 104. The adsorption coefficients are experimental values for water,[27] ethane diol, and diethyleneglycol[69] and calculated values [with Eq. (7) and Eq. (10) for the other surfaces].

A. Relative Importance of Absorption and Adsorption in/on a Bulk Phase

In order to find an answer to our first question (given earlier) it is necessary to compare the adsorption and absorption capacity of bulk phases like water or organic matter.

By dividing the adsorption constant of a compound i

$$K_{i\,\text{surf/air}} \equiv \frac{\text{amount of compound } i \text{ persurface area of sorbent (mol m}^{-2})}{\text{amount of compound } i \text{ per volume of gas phase (mol m}^{-3})}$$

through its absorption constant

$$K_{i\,\text{abs}} \equiv \frac{\text{amount of compound } i \text{ per volume of sorbent (mol m}^{-3})}{\text{amount of compound } i \text{ per volume of gas phase (mol m}^{-3})}$$

for a particular sorbent one gets a length, $D_{i\,\text{ads/abs}}$, which equals the volume-to-surface-area ratio of the sorbent at which both the surface and the volume contain equal amounts of the compound i when in equilibrium with the gas phase. If the bulk phase is planar, $D_{i\,\text{ads/abs}}$ equals the depth of the bulk phase at which the adsorption and absorption capacity of the phase are equal. Absorption will dominate the overall sorption process of a compound i if the volume-to-surface-area ratio of a phase is greater than $D_{i\,\text{ads/abs}} = K_{i\,\text{surf/air}}/K_{i\,\text{abs}}$, whereas adsorption will dominate in the opposite case.

1. SORPTION IN/ON THE WATER PHASE/SURFACE

The results discussed in the first part of this work (Section II) have shown that only adsorption is significant for extremely thin water films (up to about 10 molecular layers of adsorbed water, ~30Å) that exist on hydrophilic surfaces in contact with ambient air at relative humidities ≤90%. This is true even for polar compounds such as ethanol.[4,16,21,32,105] However, as the water, film grows thicker, absorption in the film becomes more and more important while the relative contribution of adsorption to the overall sorption decreases.[9,21,22,86,87] Calculation of $D_{i\,ads/abs} = K_{i\,surf/air}/K_{i\,abs}$ for some nonpolar compounds on/in bulk water demonstrates where the dominant process switches from adsorption to absorption (Figure 15).

Obviously, adsorption can only play a significant role for sorption to very thin (micrometer range) water compartments. These may occur in form of thin water films (covering surfaces), small droplets [fog (Ø ~10 μm)] and small air bubbles. In cases where the air/water interface carries a significant amount of compound compared to the bulk phase, the total load of the water phase (or the air bubble) cannot be correctly estimated with the absorption constant, $K_{i\,bulk\,water/air}$, alone. For such thin water compartments both sorption processes must be considered. In fact, an enrichment in fog droplets[107−111] and air bubbles[112,113] has been found experimentally and has been discussed as a surface phenomenon by different authors.[17,27,114−117] For thicker water compartments (e.g., rain drops) adsorption becomes less important, although it may still play a role.[118]
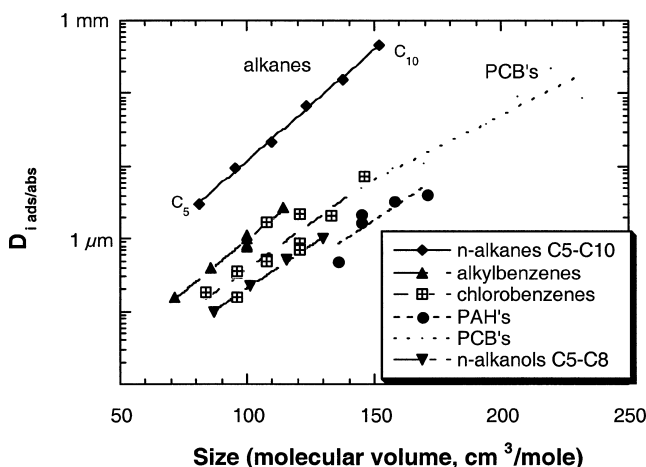

FIGURE 15. Volume-to-surface-area ratio of a planar water compartment at which equal amounts of a compound are adsorbed and absorbed when equilibrium with the gas phase is established. The absorption constants at 25°C were taken from the literature,[47,106] while adsorption data were calculated with Eq. (7) and extrapolated to 25°C according to Eq. (9).

