Contaminant Vapor Adsorption at the Gas–Water Interface in Soils

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There is evidence to suggest that the gas–water interface serves as an important retention domain for volatile organic compounds (VOCs) in vadose-zone soil. Moreover, vapor adsorption at the gas–water interface may represent the dominant retention mechanism under certain conditions. In general, vapor-phase interfacial adsorption is most significant for low organic matter soils at intermediate water contents. Among nonpolar compounds, those with low saturated vapor pressure have the greatest tendency for interfacial adsorption, as represented by higher interfacial sorption coefficients, K_{IA}. Although polar compounds may have greater tendency to adsorb at the interface than nonpolar compounds, the high aqueous solubility of polar compounds may limit the relative importance of interfacial sorption to total contaminant retention. The magnitude of interfacial retention is controlled by the specific interfacial area, A_{IA}, as well as by K_{IA}. Validated methods for measuring A_{IA} are currently lacking. However, three promising methods for measuring A_{IA} in soils have been proposed. Preliminary results indicate that the three methods are complimentary in terms of the type of information derived, as well as their applicability for different water content ranges and varying scales (e.g., laboratory vs field).

Introduction

Each phase in an unsaturated system may contribute to the total retention of gas-phase volatile organic compounds (VOCs). Phases present may include the solid mineral phase, organic matter, bulk water, and gas phase. These four phases represent the possibility for four retention mechanisms: sorption to mineral surfaces, association with organic matter, dissolution into the bulk water phase, and volatilization into the gas phase. Many studies of gas-phase VOC transport have been conducted to evaluate the relative contribution of these retention processes to the total retention. It is generally found that soil organic matter serves as the primary sorption domain in high water content systems, while sorption to mineral surfaces dominates at very low water contents (e.g., <50% RH) (*1–5*). At intermediate water contents, combinations of the above mechanisms have been proposed.

Recent studies have shown that experimentally observed VOC retention in unsaturated systems is often greater than that predicted based only on mineral sorption, organic matter association, and aqueous dissolution. For example, Karger et al. (*6*) observed greater than predicted retention of halogenated alkanes and aromatics by synthetic porous media. These results are consistent with those of Pennell et al. (*2*) and Hoff et al. (*3, 4*), who examined the retention of aromatics by soils and clay minerals. Others have also shown the retention of straight-chain alkanes and aromatics to be greater than the contributions of solid-phase sorption and aqueous dissolution (*7–9*). Underprediction of solute retention indicates the influence of additional retention mechanisms not traditionally taken into consideration. Adsorption of organic vapor to water surfaces (soil gas–bulk water interface) has been proposed as a mechanism accounting for much of the additional retention observed in unsaturated systems.

Organic vapor adsorption to thin water films and flat water surfaces is well-documented in the physical chemistry literature as early as the mid 1950s (*6, 7, 10–14*). With the exception of a few isolated studies (*15–17*), only relatively recently has the gas–water interface been studied in the context of soil systems. The potential significance of interfacial adsorption in contaminated vadose-zone systems has since been demonstrated for many types of organic compounds and a variety of synthetic and natural materials (*2–4, 6–9, 18–20*). For example, Hoff et al. (*3*) estimated that 48–56% of the observed retention of straight-chain alkanes by sandy aquifer material was due to air–water interfacial adsorption. Up to 60% of the total retention of *p*-xylene by a desert soil was attributed by Conklin et al. (*8*) to interfacial adsorption. Depending on the porous medium studied, between 29% and 73% of the total retention observed for trichloroethene was attributed by Brusseau et al. (*9*) to accumulation at the gas–water interface.

Adsorption of chemicals at air–water interfaces is an important process in many areas of environmental science in addition to VOC transport in soil. For example, Valsaraj (*19*) notes several areas of environmental chemistry in which gas–water interfacial adsorption plays a significant role. Specifically, the gas–water interface of bubbles affects the efficiency of air-stripping VOCs from wastewater. Also, the observed enrichment of organic compounds and organic particulates in the surface "microlayer" of oceans relative to underlying seawater may be due to interfacial phenomena. Valsaraj et al. (*18*) and Goss (*21*) suggest that enrichment of organic compounds in fog droplets in excess of that predicted by Henry's law may be due to adsorption at the air–water interface. Wan and Wilson (*22*) provide convincing evidence of the important role of gas–water interfaces in the transport and retention of colloids, such as clay particles and microbial cells.

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The goal of this paper is to examine the process of vapor adsorption at the air–water interface in porous media. The physicochemical properties of the porous medium and of the organic vapor influencing this process will be discussed. Incorporation of vapor adsorption into the advective–dispersive transport equation via the retardation factor will be presented, with attention given to two interfacial terms: the interfacial sorption coefficient (K_{IA}) and the specific interfacial area (A_{IA}). Methods for measuring these two parameters will be discussed, with focus on the latter, considering the current lack of an accepted method. Finally, research needs will be identified.

Vapor Adsorption on Liquid Surfaces

Theory. A mechanistic understanding of vapor adsorption at the air–water interface is required to evaluate the relative importance of this process for VOC transport. Vapor adsorption is an exothermic process and is therefore enthalpically favored. Although there is a consequent decrease of entropy in the adsorbed phase relative to the free vapor phase, adsorption is typically a spontaneous process. Experimental evidence indicates that vapor adsorption on water surfaces may be considered as an instantaneous process relative to other transport processes (*20*).

Initial studies of the extent and nature of vapor adsorption were based on measurement of changes (decrease) in the aqueous surface tension due to organic vapor adsorption. The Gibbs adsorption equation describes the relationship between the surface tension of the liquid phase, water in this case, and the vapor pressure of the organic compound above that liquid:

$$\left(\frac{\partial \gamma}{\partial p}\right)_T = -\frac{\Gamma RT}{p} \tag{1}$$

where γ is the surface tension (N m^{-1}), p is the organic vapor pressure (atm), Γ is the surface excess of the organic compound (mol m^{-2}), R is the universal gas constant (L atm (K kmol)$^{-1}$), and T is temperature (K). Often $\partial\gamma$ is replaced by π, the surface pressure, defined as

$$\pi = \gamma_o - \gamma \tag{2}$$

where γ_o is the surface tension of the pure liquid, while γ is the surface tension of the liquid as a function of the vapor adsorption. Because most organic vapors cause a decrease in surface tension, π is typically positive for organic vapor adsorption.

Using eq 1, measurement of surface tension coupled with knowledge of the organic vapor pressure above the liquid allows determination of the surface excess of the organic compound. As surface excess increases, the surface pressure also increases, indicating that the average surface area occupied per molecule decreases. Surface pressure may be considered as the two-dimensional analogue to the familiar three-dimensional vapor pressure. It is observed that adsorbed vapors behave quite similarly to gases in three-dimensional systems. The two-dimensional analogue to the familiar ideal gas law is written as follows (*23*):

$$\pi A = nRT \tag{3}$$

where A is the area occupied by one mole of adsorbed molecules (m^2 mol), and n is the number of moles adsorbed (–). As the surface pressure of a liquid surface increases, the adsorbed vapor will be compressed and A will decrease accordingly. At higher surface pressures, phase changes analogous to condensation and solidification may be observed. At high pressures, just as in the three-dimensional case, the ideal gas law no longer holds, and intermolecular (adsorbate–adsorbate) interactions and finite molecular size must be considered. The adsorbed phase remains compressible over the range observed in typical organic vapor adsorption studies. Thus, the adsorbed phase is usually considered to be a gaseous phase rather than a condensed liquid phase.