Figure 15 shows that the exact borderline between prevailing adsorption and absorption depends on the studied compound. This border line can be expressed as a function of the compound properties, $\log K_{i\,\text{hexadecane/air}}$, $\Sigma\beta_{i\,2}^{\text{H}}$, $\Sigma\alpha_{i\,2}^{\text{H}}$ if $K_{i\,\text{ads}}$ is replaced by the expression in Eq. (6) and $K_{i\,\text{abs}}$ is replaced by an analogous expression. The latter can be derived from a multiple linear regression with 400 water/air absorption coefficients at 25°C[47] ($r^2 = .86$):

$$\log K_{i\,\text{bulk water/air}}(\text{m}^3/\text{m}^3) = -0.38 \log K_{i\,\text{hexadecane/air}} + 5.75\left(\Sigma\beta_{i\,2}^{\text{H}}\right)$$
$$+ 5.10\left(\Sigma\alpha_{i\,2}^{\text{H}}\right) - 1.84 \tag{11}$$

Hence one gets the following expression for the volume-to-surface-area ratio where the absorption and adsorption capacity of a water compartment are equal:

$$D_{i\,\text{ads/abs}}(\text{m}^3/\text{m}^2) = K_{i\,\text{surf/air}}/K_{i\,\text{abs}}$$

$$= \frac{10^{0.64 \log K_{i\,\text{hexadecane/air}} + 5.19 \; \Sigma\beta_{i\,2}^{\text{H}} + 3.67 \Sigma\alpha_{i\,2}^{\text{H}} - 8.47}}{10^{-0.38 \log K_{i\,\text{hexadecane/air}} + 5.75 \Sigma\beta_{i\,2}^{\text{H}} + 5.10 \; \Sigma\alpha_{i\,2}^{\text{H}} - 1.84}}$$

$$= 10^{1.02 \log K_{i\,\text{hexadecane/air}} - 0.56 \Sigma\beta_{i\,2}^{\text{H}} - 1.43 \; \Sigma\alpha_{i\,2}^{\text{H}} - 6.63} \tag{12}$$

Equation (12) reveals that the relative importance of adsorption versus absorption increases with the hexadecane/air partition constant of a compound, whereas it decreases with functional groups that engage in EDA interactions.

The preceding calculations are valid for pure water and planar surfaces. In the case of a salt solution the results are shifted in favor of the adsorption process since absorption decreases due to the salting out effect[119] while adsorption increases.[23] On concave surfaces (e.g., drops), adsorption is somewhat lower than on planar surfaces, due to an increased distance between the interacting molecules, but this effect has been neglected here. The existence of an organic film on the water surface would, of course, also favor partitioning to the surface of the water. In this case, however, the organic film must be treated as a compartment of its own and not as the surface of a water compartment.

2. ABSORPTION AND ADSORPTION IN/ON ORGANIC COMPARTMENTS

Natural organic compartments like plants and humic material are usually considered only as an absorbent for organic pollutants. However, adsorption will also take place since these compartments possess a surface. Obviously, organic phases are much better absorbents than water while their adsorption affinity for organic molecules is similar to that of water (see Figure 14). Hence, the limiting thickness at which absorption starts to dominate over adsorption must, of course, be much smaller for any organic sorbent phase than for water. A direct assessment of the relative importance of adsorption and absorption for an organic sorbent confirms this. It follows from Figure 14 and

from our conceptual understanding of adsorption and absorption[41] that the ratio $K_{i\,\text{surf/air}}/K_{i\,\text{abs}}$ is highest for phases with a strong self-association (strong H bonds between the molecules) such as 1,2-ethanediol and would become even smaller for less polar phases. A comparison of the relative importance of adsorption and absorption for nonpolar compounds sorbing onto/into 1,2-ethanediol is given in Figure 16 and indicates that the phase would have to be very thin ($<1\ \mu$m) if adsorption was to contribute significantly to the overall sorption from the gas phase. For polar organic compounds the limiting depth of the sorbent below which adsorption dominates is even smaller than for the nonpolar compounds shown in Figure 16.

For natural organic phases like leaf lipids or humic material, the limiting thickness where adsorption becomes important must be smaller than indicated in Figure 16 because the self-association of these phases is smaller than that of 1,2-ethanediol as is shown by Hildebrand's cohesion parameter: $\delta = 29.9$ MPa$^{0.5}$ for 1,2-ethanediol; $\delta = 23\text{--}28$ MPa$^{0.5}$ for organic matter in soils and sediments.[120,121]

Hence, one may in general expect that adsorption cannot contribute significantly to sorption from the gas phase for any natural organic sorbent. In some extreme cases where the organic phase becomes very thin (e.g., aerosols or organic coatings on minerals) this general conclusion may have to be checked again.

The preceding conclusion for organic sorbents was based on the assumption that sorption kinetics can be neglected and that all organic matter can be treated like a liquid sorbent. This is not necessarily correct. It is obvious that natural organic matter has much more similarity with organic
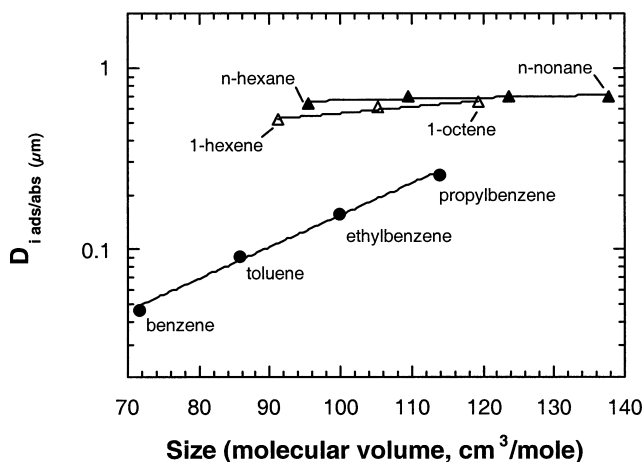

FIGURE 16. Volume-to-surface-area ratio ($D_{i\,\text{ads/abs}} = K_{i\,\text{surf/air}}/K_{i\,\text{abs}}$) of a 1,2-ethanediol phase at which the adsorption and absorption capacity are equal. Absorption and adsorption data are experimental values (25°C) from the literature.[67,69]

polymers than with organic liquids. For the sorptive properties of polymers it matters whether they are in a rigid (glassy) or in a flexible (rubbery) state.[122,123] The same appears to be true for soil organic matter[124−127] and may also apply to other natural organic phases. Rubbery polymers have a sorption capacity that is very similar to that of organic liquids with the same type and concentration of functional groups.[125] The main difference lies in the slower equilibrium kinetics since rubbery polymers are not well mixed compartments (i.e., transport occurs only by molecular diffusion) and molecular diffusion coefficients are about four orders of magnitude smaller than in liquids. Typical diffusion coefficients of VOCs in rubbery polymers lie in the range of 10^{-7} to 10^{-10} cm^2/s.[128−131] One can calculate that a compound with a diffusion coefficient of 10^{-10} cm^2/s needs about 3 min. to achieve at least 99% of the equilibrium concentration when diffusing from the edge into a 1-μm-thick compartment. Hence, even at small time scales when absorption into the organic sorbent has not yet reached complete equilibrium it may still be expected to dominate over adsorption, since the equilibration time within the first micrometer of a rubbery organic polymer is fast and this first micrometer will usually already have a higher sorption capacity than the surface of the polymer. The dominance of absorption over adsorption expected for liquid organic phases should therefore also hold for rubbery polymers, even if the total equilibration time for absorption takes days or months.