Physical System Properties Influencing the Importance of Interfacial Vapor Adsorption. The general nature of the interface as a thermodynamically favored adsorption domain provides the potential for vapor-phase adsorption. However, the properties of a given environmental system dictate the ultimate significance of this retention and the resultant impact on VOC transport. Thus, the factors influencing the presence, nature, and extent of gas–water interfaces in environmental systems must be addressed. The individual factors are intimately related, and only when considered together can the overall system be described in a quantitative manner. Nonetheless, generalizations regarding the individual effects are useful in developing a conceptual understanding of the system. Note that soils with significant organic matter content or extremely low water content are not considered in the following discussion, since in such systems retention at the gas–water interface will often be negligible as compared to partitioning into organic matter or adsorption by exposed mineral grains, respectively.

Water Content. As water content is decreased starting from a saturated system, the interfacial area can only increase from essentially zero in the saturated system to some maximum at low water content. Several theoretical models predict this general trend (*24–26*). It is believed that the maximum interfacial area corresponds to a system in which the water film is relatively thin, and pendular rings have formed across adjacent porous medium grains (*24*). At water contents below that required for pendular ring formation and resultant maximum interfacial area, the water exists primarily as thin coatings on the grain surfaces. As the system approaches monolayer water coverage, the specific interfacial area will approach the specific surface area of the porous medium. At submonolayer coverages, the interface will accordingly decrease, becoming zero at zero water content. This paper focuses on systems wetted to create a relatively homogeneous water surface, and, consequently, neglects extremely low water content systems where mineral grains may be exposed.

The interfacial area–water content relationship as well as the interfacial area maximum are expected to vary according to physical properties of the porous medium. Well-tested experimental methods for measuring the air–water interfacial area are lacking. However, several models have been proposed to quantify the dependence of interfacial area on fluid content. Early efforts by Leverett (*27*), Morrow (*28*), and more recently by Bradford and Leij (*26*) rely on a thermodynamic interpretation of experimental capillary pressure–saturation (P_c–S) plots obtained for two- and three-fluid systems. Bradford and Leij (*26*) present results for a water-wet sand system. The results indicate that interfacial area reaches a maximum value approaching the surface area of the porous medium at the residual saturation of the wetting fluid (i.e., water content after gravity drainage). The interfacial area then decreases as saturation is approached. The reported maximum specific interfacial area is approximately 450 cm^{-1}, expressed as interfacial area per unit of air-filled pore volume. This is equivalent to an A_{IA} maximum of approximately 160 cm^{-1}, using the more typical units of area per unit bulk volume of porous medium (as will be used below). The observed trend in interfacial area versus saturation is consistent with theory.

Gvirtzman and Roberts (*24*) examined the relationship between interfacial area and water saturation for two ideal packing structures of identical spheres. The ideal soil model is based on geometry variables, such as sphere radius, packing

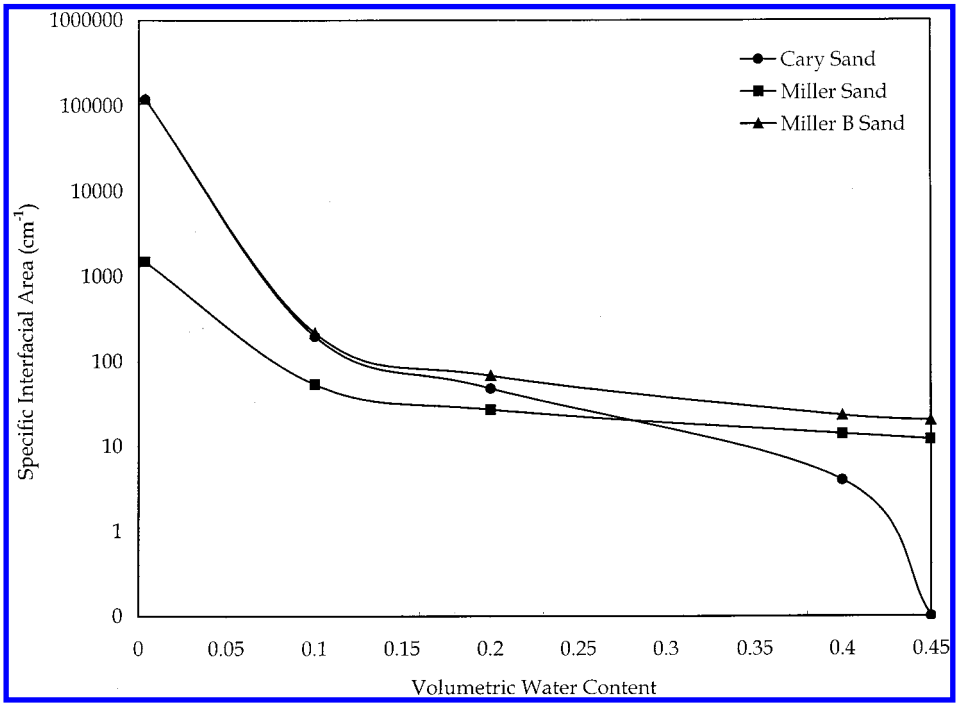

FIGURE 1. Model comparison: prediction of interfacial area versus water content for hypothetical sand system. Adapted from ref *29*.

structure, and fluid contact angle. The expected results for water content dependence are observed. The maximum interfacial area is observed to be in the range of 15−25% saturation, which is approximately 5−9% volumetric water content for a typical sand (porosity = 0.35). The maximum interfacial area is predicted to be approximately 40 cm^{-1}.

Cary (*29*) presents interfacial area versus water content data for three hypothetical soils as calculated using three semiempirical models proposed by Cary (*29*) and Miller et al. (*30*). The models are based on capillary tube pore geometries and empirically fitted parameters. Predicted trends in interfacial area versus water saturation are similar for all three models for all soils, as illustrated in Figure 1 for the sand system. Cary reports two forms of the Miller et al. model. The first model predicts interfacial areas at water saturations equivalent to monolayer water coverage that are inconsistent with the surface areas of the porous media. In the case of the sand, the maximum interfacial area is over 2 orders of magnitude lower than the porous medium surface area, while maximum interfacial areas for the silt are over an order of magnitude higher than the porous medium surface area. On the contrary, the second Miller et al. model (Miller B in Figure 1) forces the interfacial area to equal the porous medium surface area at monolayer coverage, as would be consistent with theory. Only the Cary model predicts zero interfacial area at water saturation, as is reasonable. While these models provide first-order agreement with expected trends at intermediate water contents, they provide only limited support for the current understanding of the interface due to their semiempirical nature.

Reeves and Celia (*25*) use a pore-network approach to describe saturation effects on interfacial area. The network is created by defining pore-space geometries, e.g., pore body and pore throat dimensions. By defining the pore space rather than the solid porous medium itself, the solid phase is implicitly considered. The Laplace equation and the simulated pore geometries are coupled to arrive at A_{IA} values. The expected trend of interfacial area passing through a maximum at some water content and dropping to zero area at the wet and dry extremes is observed. The maximum specific interfacial area ranges between 26 and 38 cm^{-1} and is observed at water saturations of 20−40% (approximately 7−14% water content). These values are in agreement with the results of the Gvirtzman and Roberts model.