In contrast, glassy polymers are more condensed and rigid than rubbery polymers. Absorption in glassy polymers is thought of as the filling of local unrelaxed free voids. This mechanism differs from the ordinary dissolution mechanism. Therefore, the preceding assessment of the relative importance of adsorption and absorption in organic liquids cannot be applied to glassy polymers. Diffusion coefficients in glassy polymers are several orders of magnitude smaller than in rubbery polymers.[129] Hence, the short-term reaction of a glassy polymer sorbent to a change in the gas-phase concentration of an organic compound is governed by adsorption at the surface instead of absorption into the bulk phase.[122,123] Currently, we know very little about which natural organic compartments are in a glassy and which are in a rubbery state. For lipid-like phases we can assume a rubbery state. However, for cellulose the situation already becomes difficult: Dry cellulose is in the glassy state at ambient temperatures but this changes if the cellulose is swollen with water.[132] Soil organic matter is believed to have glassy and rubbery domains.[124−126]

B. Relevance of the Adsorption Process in Different Environmental Settings

We have already discussed the relative importance of adsorption and absorption of organic vapors with respect to single sorbent phases. In the following,

the relative importance of adsorption in various environmental systems is discussed:

1. Sorption in polar regions.
2. Sorption in the atmosphere.
3. Sorption to fallow soils.
4. Sorption in terrestrial systems covered by vegetation.

1. POLAR REGIONS

Ice and snow are the major sorbent phases besides bulk water in polar regions. Due to the rigid structure of ice and snow, only adsorption but not absorption is expected to occur for most organic vapors. (However, for small, polar organics such as formaldehyde incorporation in the ice crystal volume may also be significant.[133]) Hence, adsorption must play a major role in the fate of organic contaminants in polar zones. Unfortunately, our knowledge about the sorption constants of organic compounds on ice and snow is still limited so that estimations about the relevant adsorption capacity are still vague. It is known that the ice surface is covered by a liquid-like transition layer at temperatures between 0 and about −30°C[134,135] and it has been suggested that adsorption constants to ice in this temperature range resembles adsorption constants on subcooled water.[136] However, recent measurements for a large and diverse set of organic vapors on a single snow sample do not support this hypothesis.[137] More experimental data will be needed to achieve a more comprehensive picture.

The specific surface area of ice and snow is the other important factor that determines the adsorption capacity. The few studies conducted so far have found values between 2 and 0.02 m^2/g for snow.[138−141] It is further known that the aging of fresh snow goes ahead with a decrease in the specific surface area. Cabanes et al. (2003) found that the specific surface area of fresh snow decreased by a factor 2 within 5 to 14 days, depending on temperature.[141] Hence, a snow pack may become a source of air contamination with organic pollutants that have before been scavenged from the atmosphere.[142] The melting of a snow pack also leads to a redistribution of compounds adsorbed to the snow surface, which can cause a concentration peak in the first meltwater fractions.[143,144]

For a good understanding of all these processes we must further improve our current knowledge of snow properties, that is, specific surface area and surface interaction parameters. This might then also help to assess the usefulness of the glacial record as an indicator of past atmospheric concentrations of organic pollutants.

2. ATMOSPHERE

Organic vapors in the atmosphere can sorb to fog/rain, ice/snow, and various kinds of aerosol particles. Analysis of these phases reveals the total load of

an organic pollutant but a distinction between adsorption and absorption is usually not feasible. However, this question matters for a number of reasons:

- The capacity of the sorbent depends on surface area in the one case and volume in the other.
- Direct and indirect photochemical reactions will more likely occur at a surface than inside a bulk phase.

Fog/Rain. As discussed in Section III.A.1, sorption to small fog water droplets (Ø < 10 μm) will be significantly affected by adsorption, especially for nonpolar compounds. Hence, an assessment of the sorption capacity of small water droplets in the atmosphere requires that adsorption and absorption are both considered (see ref. 118 for a detailed discussion).

Ice/Snow. The sorption capacity of ice and snow for organic compounds is still difficult to assess to due to the uncertainties considering the sorption constants and the specific surface areas. A recent manuscript by Lei and Wania[145] compares the scavenging ratio of snow and rain based on our current knowledge. However, this comparison must be regarded as somewhat preliminary until more reliable data for the sorption to snow are available.

Aerosols. Aerosol particles constitute a complex sorbent phase due to their variable and often unknown composition. Above the sea and above deserts, aerosol particles should be dominated by salt and mineral dust respectively and adsorption may be a major sorption mechanism.[146] These aerosols also dominate the aerosol mass on a global scale[147] so that the adsorption equilibrium with these adsorbents may influence the global atmospheric transport of organic compounds.