Water Distribution. Physical characteristics, such as soil texture, pore size distribution, and wetting/drying cycles, may be thought of as factors affecting the geometry of the water in the system. Water at a given saturation will be distributed differently within different porous media, essentially altering the surface area to volume ratio of the water. Knowledge of the water distribution in the porous medium is critical to evaluating the area of the gas−water interface and, hence, its significance as a retention domain. While several models have been proposed to quantify the dependence of interfacial area on water content, few have examined its dependence on pore size and pore size distribution. In all cases, the complex nature of this relationship is acknowledged, and various simplifying assumptions are made.

Gvirtzman and Roberts (*24*) provide simulated interfacial area data for two ideal packing structures of identical spheres. The behavior of interfacial area versus saturation appears very similar for both packing structures. Qualitatively, the relative interfacial area (normalized to solid surface area) is observed to increase more quickly for the more loosely packed spheres, i.e., the slope of relative interfacial area vs saturation is slightly greater.

Modeling results presented by Cary (*29*) are useful in examining the texture dependence of interfacial area. Interfacial area versus water content data are provided for three hypothetical soils calculated using three semiempirical models proposed by Cary (*29*) and Miller et al. (*30*), as discussed above. The simulated data obtained with the Cary model for the hypothetical sand, silt loam, and clay systems are shown in Figure 2. The same trend in interfacial area versus water content is observed for all three textures. However, the results indicate a strong dependence of interfacial area on soil texture. The clay is predicted to have the largest specific interfacial area at all water contents, followed by the silt loam and sand. The texture dependence is probably most influenced by the porous medium specific surface area.

Both the Reeves and Celia (*25*) and Bradford and Leij (*26*) models discussed above provide insight into the impact of soil−water hysteresis on interfacial area. Just as hysteresis

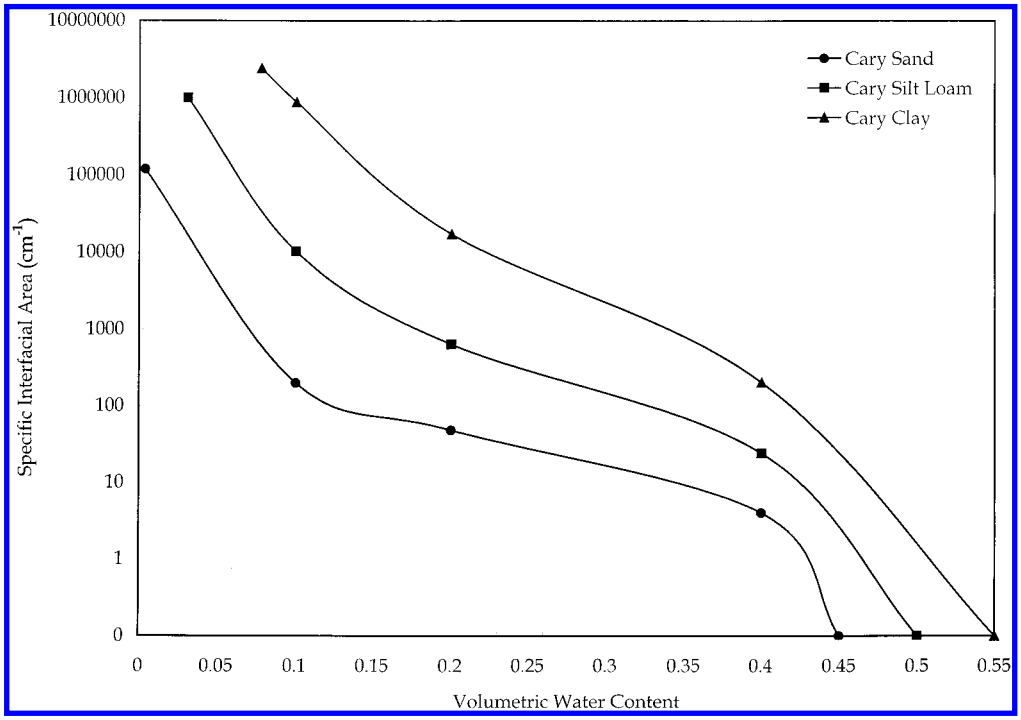

FIGURE 2. Texture comparison: prediction of interfacial area versus water content for hypothetical sand, silt loam, and clay systems. Adapted from ref *29*.

is observed in soil–water characteristic curves, it is expected that the interfacial area as a function of water content will also display wetting–drying hysteretic loops (*25*). The magnitude of hysteresis is largely dependent on the pore size distribution in the porous medium. Most models attempting to quantify the relationship between water content and interfacial area have either omitted the hysteretic region from their calculations or have chosen to consider either wetting or drying cycles, but not both. Conversely, Reeves and Celia (*25*) and Bradford and Leij (*26*) consider the interfacial area during both wetting and draining events. In both cases, the results show very little overlap of the wetting and draining curves for the interfacial area versus saturation relationship, indicating strongly hysteretic behavior.

Organic Matter Content. A property of the subsurface system that may influence the significance of air–water interfacial retention is the organic matter content of the system. It is well-documented that organic matter serves as a major retention domain in soils, especially when the mineral surfaces are solvated (*2–4*). In wetted systems with relatively high organic matter contents, the much greater mass partitioned into the organic matter will usually dominate all other retention mechanisms, rendering interfacial sorption negligible. Therefore, interfacial sorption is usually considered to be of significance primarily in wetted, low organic matter content porous media (*3*).

Chemical Properties Influencing the Importance of Interfacial Vapor Adsorption. In addition to physical properties of the porous medium, the physicochemical properties of the organic vapor (adsorbate) also exert a critical influence on the significance of the interface as a retention domain. Conceptually, the effect of the physicochemical properties of a compound on the degree of interfacial sorption can be viewed relative to its behavior on either side of the interface. It can be thought of as a result of its dissolved aqueous phase behavior or of its vapor-phase behavior. Ultimately, both aspects determine its interfacial activity.

Hydrophobicity. As a solute in the aqueous phase, an organic compound with relatively low polarity has an activity coefficient in water greater than 1. This fact is attributed largely to nonideal dissolution associated with the ordering of water molecules around the hydrophobic organic molecule. To evaluate the effect of an increased activity coefficient on interfacial adsorption, the Gibbs adsorption equation (eq 1) can be rewritten in terms of the activity of the dissolved organic compound (*31*):

$$\Gamma = -\frac{a}{RT}\frac{\partial \gamma}{\partial a} \tag{4}$$

where a is the activity, equal to the product of the solute concentration and its activity coefficient. Thus, for a given aqueous concentration, as the activity coefficient increases due to decreasing polarity, the surface excess will also increase. This effect is supported by the results of studies examining the adsorption of homologous series of straight-chain alkanes on flat-water surfaces (*10, 14*). At a given concentration, as chain length increases, a greater surface tension decrease (i.e., greater surface excess) is observed due to increased (hydrophobic) molecular surface area in contact with water. Similar behavior has been observed in environmental systems (*4*). In fact, the magnitude of adsorption enthalpy is observed to increase linearly with each methylene addition (carbon number increase) as predicted by Traube's rule (*3, 6, 14, 31*).

Saturation Vapor Pressure. Clear trends are also observed with respect to properties of the organic vapor phase. The interfacial behavior of organic vapors can be evaluated in two ways, in terms of a given vapor pressure and as a function of their respective saturation vapor pressures, p_o. At a given vapor pressure, a low molecular weight compound (high p_o) such as methane will show much less interfacial adsorption than a higher molecular weight compound (low p_o) such as octane (*10*). This is attributed to the relative volatility of smaller compounds and their subsequent tendency to remain in the vapor phase. As saturation vapor pressures are approached, however, the trend is reversed, where more volatile compounds begin to exhibit greater total interfacial adsorption. This is due to the much larger saturation vapor pressures of lower molecular weight compounds. Vapor

TABLE 1. Literature Values of K_{IA} for Selected Compounds

compound	log K_{IA} (cm) 25 °C[a]	12 °C	compound	log K_{IA} (cm) 25 °C[a]	12 °C
1 pentane	−5.28	−5.05[b]	17 1-chlorobutane	−4.35	
2 hexane	−4.96	−4.70[b]	18 1-bromobutane	−4.07	
3 heptane	−4.63	−4.40[c]	19 perfluorohexane	−5.14	
4 isooctane	−4.54		20 benzene	−4.35	−4.05[c]
5 nonane	−3.97	−3.64[c]	21 toluene	−3.95	−3.60[c]
6 decane	−3.65	−3.28[c]	22 ethyl benzene	−3.63	−3.24[c]
7 cyclohexane	−4.97		23 isopropyl benzene	−3.39	
8 cycloheptane	−4.56	−4.30[c]	24 chlorobenzene	−3.91	−3.59[b]
9 cyclooctane	−4.20	−3.96[c]	25 m-dichlorobenzene	−3.57	
10 dichloromethane	−4.73		26 fluorobenzene	−4.26	−3.96[b]
11 trichloromethane	−4.46		27 methyl formate	−3.71	−3.33[b]
12 tetrachloromethane	−4.83		28 ethyl ether	−3.27	
13 1,2-dichloroethane	−4.16		29 ethyl acetate	−2.56	
14 1,1,1- trichloroethane	−4.53	−3.77[b]	30 ethyl formate	−4.23	
15 trichloroethene	−4.58		31 *n*-propyl ether	−2.81	
16 tetrachloroethene	−4.49		32 acetone	−2.74	

[a] Data from ref *4*. [b] Data from ref *6*. [c] Data from ref *7*.

pressure is proportional to the number of molecules in the vapor phase and, subsequently, to the number of collisions with the interface per unit time. The larger saturation vapor pressures of lower molecular weight compounds provide for many more gas molecule collisions with the water surface and, hence, greater probability of adsorption. Thus, at their respective saturation pressures, a compound such as pentane may cause more than a 6 dyn cm^{-1} drop in surface tension, while octane at saturation will cause less than a 2 dyn cm^{-1} decrease (*10*).

The above discussion identifies two competing effects: less volatile compounds will dominate interfacial adsorption at lower absolute pressures, while at higher absolute pressures (near saturation pressures), adsorption of more volatile compounds will dominate. Even in the presence of bulk organic liquid, it would be rare in environmental systems for the vapor pressures to approach vapor saturation where the latter effect dominates (*32*). With this assumption in mind, it is generally stated that interfacial adsorption is inversely proportional to saturated vapor pressure.

The influences of hydrophobicity and vapor pressure have been discussed primarily in relation to the behavior of a homologous series of straight-chain alkanes. However, the arguments are applicable to nonpolar organics in general, where greater hydrophobicities and low saturation vapor pressures are indicative of increased interfacial adsorption. More polar compounds, such as aromatics and chlorinated hydrocarbons, tend to have greater K_{IA} values than nonpolar compounds due to favorable interactions with the polar water surface. Although more mass may be retained at the interface for polar compounds, this retention may often comprise a smaller fraction of total retention, since their higher aqueous solubilities may lead to dissolution into bulk water as the dominant retention process (*3, 7, 8*). For this reason, system water content becomes important for aromatics, not only because it affects interfacial area but also because solute retention via dissolution into bulk water may overwhelm interfacial contributions as water content increases. Many slightly polar compounds, such as benzene, toluene, xylene, and tetrachloroethene, have been found to be retained significantly both at the gas−water interface and in the bulk water phase (*4, 6, 7*).

Quantitative Treatment of Interfacial Vapor Adsorption

Retardation Factor. The total retention of organic solutes in a system at equilibrium can be quantified by the amount of mass present in each of the possible retention domains, as dictated by equilibrium partition constants and parameters denoting the relative "size" of each domain. The advective−dispersive equation describing solute transport in porous media can be modified to explicitly include the effect of specific retention domains. After some mathematical manipulation, the following retardation factor, R (−), can be defined for a system with immobile water and a mobile vapor phase:

$$R = 1 + \frac{\theta_w}{\theta_a K_H} + \frac{\rho_b K_d}{\theta_a K_H} + \frac{K_{IA} A_{1A}}{\theta_a} \tag{5}$$

where θ_a and θ_w are the volumetric air and water contents, respectively (−); K_H is the Henry's law constant (−); ρ_b is the bulk density of the porous medium (g cm^{-3}); K_d is the solid-phase sorption coefficient for a water-solvated sorbent (cm^3 g^{-1}); K_{IA} is the interfacial sorption coefficient (cm); and A_{IA} is the specific interfacial area (cm^{-1}). The first term in eq 5 represents the mobile (vapor) phase; the second term represents retention due to dissolution in (immobile) bulk water; the third represents sorption to the system solid phase (organic and mineral phases); and the fourth term represents interfacial retention. One or more terms in the retardation factor may be deemed negligible in a given situation.

The final term in eq 5, representing interfacial retention, is of primary interest here. The interfacial sorption coefficient, K_{IA}, is defined here in reference to the gas-phase:

$$K_{IA} = \frac{\Gamma}{C_a} \tag{6}$$

where C_a is the bulk concentration in the vapor above the interface (mol cm^3). Standard methods exist for measuring K_{IA} (*2, 7, 10−13*). Values of K_{IA} have been tabulated for many environmentally relevant compounds (*3, 4, 16, 33*). Values for selected compounds are given in Table 1.