Field studies on gas/particle partitioning have up to now concentrated on urban areas where air quality is an important health topic. A comparison of experimental sorption coefficients from field experiments with the adsorption and absorption constants for various known sorbent phases reveals some interesting features: Figure 17 shows aerosol/air sorption constants of PCBs measured at different events for mostly urban environments in USA and GB.[148,149] Data reported by others for urban aerosol particles lie in the same range.[35−40] Figure 17 also shows a plot of the maximum adsorption that one can expect for PCBs on mineral or salt surfaces (using a specific surface area of 2.5 m^2/g for aerosol particles[150,151]). It appears that this adsorption is too small to explain the sorption capacity of aerosols found in the field measurements. A similar calculation for adsorption to elemental carbon (i.e., an adsorbent that is an important soot component) comes closer to the observed field data but only with the unrealistic assumption that all of the aerosol surface area stems from EC. The estimated absorption into organic matter (OM) (here, hexadecane) assuming an OM content of 30% per weight
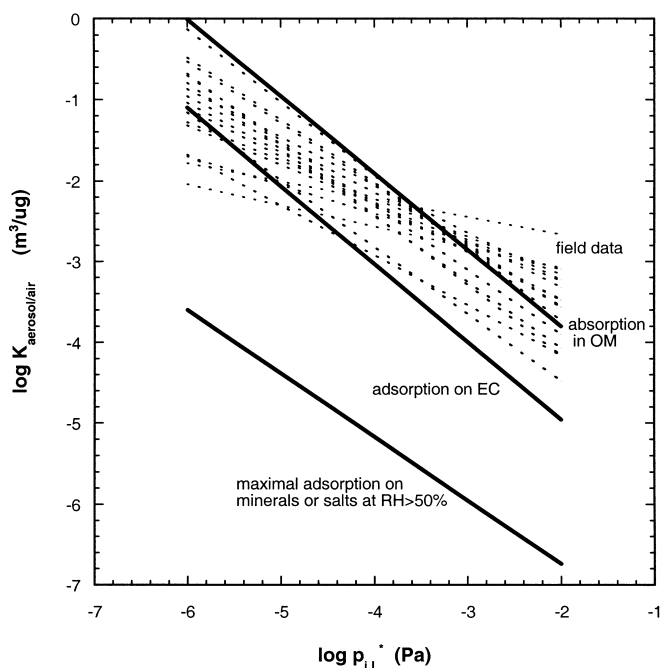
FIGURE 17. Comparison of particle/air partitioning of PCBs for different sorbent phases: aerosols measured in the field;[148,149] adsorption on minerals and salts (50% rh) and elemental carbon (EC) [predicted with Eq. (7) using the surface parameters from Figure 9 and [152] and assuming a specific surface area of 2.5 m²/g as is typical for aerosols[150,151]]; absorption in hexadecane (OM) (extrapolated from data in ref. 47) for an organic matter content of 30% per weight of the aerosols.

for aerosols suggests that absorption into an organic phase is the process that most likely can explain the reported field data.

Prediction of Gas/Particle Partitioning in Multimedia Fate Models. The outcome of multimedia fate modeling for semivolatile organic compounds may strongly depend on the estimated gas/particle partitioning.[153] Therefore, a short review of some common approaches to estimate this sorption equilibrium is included here.

It appears that multimedia models describe gas/particle partitioning either as an adsorption or as an absorption process but never consider both processes. Adsorption is typically predicted by the Junge equation,[154] which can be reduced (using $c = 0.172$ Pa m) to:

$$\log K_{i\,\text{surf/air}}(\text{m}^3/\text{m}^2) = -\log p_{iL}^*(\text{Pa}) - 0.76(\text{Pa m}) \qquad (13)$$

Obviously, an equation based solely on liquid vapor pressure as a predictor variable can never predict the influence of relative humidity or surface type on adsorption. Even the description of the compound variability of the adsorption constants must remain incomplete (see Section II of this review).
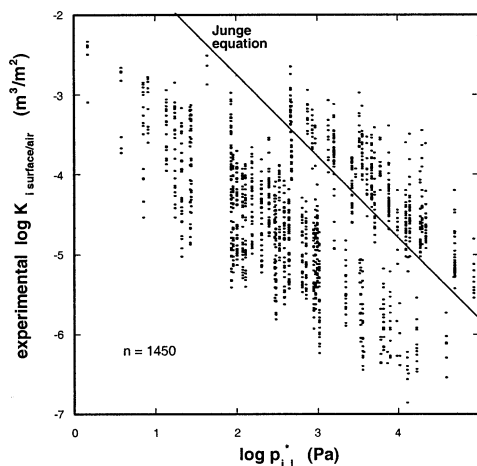
FIGURE 18. Experimental adsorption data on various mineral and salt surfaces at 15°C and 20–90% rh[21,23] plotted versus saturated liquid vapor pressure of the respective compounds at 15°C.