***K_{IA}* Estimation.** For cases where measured values are not available, empirical correlations provide a means to estimate K_{IA} values using other physicochemical constants that are more readily available in the literature. Correlations exist between the extent of vapor adsorption to the gas−water interface, as represented by K_{IA}, and several physicochemical properties of the compound, as represented by various physical constants. In many cases, the correlations are expressed in terms of K_{IW} ($K_{IW} = K_H K_{IA}$), the interfacial−water partition constant, rather than K_{IA}. For example, Hoff et al. (*4*) reported a correlation between K_{IW} and the aqueous

solubility, C_w^S (mol cm^3), for 26 relatively low solubility compounds:

$$\log (K_{IW}) = -8.58 - 0.769 \log C_w^S \quad (7)$$

For relatively nonpolar compounds, Valsaraj et al. (*18, 33*) have noted correlations between K_{IW} and hydrophobic molecular surface area, S_H (Å^2), liquid molar volume, V_m (cm^3 mol^{-1}), and the octanol−water partition constant, K_{OW} (−):

$$\log (K_{IW}) = -6.55 + 0.0156S_H \quad (r = 0.8523;\ n = 19) \quad (8)$$

$$\log (K_{IW}) = -6.32 + 0.0146V_m \quad (r = 0.8486;\ n = 19) \quad (9)$$

$$K_{IW} = 3 \times 10^{-7}K_{OW}^{0.68} \quad (r^2 = 0.936;\ n = 8) \quad (10)$$

Good correlation is also observed between K_{IW} and the first-order molecular connectivity index, $^1\chi$ (−) (*34*). $^1\chi$ is a nonempirical parameter based solely on the structure and topology of the molecule. Sabljic (*35*) provides a compilation of $^1\chi$ values for environmentally relevant compounds:

$$\log (K_{IW}) = -5.53 + 0.2735(^1\chi) \quad (r = 0.8518;\ n = 13) \quad (11)$$

For more polar compounds, Hoff et al. (*4*) suggest the following regression:

$$\log (K_{IW}) = -7.508 + \gamma_W + a_S\frac{\sigma_{WA} - \sigma_{SA} - 1.35\sigma_{SW}}{2.303RT} \quad (12)$$

where γ_W is the activity coefficient of the aqueous organic solute (−); a_S is the molar surface area of the solute at the interface (cm^2 mol^{-1}) (using a spherical approximation $a_S = 8.45 \times 10^7(V_m)^{2/3}$; V_m is the liquid molar volume (cm^3 mol^{-1})); σ_{WA}, σ_{SA}, and σ_{SW} are the surface tension at the water−air, solute(liq)−air, and solute−water interfaces, respectively (erg cm^2). Goss (*21*) suggests the introduction of a hydrogen bond acceptor term, β (−), into correlation equations for relatively polar compounds where hydrogen bonding may play a role:

$$\ln (K_{IA}) = -0.615 \ln (p_L^o) + 7.86\beta - 5.80 - (385 \ln (p_L^o) - 6037\beta - 6611)\left(\frac{1}{T} - \frac{1}{323}\right) \quad (13)$$

where p_L^o is the saturated vapor pressure at 25 °C (Pa), and T is temperature (K). Equations 12 and 13 are decidedly more complicated and require more knowledge about the system, reflecting the more complex amphiphilic interactions of polar solutes and water.

Air−Water Interfacial Area. The importance of the areal extent of the air−water interface in dictating the significance of interfacial vapor retention has been described above. Furthermore, mass-transfer processes, such as volatilization and dissolution, are strongly controlled by the gas−water interfacial area. Because aqueous diffusion rates are typically much lower than vapor diffusion rates, a larger interfacial area to water volume ratio would tend to enhance transfer rates, while a small interfacial area to water volume ratio may cause significant mass-transfer rate limitations. For instance, it is expected that thin water films coating soil grains would have minimal mass-transfer rate limitations, while diffusional rate limitations may be quite important for deeper "pools", such as water-filled pores. Therefore, interfacial area considerations may be critically important in predicting the transport and retention behavior of all VOCs, even those that otherwise have little interfacial activity.

While modeling efforts have produced qualitative and semiquantitative estimates of A_{IA} for given systems, these models remain very system-specific and lack experimental confirmation. No well-tested and accepted method exists for direct measurement of air−water interfacial areas in soils. Without such a method, interfacial retention cannot be predicted nor its significance in a system evaluated. A laboratory-scale method would be critical in increasing the theoretical understanding of the interface. Field-deployable methods would also be desirable for more practical applications, such as risk assessment and remediation planning.

Three laboratory approaches are found in the literature and will be discussed in detail below. The first two approaches can be categorized as dynamic methods (involving column experiments) and the third as a static method (batch-style experiments). The underlying principles governing these methods and their practical implementation will be discussed. Finally, the laboratory methods will be compared according to their ability to further the current understanding of the gas−water interface in soils, the potential accuracy of the results, the ease of laboratory implementation, and the feasibility of applying the method at the field scale.

Methods for Measuring A_{IA}

Dynamic Methods. The dynamic methods make use of well-established column experiment procedures in which a solute-containing fluid is passed through a packed column and effluent solute concentrations are measured over time. Typically, a pulse of the solute is introduced and then flushed from the system. The resulting graph of concentration versus time, termed a breakthrough curve, can be analyzed by the method of moments to determine the retardation factor, R, for that compound in the experimental system. As defined in eq 5, R represents the total retention of the solute by all possible mechanisms. If one retention domain in a system dominates the total retention of a given compound, that compound can be used as a "partitioning" tracer for that domain. For an interfacial tracer, eq 5 can be simplified, here given with respect to a mobile vapor phase:

$$R = 1 + \frac{K_{IA}A_I}{\theta_a} \quad (14)$$

Therefore, if K_{IA}, θ_a, and R are known, the equation can be solved for A_{IA}. Two variations of the tracer method have been proposed for interfacial area measurement: the first relies on a gaseous interfacial tracer (*9*); the second makes use of an aqueous-phase interfacial tracer (*36*). For the latter, eq 14 is altered to reflect a mobile aqueous phase.

Vapor-Phase Interfacial Tracer Test. For a vapor-phase interfacial tracer experiment, the gaseous tracer contained in a balance of some inert gas, such as nitrogen, is passed through the packed column. The interfacial tracer partitions between the mobile inert gas stream and the relatively immobile gas−water interface. Any retention of the tracer is attributed to adsorption of the gaseous tracer at the interface. A viable gaseous interfacial tracer has properties in keeping with those described above for highly surface active vapors. The compound must be relatively water-insoluble and have an intermediate saturation vapor pressure. If the compound is too volatile, it will not be measurably retarded by the system, while increased retention of less volatile compounds may result in unreasonably long retention times.

Brusseau et al. (*9*), Okamura and Sawyer (*37*), and Enright (*38*) have conducted experiments demonstrating the vapor-phase interfacial tracer method. Heptane was used as the interfacial tracer by Brusseau et al. and Enright, while Okamura and Sawyer used a variety of halomethanes. In the heptane tracer studies, interfacial adsorption was observed to be the dominant retention mechanism for heptane, comprising approximately 99% of the experimentally observed retention, while only 0.1% of the retention was due

to bulk water dissolution. Therefore, heptane demonstrated appropriate properties for a successful interfacial tracer. Okamura and Sawyer measured interfacial areas using composite data from several halomethanes, including dichloromethane and trichloromethane. Strictly speaking, the halomethanes are not interfacial tracers because of their appreciable water solubility. However, this was taken into account in their data analysis. In all cases, interfacial areas were calculated using measured retardation factors, known K_{IA} values, and versions of eq 14. Brusseau et al. measured an interfacial area of 61 095 cm^{-1} for a silica sand system with 10% water content, while values reported by Enright for a synthetic porous medium ranged between 13 031 cm^{-1} and 6 674 cm^{-1} for 4.7% and 14.1% water contents, respectively. Interfacial areas reported by Okamura and Sawyer for a Gila silt loam were similar to those reported by Enright. However, physical differences between the porous media used in these studies do not allow direct comparison of the data. The decrease in interfacial areas with increasing water content reported by Okamur and Sawyer and Enright is in general agreement with theoretical predictions. Figure 3 shows the relationship between specific interfacial areas and water content reported by Okamura and Sawyer.

The A_{IA} values obtained from the experiments reported above are significantly higher than values predicted using the theoretical models discussed previously. For a typical sand near 10% water content, the Cary model predicts an interfacial area of approximately 200 cm^{-1} (*28*). This discrepancy may be due in some cases to the use of high tracer concentrations, which force consideration of multilayer adsorption. The occurrence of multilayer organic vapor adsorption on water surfaces is well-documented in the literature (*10−12, 14*). However, this phenomenon has received limited attention for environmental applications.

With the possibility of multilayer adsorption in mind, eq 14 can be rewritten as:

$$R = 1 + \frac{K_{IA}(nA_{IA})}{\theta_a} \tag{15}$$

where n is included as an apparent number of adsorbed layers. Thus, because the values reported by Brusseau et al. and Enright were measured using high tracer concentrations, they may be considered to be "apparent" interfacial areas, nA_{IA}, rather than true interfacial areas, A_{IA}. The concept of an apparent interfacial area is an important consideration for environmental applications. In some situations, it is possible that the contaminant vapor is undergoing multilayer adsorption. In such cases, the actual contaminant mass retained by the interface may be significantly underestimated when true A_{IA} values are used in eq 14. Thus, while gas-phase interfacial tracer tests may not always allow quantification of the true interfacial area of the system, they may provide insight into the actual contaminant mass adsorbed. For example, Brusseau et al. (*9*) used a tracer-derived apparent interfacial area to successfully predict R values for trichloroethene transport based on the tracer-derived apparent interfacial areas ($R_{predicted} = 8.29$ versus $R_{measured} = 8.25$).

When considering multilayer adsorption, it is important to note that the K_{IA} term is generally measured at submonolayer coverages. Thus, it truly applies only for systems at infinite dilution. In the case of the interfacial tracer test, the use of the infinite dilution K_{IA} value at high concentrations would underestimate the tendency of the tracer to accumulate at the interface, with the resultant "excess" retention resulting in estimation of an interfacial area larger than the true value. This situation can be addressed by use of a concentration-dependent K_{IA}. This would, of course, require measurement of the full isotherm. In the absence of such data, the apparent interfacial area approach can serve as a useful construct for practical applications.

One concern regarding this interfacial area measurement technique is the redistribution of water in the system due to changes in aqueous surface tension. As discussed above, adsorption of organic vapors on water tend to decrease the surface tension of the water. This decrease in surface tension may cause pores to dewater, changing both water content and interfacial area in the system. Furthermore, the decrease in surface tension may cause the interface to become mobile. A mobile interface will tend to decrease the retention of the tracer as compared to the case where the air−water interface is immobile. Thus, a decreased interfacial area will be measured that may not be representative of the original system. These complications are important to consider, especially when high tracer concentrations are used.

The presence of disconnected pore space in wetted soils is another aspect to consider regarding the gaseous tracer method. The gaseous tracer can only easily access interfaces bounding possible flow paths, i.e., connected pores. This occurrence of disconnected pore space may therefore result in artificially low measured values of total interfacial area. It is expected that disconnected air-filled pore volume will increase with increasing water saturation.

Disconnected pores are only considered a complication in attempting to quantify the total interfacial area present in a given system. However, if one considers contaminant transport applications, the gaseous tracer may actually access the same interfaces as the contaminant vapors. It is expected that the relatively insoluble VOCs would be in contact only with interfaces bounding connected pore space, similarly to the gaseous tracer. It is possible that more soluble compounds may dissolve in and diffuse through immobile water films to an interface bounding disconnected pores. However, if the VOC has sufficient solubility to force consideration of this possibility, it is also possible that aqueous dissolution and its associated rate limitations would replace interfacial adsorption as the dominant retention mechanism. Therefore, while not providing total interfacial area measurements, which might prove helpful in furthering the theoretical understanding of the interface, the apparent interfacial area measured by a vapor-phase tracer may prove more useful in practical applications, such as predicting VOC retention and transport.

Aqueous-Phase (Surfactant) Interfacial Tracer Test. The aqueous-phase interfacial tracer method is quite similar to the vapor-phase tracer method described above, with the exception that water is the mobile phase carrying a tracer compound. Equation 14 is modified to reflect this:

$$R = 1 + \frac{K_{IW}A_I}{\theta_w} \tag{16}$$

Physical properties of an appropriate aqueous interfacial tracer include little tendency to adsorb to the solid mineral phase, low volatility, high water solubility, air−water interfacial activity culminating in monolayer coverage, and a known and constant molecular area at the interface (*37*). Anionic surfactants appear to fit these criteria.

Kim et al. (*36*) have demonstrated the surfactant interfacial tracer technique for measuring gas−water interfacial areas in laboratory-scale porous media systems. Sodium dodecyl benzene sulfonate (SDBS) was used as the aqueous interfacial tracer in a sand medium. Six experiments were performed at water contents ranging from 11% to 100%. Figure 3 shows the measured interfacial areas as a function of water content. At the lowest water content, the measured interfacial area is 46.4 cm^{-1}. It is observed that at higher water contents the interfacial area decreases linearly toward zero at saturation. A six-point regression of interfacial area versus water

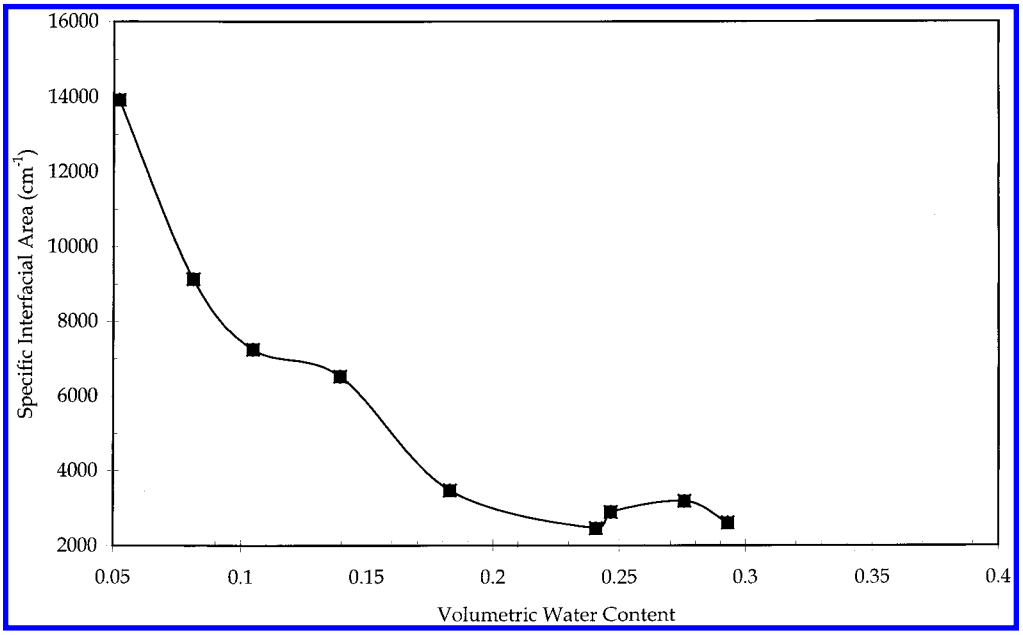

FIGURE 3. Vapor-phase tracer results: specific interfacial area versus water content for Gila silt loam. Adapted from (*37*). There is some uncertainty in volumetric water content values due to the assumption of bulk density, $\rho_b = 1.45$ g·cm^{-3}, but the trend in interfacial areas is not affected.