Figure 18 demonstrates the variability that remains when our experimental adsorption data are plotted against vapor pressure of the respective compounds. In contrast, Eq. (7) allows a very good description of the complete variability in the experimental data (Figure 5).

Figure 18 suggests a high uncertainty involved in the use of Eq. (13) unless the variability of ambient aerosol surfaces was much smaller than what could be expected from Figure 18. This could happen if one surface type would always dominate the adsorption process or if ambient aerosols surfaces were a more or less constant mixture.

Another approach predicts the gas/particle partitioning as an absorption process into the organic aerosol fraction using octanol as a surrogate for the organic aerosol phase[155,156]:

$$\log K_{i\,\text{aerosol/air}} = \log K_{i\,\text{oa}} + \log f_{\text{om}} - 11.9 \qquad (14)$$

Several conceptual problems arise with this approach:

1. Adsorption to minerals, salts, and soot is neglected although these surfaces may be relevant in rural, marine and urban environments.
2. The unity slope in Eq. (14) implies that the organic aerosol phase and octanol have the same sorption properties.[157] However, the experimental data used by the same authors exhibiting slopes of 0.79 or 0.55 give proof of the contrary.[157] See also ref. 65 for the interpretation of such slopes. The assumed similarity between octanol and organic aerosol phases also ignores any variability in the sorption properties of aerosols. Such a variability is likely to exist considering the various sources of primary and

secondary aerosols. The wide range of slopes that is found in linear regressions between field data on gas/particle partitioning and octanol/air partitioning[149] also implies that the sorption properties of the sampled particles differ from those of octanol.[65]

3. A compound descriptor such as the octanol/air partition coefficient can not describe the complete compound variability in aerosol partitioning if the sorption properties of the aerosol are different from octanol (as concluded in 2).[41]

3. FALLOW SOILS

Gas-phase sorption processes are relevant in the vadose zone of soils and for the exchange between the atmosphere and the soil surface. In principle, the following sorption processes can occur for organic vapors:

1. Adsorption at the mineral/air interface (at low rh) or at the interface between the adsorbed water film and air (at high rh).
2. Absorption in water.
3. Absorption in soil organic matter (SOM).
4. Adsorption on the mineral/water interface.

The abundant soil minerals such as quartz and clays and many other oxides are hydrophilic. Most organic compounds (except very polar compounds) do not compete successfully with water molecules for adsorption sites at such mineral surfaces. Hence, adsorption to the mineral/water interface (4) is small and usually not significant compared to the other sorption processes.[158–161] (Exceptions must be expected in saturated soils with extremely low SOM content.) The relative importance of the other sorption processes must be discussed as a function of the soil moisture content.

Air-Dry Soils (<90% Relative Humidity = Water Pressure < −12 MPa). Such dry soils can be found in arid and semiarid climates. In temperate climates only the soil surface (upper few centimeters) can become air-dry if the conditions are appropriate.

Process (a): The adsorption constants on mineral surfaces covered with a thin adsorbed water film can be estimated with Eq. (7) using the surface parameters from Figures 9 and 10. The surface area of the adsorbed water film is about the same as the surface area of the underlying minerals independent of the actual humidity.[16,25] Hence, the capacity of this adsorption process, which depends on the product of surface area and adsorption constant, decreases with relative humidity, mainly due to the decrease in the van der Waals surface parameter, $\sqrt{\gamma_{\text{surf}}^{\text{vdW}}}$ (see Figure 9).

Process (b): Absorption of organic compounds into the adsorbed water is negligible compared to adsorption at the air/water-interface below 90% rh.[4,16,22,32,105]

Process (c): Absorption into organic matter is the only other partition process that must be considered in soils with a relative humidity <90%. Soil organic matter also absorbs increasing amounts of water with increasing relative humidity. The work of Borisover and Graber[162,163] and Rutherford and Chiou[164] suggests that the humidity effect on soil organic matter partitioning is small for most compounds. Hence, it should be possible to estimate the partitioning between air and soil organic carbon (SOC) from the combination of $K_{i\,oc}$ (SOC/water partition coefficient) and $K_{i\,bulk\,water/air}$.

Based on numerous experimental data we were able to show in a recently submitted manuscript[165] that indeed both processes adsorption on minerals and absorption in SOC may play an important role. The experimental data could nicely be predicted by a model that considered both processes. Other experimental results[4–6,8,31,32,105,166–168] also support the importance of adsorption to air-dry mineral surfaces. Simple fate models that only consider soil organic matter as a sorbing phase in the partitioning equilibrium between the atmosphere and a dry soil surface may therefore strongly underestimate the sorption capacity of soils.

Moist Soils. If humidity in the soil rises above 90% rh (matric potential > −12 MPa) the water content of the soil increases rapidly and the sorptive capacity of the soil changes dramatically. At humidities >99% rh (i.e., matric potential > −0.12 MPa), which are typical for subsoils in temperate climates, water usually fills a considerable part of the pore space by capillary condensation. Hence the air/water interfacial area is reduced by several orders of magnitude compared to air-dry soils. Values as low as 0.001 m^2/g have been reported for partly water-saturated conditions.[7,169,170] It is clear that the capacity of surface adsorption is correspondingly smaller under these conditions than it is for air-dry soil. Hence, soil organic matter must be the dominating sorbent in moist soils. For less hydrophobic compounds, absorption into the water phase may also contribute significantly to the overall partitioning in moist soils. These theoretical considerations are in agreement with experiments that found sorption from the gas phase being dominated by absorption into soil organic matter in moist soils (rh ∼100%).[6,32,33,168,171] Only experiments with minerals that were almost free of organic carbon indicated adsorption to the air/water interface to be important for the overall partitioning at such high moisture contents.[7,9,10]

Figure 19 shows how the sorption capacity and hence the relative partitioning of a compound (here toluene) may change with the water content of a soil (at 25°C). The calculations are based on the following assumptions: The soil has a porosity of 40%, an organic carbon content of 0.5% (w/w), a mineral surface area of 5 m^2/g. The air/water interfacial area is assumed
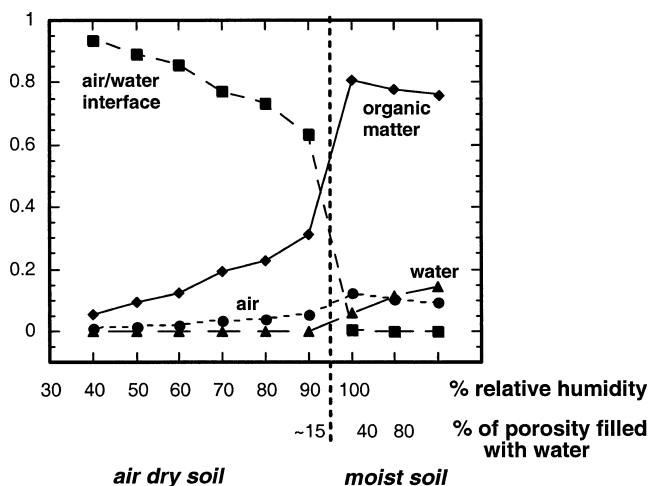
FIGURE 19. Estimated relative partitioning of toluene in different soil compartments as a function of relative humidity.

to be: 5 m^2/g for rh $\leq$90%; 0.02 m^2/g when 40% of the pores are water filled and 0.0015 m^2/g when 80% of the pores are water filled (the latter data were adapted from ref. 169). The required values for $K_{i\,oc}$ and $K_{i\,bulk\,water/air}$ were taken from refs. 172 and 47. The adsorption coefficients of toluene at different relative humidities were estimated with Eq. (7) and Eq. (9).