saturation, S_W, yielded the following bestfit line:

$$A_{IA}\ (\mathrm{cm}^{-1}) = -64.7S_W + 64.7 \quad (r^2 = 0.97;\ n = 6) \quad (17)$$

The observed behavior of interfacial area as a function of water content is consistent with the pore-filling theory, discussed above. This trend has been observed in several interfacial area modeling results and lends support to the surfactant tracer interfacial area measurement method. Specifically, note the general similarity between experimental data trends from Kim et al. (Figure 4) and the trends in the results of the three semiempirical models (A−C) evaluated and compared by Cary (Figure 1). As a first approximation, the experimental data are in agreement with the current understanding of interfacial area dependence on water content.

An aqueous transport study by Kim et al. (*39*) provides convincing support for the aqueous tracer method. In this study, the interfacial areas obtained previously were used to successfully predict the total retention of other compounds in an unsaturated porous medium. Predicted *R* values were on average within 3% of the experimentally observed retardation factors. Interestingly, interfacial retention comprised on average 60% of the total retention for the alcohols and on average only 3% of the total retention for the aromatics. These results illustrate the importance of chemical properties on the relative significance of interfacial retention.

The absolute values of interfacial area for a sand system at 10% water content reported by Kim et al. (SDBS surfactant tracer) are approximately 2−3 orders of magnitude lower than areas measured with the gaseous tracer method for similar systems. Lower interfacial area values are expected from the surfactant tracer method and may be attributed to the fact that true interfacial areas obtained, in contrast to the apparent interfacial areas obtained in the gaseous tracer method. This may explain why the surfactant tracer method yielded interfacial area values in approximate agreement with model predictions.

There are certain limitations inherent to the aqueous tracer technique. Aqueous tracer experiments are not feasible at lower water contents due to capillary pressure constraints on achievable flow rates (*36*). At low water contents impractical or impossible pressure gradients would be required to overcome the high matric potentials. Additionally, the increased fraction of disconnected, immobile water at low water contents limits measurement accuracy. This is analogous to the discussion of gaseous tracers at higher water contents. However, unlike gaseous tracers, aqueous tracers may not necessarily access the same interfaces as a vapor-transported contaminant.

Similar to adsorption of the gaseous interfacial tracers, surfactant accumulation at the air−water interface tends to decrease the surface tension of the water. As discussed above, this may induce water redistribution in the system and mobilization of the air−water interface. If this occurs, the retention of the surfactant and the measured interfacial area may not be representative of the original system. Kim et al. (*36*) suggest two ways to minimize this behavior. First, surfactant concentrations should be kept low, so as to minimize water redistribution. Second, rather than displacing pure water from the system with an aqueous surfactant pulse, (which causes the problematic change in surface tension), the system could be conditioned by introducing surfactant solution that is then displaced by a radioactive-labeled surfactant solution. In this manner, the surface tension remains constant throughout the experiment, while allowing the radioactive input pulse to be distinguished from the background solution. Despite these precautions, even if transient conditions were eliminated from the experiment, it remains that the decrease in surface tension induced by the measurement method inevitably alters the system relative to natural, surfactant-free conditions.

Static Method: Surfactant-Induced Water Mobilization. A static method developed by Karkare et al. (*40*−*43*) relies on the principles of capillary action, by which water is held in the pores of porous media. A horizontal column is packed with uniformly wetted porous media. As surfactant is added to one-half of the column, accumulating solely at the gas−water interface, the water is observed to redistribute until a new equilibrium water distribution is achieved. The surfactant causes a reduction in the surface tension of the water and forces a decrease in matric potential, which causes partial dewatering of the pores. When the system becomes stable again, it is observed that the section of the column to which surfactant was added is depleted almost uniformly of water, while the surfactant-free half has a water content much

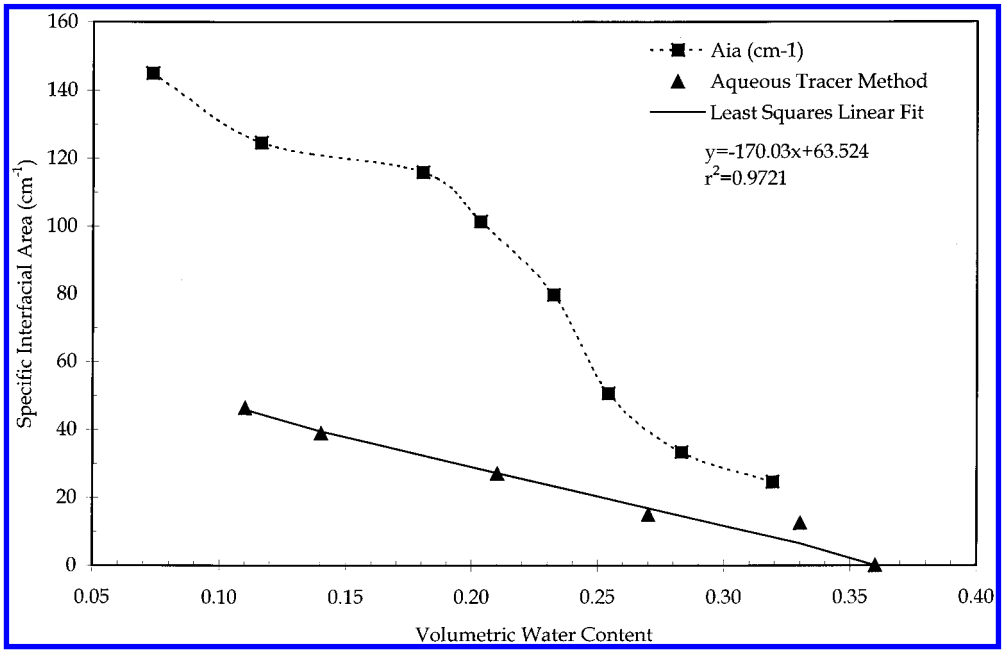

FIGURE 4. Results from aqueous interfacial tracer and surfactant-induced water mobilization methods: interfacial area versus water content for two wetted sand systems. Adapted from (*36*) and (*43*), respectively.

greater than the initial. This water mobilization is observed only for surfactant concentrations greater than a critical value, corresponding to monolayer coverage. Thus, knowing the area per molecule (inverse of surface excess) at which the mobilization occurs and the minimum amount of surfactant needed to achieve the critical mobilization concentration, allows the calculation of the interfacial area.