The decrease in adsorption to the surface of the adsorbed water film between 30 and 90% rh is due to a decrease in the respective adsorption coefficient (compare Figure 7). The decrease in adsorption above 90% rh, which is much more distinct, is due to the decrease of the air/water interfacial area, while the adsorption and absorption coefficients essentially remain unchanged in this humidity range. Again it must be stressed that the curves in Figure 19 would be completely different for soils where absorption into organic matter dominates in the whole humidity range as it is expected for soils which have a small specific surface area and/or are rich in organic carbon.[34]

The strong influence of moisture on the adsorption capacity of the air–water interface has a number of important consequences in soils where adsorption dominates at lower humidities. Increasing soil moisture will lead to a redistribution of an organic compound in favor of the other compartments: soil organic matter, water, and air. This will principally increase the mobility of the compound, since a greater amount of it becomes available for diffusive and advective transport. The availability of the compound to photolysis and biodegradation also changes with this redistribution.

This has the following practical consequences:

- An air-dry soil surface may present a significant barrier for the pollutant transport between the vadose zone of a moist subsoil and the

atmosphere.[173] Hence, for example, the performance of sniffing dogs detecting explosive vapors that leak from buried landmines will strongly depend on the actual moisture regime.[174]

- Pesticide volatilization from soil surfaces will strongly increase with increasing humidity of the surpassing air and/or with increasing soil humidity. This has also been shown in experiments.[175] For example, a rain event after a dry period can cause a sharp increase in the pesticide volatilization over a field.[176−179]
- The performance of remediation procedures like soil venting should strongly depend on an optimal soil moisture regime.
- The toxic effect of insecticides is reduced by increasing adsorption and hence by low soil moisture as shown by ref. 180.

In temperate climates adsorption will have only local and temporary effects on the fate of pesticides because it is limited to dry, fallow soils. However, the adsorption process may also be important on a global scale. Large areas of the continents are covered with deserts, that is, dry soils with little organic matter. Here, adsorption must be expected to be the dominant exchange process between the atmosphere and the terrestrial surface.

4. SOIL COVERED BY VEGETATION

Soil surfaces that are covered with vegetation are usually rather moist (water pressure > -3 MPa) so that adsorption to mineral surfaces should not be significant (see discussion under III.B.3). The sorption capacity of soil organic matter and vegetation is expected to be dominated by absorption (see III.A.2). Recent model calculations suggest that the absorption capacity of soils greatly exceeds that of vegetation growing on the soil but that the vegetation may strongly increase the transport kinetics from the atmosphere to the soil as compared to fallow soils.[181,182]

IV. CONCLUSIONS

Adsorption constants between air and uncharged surfaces have been described by a conceptual model based on the van der Waals and EDA properties of the surface and the adsorbing compound. The model also accounts for the effect of temperature and relative humidity. It provides a good explanation of the variability of more than thousand experimental adsorption constants and it facilitates a comparison of the surface properties of mineral and salt surfaces at various relative humidities with the surface properties of a bulk water surface.

The adsorption process has, so far, not attracted much attention as a possible contribution to the environmental partitioning of organic compounds. With a quantitative model for the prediction of adsorption constants for

various compounds and surfaces this gap can now be closed. A comparison of the relative significance of absorption and adsorption (Section III) allowed the identification of the following situations where adsorption likely is the dominant sorption process: (a) the exchange between the atmosphere and terrestrial surfaces in locations permanently devoid of vegetation, such as the polar regions, deserts, and high mountain ranges; (b) the air/particle exchange within the atmosphere if the particles are dominated by mineral dust (above deserts), salt (above oceans), soot (tunnels), or in the case of snowfall. Hence, it follows that the global atmospheric transport of organic compounds can probably not be understood without taking adsorption into account. With the information reviewed here it should become feasible to include the effect of adsorption into models that describe the global partitioning of compounds.

There are a number of technical systems where adsorption plays a role and where an improved understanding of the adsorption equilibrium may help to optimize the performance of the system. Here, only two applications are mentioned briefly.

- Small water droplets are used to wash exhaust gases. The possibility to predict the adsorption of organic compounds on the surface of these droplets may help to assess the capacity of such gas washing units and to optimize the droplet size.
- In air sampling it is important to know the capacity of the adsorbent. With the model presented here the adsorption capacity that has been determined for a number of different compounds on a given adsorbent can be extrapolated to all kinds of untested organic compounds and/or other adsorbents.

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