There are four surfactant properties required for the desired behavior to be observed (*40*). The surfactant must be water soluble but interfacially active. Second, the surfactant must form a condensed solid monolayer. A condensed solid monolayer is one that is relatively incompressible. This results in a well-defined surface concentration (excess) at monolayer coverage, which is required for calculating A_{IA}. Additionally, this prohibits the surfactant from being mobilized or spreading at the interface. This is discussed in more detail below. Third, surfactant coverages less than that required to form the solid monolayer must have minimal effect on the surface tension (i.e., no water mobilization), but at monolayer coverage, a measurable amount of water must be mobilized (i.e., significant decrease in surface tension). If surface tension decreases over a range of surfactant coverages, the surfactant mass necessary to achieve monolayer coverage would be unknown, and interfacial areas could not be computed. Last, the surfactant must not form multiple layers at the gas−water interface. Similar to the discussion above in relation to the dynamic vapor method, if multilayers are formed, the calculated interfacial area would be artificially high.

It is important to note that because the surfactant forms a solid monolayer, the surfactant itself remains more or less in its original location even during induced water flow. In fact, it is because the surfactant remains essentially in its initial location within the column that a surface tension (capillary pressure) gradient is maintained throughout the duration of the experiment (*42*). If the surfactant were to spread, equalizing its concentration throughout the column, the initial surface tension gradient would gradually decrease to zero. Without a surface tension (capillary pressure) gradient, the water would revert back to its initial relatively uniform water content. This is in direct contrast to the behavior discussed above for the surfactant used in the dynamic aqueous surfactant method.

In the Karkare et al. experiments, 1-tetradecanol was used as the water-mobilizing surfactant and observed to meet the above criteria. The interfacial areas were measured for sand and glass bead systems at several water contents ranging from 5 wt % to near saturation. A plot of interfacial area versus water content for the sand system is shown in Figure 4. Similar behavior was also observed in the glass bead system. At intermediate water saturations, the interfacial area decreases with increasing water content. This behavior is consistent with the results of the theoretical analyses and compares favorably with the trends observed in the dynamic surfactant tracer experiments, also shown in Figure 4. Calculated A_{IA} values for the sand system decreased from 145 to 20 cm^{-1} as water content increased toward saturation. These A_{IA} values are approximately three times larger than the values obtained via the dynamic surfactant tracer method for a similar sand system. This relatively small discrepancy may be due to physical differences between the two porous media.

Method Comparison. Three approaches have been described for measurement of air−water interfacial areas in porous media. All three appear to have potential for furthering the current theoretical understanding of the gas−water interface in soils and its complex dependence on system properties (e.g., water content, grain size). The results of experiments conducted at several water contents are consistent with predictions obtained from existing interfacial area models. Although gaseous tracer methods may in some cases yield artificially high interfacial area values, data at multiple water contents show that relative changes in interfacial area as a function of water content are observable via this method.

The surfactant and gaseous tracer methods appear complimentary, in that the two are most applicable in different water content ranges. The gaseous tracer method is expected to perform better at low to intermediate water contents, where disconnected air porosity is less significant. For analogous reasons, the aqueous tracer method is restricted to higher water content systems. Taken together, the tracer methods may be capable of elucidating trends in interfacial behavior across the full spectrum of water saturation. The water mobilization method also appears quite promising in its ability to delineate interfacial trends and

behavior. Application of the mobilization method is not experimentally observed to be restricted to certain water content ranges. However, it is expected that the method would not function at very low water contents, where the decrease in surface tension caused by the surfactant addition may not be sufficient to overcome the very high capillary pressure holding water in the pores.

The A_{IA} values obtained via the surfactant tracer and water mobilization methods are comparable to values predicted by existing models and may be considered closer to the "true" interfacial area of the system. True A_{IA} values are critical in assessing possible rate-limited mass transfer processes, such as nonaqueous phase dissolution and oxygen delivery for biological processes. The apparently high A_{IA} values obtained via the gaseous tracer method are possibly due to multilayer adsorption of the gaseous tracer, a phenomenon likely affecting the retention of volatile contaminants as well. Therefore, the gaseous tracer method may be considered as providing apparent interfacial areas that may be more realistic in predicting contaminant transport. Methods for measuring true and apparent A_{IA} yield complimentary information and address different aspects of environmental systems.

With respect to in-situ environmental systems, such as a vadose zone, it is improbable that the surfactant-induced water mobilization method could be adapted for field applications. It is not feasible to emplace surfactant in the vadose zone within a well-defined area and to monitor vertical and lateral water mobilization/re-equilibrium, as this method requires. Therefore, the dynamic tracer methods may be more applicable. While the aqueous-phase tracer is quite feasible, the gaseous tracer method would be preferred because much faster gas velocities can be induced relative to water, thereby allowing much shorter tests.

When applying tracer tests to field-scale system, it is critical to recognize that the volume-normalized interfacial area value would be averaged over the entire swept volume of the tracer test (volume swept between the injection and extraction wells). Thus, the average specific interfacial area and the subsequent average behavior of the contaminant in the system may be more useful for field-scale predictions than for isolated point measurements. While the application of interfacial partitioning tracer tests is feasible at the field-scale, their effectiveness has yet to be fully evaluated.

Discussion

While the role of the gas−water interface in environmental systems has received increased attention in recent years, many uncertainties remain. Critical questions regarding both interfacial theory as well as practical implications of the impact of gas−water interfaces on environmental systems remain unanswered. Preliminary experiments have shown general agreement with theory with regard to interfacial area as a function of water content. The surfactant-induced water mobilization method appears well-suited to seek out this theoretical A_{IA} maximum by conducting a series of experiments at small water content intervals. If it is found that the A_{IA} maximum occurs at the residual saturation, as indicated by Bradford and Leij (*26*), this A_{IA} maximum could be used as a worst-case scenario in predicting contaminant retention at the interface. Additionally, the hysteretic behavior of the interfacial area expected during wetting and drying cycles has not been investigated experimentally. Both the water mobilization and aqueous tracer methods have potential to bridge this gap between theory and observation. Interfacial areas and their maxima are expected to be dependent on soil properties, such as texture, but these effects have not been quantified.

The phenomenon of multilayer adsorption at the interface has been discussed at many points throughout this paper. Unfortunately, detailed information regarding the uniformity of multilayer coverage, the number of adsorbed layers, and the dependence of these factors on the contaminant physicochemical properties is not available for porous media systems. In terms of uniformity of coverage, it is possible that microscopic and spectroscopic methods could be employed to image the interface and provide more detailed information (*44*). Furthermore, it has been assumed throughout that interfacial adsorption is essentially an instantaneous process; and while limited studies have supported this assumption, no systematic investigation of interfacial kinetics has specifically been conducted. A kinetic investigation could possibly be accomplished by the gaseous tracer method.

The areal extent of the gas−water interface in a soil system plays a major role in dictating its importance as a source of contaminant retention. However, well-established methods for measuring the interfacial area are presently unavailable. Three methods have recently been proposed. Although these methods show potential for addressing the above theoretical questions and uncertainties, careful study of several issues regarding the methods themselves is lacking. Experiments are needed to delineate applicable water content ranges for each method. It is also important to evaluate whether retention of contaminants can be successfully predicted using experimentally measured interfacial area values. This has been performed successfully with both tracer methods at the laboratory scale. However, predictive capabilities remain to be demonstrated for the vapor-phase tracer method at a range of water contents. Furthermore, assessment of predictive capabilities at the field-scale is of critical importance. Last, it remains for all interfacial area measurement methods to be performed in a common system, allowing a direct comparison of method results.

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